Recycling plastics from waste computer equipment.

Brennan, Louise B

Brennan, Louise B (2004) *Recycling plastics from waste computer equipment..* thesis, Swansea University.
http://cronfa.swan.ac.uk/Record/cronfa43077

School of Engineering
Materials Research Centre

RECYCLING PLASTICS FROM WASTE COMPUTER EQUIPMENT

By

Louise B. Brennan
B.Eng M.Phil

A dissertation submitted to the University of Wales for the degree of

Doctor of Philosophy

July 2003

For Kenneth Lucas

My Grandad

ACKNOWLEDGEMENTS

A great big thank you, thank you, thank you, to Cris and Dave, my two tutors, for their endless time and support throughout the project and also to the Swansea Environment Centre for their funding assistance. More great big thank you's go to PMI (Wales) Ltd (who aren't actually there anymore) for supplying the materials needed, and also to Phil, Idris and Paul from Merthyr College, and 4 The Environment (who aren't there anymore either) for their technical expertise and assistance with the recycling process. A big cheers goes to Carwyn for the many hours spent extruding plastics with me instead of doing his own project (oops did I say that?) and everyone else who devoted their time and effort to helping throughout the project, including James, Tom and Stew who's social time and assistance was invaluable. Also a special mention for Brian, the best ever lifesaving and swimming coach from the days when the University had its own pool!!

SUMMARY

In light of recent European legislation, an increase in recycling and recovery activities is required in the electrical and electronic sector in order to meet stipulated targets. For waste plastics this also includes the separation of plastics containing brominated flame retardants from those that do not.

Studies into the FTIR (Fourier transform infrared) spectra of a collection of plastics from waste housings for computer equipment and comparisons with spectra from a selection of flame retardants, as well as testing different plastics identification systems have concluded that infrared spectroscopy cannot be used to detect flame retardants in plastics in the current state of technology. However flame retardants may be detected by using a combination of identification techniques such as IR (infrared) for plastic identification and pyrolytic spectroscopy for additive detection.

The effects of recycling and blending on a commercial scale have been assessed on mechanical properties of the four most used plastics in computer equipment housings. Recycled ABS (acrylonitrile-butadiene-styrene), HIPS (high impact polystyrene), modified PPO (polyphenylene oxide) and PC (polycarbonate) /ABS alloy were tested in the pure form and as various blends of ABS and HIPS, HIPS and modified PPO (mPPO), ABS with PC/ABS and a blend of all four plastics. Properties tested were tensile and impact properties, DMTA (dynamic mechanical thermal analysis), viscosity, molecular weight and surface and bulk microscopy.

Generally changes to mechanical properties following recycling of pure ABS, HIPS, PPO and PC/ABS are quite small, although there are slight reductions in ductility for HIPS and mPPO. All plastics used in this study appear unaffected by the presence of a small proportion of another plastic, although at higher blend proportions impact strengths of ABS/PC/ABS deteriorate, properties of ABS/HIPS blends remain unaffected and larger proportions of HIPS/PPO are beneficial to all properties. These results indicate that a plastics identification system probably does not need to be exactly 100% accurate.

CONTENTS

CHAPTER 1:

INTRODUCTION

Plastics have had a strong influence in the way we live today and over the past several decades plastics have also had revolutionary effects in most industrial sectors. This is largely due to properties found in plastics such as ease of processing, colouring and forming [1] as well as being lightweight and highly adaptable. Due to the availability of such a wide variety of different plastics, they can be adapted to fulfil both low and high-grade applications from packaging materials to automobile components. Over the past several decades, there has been a tremendous increase in the growth of plastics production and consumption, which has been seen world-wide. Producers are recognising that by using plastics they use less total material, which leads onto less energy in production, less fuel and pollutants in transport and delivery and therefore less waste at the end of life [2].

Plastics are produced from oil and in 1997 the world production of plastics was estimated at around 150 million tonnes [1,3]. Although this amount does seem rather substantial, it does in fact account for just 4% of world oil consumption each year [4]. Figure 1.1 illustrates the various applications in oil consumption. Therefore, as most oil is used as a source of energy and the production of plastics help save energy, it can be observed that plastics use in various applications actually save more oil than is needed for their manufacture [5].

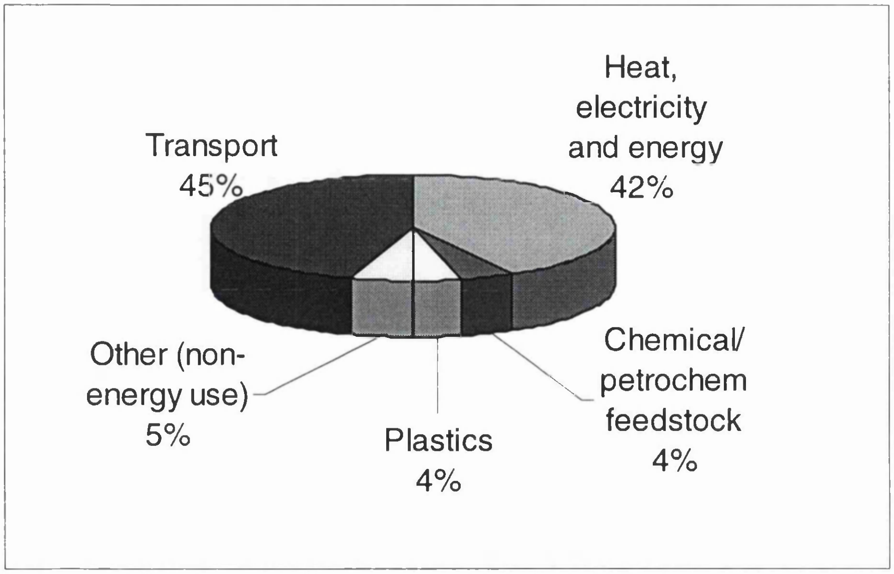


Figure 1.1. World Crude Oil Consumption, by Use [4]

As previously stated, the consumption of plastics has increased substantially over the past few years. Since 1995 the average rate of plastics consumption in Western Europe has risen by more than 5% each year [6] and has been predicted to continue over the next few years [7]. Therefore, at the same time the amount of waste generated from post-user plastic products (which stays at approximately 60% of plastics consumption each year) is also increasing [5,6,8]. Although plastics account for just a small weight proportion of total waste, it must be remembered that because of their low density, plastics waste can actually appear more significant when considering their volume. For example, although the plastics proportion of Municipal Solid waste (MSW) is just 7% in weight, it accounts for about 18% in volume [9]. This consideration highlights the importance of finding alternative methods for the disposal of plastics waste as opposed to landfill.

Numerous environmental impact studies have demonstrated that the main environmental goal should be the diversion of waste from landfill [6,7,10-13]. In the case of plastics there are several options as an alternative to landfill, including mechanical and chemical recycling and energy recovery. The Association of Plastics Manufacturers in Europe (APME) have suggested that the only way to effectively divert the highest proportion of plastics waste from landfill would be through an integrated management policy of a combination of such recovery options [10].

In addition to the yearly growth in plastics consumption and waste, the amount of plastics recovered for alternative recovery options is also increasing. In 1994 20% of plastic waste from Western Europe was recovered, which has grown to a 36% recovery rate in 2000 [14]. The challenge for plastics is for waste recovery to keep pace with continual growing consumption, which would mean that each year the actual amount of plastics waste recovered would need to increase proportionally according to increases in consumption and waste. A survey undertaken by TN Sofres Consulting showed that in 1998 plastics waste recovery was 30% of the total plastics waste stream [5]. This contributed to a 9% reduction by weight of in the total volume of plastic waste being landfilled [15]. Continual research has shown that year after year not only does the recovery of plastics waste keep pace with demand, but the annual recovery rate is actually increasing [5,6,14]. In 2000, growth in recovery not only kept pace with consumption, as it had in previous years, but actually outstripped it due to considerable growth in recycling and energy recovery [14]. This means that as a higher proportion of plastics waste is being recovered, the proportion of plastics waste being disposed of to landfill is reducing each year.

However, this annual increase in plastics waste recovery rate in Western Europe is not equally representative of individual countries, as some countries are actually recovering a higher proportion than others [6]. Germany for example, is not only the highest plastics consumer in Western Europe it is also the highest mechanical recycler [5] and one of just two countries to use feedstock recycling [6,14]. Although countries such as Switzerland and Denmark recycle just 7% of plastics waste they are also recovering the energy from up to 75% of such waste, so that more than 80% of plastics waste is currently being diverted from landfill [14]. On the other hand Ireland consumes the lowest amount of plastics by weight but is also recovering the smallest percentage of plastics waste. The UK is also one of the worst countries to recover plastics waste and despite being one of the higher plastics consumers in Western Europe, the total recovery rate is at 13%, with just under 7% of plastics waste being mechanically recycled [14].

The continual increase of plastics waste has become a world-wide concern, therefore it is no surprise that organisations such as the European Commission have introduced legislation with the aim of increasing recycling and recovery activities, especially in those countries that could recover a larger proportion than they do already. There are currently several directives that deal with the issue of waste from

MSW, the automotive sector and the electrical and electronic sector. Sectors such as Agriculture, Distribution and Industry already have fairly good recovery rates and with such amounts being recycled voluntarily, there is little legislation needed in these areas [6].

The electrical and electronic (E&E) sector currently has the lowest sector recovery rate of just 5% despite enjoying the highest percentage growth of consumption in 2000 [14]. European legislation for this sector is currently being proposed and there are now three different directives covering different aspects that will be discussed in more detail. Recovery of E&E plastics waste is a developing area and although recycling is increasing, it can be restricted due to technical feasibility and economics [16]. Within the E&E sector, areas that consume the most plastics and who also produce the most waste are large household appliances and IT (Information Technology) & Telecommunications. By concentrating on areas such as these, recovery levels within the E&E sector could potentially increase as only large appliances such as copying machines, refrigerators or computer monitors could provide the volumes of plastics necessary for successful recycling operations [16].

A report by the APME (Association of Plastics Manufacturers in Europe) has suggested that the recycling rate of the E&E sector could increase if more PS (polystyrene) and ABS (acrylonitrile-butadiene-styrene) recyclate become available [7]. Previous work concluded that ABS and HIPS (high impact polystyrene) are two of the more used plastics in computer equipment [17]. Therefore by recycling more computer equipment, the recycling rates for the E&E sector could increase.

Over the past few years it has been found economical to recycle the electrical insides of computer equipment, however the plastic casings of such equipment are all too frequently landfilled. Reasons for this include difficulties in identification, separation, and the detection of additives present in the plastics, as well as dismantling difficulties and insufficient knowledge as to the effects of recycling on the properties of the plastics used in these applications.

The purpose of this study is to address some of the issues that hinder recycling activities of plastics from computer equipment. All options for the recovery of plastics are reviewed as part of the literature review in Chapter 2. This chapter also contains an outline of the aspects of current legislative directives for the recovery and disposal of plastics waste from the packaging, automotive and electrical and electronic (E&E) sectors. Subsequently, brominated flame retardants are then reviewed in order to assess their merits as a flame retardant, as well as reasons why legislation is requiring that these substances are to be banned from use. This is followed by a review into current research and technology of plastics identification, in order to determine possible solutions to overcome this barrier that is currently impeding recycling activities in the E&E sector. The final sections of the literature review include an overview on the structure and degradation of ABS, HIPS, PPO and PC/ABS, which are the four plastics that are used in the mechanical recycling part of this study, as well as a brief summary of the main findings of recycling these plastics that were concluded from previous work. The following section brings Chapter 2 to an end with the background and explanation to the methods used to compare the effects of recycling and blending on various properties of the four recycled plastics that were taken from disused computer equipment.

The subsequent chapters follow the experimental side of the project, which has been divided into two parts covering studies into plastics identification methods and also the effects of mechanical recycling and blending on four of the most used plastics in computer equipment. Chapter 3 is an outline of the experimental procedures of the various studies undertaken on plastics identification technology, the results and discussion of which can be found in the subsequent chapter, Chapter 4. Chapter 5 consists of the experimental procedure for mechanical recycling and blending, the results of which are found in Chapter 6 and the findings of which are discussed in Chapter 7. The remaining Chapter 8 states the main conclusions drawn from this study as a whole with recommendations for any future work. It is hoped that the issues addressed in this project will be useful to such areas that need developing in order to increase confidence in the area of recycling plastics from waste computer equipment.

CHAPTER 2:

LITERATURE REVIEW

2.1 INTRODUCTION – PLASTICS IN THE ELECTRICAL AND ELECTRONIC SECTOR

Due to the emphasis of constant innovation and research, the role of plastics has become key to technological development within E&E industries. Plastics are being used more and more in this sector and properties such as weight reduction and electrical and thermal insulation are exploited extensively in the production of E&E equipment. As well as the more highly visible packaging and structural applications, the use of cables also require properties including high strength, corrosion resistance, flexibility and durability, all of which are found in plastics and the progress of this sector can be generally attributed to the versatility of plastics developed to meet specific needs [16].

In 2000 production in the E&E sector was more than 13 million tonnes, with an average annual growth rate of 4.3% since 1995 [16]. Within this sector, plastics consumption for 2000 was just over 2,680,000 tonnes [14], an increase of more than 25% since 1995. Although this level of plastics consumption accounts for almost 20% by weight of all E&E equipment [16], it must be remembered that almost half of all the plastics produced in this sector are used to sheath cables and electrical equipment. However, excluding this application, the main areas accounting for 87% of the remaining plastics use are large household appliances, IT and telecommunications and consumer equipment (illustrated in Figure 2.1).

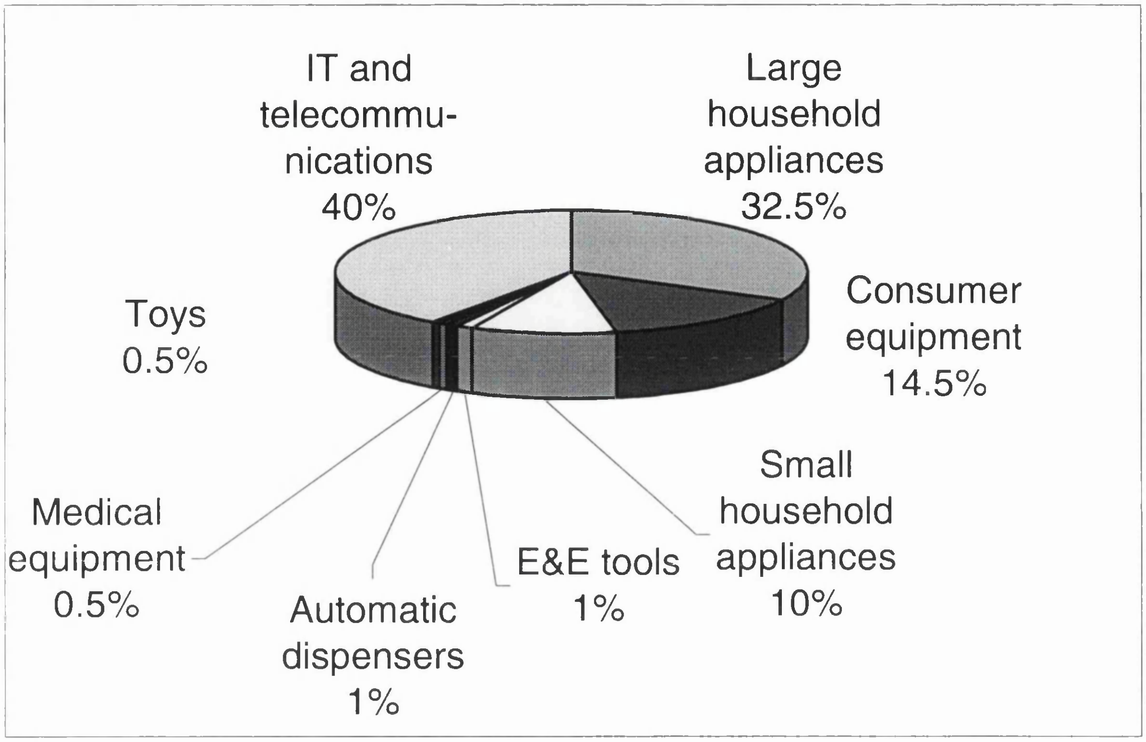


Figure 2.1 Plastics Consumption In E&E Equipment By Sector, Western Europe 2000 [16].

The main growth of plastics consumption within the E&E sector has been seen in the most innovative areas. Technological advancement especially within IT and telecommunications has been so considerable that the average product life of items such as computer equipment has been reduced to two years in some cases [18]. Data processing equipment, which includes computer equipment has now expanded and accounts for 29% out of the 40% of IT and Telecommunications compared with just 5% in 1995 [16]. Along with an expansion of the area in general, the amount of plastics used in IT and telecommunications has also increased and now makes up more than 25% of all materials used. However, it must be realised that the largest areas of plastics consumption also produce the most waste.

A study by Carnegie Mellon University in the United States predicted that almost 150 million personal computers (PC's) in the USA would be landfilled by the year 2005 [19]. However, an updated model of the study suggested that the same amount of PC's previously predicted for landfill would instead be recycled and just 55 million PC's would be landfilled [20]. Considering that most computer equipment is housed in plastic casings, it appears that a significant amount of plastic is available for recycling in the US and it could be estimated that a similar quantity of such plastics waste could also be available for recycling in Europe. Although it has been found economical to recycle the electrical components of computer equipment, the plastic casings of such equipment are often landfilled. This is unfortunate as such plastics would be ideal for material recycling as they have been defined as high quality waste [16] due to being high quality engineering plastics and being relatively contaminant free when compared with mixed plastics packaging waste from MSW. Since these components are relatively large and also subject to constant upgrade and innovation, they are available in large volumes.

It has been suggested that the recycling levels in the E&E sector could increase if more polystyrene and ABS (acrylonitrile-butadiene-styrene) recyclate become available [7]. ABS and HIPS (high impact polystyrene) are the two most used plastics in casings for computer equipment [17], as well as two of the most used plastics within the E&E sector [16] (excluding cables). Therefore it is quite possible that an increase in recycling activities in this area could do just that. With impending legislation about to come into play it is essential that recycling rates in the E&E sector increase as soon as possible if imminent recovery targets are to be met. Although waste plastics from computer casings are ideal for material recycling, this would not be the solution for all E&E waste due to the complexity of some products [21]. The mobile phone is the perfect example of such a product. A complex variety of plastics are used to provide these small, lightweight, yet strong devices and make up to 75% of the weight of a mobile phone. However this produces a fairly complex waste stream consisting of a blend of small amounts of different plastics and other materials that are particularly hard to separate. Therefore where mobile phone recycling schemes have worked, it has been due to reclaiming the value of the precious metals that they contain [16]. As the E&E sector accounts for so many different products it would appear that the most sensible and economic approach to optimising recovery rates would therefore be to adopt a combination of all waste recovery options.

2.2 INTEGRATED WASTE MANAGEMENT

When considering alternative options to landfill, most people automatically think material recycling to be the only option. For some materials such as metals for example, this is probably the only choice available. However, with plastics there is more than one alternative. For a number of years the APME has championed the adoption of an integrated approach to waste management [22]. This policy, or strategy, which has been emphasised in many reports and studies [2,4,6,10,11,14,22-25], encompasses an optimal balance of technical, environmental and economic factors in order to ensure highest total recovery in the most economically sensible way. A model of plastics recovery options is illustrated in Figure 2.2.

2.2.1 Prevention or Reduction at Source

The first option for integrated waste management is not to create the material to become waste in the first place [26]. The aim of reduction at source is in minimising the volume of potential waste at the production stage whilst maintaining the quality of the product. A major contribution of source reduction is the constant redesign and innovation of products, which helps manufacturers to use less material to achieve more [27] without compromising the quality of the product.

One of the most graphic examples of source reduction is that of plastics packaging. Statistics show that today's plastics packaging is up to 80% lighter than it was 20 years ago [28]. Another excellent example of reduction at source is that of the laptop computer. This innovative device has only seen success due to the application of high quality engineering plastics enabling it to achieve substantial reductions in size and weight [16], bringing benefits in the saving of resources as well as convenience for the consumer.

2.2.2 Re-use

Re-use of plastics products is a popular concept as it extends the life of a product, thus delaying waste and at the same time preventing more plastic from becoming potential waste. However, this can only be successful if the environmental and economic costs do not counter the material savings. One of the most successful re-use items in Europe is the plastic carrier bag [28]. One UK retailer was able to reduce plastics bags usage by 60 million per year, equivalent to 1000 tonnes of plastics, by offering a penny refund on every re-used bag. Also, many electrical and

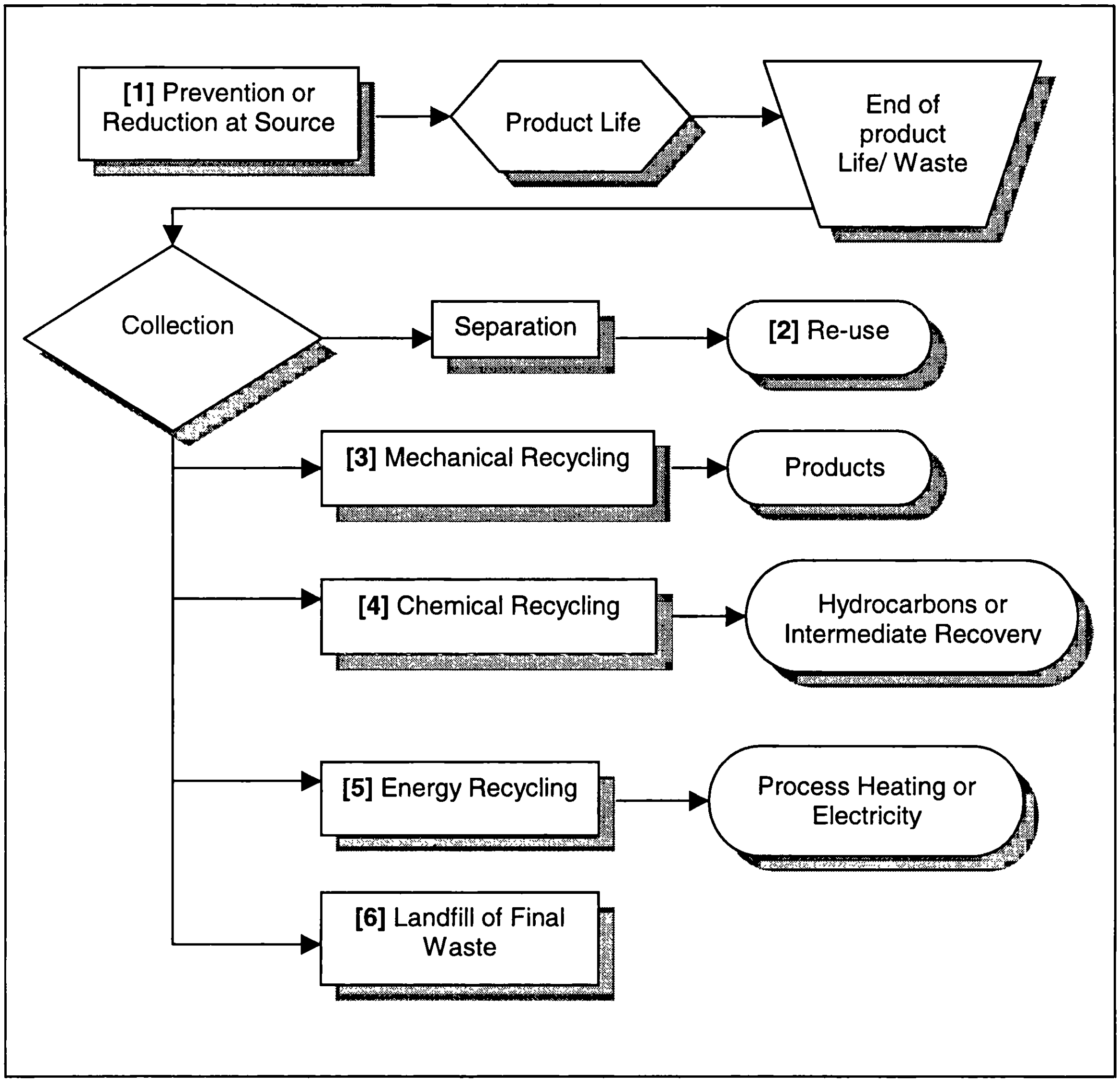


Figure 2.2 Model of Integrated Waste Management of Plastics Waste

electronic items that have been discarded may be refurbished and reused, diverting the product from the waste stream and giving it a second life, which thus saves on potential waste through buying a new product. However, it must be remembered that within the E&E sector the rapid pace of innovation and development often means that the latest models replace the older ones, thus shortening product lifespans in particularly innovative sectors such as IT and telecommunications. Although many specific parts from this type of E&E equipment could be reusable, the pace of development will more than likely render such items obsolete, which often means that re-use is not always feasible [16].

2.2.3 Mechanical Recycling

Mechanical recycling is the preferred recovery technique for plastics waste so long as plastics recyclate can replace virgin plastics on a ratio close to 1:1 [6]. High quality recyclate is usually only achieved by recycling clean, homogeneous plastics waste. Contaminated mixed waste is not ideal for recycling as the cost of intensive cleaning and separation cannot be justified in terms of environmental or economic gain. Therefore in some sectors such as distribution and agriculture, recycling rates are higher than other sectors, due to the quality and availability of clean homogeneous waste [21]. In 2000, the amount of post-use plastics waste recovered in Europe through mechanical recycling was 17% higher than in 1999, which pushed overall mechanical recycling rates up to 11%. This increase was attributed to increased collection rates in several countries as well as relatively high process of virgin plastics in that year [14].

However, despite mechanical recycling being the favourable option for plastics waste, a study has shown that to increase mechanical recycling rates of plastics from plastics packaging waste to a rate above 15% would have actually no major benefit in terms of eco-efficiency [11]. Economic costs would probably increase quite significantly but environmental impacts would remain broadly similar. Reasons for this include the imbalance between collectable waste and potential end-markets as well as the availability of large quantities of mixed plastics waste [14], where energy consumed in separating and cleaning clearly outweighs the environmental gain of mechanical recycling. Nevertheless, there are sectors such as the electrical and electronic sector that are still in their infancy regarding recovery of waste plastics. As similar studies have not yet been conducted for this sector, it is unclear what the optimum recycling level for this sector would be. However, there is a potential supply of relatively uncontaminated high quality plastics waste from this sector, and because more will be required to be recycled when legislation for this sector comes into play, this could contribute to mechanical recycling rates in the near future.

Figure 2.3 illustrates a typical mechanical recycling process for waste plastics, each step of the process being essential to the quality of the recyclate. Following collection the plastics waste is sorted and separated into homogeneous material, as mixed plastic waste usually reduces recyclate quality. For sectors such as plastics packaging, where there are large amounts of mixed plastics waste due to extensive food contact applications, the difficulties and energy consumed in separating such waste into homogeneous fractions clearly outweigh the environmental gain of mechanical recycling [25]. Other recovery methods would therefore be more suitable, although various facilities have been set up and there appears to be some success in the collection and recycling of plastic bottles. As long as such items can be separated from the main waste stream, mechanical recycling is a viable option. Identification methods can be kept fairly simple as there are generally just two or three plastic types used for this application [29]. However, separation methods for the E&E sector are not always so simple despite being a source of higher quality waste streams. As well as dismantling difficulties, recyclers are faced with the task of identifying a broad range of plastics types and their blends, many of which contain additives such as flame retardants. These pose an additional problem as due to impending legislation, it is imperative that plastics containing certain flame retardants are identified, separated and not recycled. Therefore, with greater demands on the capabilities of identification equipment, a higher level of technology is needed. A considerable amount of research is being undertaken in this area and different types of identification and separation technologies are discussed in Section 2.5.

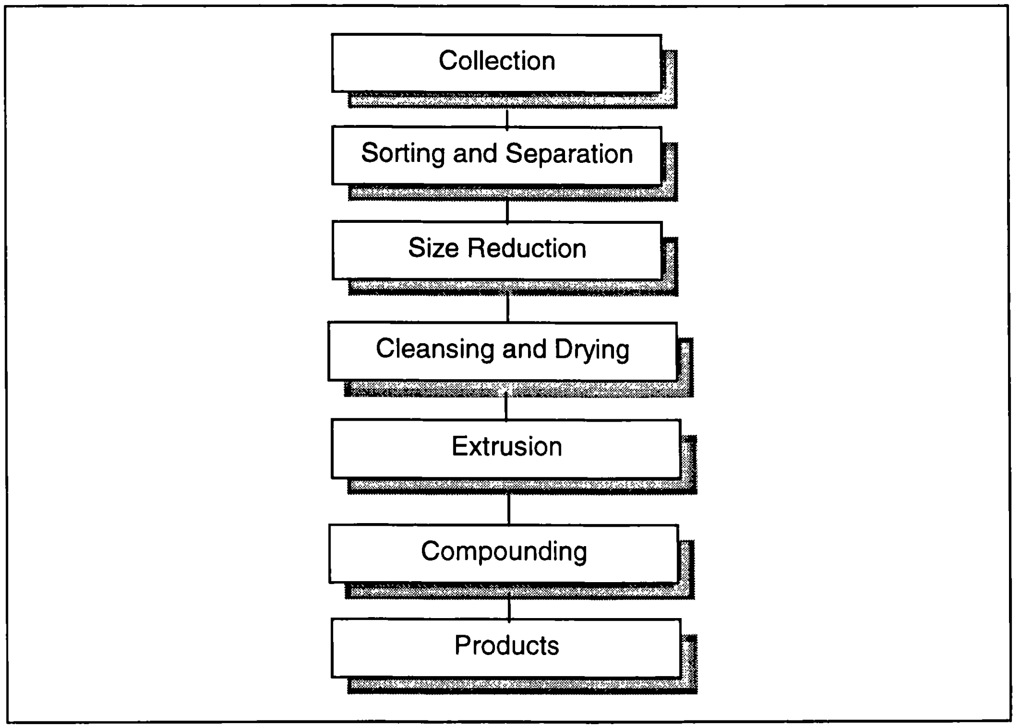


Figure 2.3 A Typical Plastics Mechanical Recycling Process

Size reduction is necessary for any subsequent processing and usually occurs before the cleansing process. Plastic waste that is highly contaminated, as is usually the case with most plastics packaging waste, requires extensive washing which is both time and energy consuming, and the costs of this part of the process often outweigh the environmental gains of mechanical recycling. Plastic waste from the E&E sector is usually fairly uncontaminated and so washing may be at a minimum. Following cleansing, it is important that the granulated plastic is dried thoroughly before commencing the thermal process in order to reduce the possibility of water vapour bubbles forming in the recyclate during processing.

Extrusion and compounding are usually the final parts to a mechanical recycling process, resulting in a compounded recyclate that is ready to manufacture into products. The extruder is the centrepiece of any recycling plant and is an important factor regarding the economic viability of the plant, as it is commonly the biggest energy consumer. The quality and homogeneity of the recyclate are heavily influenced by the geometry of the extruder screw and as a result, recycling screws are designed to be as gentle as possible on the material being processed [30]. Following extrusion the recyclate is compounded or pelletised, making it ready for distribution to manufacturers.

2.2.4 Chemical Recycling

Chemical or feedstock recycling, which is a process exclusive to plastics, is understood as the conversion of plastic materials into low molecular products [31]. The petrochemical feedstock can be repolymerised into plastics [32], converted into commercial chemical compounds or used as fuels [33]. Table 2.1 is a brief overview of the main types of chemical recycling processes.

Pyrolysis is a thermal treatment under inert conditions that causes the degradation of macromolecules into smaller fragments. This process can generate monomers or products similar to crude oil, which can either be repolymerised or be reused in the original market [31]. Gasification involves cracking the waste plastic in air under high temperatures and pressures to produce a synthesis gas (normally comprising carbon monoxide and hydrogen) that can be used in the production of methanol or ammonia or can be converted into heat and electricity [31].

Hydrogenation is the depolymerisation of plastics either alone or with heavy crude oil, followed by hydrocracking using molecular hydrogen at higher pressures, and temperatures around 500°C. Products include hydro-bitumen and syncrude, which can be converted further into chemical raw materials.

Table 2.1 Chemical Recycling Processes [31]

Process	**Reaction Conditions**	**Products**	**Comments**
Pyrolysis	400-900°C	Wax, oil, gas, energy	Mainly pilot plants
Gasification	~150 bar ~1600°C	Synthesis gas, electrical energy	Co-gasification with municpal waste, coal, heavy oil
Hydrogenation	~200 bar 500°C	Hydrogenation bitumen, syncrude	KAB coal/oil plant: -25% mixture with vacuum residuals, capacity appr. 40,000 t/a
Reduction in a blast furnace	~2000°C	Pig iron, furnace gas	Bremner Stahlwerke site: 40,000 t/a projected
Solvolysis	Depends on reactants. Higher pressure ~200°C	Mainly monomers	Small plants at producer or manufacturer sites

A variant of feedstock recycling is to use plastic waste as a reduction agent in the blast furnace. At 2000°C the polymer evaporates instantly, creating gases essential for blast furnace reduction, thus saving oil [31]. This process is an effective way of recovering metals mixed with plastics that are otherwise difficult to separate, although there is probably a lack of pollution control with this method and it is likely to produce more dioxins than incineration. However, research has also suggested that a safe way of recovering PC scrap is as feed stream in non-ferrous smelting plants [16]. Solvolysis is a general expression comprising of the following chemical recycling processes; glycolysis, methanolysis, hydrolysis, acidolysis and alcolholysis. This is basically the reaction of waste plastics with different reaction agents such as methanol or ethanol for example, and at higher pressures and temperatures, although this varies according to the reactant. Products are mainly monomers that are repolymerised.

Feedstock recycling has the potential to boost plastics waste recovery levels and still produce high quality end products, due to the possibility of using mixed plastics waste such as small lightweight packaging that is not ideal for mechanical recycling. However the amount of waste treated this way has not changed significantly since 1997 [6]. This is probably due to economic considerations such as the initial capital investment as well as the necessity of a constant supply of the quantity and quality of plastics needed for this process. Currently feedstock recycling only recovers waste plastic from municipal solid waste [6] although research into different feedstock recycling technologies is continuing.

2.2.5 Energy Recycling

A key recovery option for plastics that is also not possible with many other materials is energy recovery. Through the combustion of plastics waste, latent heat can be released and recovered to generate power and energy for domestic and industrial users, sparing other finite fossil fuel resources. Because the basic raw material of plastics is derived from oil, plastics waste has a calorific value often greater than fossil fuels such as oil and coal. For example, just one plastics yoghurt pot contains enough energy to power a light bulb for one hour and the amount of waste in one year from the average dustbin, contains enough energy to heat 3,500 showers or power 5,000 hours of television viewing [34]. However, all too often, too much of this valuable resource is lost to landfill (although the incineration of waste without using the energy produced is just as great a waste of resources). Energy recovery alongside material recycling has a vital role to play in diverting plastics waste from landfill and maximising environmental gain [16]. In the E&E sector, energy recovery is a key recovery option for items such as small appliances for example, that may have many small parts that are difficult to dismantle and are therefore not appropriate for mechanical recycling [16]. In terms of economic and environmental impact, studies have also shown that the combination of 15% material recycling combined with 85% energy recovery appear to be the most eco-efficient [11].

Energy recovery is extensively used in countries such as Switzerland and Denmark where up to 74% of waste is diverted from landfill in this manner. An example of energy from waste in action can be seen in the city of Gothenburg, Sweden where more than 70% of the city's heating is provided by waste incineration [6]. In addition to saving fuel, energy recovery reduces the volume and weight of waste by 70 and 90% respectively, and turns it into a safe inert residue, which can then be landfilled [34]. However the safety of this residue is still highly debated as any heavy metals in the plastics will probably end up in the ash. Also, in the past there has been a certain degree of animosity towards the incineration of plastics, which can be attributed mainly to the poor environmental performance and emissions produced from old incinerators. However, emission levels from today's incinerators have been reduced so significantly that energy recovery has now been endorsed as an environmentally sound option [6].

2.2.6 Landfill

The landfilling of plastics waste is the last resort. Although waste disposal by landfill currently has the lowest economic costs despite the imposition of landfill tax, the environmental costs are the highest [11]. Only when all of the above recovery options have been used to divert waste in the most economically and environmentally efficient way will landfill site usage be at a minimum.

2.3 RECYCLING LEGISLATION

There are several European Union legislative directives attempting to reduce the volume of waste being landfilled, which are aimed at several different sectors including packaging, automotive and electrical and electronic. Not all of these directives are in force as of yet, however they are imminent, which is why it is important to be prepared for the recovery targets that will soon be legal requirements. As previously stated, other sectors such as agriculture and distribution do not yet need the same legislative attention as substantial quantities are already being recovered [6].

2.3.1 Directive On Packaging And Packaging Waste

The Packaging and Packaging Waste directive deals with plastic from all packaging activities, and such a considerable proportion of this waste consists of plastics packaging, usually from food applications. The purpose of the directive is the prevention and reduction of packaging waste through principles of re-use, recovery and recycling. The directive was entered into the Official Journal of the European Communities in December 1994 [35] and since that time, there have been a number of targets and guidelines mandatory to each member state.

Targets include a minimum recovery rate of 50% by weight of all packaging waste as well as a recycling rate of 25% by weight. There is also a minimum recycling target of 15% by weight for each different packaging material i.e. plastics, glass, paper etc. These initial targets were to be met by the year 2001 [36,37]. Once the initial target deadline was met, the directive specifies that target levels would be subject to review by the European Council (EC), with the intention of increasing recovery and recycling rates. These targets have been reviewed each year since 2001 and targets for 2002 were increased to 59% recovery and 19% material specific recycling [38]. However targets in the UK for 2003 are unclear and will remain at the 2002 level of 59% overall recovery as new EU packaging directive targets and deadlines for the coming years remain undecided [39,40]. Over the long term, targets could be set to a maximum recycling level of 80%, with minimum targets for specific materials to be between 15 – 60% depending on the material. These targets would not have to be met until 2008, however it appears that the directive is currently awaiting a parliamentary reading to finalise such details [38].

Current guidelines within the directive also encourage the use of recycled materials from packaging waste to be used in the manufacturing of packaging, as well as the design of packaging to take into account the subsequent recyclability and recovery of the material. The directive stipulates the importance of the provision of return and collection facilities and specifies that packaging material should be labelled in accordance with a marking system in order to facilitate separation on recovery. Figure 2.4 is an example of the type of coding system used by the Society of the Plastics Industries Inc. (SPI) in the US that can be used on packaging materials [41]. The EC has adopted a similar system, with numbering as follows [35];

1-19: plastics
20-39: paper and cardboard
40-49: metal
50-59: wood
60-69: textiles
70-79: glass

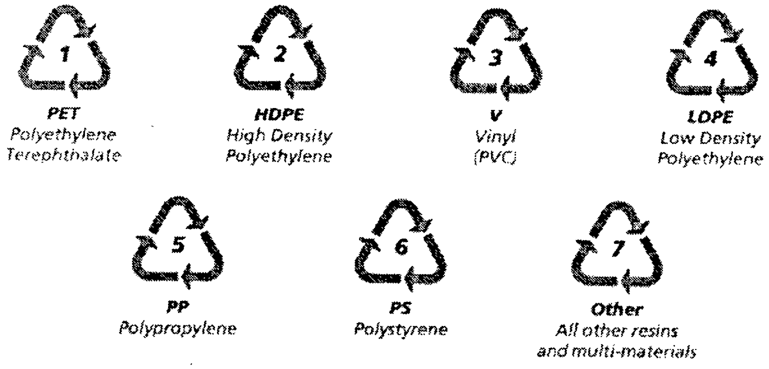


Figure 2.4 SPI coding system for identification of packaging materials.

In 1999, seven countries achieved recovery rates of around 50% and above, these being Denmark 85%, Sweden 79%, Netherlands 73%, Germany 70%, Austria 66% Belgium 55% and France 49% [6]. Despite being one of the highest plastics consumers in Europe, the proportion of plastics packaging waste recovered by the UK, at 17% was one of the lowest. With just 11% being mechanically recycled, the UK is not even meeting the minimum recycling target rate of 15% [6]. It is interesting to note that countries such as Greece, Portugal and Ireland have actually been allowed a lower target of 25% minimum recovery due to the geographical nature of these countries i.e. the number of small islands and the presence of rural and mountainous areas [35]. By 1999 Greece was almost at this target at 21% recovery, whereas Portugal at 14% and especially Ireland at 4% [6] still need to do more to attain this. Therefore although some countries are recycling well above the minimum requirements and others are improving their recovery rates, challenges still remain for a number of countries to meet the minimum recycling rate of 15%.

It has been found that plastics packaging recovery is most successful when individual streams are targeted such as plastic bottles [6] or industrial or distribution films [14]. However, it still remains clear that the optimum recovery level for packaging waste will only be achieved through a combination of recovery options.

2.3.2 End Of Life Vehicle Directive

The End of Life Vehicle (ELV) Directive covers legislation for the automotive sector. It was entered into the Official Journal of the European Communities in October 2000 [42] and is one of the most recent recycling directives to come into play. The aim of this directive is the prevention and reduction of waste from vehicles through re-use, recovery, and recycling, while improving the environmental performance of the vehicle life-cycle.

In order to prevent waste from ELV's, the directive has stipulated that future vehicles be designed with the view to easier dismantling and recyclability, as well as to integrate an increasing amount of recycled material in vehicles. Manufacturers are advised to use less hazardous materials in vehicles and vehicle components containing lead, mercury, cadmium or hexavalent chromium are to be phased out by 2003. Facilities are also to be set up by member states for the collection and treatment of ELV's with the view that eventually owners will be able to return them free of charge [40]. Recovery targets (that are currently on average 75% per vehicle by weight) are to increase to 95% [43], although this is not expected to happen overnight. The directive aims to increase minimum recovery rates to 85%, and reuse and recycling rates to 80% by average weight per vehicle, by the year 2006. This will subsequently be increased to 95% recovery, and 90% reuse and recycling by the year 2015. In general, vehicles put on the market following the adoption of this directive will have to be recoverable and recyclable in compliance with such targets [42].

The average vehicle is comprised of 70.2% ferrous metals, 21.1% non-metals and 8.7% non-ferrous metals by weight [44]. Plastics account for approximately 9.3% by weight [45] and the average car may typically contain more than 20 plastic types [44]. The volume of plastics used in cars is increasing and it has been estimated that without plastics, cars today would be at least 200 kg heavier, resulting in increased fuel consumption [45].

Currently, on reaching its end of life, about 75wt% of the average vehicle is recycled which is believed to be the highest recycling rate in durable goods [44,46]. However, this proportion is generally limited to the metal content of the vehicle such as steel, iron, zinc, copper and aluminium. The remaining proportion consisting of a mix of materials from shredder residues such as plastics, rubber, glass, textile, paint, oils and lubricants, paper and cardboard, and these are generally landfilled [44,46]. If recovery levels are to be increased to 95%, this will only happen if a proportion of the shredder residue is recycled instead of landfilled. Figure 2.5 illustrates the proportion of materials found in the shredder light fraction of an average car, where almost a third of the shredder residue consists of plastics. Therefore one solution to increase recovery levels in end of life vehicles that comply with legislation would be through the recovery of the plastic fraction. Although larger parts such as bumpers provide good quality single type plastics and are therefore suited to mechanical recycling, it is the smaller components, especially those encasing other materials that are generally difficult to recycle due to dismantling difficulties as well as problems with identification [45]. Feedstock recycling offers the advantage that mixed and soiled plastics may be used without sorting, and may also tolerate a level of contamination unacceptable to mechanical recycling [44]. However, it must be recognised that feedstock recycling is not a low-cost option and must be used as part of a combination of recovery options in order to ensure maximum environmental gain at lowest cost to society.

The plastics industry has recognised the need to enhance the recovery of automotive plastics in order to meet legislation targets and new cars are being designed with recovery in mind. However, for older cars that have not been made with such environmental considerations, there is a considerable amount of research in areas including ways of avoiding or reducing shredder light fraction, identification of different plastics [44], as well as novel feedstock recycling techniques [47]. It is such research that will hopefully play a part in overcoming many of these barriers to recycling in the near future.

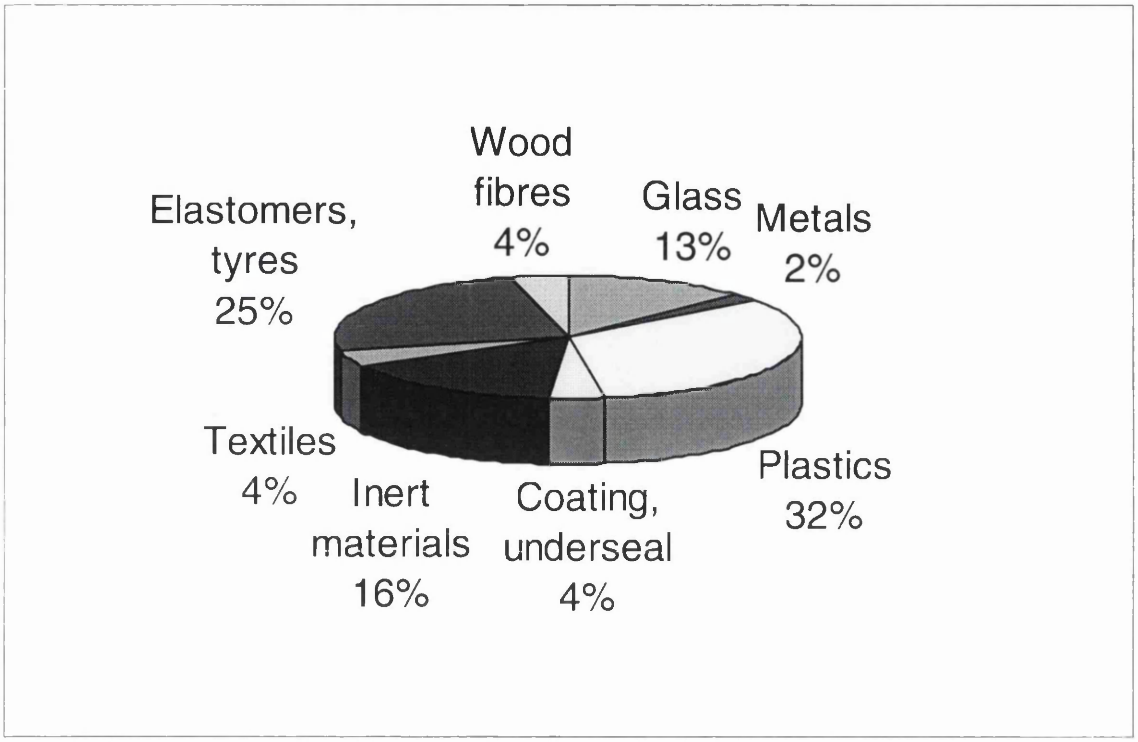


Figure 2.5 Shredded Light Fraction in a car [44]

2.3.3 Legislation For The Electrical And Electronic Sector

The production of electrical and electronic equipment (EEE) is one of the fastest growing manufacturing sectors in the world [48]. This is mainly due to the acceleration of technological innovation and market expansion, and new applications of EEE are increasing significantly. An effect of such development is seen as an increase in the volume of waste electrical and electronic equipment (WEEE). The growth of WEEE is about three times higher than the average growth of MSW and is a complex combination of materials and components, some with hazardous content [48]. If not treated and managed properly, these substances may become harmful to the environment. In order to minimise the potential environmental effects of such a growing waste stream, legislation has been drafted by organisations including the European Commission.

Legislation in the electrical and electronic sector started out as just one potential directive called the WEEE directive. The main aims of this directive were to protect soil, water and air from pollution caused by WEEE disposal, to avoid the generation of waste and to reduce the harmfulness of WEEE while preserving valuable resources such as energy. This proposed directive suggested recovery, recycling and re-use targets for such equipment, set restrictions on hazardous substances contained in such waste, as well as proposing guidelines for manufacturers with the view to designing more recyclable products. However as the WEEE directive developed it has now become three separate directives which deal with each of the above aspects in the details necessary for each one.

2.3.3.1 Directive on Waste from Electrical and Electronic Equipment

The 'Proposal for a Directive on Waste from Electrical and Electronic Equipment' (WEEE) was adopted by the European Commission in June 2000 and started the parliamentary process in Autumn 2001 [49], becoming part of European law at the end of 2002. The aim of the directive is the prevention of waste electrical and electronic equipment by requiring end of life equipment to be collected for recovery, recycling and re-use, and by 1 January 2006 aims to be collecting on average 4kg of WEEE per inhabitant per year from private households. The main targets include minimum recovery rates of 70-80wt% and minimum material and substance recycling and re-use rates of 50-75wt% for some materials. For IT equipment, which includes computer equipment, the minimum targets are 75wt% materials recycling and 65wt% material re-use [49]. In order to meet such targets, some countries will have to drastically increase recycling activities of waste from this sector. The WEEE directive also states that private households should be able to return such waste free of charge and it will be the responsibility of producers to finance the collection, treatment, recovery and environmentally sound disposal of WEEE from households. Such disposal of WEEE from other sources however, is to be agreed between producers and users of such equipment. Part of the directive requires certain substances to be removed from separately collected WEEE, including plastics containing brominated flame retardants [49], although the disposal of hazardous substances is now covered in greater detail in a separate directive.

2.3.3.2 Directive on the Restriction of the Use of Certain Hazardous Substances in Electrical and Electronic Equipment

The 'Draft Proposal for a Directive on the Restriction of the Use of Certain Hazardous Substances in Electrical and Electronic Equipment (RoHS)' was originally part of the WEEE directive and proceeded through the parliamentary process in tandem with the WEEE directive. The aim of this directive is to restrict the use of hazardous substances in electrical and electronic equipment (EEE) by phasing out the use of certain substances by the year 2008. Materials that will need to be substituted in EEE include lead, mercury, cadmium and hexavalent chromium as well as PBB (polybrominated biphenyls) and PBDE (polybrominated biphenyl ethers) flame retardants found in plastics [50]. The production of PBBs has already ceased [51], however out of the different types of PBDE's, Penta-BDE is expected to be phased out by the end of 2003 as a result of the widespread occurrence of its constituents in the marine environment [50]. Although not yet banned from use at present, Octa-BDE and Deca-BDE are currently under assessment [52].

2.3.3.3 Directive for Electrical and Electronic Equipment

The 'Draft Proposal For An Electrical And Electronic Equipment Directive (EEE)' is being developed in order to minimise the impact of products over their whole life cycle. Although it is still at a very early stage, the directive covers aspects of a product's life cycle including designing with a view for refurbishing, re-use and recycling. It also makes provision for production considerations and the incorporation of recycled materials in new products, product use, and the ease of disassembly at end of life, while focussing on the need to minimise waste and energy used during all aspects of a product's life cycle. The directive also requires correct labelling of components and as well as encouraging constant innovation of products in order to achieve continual technological efficiency [53].

Now that the WEEE and RoHS directives have been passed as European law, member states including the UK have until August 2004 to transpose these directives into national law [54]. However if the UK is to meet the tough recovery and recycling targets of 80% and 75% respectively, a lot of work is yet to be done and it is thought that current targets suggest that the amount of WEEE that will have to be collected over the next few years is a tenfold increase in the amount that is recycled and reclaimed today [55]. It is thought that local authorities will be used to collect WEEE (at the expense of producers of course) [54], and one forward thinking local council has just recently set up the first WEEE recycling facility [56]. Initially the plant will be set up to take in fridges, freezers, washing machines and other white goods, however, if the scheme proves successful, then other forms of WEEE can be recovered, such as computers and IT equipment for example [56]. This is not the only venture currently taking place and three leading companies in their respective sectors, Endeva, Biffa and European Metal Recycling (EMR), have joined forces to create the working venture Transform [57]. The aim of this venture is to meet WEEE targets by building on each company's existing networks. Endeva is to provide consumer take back, Biffa will collect from businesses and retailers and EMR will recycle the waste [58].

Of course, despite these positive steps some products, especially IT equipment, are up against various barriers and successful target attainment depends on the ability of recyclers to overcome such obstacles. One obstacle that researchers have recognised is that information on dismantling, recycling and other attributes is inadequate [59] and that the key to the provision of such information is the need for improvement of relationships between the designers, manufacturers and the end-of-life equipment managers [60]. Plastics form approximately 30% of E&E products and this is an area requiring attention. It is believed that to recycle such plastics, the overall recycling efficiencies of E&E products would need to be increased. However in order to accomplish this, there first needs to be an improvement in the identification of these plastics, which has been recognized as an existing recycling obstacle and also the first stage of developing better mechanisms for end-of-life management. Until this and other barriers are overcome, it has been concluded that it will be uneconomical to recycle such plastics [59]. If these and other issues are not dealt with in the near future, then such problems with identification and other barriers could impede the development of the recovery activities needed to ensure compliance with legislation for the E&E sector once it becomes part of UK national law [61].

2.4 BROMINATED FLAME RETARDANTS

2.4.1 The Need For Flame Retardant Plastics

Organic polymers are essentially based on chains of carbon mainly with the addition of hydrogen, and also with quantities of other elements such as nitrogen, oxygen, sulphur, fluorine and chlorine [62]. When exposed to sufficient heat, all of these polymers undergo thermal degradation, which involves the breaking of bonds in the polymer backbones. This generates lower molecular weight products that are fairly volatile and if the thermal degradation occurs in the presence of oxygen, other products may also be formed producing a gaseous mixture that is now inherently flammable, thus providing more fuel in a fire situation. Although some polymers are more stable than others due to structural differences, almost all polymers will ignite and burn at temperatures in the range of 350 – 450°C.

The essential requirements for a fire are heat, fuel and oxygen [63]. A fire needs the presence of all three and the removal of any one of the three elements results in the fire being extinguished. A fire is said to develop in three stages; fire initiation, fire propagation, which involves flame spread and flashover where enough heat is generated that all combustible material bursts into flames [52], and a fully developed fire [63]. As well as hazards concerned with the combustion or burning part of a fire, there are also concerns as to the smoke and toxic gases that are produced as a result of a fully developed fire. Fatalities may occur due to inhalation of such gases, and suffocation due to lack of oxygen. The corrosivity of the acid gases released in a fire has also been identified as major problem inherent in electrical and electronic components [62].

Over the years plastics users have demanded progressively improved fire performance [64]. The flammability of polymeric materials is a major concern, especially in applications such as E&E equipment, that have seen an increase in amount of plastics used, and where electricity is a primary fire hazard [52]. As most polymers are flammable in their pure form (except those containing significant amounts of chlorine and/or fluorine) the flammability resistance of combustible polymers may be enhanced by using additives known as flame retardants [65].

Flame retardants are additives that reduce the flammability of a polymer by restricting the supply of one or more of the three elements required for a fire (heat, fuel and oxygen). All flame retardants function during the early stages of a fire, however it must be remembered that no amount of flame retardant can make an organic polymer totally fireproof and virtually all retarded polymers will ignite during extremely severe temperature conditions and high oxygen concentrations [62].

The role of the flame retardant is to reduce flammability by interfering with the chemistry or physics of the combustion process. Owing to the wide variations in the chemical compositions of commercial polymers, there is no universal flame retardant that is applicable every time, as the flammability of plastics can vary considerably. Therefore there exists quite a variety of compounds that are effective flame retardants, each one reducing the flammability of polymeric materials in different ways. Their various mechanisms are listed below [62]:

1. **Inhibition of vapour phase combustion:** Most polymers decompose at certain temperatures producing volatile low molecular weight products, which are highly combustible. This type of flame retardant will act by producing decomposition products at the same temperature that the polymer decomposes, which react with the products of the polymer rendering them less volatile and thus inhibiting the combustion process. Organobromine and organochlorine flame retardants work in this manner by emitting hydrogen halide gas during decomposition. This gas readily reacts with high energy H and OH chain branching radicals producing a low energy radical that is incapable of propagating the oxidation process. This helps to decrease the burning rate and extinguishes the flame.
2. **Dilution of volatile products:** This type of flame retardant works to produce an inactive diluent, commonly water, at the same temperature of polymer decomposition, which slows down the reactions of flame. This does not result in the emission of any toxic or corrosive gases. Compounds such as alumina trihydrate and magnesium hydroxide are well suited to this application as both produce high proportions of water during breakdown. A drawback to these systems however is that high loadings are needed to obtain a reasonable degree of flame retardancy.
3. **Removal of heat of combustion:** This flame retardant reacts, decomposes or changes state endothermically, which absorbs heat, removing it from the fire cycle so that combustion will slow down or stop. Several flame retardants have a breakdown reaction that releases water in an endothermic reaction resulting in dilution as well as heat removal. Both alumina trihydrate and

magnesium hydroxide reduce flammability in this way as the breakdown process to release water is a highly endothermic reaction.

4. **Promotion of char forming reactions:** This flame retardant is involved with the alteration the mechanism of oxidative thermal degradation of the polymer. Instead of the emission of volatile products, low energy solid state reactions are promoted, which lead to the carbonisation of the polymer and a carbonaceous char on the surface that protects the polymer underneath. Many phosphorus and boron additives behave in this way.
5. **Formation of a protective coating:** As opposed to forming an insulating char barrier, some compounds may act as a flame retardant by forming a thermal shield on the polymer surface without increasing the char content. The thermal shield insulates the polymer and slows down the degradation process and subsequent formation of volatile gases. For example, zinc borate forms a glass-like coating on the plastic surface.
6. **Smoke suppressants:** As smoke is one of the hazards associated with polymeric materials and has been the cause of death in many cases, an additive that reduces the smoke generated of a material is beneficial. Char forming flame retardants tend to be good smoke suppressants as they increase the amount of char at the expense of the emission of volatile gases that could be potentially toxic. The production of smoke has been a concern with PVC, which emits a considerable amount of smoke when burning. However compounds based on iron, tin and zinc act as smoke suppressants in PVC by increasing the amount of char and reduces the emission of volatiles.

Almost all flame retardants and smoke suppressants that are commercially available today are based on the following elements; aluminium, antimony, boron, bromine, chlorine, iron, magnesium, molybdenum, phosphorus and tin [62]. Most flame retardants that were used up until the 1970s mainly reduced the ignitability of the polymer and the surface spread of the flame. However since then, more attention has been focussed on flame retardants that impede the rate of heat release and reduce the emission of smoke and toxic gases as these were significant causes of fatalities in the outbreak of a fire [17].

2.4.2 The Role of Bromine as a Flame Retardant

Bromine is a chemical element that belongs to the group called the 'Halogens' along with chlorine, iodine and fluorine. These elements are found in nature and are generally reacted with metals to form salts [51]. Bromine is mainly found in seawater and salt lakes and despite being used in many different applications, one of the largest uses is in flame retardants [52].

Brominated flame retardants (BFR's) are a family of approximately seventy-five substances all with different properties, characteristics and performance, with bromine being their only common factor. Along with chlorinated flame retardants, BFR's are said to act by a flame poisoning mechanism in the vapour phase, by producing the gas hydrogen halide during their decomposition. Although the exact mechanism is not fully understood, it is believed that the halide gas produced interferes with the flame reactions by producing a low energy radical, which reacts with oxygen to produce water. This reduces the rate of heat transfer at the polymer, decreases the burning rate and leads to extinction of the flame [62]. Halogenated flame retardants are often used together or with other synergist compounds such as antimony trioxide (Sb_2O_3). On its own, Sb_2O_3 is not an effective flame retardant, however in combinations with halogenated flame retardants, it acts to reduce the amount of halogen needed to impart a given level of flame retardancy. The actual flame retarding mechanism is complex and not entirely understood [62]. Some of the main types of BFR's include TBBPA (tetrabromobisphenol – A), HBCD (Hexabromocyclododecane), PBB (Polybrominated biphenyls) and PBDE's (polybrominated dephenyl ethers) of which there are three main types; Deca-BDE, Octa-BDE and Penta-PDE.

The main advantage of BFR's is that they are very efficient and only relatively small quantities of product are needed in a material in order to provide the highest level of fire resistance [51]. BFR's are usually present at a loading of 10-20% in plastic compositions in order to pass high standards of flame retardancy [66]. In order to achieve the same level of fire protection, higher quantities of other products would need to be used, which not only will increase production costs, but can have effects on material quality. BFR's not only keep down production costs whilst maintaining the highest fire protection standards, they also allow a plastic resin to retain its durability and other properties during recycling. In certain plastics such as ABS and HIPS, there are currently no cost-effective alternative flame retardants that can provide good flame retardancy and good mechanical properties [52].

More than half of BFR production is used in the E&E sector, the major proportion being used in equipment housings, for computer monitors and television sets for example. The increased use of electronic equipment in the home or at work means that BFR's in plastics contribute greatly to reducing the risk of fire outbreak and the improvement of fire safety [51]. However, despite excellent fire retardant properties, the main disadvantage of halogenated flame retardants, including BFR's, is that they tend to emit more smoke than the untreated polymer formulations, a part of which is the corrosive hydrogen halide [62].

2.4.3 Issues with Recovery and Legislation on Brominated Flame Retardants

Brominated flame retardants currently provide the most efficacious and cost-effective means of flame retardancy in the plastics applications in which they are used [67]. However, there are concerns that some of these flame retardants have the most environmental impact while performing their action or when burned during the incineration of plastic waste [68] and have been named as one of the most environmentally problematic substances contained in EEE [48]. Current waste management practice does not adequately deal with the environmental risks associated with this waste stream and more than 90% of WEEE is landfilled, incinerated or recovered without any pre-treatment.

This growing waste stream of WEEE has become a concern in many countries and the objective of the most recent directive is to increase the recycling and recovery of WEEE in order to reduce the amount going to landfill. The directive on WEEE also includes the separation of plastics containing BFR's prior to recycling or other means of disposal [69], and it will require the eventual phasing out of BFR's due to concerns that some flame retardants form highly toxic and potentially carcinogenic brominated furans and dioxins during combustion [68]. However, some reports into the toxicity of BFR's have concluded that most BFR's are neither toxic nor harmful to the environment and that out of the commercially available seventy-five BFR's only two are of recognised concern to the environment [51].

The RoHS directive, which has been brought out in tandem with the WEEE directive, is now only specifying that these two BFR's, Penta-BDE and PBB, will be banned from the production of new E&E equipment as of January 2006 [69], although

PBB production actually ceased in May 2000 and is no longer used in E&E equipment [52]. Reasons for banning these particular BFRs are due to conclusions drawn from a number of studies. Various scientific observations have indicated that PBDE's may act as endocrine disrupters and have shown effects on reproduction and tumour formation on the liver. PBB's are believed to be equally as toxic [48]. Neither uptake nor degradation of PBB's by plants have been detected, however, in contrast, they are easily absorbed by animals either through absorption into the blood on exposure, or by ingestion of fish that absorb PBDE's and PBB's from polluted rivers and lakes [70]. The presence of PBB's in arctic seals indicate a wide geographical distribution and studies have indicated that the concentration of PBDE's in human breast milk has been rising exponentially since the 1970's [71].

However, although this recent legislation involves banning such substances from new E&E equipment, the waste plastics will still contain such substances, and it could be another fifteen years before the flowback of plastics waste containing PBBs and PBDEs ceases [72]. Therefore unless it is possible to identify individual flame retardants, all plastics from WEEE containing BFR's will have to be treated as hazardous and will not be able to be recycled for reuse as new products, which could impede many countries from reaching the recovery targets set by this legislation.

It appears then, that in the current situation, any traditional disposal method of plastics containing BFR's is undesirable. Although the cheapest and what seems to be the only option, landfilling, is an undesirable means of disposal of plastics containing BFR's. No landfill site is completely watertight, so when substances including brominated flame retarded plastic are landfilled, PBDEs and PBBs may leach into the soil and groundwater, which may spread into the surrounding environment. As leaching of such compounds on a short-term scale is small, and the amount of leaching is relative to the degradation of the plastic, the question is whether the compounds will degrade before ending up in the leachate. However, as compounds such as PBB's are more then 200 times more soluble in landfill leachate than in water [48], long term diffusion of emissions over a wider release into the environment are highly likely. There is also the risk that in the occurrence of a landfill fire, polybrominated dioxins and furans can also be emitted [48].

The mechanical recycling of plastics containing BFRs is actually advantageous, as the presence of BFRs in plastics offer a high level of stability during the recycling process [69]. However, there is the concern that dioxins and furans from brominated plastics may also be generated during a recycling process, especially during the extrusion of plastics. The particular concern is that of the exposure to the PBDE's of personnel working in such an environment and various studies have demonstrated that workers in a recycling plant have significantly higher levels of PBDE's in the blood than in other work environments [73]. However, another study has concluded that these plastics may be processed at least five times before debromination occurs [74].

Disposal by incineration could also be considered undesirable because many studies have shown that there is the risk of generating extremely toxic polybrominated disbenzo dioxins (PBBD's) and polybrominated disbenzo furans (PBDF's) at low temperatures 600-800°C, and that such dioxin formation is maximal even at 300°C. However, data from MSW waste incinerators in the Netherlands did not show any significant relationship between dioxin formation and the bromine content of the waste [48] and other studies have also demonstrated that waste containing bromine can be safely incinerated to generate useful energy in an environmentally sound manner well within emission levels [52].

However, one option of BFR recovery that does not seem to have had any bad press as of yet is that of feedstock recycling. Tests have concluded that this would be an environmentally sound and feasible option for recovering bromine from plastics containing BFRs [75]. This would close the bromine loop and ensure the sustainability of bromine production as well as providing a solution for the diversion from landfill of BFR plastics from WEEE [62].

2.5 SEPARATION AND IDENTIFICATION OF PLASTICS FROM WASTE COMPUTER EQUIPMENT

In order to achieve the highest quality recyclate material from mechanical recycling, the waste plastics need to be homogeneous and clean. Previous work [17] has shown that casings from waste computer equipment can be any one of approximately ten different types of plastic. Aesthetically, many of these plastics appear very similar and would thus be difficult to distinguish and separate just by looking with the human eye. It could be possible to separate them according to markings put on individual casings by manufacturers, however as previous work has shown [17], not all casings are actually marked and the ones that are may not always be correctly so, and it is believed that an improvement in the identification of plastics would lead to greater overall recycling efficiencies for many E&E products [59]. There are many different ways of identifying different plastics types, from simple density tests to spectroscopic methods. For a mechanical recycling process to be as efficient and as economic as possible, the different waste plastics types need to be identified as quickly and as accurately as possible. Usually the faster, simpler methods are not so accurate and it is the slower more complicated ones that are. However, as plastics recyclers have identified the need for fast and accurate identification methods, technology has been developing to provide just that and it is now possible to obtain rapid plastics identification equipment for different waste streams.

As part of the legislation imminent for the electrical and electronic sector, certain hazardous substances are to be phased out and eventually banned from use. This includes plastics containing brominated flame retardants. Now, not only do recyclers need to be able to distinguish the different plastic types in order to recycle high quality material, they need to separate out those plastics containing brominated flame retardants from those that do not. As approximately 30% of plastics casings from computer equipment contain bromine, accurate detection is essential, otherwise either such plastics may be recycled and put back again into the production cycle or all plastics may have to be treated as hazardous until accurate detection methods are established. Therefore there is a considerable amount of research examining rapid plastics identification methods that will also detect other additives or elements present in such waste. In view of the lack of proper identification of plastics containing flame retardants, and the difficulty in distinguishing flame retardant plastic from ordinary plastic, most recyclers do not generally recycle plastics from WEEE. However as plastics identification technology develops hopefully this will change in the near future.

This section is a review on some of the many different methods that may be used for plastics identification and separation purposes, in order to illustrate the type of technologies available for this application and also the feasibility as to the ease of additive detection in such plastics.

2.5.1 Identification and Separation using Density

The sorting of plastics scrap into homogeneous material streams requires procedures that exploit the differing properties of plastics undergoing the process. One of the simplest properties to exploit is the difference in density between different plastics. Simple methods include the sink or swim method, froth flotation (a method that influences the affinity of bubbles for different types of plastic allowing them to float while the other sinks), the hydrocyclone or even a sorting centrifuge [76]. However, a common problem with separating plastics is that most have densities between 0.9 and 1.5g/cm^3 [77]. Plastics such as PVC and PET have such similar densities that it is not possible to separate them using just water. A way to solve this problem would be to use different wetting solutions for the sink or swim or froth flotation methods that would achieve selective separation by creating an affinity to one plastic and not the other [78].

Despite being one of the cheapest fairly rapid separation methods, it must be remembered that the presence of additives (especially heavier mineral fillers) will modify the densities of the plastics, giving poor results from density separation methods. As these additives cannot be detected anyway, these types of methods would not be suitable for plastics generated from waste computer equipment.

2.5.2 Identification and Separation using Electrostatic Properties

Plastics have a range of electrical properties and when there are differences between different plastic types, these can be used as a method of differentiation [79]. All plastics will have slightly different electrostatic charging; some more negative or positive than others and in principle plastics can be separated from each other by electrostatic separation. Table 1. shows the order of triboelectric charging of some common plastics.

The triboelectrification theory stipulates that when two materials come into contact with each other, an electronic transfer takes place from the surface of the one with the smaller work function to the surface with the greater work function, resulting in the material with the greater surface work function becoming more negatively charged [80]. The principle behind electrostatic separation techniques involves electrostatically charging the plastics and then exposing them to two high voltage electrodes that are either positively or negatively charged. The particles will be deflected to one or the other depending on their charge and laboratory experiments have concluded that it is feasible to separate mixtures of two different plastics in excess of 99% purity [80].

Table 2.2 Triboelectric series of some common plastics

PTFE	Negative Charging
PVC	
PP	
PE	
PS	
ABS	
PC	
POM	↓
PUR	Positive Charging

Electrostatics may also be used in the identification of plastics. The tribopen is one such device, developed by Peter Walker Systems, Wolfson Electronics and Southampton University for the Ford Motor company [81]. It is hand-held and about the size of a small flashlight. Although it cannot identify specific polymers, it can differentiate between two polymer groups by collecting and analysing the triboelectric charge generated when the tip is dragged across the surface of the plastic [79]. In order to ensure a correct reading it is probably necessary to know that the polymer tested is one of the two for which the tribopen is calibrated [82].

Japanese researchers have also developed a hand-held dielectric device for distinguishing between selected plastics. Instead of a pen-like instrument, this is in the form of a clamp equipped with a pair of electrodes and a potentiometer that measures the dielectric properties of the plastic clamped between the electrodes. The advantage of this device over the tribopen is that it is able to measure through paints and such contamination, as it is a bulk analysis technique rather than a surface analysis technique. However despite both of these devices being relatively cheap and easy to use, they are extremely limited in the variety of plastics between which that they can differentiate. They will never be able to differentiate between two or three different polymers at a time and will make mistakes if presented with a polymer to which they are not calibrated.

Although current electrostatic methods can be useful in separating and identifying waste streams such as automotive plastics for example, the inability to detect more then a few different polymers along with the incapability of detecting additives make the present technology not so suitable for identifying unknown plastics from waste computer equipment.

2.5.3 Selective Extraction of Plastics Waste

Selective extraction or dissolution is a fairly novel recycling process that involves organic solvents to dissolve the thermoplastic and separate them from either insoluble materials such as metals, dirt, or glass, or the separation of multi-polymer mixes. The dissolved polymer may then be precipitated from the solution to become a high-grade quality recyclate. Materials suitable for this method are technical polymers such as ABS, SMA, PVC and PMMA that were originally bumpers and dashboards from automotive scrap and casings of computers and printers etc, from electronic waste [83]. Examples of what may be achieved by this process are shown in Table 2. It appears that this method may be useful for the treatment of waste plastics not only from end of life vehicles, but also from waste computer equipment. This could also be a solution for the treatment of those plastics that contain brominated flame retardants. Work on this method of recycling was realised in a pilot plant and involves washing, dissolution, mechanical refining, precipitation and formulation into granulate. It has been estimated that the proportional production cost of the recycling process reaches about 50% of costs for production of new material [83] and it is hoped that this method of recycling will be realised on a commercial scale in the near future, although there may be concerns over environmental hazards due to large quantities of solvents.

Table 2.3 Examples of types of waste mixtures separated by dissolution [82]

Material	Result
PE/PP/PET/PVC/ABS	Separated
PS (plastic foam wrappings)	Colour is removed
PS (flame retardant)	Dehalogenation

2.5.4 Rapid Identification of Plastics by Spectroscopic Methods

Rapid spectroscopic methods can be divided into two main groups, electromagnetic and pyrolytic techniques. The first group is those that analyse the whole polymer macromolecules without altering their composition or structure in anyway. These methods include near infrared (NIR), medium infrared (MIR), Fourier Transfom infrared (FTIR), X-Ray analysis and Raman spectroscopy. These types of polymer spectroscopy generally refer to the measurement of absorption or emission of electromagnetic (EM) radiation of photons from a polymer sample under examination.

The second group consists of methods using pyrolytic decomposition of the macromolecular chain into smaller elements, which are then subjected to analysis [84]. Some of these methods include pyrolysis mass spectroscopy, infrared pyrolysis spectroscopy, laser-induced emission spectral analysis (LIESA) and spark induced spectral analysis. The choice of the type of identification method depends on several factors of the plastic waste including the potential types of plastics, sources of origin, and colouring.

2.5.4.1 Group 1. Electromagnetic Methods of Spectroscopy:

As already stated, spectroscopy techniques are generally involved with the measurement of absorption or emission of electromagnetic (EM) radiation of photons from a polymer sample under examination. The absorption and emission of radiation is when an atomic or molecular system undergoes a transition between energy states to either a higher state, which requires the absorption of photons, or a lower state, which involves photon emission. These transitions to a higher or lower energy state can be measured using electronic, vibrational, rotational or magnetic states of energy, all of which detect photon transitions over different wavelengths of the EM spectrum [85]. Electronic states have large energy separations. Photon transitions in this state lie in the ultra-violet (UV) and visible part of the EM spectrum, corresponding to a range of wavelengths (λ) of 100-1000nm. Vibrational states have lower energy separations and correspond to the infrared range ($\lambda \sim 1\mu m$ to 1mm). Rotational states correspond to the lower part of the IR region and the upper part of the microwave region, whereas transitions between different magnetic states (of a spinning nucleus or unpaired electron) require even less energy and usually occur in the microwave regions ($\lambda \sim$ 1mm to 1cm) [85].

Vibrational spectroscopy is concerned with the detection of transitions between energy levels in molecules resulting from vibrations of the inter-atomic bonds, usually occurring in the infrared region of the EM spectrum. Molecules consist of atoms that vibrate due to thermal energy. Because atoms are held together by valence forces, each inter-atomic bond will vibrate at a frequency characteristic of its atomic structure. However these bonds display a sensitivity to their molecular environment, chain conformation and morphology. A polymer molecule will have a set of resonance vibrations characteristic to that molecule and when exposed to radiation, will absorb the radiation only at frequencies corresponding to the molecular modes of vibration. Therefore as no two compounds have the same structure, neither will they have exactly the same vibrational frequencies and intensities, hence the IR spectrum is often referred to as the fingerprint of a molecule [86].

Infrared spectroscopy is the most widely used technique for polymer identification and may also provide qualitative and quantitative information on the polymer being analysed. Within infrared spectroscopy, there are a number of techniques that measure vibrational frequencies over different parts of the infrared spectrum. Some spectrometers operate in the near infrared region (NIR) over the range $\lambda \approx 0.7\text{-}2.5\mu m$ or 4000-1400 cm^{-1} as expressed in wavenumbers (ν) (i.e. the number of wavelengths per centimetre νcm^{-1}). Some operate in the mid infrared (MIR) 1400-200 cm^{-1} (2.5-50μm) and others in the far infrared (FIR) 200-12cm^{-1} (50-80μm). With Fourier Transform infrared spectroscopy (FTIR), measurements are taken over the whole infrared region, although it must be realised that the molecular vibrational energies most useful in analytical work are usually in the wavenumber range 4000-400cm^{-1} (λ range 2.5-25 μm) [85].

Raman spectroscopy is concerned with the detection of scattered light due to the interaction of molecules with the incident monochromatic radiation [85]. When a beam of light is directed at a sample, the majority of the radiation is scattered elastically but at the same frequency. This is known as Rayleigh scattering. However a small amount of radiation is scattered inelastically and at a different frequency and this is Raman scattering [87]. It is this inelastically scattered light that carries information about molecular vibrations in the material and just like infrared spectroscopy, will be characteristic of different functional molecules. Although not used extensively on a commercial recycling basis, Raman spectroscopy has been found most useful in the characterisation of composites and will probably contribute greatly to recycling activities in this area.

As far as practical applications are concerned there is a considerable amount of research covering most aspects of rapid plastics identification technology. It has been found that NIR spectroscopy has proved to be an appropriate method in identifying the plastics of packaging materials predominantly found in domestic waste [1]. The spectral quality of the plastics is high, as such material contains little or no additives, and allows the analysis of fast moving pieces of up to 400kg/h [88]. A simple variation of NIR spectrometry is the development of a two-colour NIR sensor that has been shown to be an inexpensive but rapid and reliable method of sorting PVC from PET plastic bottles [89]. It has also been suggested that NIR is suitable for identifying plastics from electronic devices such as computer casings [90]. However, the most prominent disadvantage is the fact that NIR is entirely unsuitable for black plastics [88], because carbon black (the black pigment used) is a strong absorber in the NIR region and produces a featureless spectra. Also the recognition of additives such as flame retardants is practically impossible using NIR spectroscopy, therefore other methods would probably be more suitable for such plastics waste.

For waste plastics from end of life vehicles, identification technology has looked mostly to the MIR region [91]. Since black formulations are widely used for cars, and also in some electrical and electronic applications, it is essential to be able to identify black plastics and this is the clear advantage of the mid-infrared [76]. Since

September 1993, a piece of MIR research equipment has been in use in a car dismantling plant in Germany [92] greatly improving the identification accuracy and speed of identification. Undoubtedly, MIR also has its disadvantages. Essentially it is a pure surface method with a negligible depth of penetration, therefore surface dirt, paint layers or other surface contamination must be removed before measurement. The surface roughness must also be minimal in order for an identification analysis to be made. For the MIR research equipment on trial in the car dismantling plant, these disadvantages have proven to be less of a problem than previously thought [76]. Mid infrared spectroscopy may also be used for the identification of plastics from waste computer equipment. However, the accuracy of detecting plastics additives is an area currently being researched.

FTIR spectroscopy involves the measurement of wavenumbers over the whole infrared region [85]. The measurements of the response of a material are then transformed to a single excitation by digital computer into a spectral scan. The process is repeated many times and the results are averaged in order to attain high accuracy [63]. With some methods of FTIR, it is possible to scan a material in bulk form without significant sample preparation. This makes the technique fast and relatively easy to use. For example, the Perkin Elmer System 2000 FTIR Spectrometer used in this study required almost no sample preparation. This technique is known as attenuated total reflection (ATR), and involves contact sampling with a highly refractive crystal with low IR absorption in the IR region of interest. Careful calibration is required in order to account for the level of water absorption in the surrounding atmosphere.

Although FTIR spectrometry is one of the most widely used techniques in plastics identification, it must be noted that applications are generally limited to laboratory analysis and are not suitable for rapid analysis. Such systems are generally not sufficiently robust for the intensity of commercial use and they are not able to produce clear spectra in such short times (several seconds for example) that are required for a commercial system. They are more accurate with time, and despite producing good quality spectra, they are just too slow for a commercial recycling process.

2.5.4.2 Group 2. Pyrolytic Methods of Spectroscopy:

The basic principle behind such methods usually involves a form of material decomposition in order to break down the molecules, followed by analysis of the particles often with an infrared spectroscopic technique. Researchers in Japan have been developing a pyrolysis infrared spectrometer for identification of automotive waste [93]. Using a NIR lamp as the heat source, a pyrolysis probe pyrolyses a 5mm area from the surface of the sample within 2s. The pyrolysed particles are then carried through a gas guide by a carrier gas, into the gas cell where the parts are analysed by an FTIR spectrometer. The spectrum of the pyrolyzate is then analysed by comparing with a library of spectrum. A main advantage to this method is that the depth of sampling is approximately 100μm, compared with just a few microns as analysed by reflectance spectroscopy. Therefore any surface contamination such as dirt etc will not impede the analysis. Due to the nature of the spectroscopic system, this technique is able to measure black samples and it is also expected to be suitable for identifying fillers and other additives, including flame retardants, which could even be a suitable method for identifying plastics from WEEE. However, a disadvantage to the system is that the gas tube and cell may eventually become plugged with impurities if the particles are not flushed away following analysis.

Another method has been developed by researchers in Germany that uses a similar technique to the one above [94]. This method uses sliding spark spectroscopy to identify plastics, which is the thermal vaporisation of a small amount of the plastic surface using a train of defined high current sparks. The vaporised particles that are in the spark plasma are then atomised and activated to emit radiation, which is detected and characterised according to the spectral library. This hand-held method allows the identification of plastics regardless of colour as well as fillers including flame retardants, and has been developed as a cheaper alternative to some of the more expensive identification equipment.

2.5.5 Other techniques for the rapid identification of plastics

It appears that despite the technological development, it is still difficult to find a fast enough method that can identify high quality engineering plastics waste as well as being able to accurately detect plastics additives. Although NIR appears to be one of the fastest methods of identification, it has limitations especially in the identification of black plastics and detection of additives and flame retardants. In order to overcome such limitations, research is currently developing a novel identification system incorporating the combination of more than one technique. For example a NIR spectrometer coupled with an LBDS (Laser break down spectrometer), so that the LBD spectrometer can identify black samples and also detect the presence of additives such as fillers and flame retardants [95].

One novel and futuristic idea is to apply radio frequency identification (RFID) tags to computers [96]. Already used in a number of applications from personnel identification and access control, to refuse collection identification, the RFID, a read only tag, acts similar to a barcode. This means that it could be placed anywhere around a computer casing. Information provided could include the component material, any additives and flame retardants used and also information on components contained inside the casing. Current identification problems could be overcome and all that recyclers would need is the tag reading equipment, which would probably be compact and light weight. Of course for this method to come into effect it would probably take several years for the tags to filter through the product life cycle and would in no doubt require the co-operation of computer manufacturers around the world. However, this would not be easy to set up and it is possible that the cost could outweigh the benefits.

A less expensive concept developed by researchers in the UK is the idea of using fluorescence tracers for automatic sorting of plastics. Fluorescent tracing is not a new concept and is already used extensively in the authentication and detection of passports, bank notes and identity cards [97]. The tracer, probably a commercial dye, will have to be added in the plastic during manufacturing. At the end of life of the product, the tracer can be detected using UV spectroscopy. Because there is more than one plastic type in any plastics waste stream, there needs to be more than one tracer in order to distinguish the different plastic types. Several commercial dyes have been examined for suitability, each having distinct UV spectra and up to fifteen different plastics may be identified through combinations of just four different dyes. With the UV spectrometer as part of an automatic sorting device, it is feasible to sort plastics from packaging materials, electrical and electronic applications and even automotive plastics quickly and at low cost. However, in order for this to occur on a commercial basis, there needs to be a large-scale co-ordination between manufacturers and recyclers everywhere, so that all plastics will contain the same combination of tracers. Although setting up a fluorescent tracer system could happen fairly quickly in the plastics packaging sector, longer term applications such as those from automotive or electrical applications would take a lot longer to filter through and would be a lot more difficult to implement.

2.6 PLASTICS MORPHOLOGY, DEGRADATION AND RECYCLING

Polymeric materials are essentially made up of relatively long macromolecular chains. These polymer molecules, or macromolecules are chains of atoms that contain repeat units of a particular grouping of atoms that are linked together by covalent bonding. Many repeat units are derived from unsaturated monomers, which are usually hydrocarbons (molecules of carbon and hydrogen) in different configurations. Polymer chains can be linked by any atom that will form two or more covalent bonds, and as carbon atoms are able to form at least four covalent bonds, most macromolecules are in the form of long chains of covalently bonded carbon atoms with additional side groups of atoms, for example aromatic structures [98]. A typical polymer is made up of CH_2 arranged tetrahedrally (see Figure 2.6), although the hydrogen atom may be replaced with different atoms or benzene rings depending on the polymer type. Polymer chains may be flexible according to the chemical structure, and the rotations of the chain enable different chemical configurations as well as varying the flexibility of the material. Some molecular arrangements may only permit the polymer chain to be fully extended, whereas other configurations may have many different chain conformations.

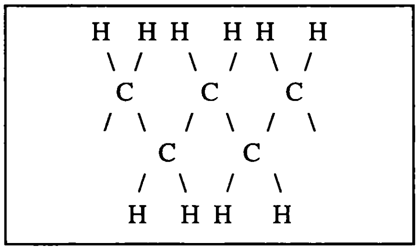


Figure 2.6 Tetrahedral structure of Polyethylene, a typical CH_2 based polymer chain

In a covalent bond between two atoms, the electron pair is seldom shared equally between the two atoms, which gives one end of the bond a small negative charge and the other a small positive charge. This is said to be polar with the strength and direction of the polarity being determined by the atoms forming the bond. Polymer chains that are held together in condensed phases are bound by Van der Waals forces and hydrogen bonding. Van der Waals forces are dipole/dipole attractive interactions of a positive end of a grouping of atoms in a molecule, to the negative end of a nearby grouping. If hydrogen is part of the link then it is known as hydrogen-bonding [98]. Van der Waals and hydrogen bonding are what link polymer chains side by side together. These types of bonds are not as strong as covalent or ionic bonds and so will be the first bonds to break on deformation, allowing polymer chains to slide past each other.

Due to their long chain nature polymer liquids have relatively high viscosities when compared with small molecular liquids, such as water, for example. The higher the molecular weight, the more difficult will be the processing of a polymer melt. For many polymers, chains can arrange themselves in a three–dimensional repeating array of atoms. Some polymers may crystallize into more than one conformation. However many polymers are not able to crystallise into any particular conformation and these structures tend to be an entanglement of chains in no particular order, which is termed amorphous. Amorphous polymers occur, as the molecular configuration will usually contain side branches that interfere with crystallisation. Even crystallisable polymers are termed semicrystalline, having both amorphous and crystalline regions [65].

The physical and mechanical properties of a polymer, including its response to an applied stress, depend on the morphology and molecular structure of the sample. Factors that affect polymer morphology include; fabrication of the polymer, the sample processing method and thermal history of the material, as well as the component of the polymer (i.e.whether it is a single polymer or copolymer). Physical properties and the response to an applied stress depend on the amount of chain extension and mobility of the polymer, as well as the amount of phase separation that could occur in a blend/block co-polymer, and sample homogeneity (i.e. how well mixed or miscible). Other factors include direction of chain orientation, size of separated domains and sample continuity, as well as test conditions (rate of test and temperature). Any changes to morphology that could be brought on by an interactive environment or a change in temperature for example, will cause changes to physical properties and response to an applied stress [98].

2.6.1 Polystyrene

The structure of the styrene monomer can be thought of as the replacement of one of the hydrogen atoms in ethylene (C_2H_4) by a benzene ring (C_6H_6) [99]. The production of styrene is a three stage process known as the Dow process. Stage one is the reaction of benzene and ethylene forming ethylbenzene, followed by degydrogenation at stage two, which creates styrene. These stages are illustrated in Figure 2.7. Stage three then involves purification of the styrene monomers through several distillation processes. The styrene monomer is then polymerised to make polystyrene [64].

Polystyrene (PS) has a simple repeat structure (Figure 2.8), and the linearity of the chain makes it a thermoplastic. It is generally amorphous in nature, as the position of the benzene ring is random enough to inhibit crystallisation, although the presence of the bezene ring does have a chain-stiffening effect. Because of this chain stiffening effect, the glass transition temperature (T_g) is approximately 100°C and a consequence of this T_g value and the amorphous nature of the polymer means that it is hard and transparent at room temperature. The hydrocarbon nature of PS gives it excellent electrical insulation properties, which can be maintained in humid conditions as this nature also exhibits low water absorption [64].

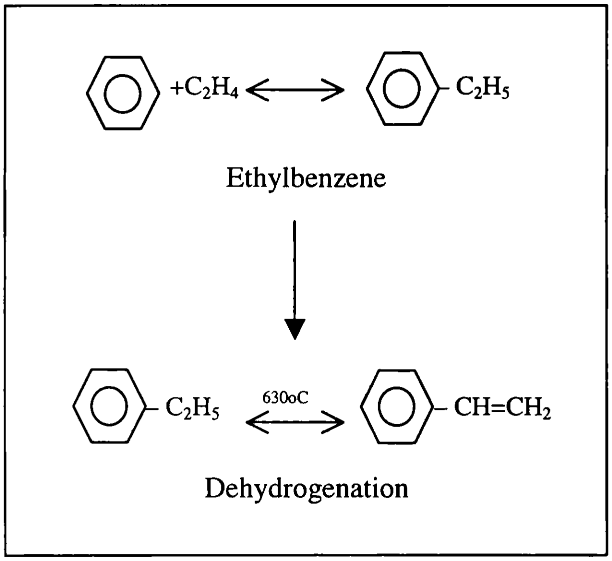


Figure 2.7 Production of styrene by
1. Production of Ethylbenzene
2. Dehydrogenation

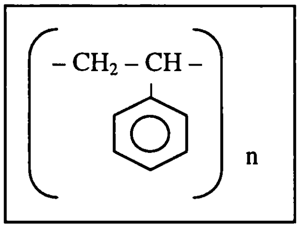


Figure 2.8 Repeat structure of Polystyrene

Mechanical properties of PS are generally dependant on several factors including molecular weight, methods of sample preparation / processing and the variable parameters of the test measuring specific properties. On the whole PS is a rigid transparent thermoplastic and is a relatively low cost material with a range of beneficial properties including; good mouldability, low moisture absorption, good dimensional stability, good electrical insulation, colourability and reasonable chemical resistance. Its main limitations are brittleness, the inability to withstand the temperature of boiling water and poor oil resistance, and although it has generally good optical properties, it can be prone to hazing or yellowing over time, which could be related to aging among other factors. In order to overcome some of its limitations and to take advantage of others, PS has been developed into several different grades [64]. Some of the main grades of polystyrene are as follows;

1. General purpose grades. A balance is attempted to obtain good heat resistance, good flow properties and reasonably high impact strength.
2. High molecular weight grades. PS has very little strength if the molecular weight is below 50,000, but if it is above 100,000, there are adverse effects on ease of flow without any significant effects on tensile strength. Therefore molecular weight is better between 50,000 and 100,000. These grades are used where improved impact strength is required, without the loss of clarity.
3. Easy flow grades. Flow properties of PS can be improved with little effect on other properties by incorporating an internal lubricant such as butyl stearate or liquid paraffin or by using a polymer of lower molecular weight. Other ways include controlling granule shape and size and adding an external lubricant such as zinc stearate. These grades are useful in applications such as thin wall mouldings, or for other intricate moulding.
4. Heat resistant grades. Within the structure of PS, there can often be a small volume of styrene monomers. Increasing the amount of monomer in the polymer has the effect of lowering the softening point of PS. By reducing the amount of volatile matter within the PS structure from 5% to 0% for example, the softening point of PS may be raised from 70°C to 100°C.
5. High impact grades. These are combinations of PS with rubbery materials such as polymerised polybutadiene rubber and are discussed in more detail shortly.

2.6.2 Polyphenylene Oxide

Polyphenylene oxide (PPO) is produced by the oxidation of 2,6-xylenol, as shown in Figure 2.10 [100]. As can be seen from Figure 2.6.5 the structure of PPO will be fairly stiff as the chains are bonded by benzene and oxygen. Due to this rigid structure the polymer PPO has a high T_g between 200°C and 212°C [101, 102,103], which means that processing temperatures will be high [64].

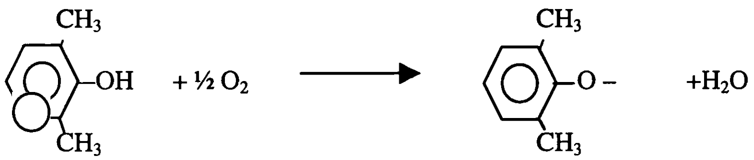


Figure 2.10 The oxidation of 2,6-xylenol forming PPO and water

The structure of PPO is crystalline on polymerisation. However, due to a surprisingly low melting point (T_m) of 257°C, PPO is generally amorphous on cooling from the melt during processing as there is insufficient time for crystallisation to occur because of the relatively small difference between T_g and T_m. Despite the rigidity of the polymer, PPO exhibits a reasonable degree of toughness at room temperature. Moulding may be carried out to tight specifications due to properties such as low moulding shrinkage and low water absorption. Other favourable properties include exceptional dimensional stability, chemical resistance and excellent electrical insulation properties. The main drawback to this polymer is that the cost of production is high, and the price is usually too great to justify more than very restricted applications. However in order to reduce this cost it can be blended with styrenic materials or polyamides, which are less expensive than unblended PPO [64] and will also have the effect of reduce the processing temperature.

2.6.3 Polycarbonate

Polycarbonate (PC) is a transparent, predominantly amorphous, thermoplastic polymer, possessing unusually high impact strength and toughness. It has good heat, chemical and electrical resistance and good oxidative and thermal stability, although ESC is a big problem and it hydrolyses in hot water [104]. PC is commonly derived from the reaction of bisphenol-A with phosgene [100], where bisphenol-A is a petroleum-based product and phosgene is produced by reacting chlorine from the electrolysis of sodium chloride with carbon monoxide produced from the pyrolysis of coal oil or gas [104] (Figure 2.11).

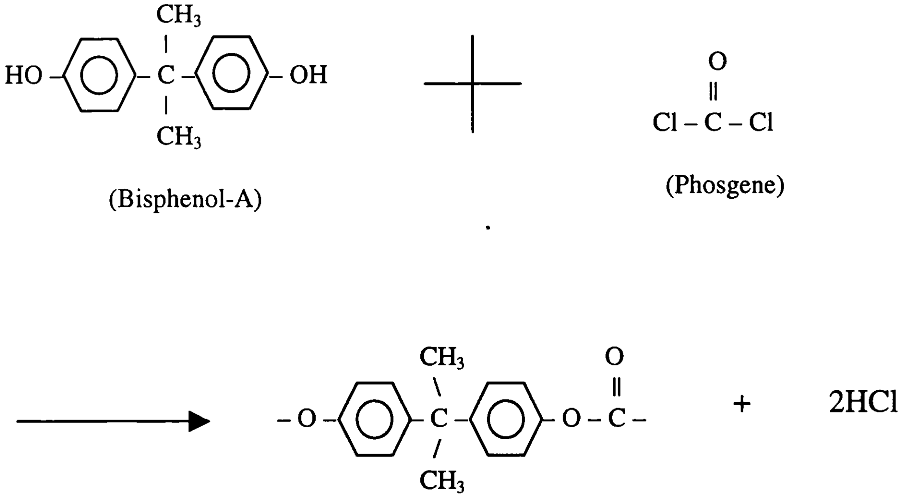


Figure 2.11 The reaction of bisphenol-A and phosgene, which forms polycarbonate and 2HCl

As can be seen from Figure 2.11, the PC molecule is fairly symmetrical in structure. The carbonate groups are polar but are separated by aromatic hydrocarbon groups. The presence of benzene rings in the chain restricts flexibility of the molecule, although the repeating unit of the PC molecule is quite long. Because of the regularity of the structure it could be expected that this polymer would be capable of crystallisation. Although PC does crystallise, the degree of crystallinity in most commercially produced mouldings and extrusions is so low that it is virtually unmeasurable. Crystallinity of PC is normally achieved through solution casting. The excellent impact and strength properties are therefore due to the amorphous structure and limited crystallinity of PC [64].

There is a considerable range of polycarbonates commercially available and the differences between grades include differences in molecular weight and the presence of different additives for example. As well as the properties already mentioned PC is also virtually self extinguishing, requiring just small amounts of flame retardant additives. However drawbacks include limited resistance to chemicals and ultraviolet light, as well as not being as easy to process as some polymers and it is also more expensive than polymers such as PE, PS and PVC. PC may also be blended with other polymers to improve properties such as ABS, the merits of which are discussed in the following section.

2.6.4 Polymer Blends and Alloys

The demands on properties of plastics have increased with their widespread use and many applications require higher performance from polymers, or the need for many properties that may not be possible in a single polymer system. To develop a new polymer for every situation that comes along could prove quite costly and may not always be physically possible. Even the higher performance thermoplastics for example, polysulphone and polyarylate, which may offer exceptional heat resistance and resistance to various chemical environments [100], are difficult to process due to high melt viscosity, and also have low stress crack resistance. Therefore an excellent strategy for achieving a specific collection of properties without the need to create specialised polymer systems would be to mix two or more polymers together to produce a blend or alloy [105].

Engineering plastics possess excellent properties including high specific strength, dimensional stability, low creep and good electrical and chemical properties. However issues of toughness, processibility and cost often hinder such plastics from becoming commercially useful [106]. This is why blending is an effective method of resolving such problems [107] as it is often more economical than to use a simple homopolymer [108]. Blending two polymers is therefore a way of eliminating the poor properties of each plastic while keeping the most advantageous. Although a polymer blend can be loosely considered to be a mixture of more than one polymer, these mixtures can be further classified into polymer blends, polymer alloys and polymer composites. Utracki [109] defined a polymer blend as a miscible polymer system. An immiscible polymer system is a polymer alloy, while a polymer mixed with fibres or a filler, is classed as a polymer composite. Properties of polymer blends, alloys and composites largely depend on the compatibility and molecular miscibility of the polymeric components [107].

A miscible polymer system comprises of a pair of polymers that mix on a molecular scale producing a single phase material. An immiscible system will have two or more phases at all temperatures and compositions, which is often seen as segregated particles of one polymer in a matrix of the other. Some systems are partially miscible in that such blends are miscible at certain concentrations and temperatures and not at others [101]. A number of factors may contribute to the miscibility or immiscibility of polymer blends, some of which include the following. Polymers with a similar structure or similar in polarity are less likely to repel and more likely to form miscible blends [110], whereas diverging polarities will produce immiscibility [107]. Lower molecular weight favours miscibility [111] as such polymers are easier to mix. Also, polymers with similar molecular weight will be more miscible while polymers with very different molecular weights may be immiscible [107]. The crystallinity of a polymer also affects miscibility. When a polymer crystallises, it adds another phase to the system. If both polymers crystallise, they will usually form two separate (immiscible) crystalline phases, as it is quite rare for two polymers to co-crystallise into a single crystalline phase [107].

A polymer blend can be considered compatible when it possesses a set of useful practical properties, regardless of whether the system is miscible or immiscible. In many cases mixing two polymers often results in polymer alloys that are weak and brittle. This is often due to the segregation of phases during melt processing which results in a weak interface between the two phases [105]. The difference between incompatible and compatible polymer blends is usually a sharp weak interface and a strong broad interface between phases [107]. Some polymers may naturally form compatible two-phase blends without any additional processing. Some examples of these are crystallisable polymers, which have crystalline and amorphous phases, and block or graft copolymers, which still separate into two phases despite the macromolecules being joined or grafted together. Due to the nature of copolymers and crystalline polymers, the two phases are joined by primary covalent bonds across the interface. This gives the greatest interfacial stability and such interfaces are able to better transmit stress and resist failure. For other polymer blends that are not so naturally compatible, it is common for the compatibility of a polymer blend to be controlled by physical processes, the addition of physical additives or reactive processes, in order to modify the interfaces between phases [107]. Therefore the final properties of a polymer blend are not only determined by the properties of its components but also by the phase morphology and interphase adhesion [105].

The range of polymer blends and alloys is vast and the manner in which two or more polymers are compounded together is vitally important in controlling blend properties [105]. Most polymer blending is done by melt mixing of molten polymers. Temperature, shear rate and time are fundamental to blend morphology, which in turn will have an effect on properties. Many compatibilisers can be added during melt processing. The added ingredient could be a third polymer or a copolymer. It has also been found that reinforcing fibres can often be used to bridge across the weak interfaces and connect the stronger separate polymer phases with each other, thus improving properties. Some other ways to compatibilize a polymer system could be to modify one or both polymers to prepare for subsequent blending. This could be done during polymerisation, through block copolymerisation or even by control of molecular weight. Polymers could also be blended by initiating a chemical reaction during the mixing process. This is known as reactive blending. Often the polymers may not be sufficiently reactive to be compatibilized directly and so such polymers could be modified during or following initial polymerisation reactions [107].

2.6.4.1 Polymer Blends

As already stated, a polymer blend is a polymer system where two polymers are completely miscible on a segmental level forming a single homogeneous phase. Properties are generally proportional to the ratio of the two polymers in the blend and can be controlled fairly easily in order to comply with application specifications [107]. A simple way of calculating properties of a blend would be to use a simple linear rule of mixtures [108]

$$X = w_1 X_1 + w_2 X_2 \qquad \text{Equation 2.1}$$

where X is a measurable material property and w is the weight fraction of a component. However it must be noted that this may not be suitable for every blend.

One way to establish the miscibility in a binary blend is the presence of a single glass transition temperature (T_g) that will be between the T_g's of its constituents [107]. However, although miscibility between two polymers is often good, it must be noted that occasionally a system that mixes on a molecular level could show little improvement to properties such as toughness for example as they may be too well mixed for any fracture toughness mechanisms to occur.

An excellent example of a polymer blend is that of PPO and PS. A necessary factor for the formation of a miscible polymer is an exothermic heat of mixing between component repeat units [112]. This is thought to arise in PPO/PS blends from phenyl group coupling between the aromatic ring of PPO and that of PS [113]. PPO and PS have similar molecular weight values, which is advantageous to blending on a molecular level and as both are amorphous polymers they can therefore be blended fairly easily during melt processing [101]. A PPO/PS blend will exhibit a single T_g, an excellent indicator of molecular mixing and will be at a temperature between those of PPO (212°C [101]) and PS (100°C [114]) according to blend composition. As a PPO homopolymer will need to be processed at higher temperatures due to such high glass transition and melting temperatures, blending with PS has the effect of reducing processing temperatures and also cost of material without compromising properties. There is a broad spectrum of PPO/PS blends, usually known as Modified PPO, that are commercially available which can vary in properties from heat resistant grades to high impact grades. Many of these grades have found applications in the automotive and electrical industries [64].

2.6.4.2 Polymer Alloys

A polymer alloy is an immiscible polymer system forming more than one phase. While many polymer alloys will be weak and brittle due to phase segregation, it is those that are compatible that will have significantly better properties. As already mentioned the excellent properties of polymer alloys may often only be achieved if there is good interfacial adhesion between phases. In other words, if there is some amount of covalent bonding linking the two phases together. A good interphase usually indicates a partially miscible system, which for some naturally compatible alloys is often a good explanation for their good properties.

The proportion of each polymer in an immiscible system has an effect on morphology, which in turn will affect properties. Rather than a block of polymer A next to a block of polymer B, the phases of a polymer alloy will be a solution of polymer B in polymer A or vice versa. The major phase generally forms the continuous matrix and has the greater influence on properties, whereas the minor phase will form dispersed microdomains within the matrix and will contribute to more specialised properties to the mix [107]. However, if the viscosity of each component is significantly different, then the less viscous phase will tend to form the matrix even if present in the minor amount, while the more viscous phase will form the dispersed domains [107]. The ratio of each polymer in a two phase system can give an assorted degree of miscibility and compatibility as well as a varying range of properties according to blend proportions. Optimum properties of alloy A and B could be at

20/80 or 50/50 for example, however it is usually down to product specification to dictate required properties and therefore blend proportions.

Whereas a miscible or single phase polymer blend will exhibit a single glass transition temperature (T_g) according to blend composition [63], an immiscible system will actually show a distinct T_g for each phase of the system. If the two polymers are partially miscible, the temperature locations of the peaks will move closer together and can vary for different ratios of the two polymers. Such shifts in transition peaks indicate that blend proportion will have some effect on the miscibility and compatibility of an alloy [107].

A PC/ABS system is a good example of a polymer alloy as it is classed as a 'natural' alloy, which means that there is no need for any compatibilization techniques in order to obtain good properties [107]. Because ABS is already a two phase system, a blend of PC and ABS is therefore a three phase system consisting of a PC-rich phase, polybutadiene (PB) particles and a poly (styrene-co-acrylonitrile)(SAN) rich phase [115], with some grafting between SAN and polyacrylonitrile (PAN) with PB [107]. As a three phase system, it would be quite logical to suppose that three glass transition regions would be observed. However, because the weight fraction of the PB in the overall composition is very low, the magnitude of transition for PB can be very small and is not always detected by some thermal property measuring systems, and so the T_g's of the PC and SAN phases are those commonly reported for PC/ABS blends [115].

PC/ABS is known as a partially miscible system, which is due to the compatibility between PC and SAN and the incompatibility of PC and PB [106]. A study into the morphology of PC/ABS over a range of compositions [116] found that PC-rich blends consisted of a continuous PC matrix, containing spheres of ABS in the form of butadiene and SAN particles. As the ABS content increased, the ABS-rich domains were seen to increase until coalescence occurred between particles. As the ABS phase became continuous, the PC phase appeared initially to also be co-continuous and contained SAN inclusions. At higher ABS content, the ABS rich blends showed PC domains dispersed within a continuous ABS matrix.

Blending ABS with PC has been said to improve the processibility of PC [117, 118] while increasing the performance of ABS [107]. The processibility of PC is improved because the addition of ABS decreases the viscosity of PC [118] whereas mechanical properties of ABS are better when blended with PC. Although PC generally has good mechanical properties, notch sensitivity is high which means that even a small surface scratch could drastically reduce impact strength. PC also has relatively low resistance to stress cracking, especially when subjected to a chemical environment. However such limitations are reduced when blending with ABS. Although tensile properties compared with PC may decrease with ABS content, just a small amount of ABS dramatically improves notched impact strength [117] and has been said to reach a maximum at a ratio of 70/30 PC/ABS [119].

2.6.4.3 Polymer Composites – Toughened Plastics

A polymer composite is essentially a two phase material comprising of a continuous matrix that surrounds the other phase, often termed the dispersed phase. The dispersed phase may or may not be another polymer. There are several different types of composites including fibre-reinforced, structural and particle-reinforced [65]. Fibre-reinforced composites have the dispersed phase with fibre geometry i.e. a large length to diameter ratio. Fibres can be long and aligned, short and aligned, or with random orientation. Common materials used are glass fibres and carbon fibres. Structural composites can be laminar i.e. layers of aligned fibres cemented together in a polymer matrix, or sandwich panels which consist of two strong outer sheets separated by a layer of less dense material. Properties of structural composites depend not only on those of the constituent materials but also on geometrical orientation of each element. Particle-reinforced composites can either be large particle or dispersion strengthened. For large particle composites the particulate phase is harder and stiffer than the matrix and bears some of the load experienced by the matrix. Mechanical behaviour is strongly dependant on good bonding at the matrix-particle interface. For dispersion-strengthened composites, the particles are much smaller and any improvement to properties will occur on a molecular level. While the matrix will bear the applied load, the particles will restrict molecular movement such that plastic deformation is restricted, resulting in improvements to properties such as yield strength, ductility and toughness [65]. This section will focus on dispersion-strengthened composites.

A commercially important type of dispersion-strengthened composites, are the rubber-toughened plastics. These essentially consist of rubber particles dispersed throughout a polymer matrix [120]. The rubber toughening process is a very successful way of modifying properties of a polymer and properties such as impact strength, strain to failure, and fracture toughness can be increased up to seven times that of the parent polymer. An inevitable effect is usually a reduction to the modulus, tensile strength and transparency whereas melt viscosity is usually increased [120]. However such losses are usually far outweighed by improved properties and the better balance of properties often has more commercial significance than the parent polymer.

There are several different ways to toughen plastics. Some methods include melt processing or processes such as bulk polymerisation, bulk-suspension polymerisation and emulsion polymerisation. These latter processes mainly involve the addition of the rubber at some stage either before or during polymerisation and depending on the plastic, often with a catalyst to initiate the mixing reaction. The results are therefore rubber particles dispersed throughout the polymer matrix. As an effect of processing the rubber particles are usually cross-linked with some grafting occurring between the rubber and the matrix giving a strong interface. The crosslinking of the rubber particles is essential with rubber-toughened plastics as un-crosslinked particles tend to break down when subject to shearing forces during processing, which leads to reduced properties [120]. The size of the dispersed rubber particles is also important, especially if optimum toughness for a polymer is to be achieved. Critical particle sizes for optimum toughness vary from 0.1-2.0μm [120] and are different for each polymer type. For example particle sizes less than 1μm in diameter do not provide effective toughening for HIPS [121], however PVC may be toughened by particles less than 0.1μm diameter [120] and ABS has a critical particle size of 0.26-0.46μm [105].

The ductility and toughness of a polymer depends on its ability to undergo plastic deformation under stress. The incorporation of rubber particles increases the toughness of the polymer matrix by enabling more plastic deformation to occur within the matrix, than could occur without fracturing, in an un-toughened polymer matrix. The rubber particles in the matrix act as stress concentrators and depending on the polymer and the toughener used, different toughening mechanisms may operate in different toughened materials [105]. Shear yielding, crazing and combinations of shear yielding and crazing are well known toughness mechanisms in different polymers [120].

Shear yielding of a polymer matrix involves drawing the material without any change in volume [105, 120]. In crystalline polymers, shear yielding takes place by slip on slip planes as a result of dislocation glide. In non-crystalline polymers, shear yielding involves more movement of molecular segments and is therefore less localised than crystalline polymers. Shear yielding can often be seen in tensile testing as the necking of a sample. The shear yielding process generally takes place at 45° to the direction of stress. For rubber toughened polymers, an effect of strain softening leads to the formation of shear bands which are thin planar regions of high shear strain. Shear bands are initiated at internal or surface flaws or stress concentrators such as rubber particles for example, as these are generally regions with lower resistance to deformation than the surrounding material [120]. The rubber particles in a toughened plastic not only act as initiators but will prevent propagation of shear yielding across the entire matrix if the inter-particle distance is smaller than a critical value. This mechanism dissipates a large proportion of the total fracture energy [122], thus requiring more energy to fracture than an un-toughened glassy polymer.

Crazing is the alternative deformation mechanism to shear yielding and is both a localised yielding process and the first stage of fracture. Although crazes, like shear yielding are formed as a result of shear softening, unlike shear yielding, they actually involve a large increase in volume. Therefore the plane of a craze is not restricted to an angle of 45° but may form at 90° to the tensile axis. When a tensile stress is applied to a glassy polymer, small voids form perpendicular to the stress direction. Instead of these voids coalescing to form a true crack, they are stabilised by fibrils of oriented polymeric material, which span across the voids and prevent them from becoming wider. A network of voids and polymer fibrils is known as a craze. Although crazes may appear to resemble cracks, they have significantly different properties including higher tensile strength [120]. Crazes are initiated at points of high stress concentrations, such as near the equator of rubber particles. The craze can then propagate out along a plane of maximum principal strain until either the stress concentration falls below a critical level of propagation or when an obstacle such as another rubber particle is encountered. The rubber particles in a toughened polymer are therefore able to control craze growth by initiating and terminating crazes [123].

While some polymers can be toughened by shear yielding and others by crazing, it is not uncommon for some polymers to be toughened by both mechanisms.

While crazes grow perpendicular to the direction of tensile stress, the shear bands develop along a path 45° to the direction of an applied stress. The interaction between the crazes and the shear bands stabilizes the growing crazes and prevents them from becoming harmful cracks. The shear bands are therefore not only energy absorbers but also act as terminators of growing crazes [124]. A HIPS/PPO blend is a good example of being toughened by more than one deformation mechanism [107]. Studies have shown that a combination of both multiple crazing and localised shear yielding (shear band formation) is responsible for the enhanced toughness of a HIPS/PPO blend [124]. As different polymers are toughened by different mechanisms, this can explain why the critical size of rubber particles is important. Larger particles are necessary to initiate and terminate crazes, whereas relatively small rubber particles generate shear bands [125].

High impact polystyrene (HIPS) is the dispersion of polybutadiene (PB) rubber within a polystyrene matrix. The improved toughness of HIPS compared to PS is brought about by an increased absorption of impact energy due to the crazing mechanisms that are initiated and terminated by the rubber particles [107]. PB rubber has a structure similar to natural rubber. Both materials are unsaturated hydrocarbons, which means that the carbon-based molecule has a double or triple bond that permits easier addition of another atom or molecule to the original molecule. PB is a less reactive rubber than natural rubber, however it has poor tensile properties among others and is seldom used alone. It is the preferred rubber as a toughener in HIPS for several reasons including solubility in styrene monomer and participation in grafting and cross-linking reactions [120]. The repeat unit of PB rubber is shown in Figure 2.9 [64].

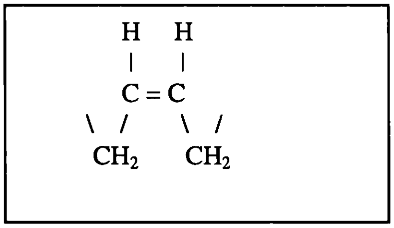


Figure 2.9 Repeat structure of Cis-1,4-polybutadiene rubber

A common way of blending polybutadiene with polystyrene, in the manufacture of HIPS is by the bulk polymerisation process [120], which involves dissolving the rubber into the styrene monomer followed by polymerisation. The resultant HIPS polymer will not only contain rubber and PS, but also a graft polymer where short styrene chains are attached to the rubber molecules, which will give a strong interface between the HIPS matrix and the PB particles. As a result of blending PS with PB, HIPS has an impact strength seven times that of ordinary PS, although this is at the cost of properties such as tensile strength, which may be reduced to about half that of PS. Compared with the clarity of PS, HIPS is opaque, and can be less stable to light and heat. HIPS may oxidise in air, on exposure to UV light and at elevated temperatures although stabilisers are often added to counter this effect [64]. Prolonged exposure could result in a deterioration of mechanical properties, however a visible sign before such effects become appreciable, is seen as discolouration of the polymer [99].

ABS copolymers are a large group of thermoplastics of various combinations of acrylonitrile ($CH_2=CH–CN$), butadiene ($CH_2=CH–CH=CH_2$) and styrene ($C_6H_5–CH=CH_2$). They are a two-phase polymer system consisting of a glassy matrix of styrene-acrylonitrile (SAN) with a dispersed phase of styrene-butadiene copolymer [107, 120, 126]. The SAN is partially grafted onto the dispersed rubber, which means that ABS copolymers will also contain an amount of polybutadiene, and polybutadiene grafted with both acrylonitrile and styrene [64, 107]. This reduces domain size and obtains a good dispersion of rubber into the matrix. The presence of these graft polymers are essential as just straightforward mixtures of polybutadiene and styrene-acrylonitrile copolymers are too compatible to give any improvement to properties. Optimal properties are therefore achieved by appropriate grafting between the glassy and rubbery phases [126].

ABS can be manufactured by several procedures including mechanical blending of SAN with a SAN/Butadiene copolymer and several polymerisation processes such as emulsion, suspension and bulk polymerisation [107]. Emulsion polymerisation offers considerable scope for the control of the structure and morphology of ABS polymers, however mechanical blending offers a good level control on the particle size and distribution, degree of crosslinking and grafting of the rubber phase [120]. The main toughening mechanism of ABS, was initially suggested by Newman and Strella as being due to the formation of shear bands in the SAN matrix [127]. However, later work found that ABS experiences both crazing and shear yielding, with shear yielding being the dominant toughening mechanism. When subjected to a tensile force, ABS will undergo stress whitening and yielding followed by localised necking, with the neck becoming intensely white prior to failure [120].

ABS is the fifth most used plastic type, being surpassed in tonnage terms only by plastics such as PE, PP, PVC and PS [64]. ABS sees considerable use in applications such as quality equipment housings among many others, as it displays excellent properties including excellent toughness, sufficient thermal stability, good processibility, and moderate chemical resistance [107]. The main drawbacks include lack of transparency, poor weathering resistance, poor environmental stress cracking (ESC) resistance and poor flame resistance. The increase in demand of ABS for applications in the automotive and electrical and electronic industries requires a higher level of flame resistance. This can be achieved by adding flame retardants, although this can often be at the cost of mechanical properties. Blending with PVC is also an effective method to improve flame resistance of ABS, although this can reduce processing stability [64].

2.6.5 Polymer Degradation

The term polymer degradation is used to denote changes in physical properties caused by chemical or physical reactions involving bond scission in the backbone of the macromolecule [128]. The most damaging effect of this chain scission is the decrease in molecular weight, and as a consequence various physical and mechanical properties may be modified [63], which is commonly in a detrimental manner. There are several different modes of polymer degradation, the main types being thermal, mechanical, chemical, photochemical, and biological degradation.

A polymer may be exposed to any of these degradation types during initial production processing and throughout its service lifetime. A recycling process following the end of life of the polymer may continue such exposure resulting in a polymer with properties inferior to those of its virgin counterpart. It is therefore useful to understand the mechanisms of polymer degradation in order to recognise such exposure and in order to engage ways of reducing such effects so that the quality of recyclate can be comparable to that of virgin polymers.

Thermal degradation refers to the case where at elevated temperatures the polymer will undergo chemical changes without the involvement of another compound. The macromolecules of a polymer are stable only below a certain limiting temperature range (usually between 100–200°C). When the temperature exceeds this range, the macromolecules can start to degrade. This happens because polymer molecules are linked together by covalent bonds. The strength of these bonds is limited and they are stable at ambient temperatures because there is insufficient energy to break such bonds. However chain scission is feasible at higher temperatures, and bond breakage occurs when the vibrational energy of the bonds reaches a critical level. Typical reactions occurring within the polymer during degradation include main chain, or side group scission. In the case of linear polymers crosslinking can occur, which actually increases the molecular weight, although at extreme temperatures depolymerization may occur [128].

Mechanical degradation generally refers to macroscopic effects brought about by the influence of shear forces. In other words, this covers the fracture phenomena as well as deformation mechanisms and chemical changes that are induced by a mechanical stress. Examples of such stress inducers include mechanical processes, such as machining, grinding, milling and extrusion, and modifying processes, such as cutting, sawing and drilling, as well as tensile or shear forces. Such stress induced processes are frequently accompanied by bond ruptures in the polymer main chains. Bond rupture occurs when sufficient energy is concentrated at a certain point of the macromolecule, which is a consequence of the non-uniform distribution of residual stresses. Although the extent to which chain scission occurs depends on the polymeric material, it is difficult to define a single mechanism for stress induced chemical reactions. This is because there are so many different bond scissions that depend on the state of the polymer i.e. rubbery, glassy or viscoelastic (molten), as well as the mode of mechanical imposition of stress. Therefore it seems that during the formation of a fracture plane in a polymer, strains can be generated, which result in bond rupture [128].

Chemical degradation refers to structural breakdown processes that are induced by the influence of chemicals (acids, bases, solvents, reactive gases etc) that are brought into contact with polymers. Although many reactions start spontaneously, the rate of chemical reactions is strongly dependant on temperature i.e. reaction rate increases with temperature. This implies that thermal and chemical degradation overlap, which is a realistic assumption considering that practically all polymers will contain some form of additive that will essentially react chemically with the macromolecules as the temperature is increased [128]. However chain scission due to a chemical reaction can occur regardless of temperature on exposure of a polymer to an environment. It should be noted that this breakdown of a polymer structure is not necessarily caused by concentrated acids or solvents, but can occur due to apparently harmless media such as oxygen (known as oxidation) or water (hydrolysis). In some polymers, it can be therefore necessary to incorporate stabilisers and antioxidants into the plastic in order to maintain properties and delay subsequent chemical degradation for a long time [63].

Photochemical degradation concerns the physical and chemical changes that are caused by irradiation of polymers with ultraviolet (UV) or visible light [128]. In order to be effective, light must be absorbed by the substrate. Plastics containing carbonyl or unsaturated groups are directly photosensitive as they readily absorb UV radiation. Sunlight can be detrimental to polymers as they are transparent to radiations of wavelengths over 400nm. The UV portion of the sunlight spectrum is therefore the most damaging part of the sunlight spectrum as it is over the wavelength range 290 – 400 nm. Occasionally photochemical degradation can occur in radiation levels lower than expected. This is due to the presence of active groups called chromophores, which occur during processing and promote photochemical reactions. Photochemical degradation can be reduced by incorporation of specific additives that absorb the radiation. However there are also additives that promote photochemical degradation known as photosensitisers. These are usually employed as self-destruction methods for the elimination of litter [63].

Biological degradation involves microbial attack of the polymer. Microorganisms can produce a variety of enzymes that can react with a polymer. This type of enzymatic attack of the polymer is a chemical process that is induced by the microorganisms in order to obtain food – the polymer. The microbial attack of a polymer can occur over a range of temperatures and can be as high a 70°C in some cases [128].

2.6.6 Recycling Plastics

The plastics ABS, HIPS, PPO and PC/ABS are four of the most commonly used materials as housings for data processing and computer equipment [17]. With continual technological advancement there is constant upgrading of equipment of this kind, which means that the amount of obsolete and disused equipment is increasing. Some of this equipment may be reconditioned for re-use, however this is not always a viable option. New recycling legislation in the electrical and electronic sector is setting minimum recovery and recycling targets. The recycling of computer equipment would have a significant contribution in meeting such targets, however at the present time the plastic and glass content of computer equipment is not being reprocessed. Hopefully this will change once a better understanding of the effects that recycling has on these materials has been established [36].

Although there is not a great deal of information available as to the recyclability of the above plastic types, results from recent research studies look fairly promising. Several studies have been conducted into the recyclability of PS and HIPS over a series of recycling passes. Covavisaruch et al [129] looked at the effects that a number of recycling passes had on physical and mechanical properties of two different types of scrap HIPS; scrap from a HIPS manufacturer containing no additives, and industrial post-fabricated waste HIPS containing the colourant titanium dioxide (TiO_2). A recycling pass consisted of extrusion (including repelletization) followed by injection moulding. Further recycling passes involved grinding the injection moulded plastic into scrap and then injection moulding again. This was repeated until five recycling passes had been accomplished, while segregating a portion of material after each recycling pass for testing. Properties investigated included tensile properties and impact strength, the melt flow rate and molecular weight. The first five recycling passes of HIPS produced insignificant changes to tensile properties however the impact strength decreased with each successive recycling pass. This was believed to be due to chain scissions induced by high shear stresses during each recycling process. This was verified by reductions to weight average molecular weight (M_w) and increases in the melt flow rate. The presence of TiO_2 in the HIPS scrap lead to greater reductions in impact strength and M_w and was said to be due to poor interfacial adhesion between the TiO_2 phase and the HIPS matrix. The incorporation of an appropriate impact modifier such as styrene-butadiene-styrene (SBS) block copolymer into the HIPS scrap was suggested to remedy the loss of impact strength.

Investigations by Jamil et al [130] compared the effects of recycling HIPS using different thermal processing methods, such as a laboratory extruder, and a Braebender plasticorder. All results showed a decrease in shear stresses and consequently, viscosity at constant shear rate. The elongation of recycled HIPS also decreased for both processing methods and although tensile strength values progressively decreased with the laboratory extruder, they were increased in the case of the Braebender mixer. This was explained by insufficient compaction resulting from lower working pressure in the extruder.

Salman et al [131-134] also conducted studies into recycling HIPS over several passes. These studies investigated the effects of thermal aging and photochemical degradation of recycled HIPS and measured properties mainly including optical properties such as absorbance, transmittance and reflectance, as well as dynamic thermal analysis (DTA). It was found that transmittance and reflectance decreased whereas absorbance increased with each successive recycling pass in both thermally and photochemical aged HIPS, and was generally seen as discoloration of the material. DTA of aged recycled HIPS indicated a rapid deterioration in thermal stability following each recycling pass of thermally aged HIPS, but did not show any affects for un-aged recycled HIPS.

Other work on the effects of recycling on PS over several recycling passes [135, 136] also concluded no change to the tensile modulus of PS but saw decreases in tensile strength. Results from these studies were unanimous with all previous work in that continual recycling caused a significant drop to impact properties and elongation as well as a reduction to M_w.

Similar studies were carried out by Kim et al [137], on the recyclability of ABS. Three different grades of ABS, general use, colour improved and high impact strength, were recycled using twin screw extruders. The recycling pass was repeated five times, segregating a portion of material for testing after each pass, which was then injection moulded into test specimens. Properties measured include tensile strength and elongation, impact strength, hardness, the yellowing index, glass transition temperatures (T_g) and molecular weight. The main findings saw no change to tensile strength, elongation, hardness, T_g and molecular weight, even after several recycling passes. However the impact resistance was decreased after recycling for all grades of ABS although this decrease was greater in the high impact strength ABS. As this grade contained the most polybutadiene (PB) it was suggested that the decrease in impact strength is likely to be due to degradation of the polybutadiene content. All materials turned yellowish from recycling, the high impact ABS seeing a faster change in colour than the others, and morphological studies using transmission electron microscopy (TEM) found no change to the structures of each material tested. Therefore, while recycling appears to have little effect on most properties studied of

ABS, it has been found that the PB content in ABS is vulnerable to impact strength and the decomposition of PB can be indicated by a change in colour.

Very little information was found on the recycling of PPO, although it is said to possess a good melt thermal stability. It has been claimed that under correct processing conditions the polymer has shown little change in physical properties even after seven regrinds [64]. A study into the recycling of Nylon 66 / PPO alloys [138] containing different impact modifiers (PB and polyisoprene block copolymer) compared the effects of multiple extrusions and multiple injection moulding passes on properties including impact properties, TEM and molecular weight. It was found that although impact strength of Nylon 66 / PPO was lost for both multiple extrusion and multiple injection moulding, the results showed a more gradual loss for the latter for both types of alloys. However results for the Nylon 66 / PPO alloy with PB showed the greater loss of impact strength for both process types. Morphological investigations found that the cohesion of the nylon 66 / PPO interface deteriorated during the later cycles of multiple processing and indicated PPO particle agglomeration which increased PPO particle size. Molecular weight results found that the weight average molecular weight (M_w) was increased following the seventh recycling pass indicating that extrusion probably causes more crosslinking than chain scission. This increase in M_w was probably the cause of an observed increase in melt viscosities. However the main observation was that the presence of PB as an impact modifier in Nylon 66 / PPO alloys will produce a serious loss to impact strength due to the thermal/oxidative degradation of the unsaturated polymer backbone.

Studies have also been conducted into the recyclability of ABS and PC/ABS. Tall et al [139] suggested that it is plausible to recycled recovered ABS, PC and PC/ABS as one fraction, although the blend ratio would need to be controlled as PC/ABS blends exhibit a minimum impact strength at approximately 30% PC content. Liu et al [140,141] conducted various studies into recycling ABS and PC/ABS taken from waste car scrap and looked at properties including tensile and impact properties. The fall in impact toughness has been the main concern when recycling blends of PC and ABS, which has been attributed to the oxidative degradation of the butadiene rubber phase in ABS during service time. On its own recycled PC has been found by Bledzki et al [142] to retain impact strength and it is the presence of other materials or contaminants that deteriorate this property. These studies have found that blending recycled PC/ABS with a small amount of methyl-methacrylate-butadiene-styrene

(MBS) core-shell impact modifier gives the mixture better impact properties than the individual components [140,141].

A couple of studies investigated the effects of recycling blends of ABS and HIPS. Tall et al [139] looked at the stress strain behaviour of blends of ABS with HIPS in proportions of 4, 8 and 12% HIPS. The tensile strength was seen to decrease with successive proportions of HIPS when compared with 100% ABS. At a HIPS content of 4% there was a substantial increase of strain at failure, but this dropped back as the HIPS content increased, and at a HIPS content of 12% the strain to failure was slightly less than that of ABS. The initial elastic part of the stress/strain curve for all blends appeared to overlap indicating little or no change to tensile modulus with the addition of such small proportions of HIPS.

Other work by Brennan et al [17, 143] also looked at the effect of recycling on blends of HIPS and ABS that were taken from equipment housings of computer scrap. Blend proportions of ABS and HIPS were as 90/10, 50/50 and 10/90 and were compared with properties of the recycled constituents. The recycling process was laboratory based and consisted of granulation, thermal mixing in a torque rheometer, re-granulating followed by injection moulding into test specimens. Properties measured include tensile properties, impact strength and T_g. Recycling and blending brought about no significant change to tensile strengths, tensile moduli and T_g's of all blends. The presence of 10% HIPS in ABS and 10% ABS in HIPS had a favourable effect on the strain at failure providing some recovery of the significant amounts of ductility that were lost in both ABS and HIPS due to recycling. The impact strength of ABS deteriorated on recycling and blending with proportions of HIPS only served to decrease the impact strength further. Likewise the impact strength of HIPS was decreased due to recycling, although blending with proportions of ABS did not affect impact properties further than those due to recycling.

2.7 TESTING OF PLASTICS

2.7.1 Tensile Properties

The conventional stress-strain, or tensile test is often used to describe the short-term mechanical properties of plastics. It is a widely used method for characterising metals, but is easily adapted for use with plastics [65]. Thermoplastic materials are generally viscoelastic in nature. This means that their mechanical properties reflect characteristics of both viscous liquids and elastic solids. So, on experiencing a stress, a thermoplastic can either exhibit viscous flow, which dissipates energy, or it can displace elastically, which stores energy that can be used to recover the plastic to its original form on removal of the stress [114]. Generally the properties of viscoelastic materials are dependant on time, temperature and strain rate and the mechanical properties can vary quite significantly according to these factors [63, 114]. Tensile testing would therefore be unsuitable in classifying long-term properties and care should be taken with test conditions in order to obtain valid results.

A basic tensile test involves the deformation of a specimen in tension at a constant extension rate, whilst recording the stresses and strains experienced by the sample until sample failure occurs [17]. Most tensile results will be recorded as the load or force exerted on the sample (in Newtons) versus the extension or displacement of the sample (in millimetres). However, as samples may differ in size and dimensions, the load and displacement are converted into units of stress and strain in order to take into consideration relative sample geometry. Tensile stress (σ) is defined as [144];

$$\sigma = \frac{F}{A} \qquad \text{Equation 2.2}$$

where F is the force exerted onto the sample (N) and A is the cross-sectional area of the sample (m^2). The units of stresses are therefore in Newtons per metre squared (Nm^{-2}) or Pascal (Pa). As this unit is relatively small, the normal unit of stress is expressed as mega pascal (MPa). The nominal tensile strain (ε) is defined as [144];

$$\varepsilon = \frac{l}{l_o} \qquad \text{Equation 2.3}$$

where l_o is the original gauge length of the sample in mm and l is the amount of extension parallel to the tensile stress in mm. Strain is therefore the amount extended as a proportion of the original length (often converted to a percentage). Strain can be either elastic or plastic. Elastic strain is reversible and disappears once the stress is removed. It is roughly proportional to the applied stress. Plastic strain occurs when a material is stressed to the extent where its elastic limit is exceeded. On removal of the stress, only the elastic strain disappears and any plastic strain produced is retained [145]. As polymers exhibit viscoelastic behaviour, the strain can be recovered over a finite time period.

The stress/strain data recorded from a tensile test can be plotted as a curve of stress versus strain. Three different types of stress/strain behaviour can typically be found for polymers and are represented in Figure 2.12. Curve (a) represents the behaviour of a brittle polymer. This type of polymer experiences elastic strain only, with fracture occurring before plastic deformation. Curve (b) represents a more plastic stress strain curve, which is highly characteristic of many plastics and some metallic materials. The polymer initially shows approximately linear deformation until yielding occurs [65], where the yield point is the first point on the stress/strain curve at which an increase in strain occurs without an increase in stress [146]. This type of curve has a definite yield point with a definite drop in stress as localised polymer chains slide past each other. Following this drop is a period of cold drawing [63], which can often be seen as necking [65] and is where polymer chains start to unfold and can slide past each other relatively easier. Plastic deformation continues with little change to stress levels until the polymer chains are sufficiently stretched and aligned. This is known as orientation hardening or stiffening [63] and requires an increase in stress to continue deformation until failure occurs. Curve (c) is characteristic of highly elastic materials such as rubbers or elastomers [63]. These materials are highly extensible and deformation is predominantly elastic with large recoverable strains produced at low stress levels [65]. No one stress/strain curve will completely describe a family of polymers and tensile behaviour will vary according to variables such as additives and fillers present, testing conditions, and processing history, however the curves described above serve only to illustrate the general types that can be encountered.

A substantial amount of information regarding properties of polymers can be derived from stress strain curves and the properties are defined as follows with reference to the illustration of these properties in Figure 2.13. The tensile strength is the maximum tensile stress supported by the specimen during a tensile test. In Figure 2.13 it is at (a), which also happens to be the tensile stress at failure, although these

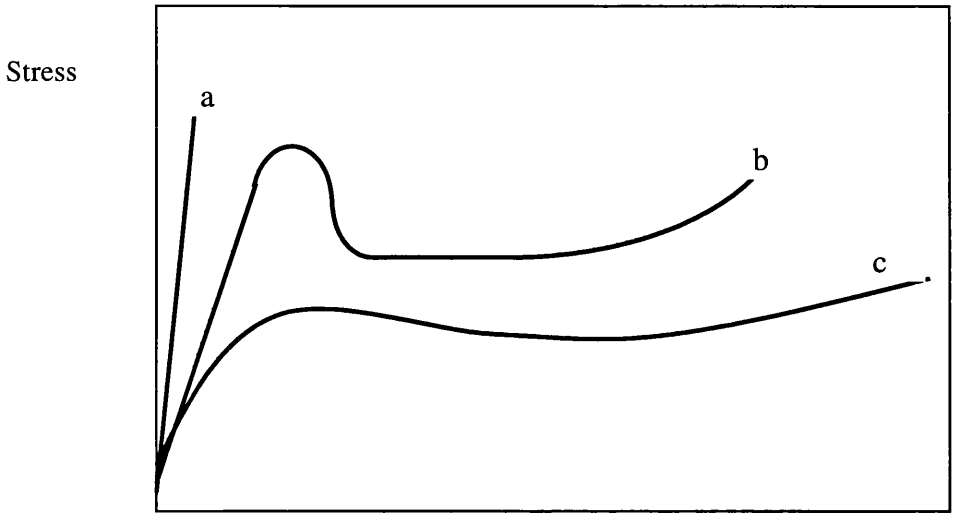


Figure 2.12 Various stress/strain behaviour for polymers

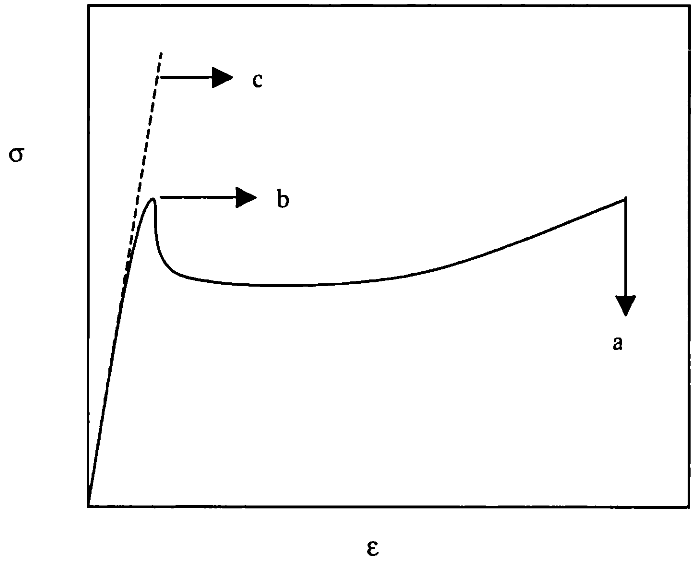


Figure 2.13 Typical features of a stress/strain curve

two properties are not always at the same point on the curve. The strain to failure is the percentage elongation of the test specimen in relation to the original length and is also at point (a). This property is important as it can give an indication as to the ductility of the plastic. The yield point is the first point at which plastic flow is said to occur. On the diagram in figure 2.13 it is fairly easy to define and is at (b). However it must be remembered that in many polymers the yield point is not so well defined and can be difficult to determine the exact point accurately. For some very ductile plastics it is sometimes necessary to know when plastic flow will begin to occur, so the yield strength can often be a more important parameter than the maximum tensile stress [145]. The line at (c) is a tangent to the proportional or elastic part of the curve. This part of the curve is used to calculate the modulus of elasticity (E) of a material, which can be defined as the ratio of stress to corresponding strain below the proportional limit of the material [146]. In other words, it is the stress required to produce a unit quantity of elastic strain. It is therefore calculated as the gradient of that proportional elastic part of the curve and is defined by the following expression [145];

$$E = \frac{\sigma}{\varepsilon} \qquad \text{Equation 2.4}$$

The elastic modulus is a measure of the rigidity or stiffness of a material [145] and the higher the modulus the stiffer the material [65].

2.7.2 Impact Properties

For many applications the resistance to impact is an important property of plastics materials. The ability to withstand accidental knocks can be key to determining success or failure in a particular application as a plastics product is more likely to fail when subjected to an impact blow in comparison with the same force being applied more slowly [63]. The energy required to break a sample is approximately given as the area under a stress strain curve [64]. A brittle polymer that has very little deformation prior to fracture will require a lot less energy to break, despite having a high modulus and tensile strength, than a more ductile or rubbery polymer with a lower tensile strength due to the large extensions of the sample before fracture occurs (Figure 2.14). If the rubbery polymer is struck a sudden blow, a lot more energy will be required to break than for the brittle polymer and it will be therefore regarded as tough [64].

The toughness or impact strength of a material depends on a number of variables, and polymers can experience ductile or brittle fracture depending on temperature, strain rate, specimen geometry and sample processing history [114]. As with metals, both crystalline and amorphous polymers experience a ductile to brittle transition over a temperature range [65]. At lower temperatures below the glass transition temperature (T_g), they are brittle with low impact strengths, becoming more ductile with greater impact strengths at higher temperatures above T_g [64]. An ideal plastic would therefore be rigid with high impact strength at ambient temperature [64,65].

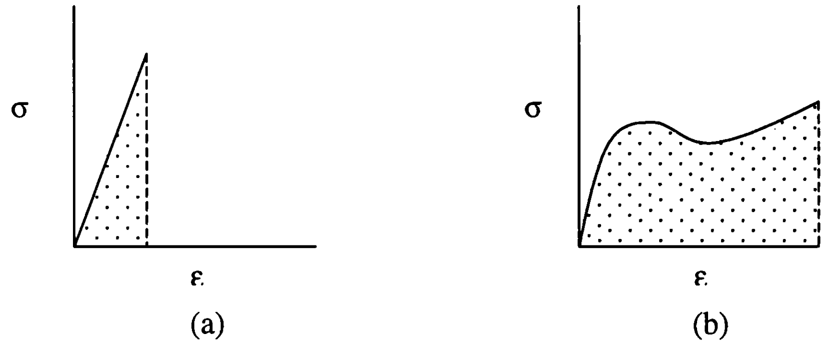


Figure 2.14 Stress/strain curve for (a) brittle and (b) ductile polymers. The area under the curve is a measure of the energy required to break the test piece.

In order to comparatively quantify impact strength data, careful consideration needs to be given to impact test conditions so that they resemble specified product service conditions as closely as possible. However impact tests can also be used to compare impact strengths of different materials. Practical methods used for measuring impact toughness differ from tensile tests used to produce stress/strain information in that they employ shock loading [145]. The main impact test procedures include Izod, Charpy, Tensile-impact and Falling weight tests. Izod, Charpy and Tensile-impact tests are all types of standard pendulum tests, whereby a notched or un-notched specimen is held or clamped in a fixed position and subjected to a blow imparted by a pendulum impactor. A Charpy test is an impact three point flexure test, the Izod method a fixed cantilever beam and the tensile-impact test represents a high strain rate version of the conventional tensile test [63]. The different test geometries are illustrated in Figure 2.15 [17].

The principle behind pendulum tests involves calibration of the system in the absence of a sample in order to take account of the frictional forces, and determine the height the pendulum reaches during a "free" swing. During testing the energy absorbed by the sample will be seen as a loss of potential energy or height, suffered by the pendulum and is calculated as energy to break in Joules. Different sample geometry will absorb different quantities of energy and so in order to obtain a comparable result, the cross-sectional area of the sample must be taken into account.

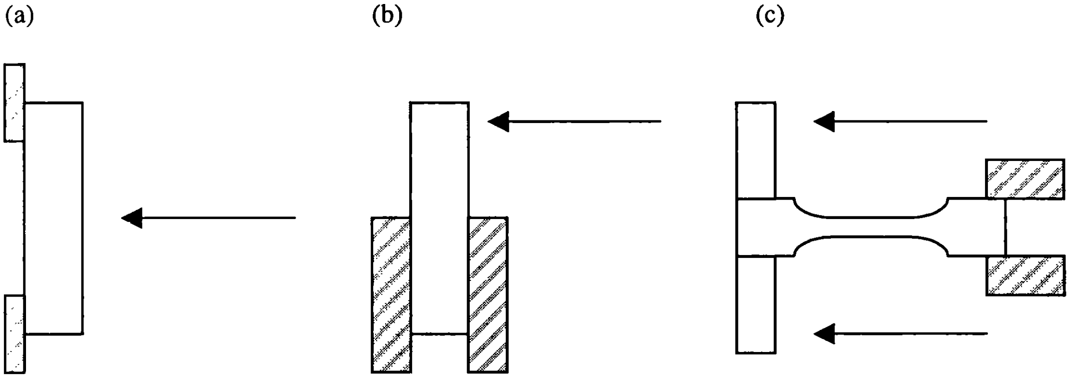


Figure 2.15 Test geometry, loading mechanism and clamping mode for (a) Charpy (b) Izod and (c) Tensile-impact, impact tests.

The impact strength will generally be quoted as the energy to break per fractured area [64]. This can be defined by the equation [114];

$$\text{Impact Strength} = \frac{\text{Energy to break}}{\text{X-area of sample}}\ (\mathrm{Jm^{-2}}) \qquad \text{Equation 2.5}$$

A falling weight impact test is where a missile is allowed to fall by gravity onto a supported flat or domed surface from a predetermined height. The degree of imposed energy is calculated accordingly as

$$Energy = mgh \qquad \text{Equation 2.6}$$

where m is the mass of the missile being dropped, g is the acceleration caused by gravity (approximately 9.8 $\mathrm{ms^{-2}}$) and h is the predetermined height. This is a less sophisticated but more qualitative method but can be more realistic. Test results are usually as a criterion of pass (if the object remains intact) or fail (if the object is damaged) [63].

2.7.3 Glass Transition Temperature

As previously stated, the properties of plastics are considerably dependant on temperature. At lower temperatures a plastic may be hard, brittle and glassy, whereas on increasing the temperature the plastic may become soft and flexible. Properties may vary according to the glassy or flexible state of the plastic. This behaviour is a result of the molecular structure of polymers [114]. At lower temperatures the material is solid having a structure of covalently bonded molecular chains, the atoms of which vibrate over small amplitudes and are relatively independent of each other. As the material is heated up and the molecules receive more energy, there is an increase in their relative movement, and rotational chain movement may occur which is seen to make the material more flexible [65]. The temperature at which this change in properties takes place is known as the glass transition temperature [145].

The glass transition temperature (T_g) is a property more associated with the amorphous region of a polymer [145], as a crystalline polymer is more likely to just experience a melting temperature from a solid into a viscous liquid [147]. The T_g of a polymer is described as the temperature corresponding to the transformation from a rigid material to one that has rubber like characteristics [65]. In other words, if a plastic is heated, the T_g is the point at which the material first acquires significant molecular motion [63]. Below the T_g a plastic will behave like a glass i.e. hard and rigid, whereas above the T_g the same material will have rubber-like properties. As the T_g is not the same for every polymer, this can help to explain some of the differences observed between plastic types. For example PMMA is seen as a glassy brittle polymer at room temperature as it is well below its T_g value of 105°C. On the other hand, the T_g of polybutadiene is about –100°C, which is why at room temperature it appears to be a very flexible material [114]. With semi-crystalline materials, the crystalline melting point (T_m) is higher than T_g, the relationship between the two being approximately [148]

$$T_g = {}^{2}/_{3} T_m \text{ K} \qquad \text{Equation 2.7}$$

The crystalline regions will give strength and rigidity to a higher temperature and the semicrystalline material will exhibit both T_g and T_m.

As the magnitude of T_g varies over a wide range of temperatures for different polymers, there are several factors that affect the T_g of a polymer. As the T_g depends largely on the amount of thermal energy required to move the polymer chains, these factors are mainly associated with rotation about the polymer chains [147]. The molecular structure of a polymer has a significant influence on T_g. Generally, polymer chains that are based on the aliphatic C – C and C – O bonds are quite flexible. However the introduction of ring structures such as a phenylene group can have a stiffening effect, which means that more energy will be required to transform into a flexible polymer and therefore such polymers will exhibit higher T_g. The size of side groups attached to the main polymer backbone also has a similar effect on the T_g of a polymer, in that the larger the side groups, the less flexible the polymer and the more energy is required to bring about any chain movement, thus the higher the T_g [64, 147]. Another factor influencing the T_g of a polymer is the molecular weight of a material. At higher molecular weights, the T_g is constant and independent to any molecular weight changes. On decreasing to a critical molecular weight and below, the T_g decreases as molecular weight decreases [65]. This is due to an increase in the number of chain ends in a polymer. A chain end is able to rotate and move more readily than a chain segment and so the more chain ends a polymer has, less energy will be required to move the chains and thus the T_g is lower than that of a higher molecular weight polymer with less chain ends [147]. However for some of the most common used polymers such as PS and PVC for example, the critical molecular weight above which T_g is independent is generally between 100 and 1000 [149]. Other factors affecting the T_g of a polymer include thermal processing history as well as the presence of fillers and additives. The effect of plasticisers for example, reduces the T_g of a polymer.

The transition from a glass to a rubber-like state of a polymer is accompanied by evident changes to properties including the specific volume, the modulus, and heat capacity [147]. Therefore the T_g of a polymer can be determined using one of several different techniques. These techniques are generally dynamic or static methods. For static methods, changes in the temperature dependence of properties such as density and heat capacity are followed. A common static method is a dilatometric technique that derives the T_g by looking at marked changes to specific volume with temperature [63]. A polymer sample is placed in a dilometer and a confining liquid such as mercury is added. Any change to the volume of the polymer is registered by movement of the mercury level. Results come in the form of specific volume/ temperature curves as shown in Figure 2.16. The curves generally consist of two linear portions of differing slopes. Between slopes, the curve changes continuously over a narrow temperature range. The T_g is determined by extrapolation of the two linear portions and is taken to be at the intersection point [147].

In dynamic methods, a rapid change to the modulus is indicative of the T_g [147]. A common method for determining the T_g of a plastic is dynamic mechanical thermal analysis (DMTA). This technique is based on characterising the T_g by measuring changes to the modulus of a material. The principle of DMTA involves the application of a small sinusoidal stress to a sample at a single frequency or over a selection of frequencies. This causes cyclic deformation of the sample and the

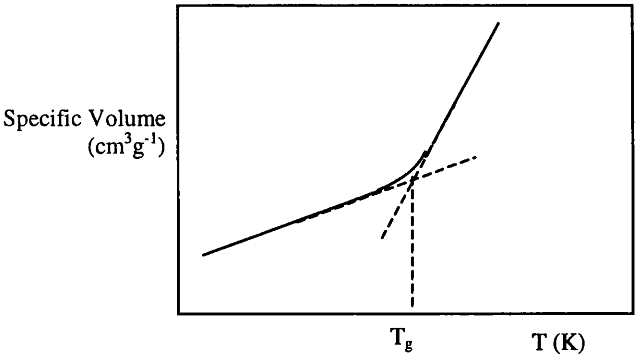


Figure 2.16 Diagram illustrating a typical specific volume versus temperature curve. T_g is at the point of intersection of the extrapolated linear sections of the curve

response of the stress/strain relationship of the sample is normally monitored over a designated temperature span. The mode of deformation is sometimes in tension or shear, but a more common method is three point bending [63].

As the sample oscillates, the stress/strain response is measured as a real or in-phase modulus (E') and an imaginary or out of phase modulus (E'') [150]. The two moduli represent the elastic and viscous behaviour of the sample. The elastic modulus (E') (or bending or storage modulus) is the absolute energy contained or stored within a sample or in other words, the amount of recoverable strain energy in the deformed body. The viscous or loss modulus (E'') is related to the energy lost due to viscous flow or dissipation of energy, and is unrecoverable by the sample. The ratio of the two moduli defines the loss tangent or damping tanδ, and is described as

$$\tan\delta = \frac{E''}{E'} \qquad \text{Equation 2.8 [150]}$$

This is a measure of the proportion of energy lost by the sample or damping that occurs as the temperature increases.

Results of a DMTA test are normally recorded as the bending modulus (Log E') and the damping or loss tangent (tanδ) as a function of temperature as shown in Figure 2.16. At temperatures lower than the T_g, the sample is relatively stiff. Therefore the absolute energy within the sample will initially be high as a higher amount of energy will be required to bend it. This is seen as a higher proportion of E' and while the material is in its glassy state, E' is relatively independent of temperature. As the sample is stiff, most of the strain will be recoverable i.e. elastic and therefore not much energy is lost initially which is seen as a lower tanδ.

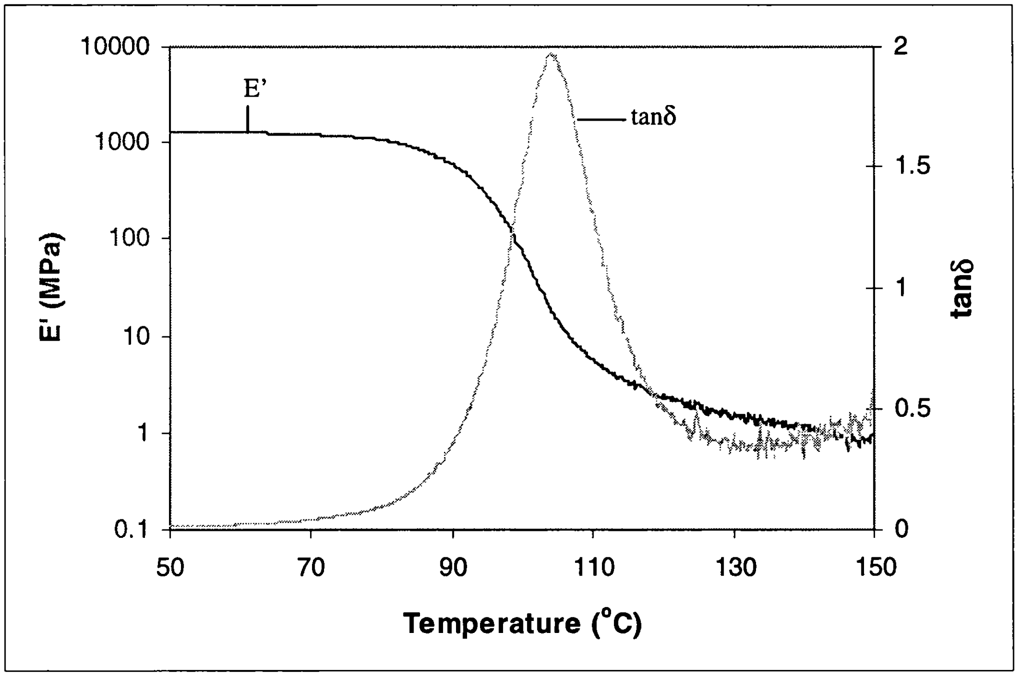


Figure 2.16 Typical results from DMTA test of recycled ABS showing bending modulus E' and loss tangent tanδ as a function of temperature

As the temperature increases, the levels of elastic recovery and damping remain relatively constant. However on approaching the T_g, the proportion of the material that is flexible starts to increase, slowly at first and then more rapidly as the temperature increases. As the material becomes less stiff and more flexible the amount of energy needed to bend the sample is reducing, which can be seen as a decrease in E', initially at a slow rate than at a rapid rate on reaching the T_g. At the same time the increase in the flexible proportion of the sample is seen as a sudden increase in the damping tanδ as the proportion of energy dissipated by the sample increases despite needing less energy. The damping tanδ is seen to peak at the T_g, which is probably due to equal proportions of the sample being stiff and flexible.

On exceeding the T_g the rapid decrease of E' continues as even less energy is being put into the system. The amount of energy being lost will also start to go down at this point and the damping tanδ falls rapidly. As the temperature continues to increase past the T_g, E' then continues to decrease at a much slower rate as even less energy is required for bending once the whole sample is more or less a rubbery flexible material. The damping tanδ continues to decrease to a minimum although this is not as low as it was initially because there will be a higher proportion of energy that will need to be dissipated. The damping tanδ will then start to increase as the sample tends towards the next transformation to a viscous liquid.

As well as determining the T_g of a homopolymer, DMTA can be useful in characterising the T_g of a blend or copolymer. If a two-component polymer is miscible, there will be a shift of the T_g to an extent determined by the blend composition in relation to the T_g's of each constituent homopolymer [63]. If the two polymers do not blend homogeneously but remain as segregated materials in a coarse two-phase structure, there will be more than one transitional temperature, as shown in Figure 2.17.

It must be noted however that care must be taken in determining comparable results as this test is frequency sensitive and will give slightly different glass transition temperatures according to the frequency of oscillation [147]. However the main advantage to this method of testing is that it is a direct method, directly measuring a material's mechanical response to a range of conditions. This means that the T_g can be measured under conditions that resemble the material application as closely as possible [150].

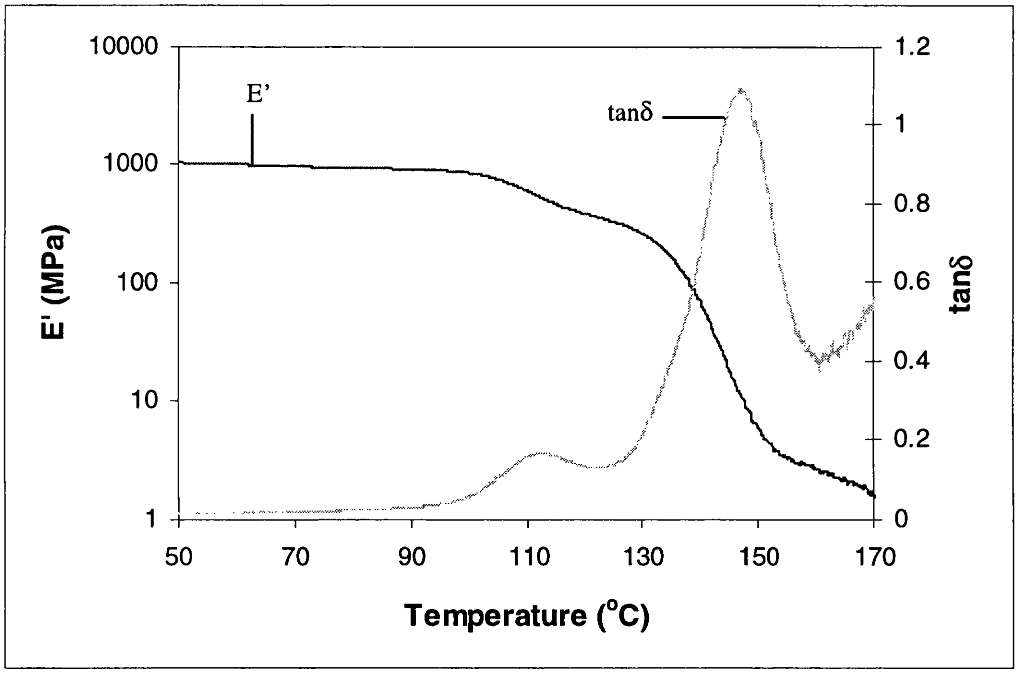


Figure 2.17 Typical results from DMTA test of recycled PC/ABS blend showing two distinct glass transitions which are seen as peaks in tanδ and inflexions of LogE'

2.7.4 Viscosity

All polymer processing methods involve heating, shaping and cooling, and although this sounds straightforward the apparent simplicity can be deceiving [114]. The flow properties of polymer melts are complex, which is hardly surprising when trying to deform variously entangled long chain molecules of a range of molecular weights [64]. It is therefore essential to be able to make quantitative predictions on material properties such as viscosity [114] so that the polymer can be processed in the optimum way.

If a stress applied to a material is removed once deformation has occurred, the strain may or may not return to zero. If the strain returns to zero, the material is deemed to be fully elastic. If the strain does not return to zero, then it is deemed that flow has occurred [151]. Viscosity is the measurement of resistance to flow [152] or in terms of plastics, the melt viscosity of a polymer is the measure of the rate at which chains can move (or flow) relative to each other [64]. Polymer melts generally exhibit a viscoelastic response to an applied stress and can behave like a liquid (continual deformation under applied stress), or an elastic solid (recovery of deformation on removal of stress), or even a combination of the two, depending on certain conditions [63]. Figure 2.18 illustrates this viscoelastic response to an applied stress.

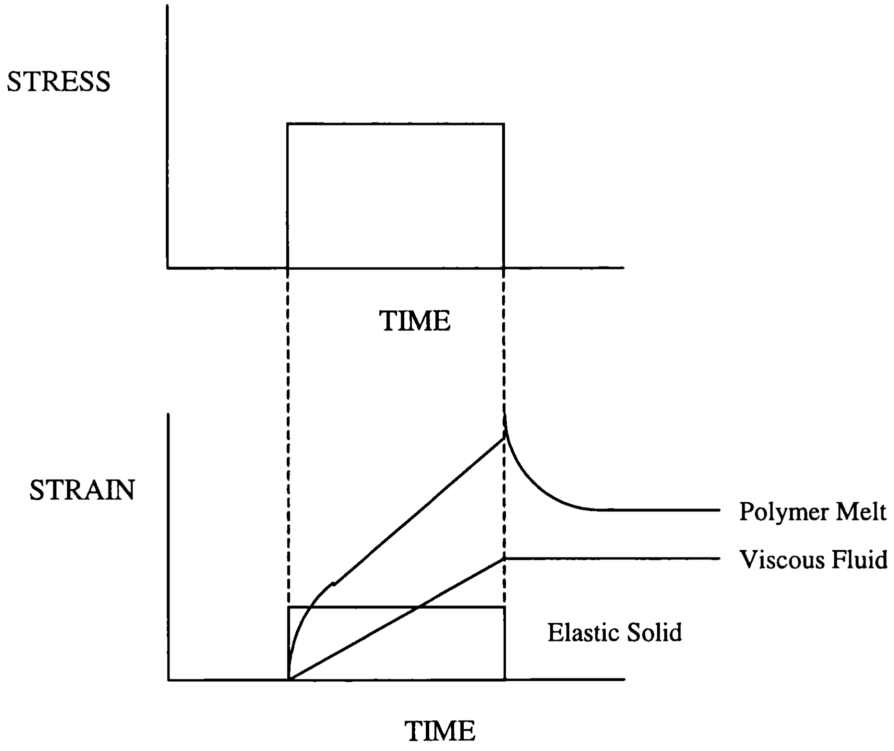


Figure 2.18 Viscoelastic behaviour of polymer melts [63]

Viscosity (η) is quantitatively defined as the ratio of shear stress (τ) to the shear strain rate ($\dot{\gamma}$) as shown in the following equation:

$$\eta = \frac{\tau}{\dot{\gamma}} Nsm^{-2} \qquad \text{Equation [2.9]}$$

Standard units are Nsm^{-2} or Pas^{-1} (pascal-second). Table 2.5 compares viscosities of different liquids.

Table 2.5 The viscosity of some familiar materials [63,128]

Liquid	**Approximate Viscosity (Pa-s)**
Glass	10^{21}
Pitch	10^{9}
Molten Polymers	$10^{2} - 10^{7}$
Glycerine	10^{0}
Olive Oil	10^{-1}
Water	10^{-3}
Air	10^{-5}

There are several factors that affect the viscosity of materials. These include shear strain rate, temperature and time of shearing. The shear strain rate can increase, decrease or have no effect on viscosity whatsoever. The viscosities of different materials can vary considerably in their responses to strain rate changes. Attempts to describe these responses have defined several different categories, which are illustrated in Figure 2.19.

The simplest model describing the behaviour of fluids is Newtonian. This type of material is purely viscous and the applied stress is proportional to the strain rate [153]. The viscosity is characteristically constant and is therefore independent of shear rate [63], as well as time and pressure [114]. An example of a Newtonian fluid is water.

A Bingham body is when a material does not deform below a certain yield stress, but essentially behaves as a Newtonian fluid once this yield stress is exceeded. The viscosity of a Bingham body will therefore be similar to a Newtonian viscosity flow curve. Plasticine and some clay slurries are examples of Bingham bodies [63].

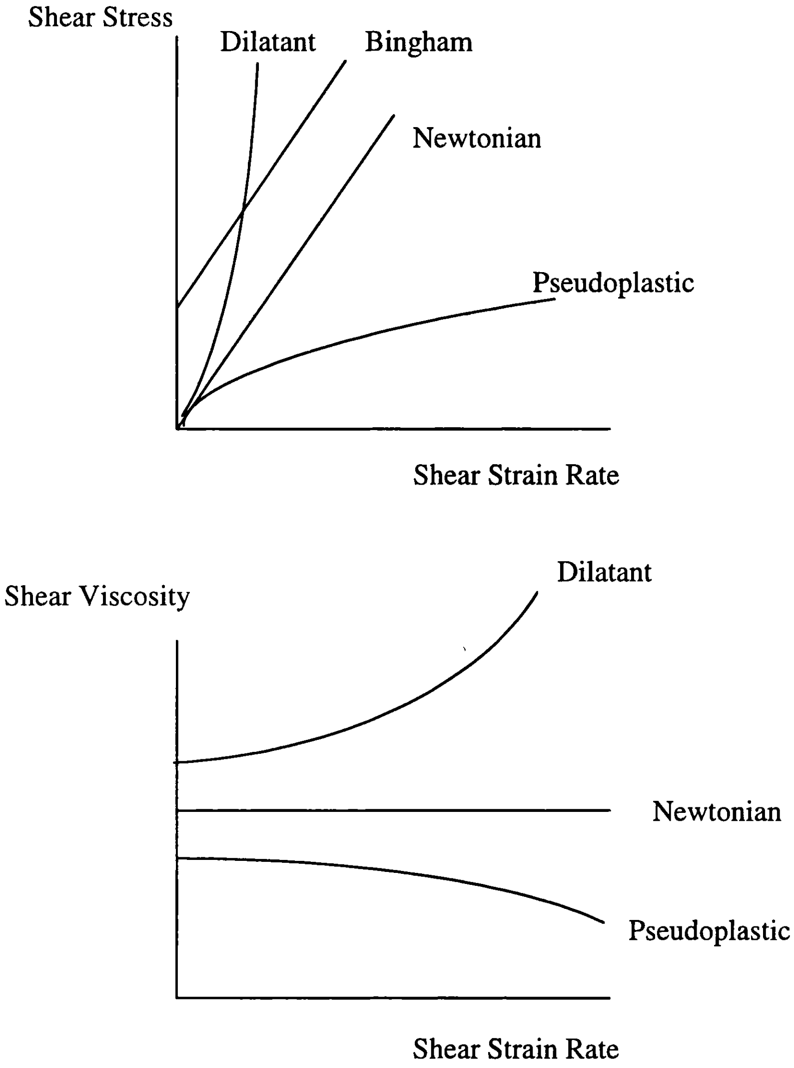


Figure 2.19 Flow curves of idealised fluids

Dilatant or shear thickening [153] materials, exhibit an increase in viscosity as shear rate increases. This is a non-Newtonian reponse and dilatancy is found to occur in certain PVC plastisols but only over a limited range of shear rates [63].

Pseudoplastic, which is also known as shear thinning [153], is the most common response for polymer melts. For this type of material the shear stress is not proportional to the shear rate, and the viscosity decreases as the shear rate increases [63]. As the shear rate tends towards zero, the viscosity tends towards a constant value and may initially appear to be almost Newtonian. Likewise when in the limit of very high shear rates, the viscosity again tends towards being constant and these two extremes are sometimes known as the upper and lower Newtonian regions (referring to regions of shear rate and not viscosity) [152]. Therefore when quantifying the viscosity of polymers it is equally important to specify the shear rate [63].

Another important parameter to note, especially when specifying the viscosity of polymers, is that of temperature. Generally viscosity decreases with an increase in temperature and the strong temperature dependence of viscosity is such that care needs to be taken with temperature control in order to maintain accuracy of results [152]. Therefore, with polymers, it is equally important when quantifying viscosity to also specify temperature.

The flow curves shown in Figure 2.19 do not take into account the effects of time on viscosity. Time-dependant materials usually exhibit a more complicated rheology and, with some materials, the time dependance on viscosity is so great that the viscosity will change during an experiment. This is not due to elasticity but to structural changes and is usually characterised by a change to viscosity with time for a constant shear rate or applied stress [153]. A reduction in viscosity over time is known as thixotropy and is exhibited by some polymer systems and paints, whereas an increase in viscosity over time is referred to as negative thixotropy [63].

Measurement of the viscosity of materials is generally conducted using a viscometer [152]. There are basically two types of viscometer; rotational and extrusion [63]. Experiments to measure viscosity can be conducted whilst varying shear rate, temperature and time as well as other parameters involved with the geometric set up of the viscometer.

2.7.5 Molecular Weight

A polymer is made up of long molecules in a chain like structure. During polymerisation, these large macromolecules are synthesized from smaller molecules and as their formation is the product of a succession of random events [63], polymer molecules will usually be of different chain lengths. This results in a distribution of chain lengths [65] and one way to characterise such a distribution is to quantify the weight of these chains into a distribution of molecular weights or an average molecular weight for that polymer.

There are several ways of defining molecular weight. There is the number average molecular weight (M_n), where each chain is of equal importance, or the weight-average molecular weight (M_w), where it is the weight of the chains and not their quantity that is important. These are defined as;

$$M_n = \frac{\sum n_i M_i}{\sum n_i}$$ Equation 2.10

$$M_w = \frac{\sum w_i M_i}{\sum w_i}$$ Equation 2.11

M_n is the summation of the product of each molecular weight value M_i and the number of such molecules or chains n_i divided by the total number of all molecules present. In contrast the M_w sums up the weight fraction for each species as the summation of the product of each molecular weight value M_i and the weight of all chains w_i for that M_i, divided by the total weight of all chains. Although M_n is easier to derive, it is usually the lower value and as it is very dependant on small chains it is not representative for most properties. M_w is less dependant on large numbers of small chains and is a more representative value of a polymer [154]. Figure 2.20 illustrates the distribution of molecular weights for a typical polymer [65].

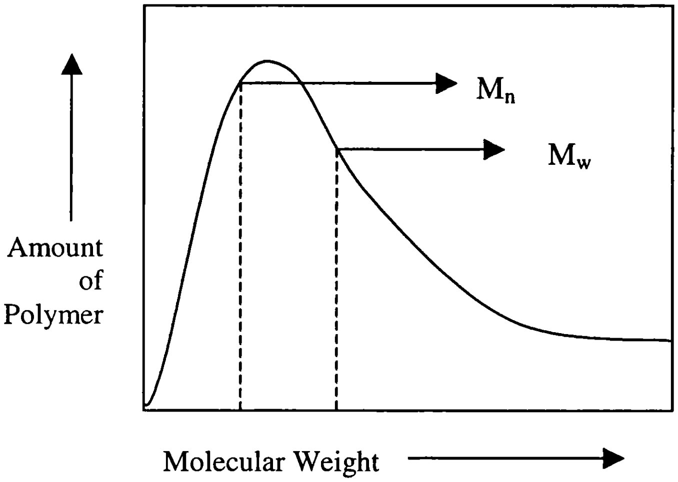


Figure 2.20 Distribution of molecular weights for a typical polymer

Another parameter that is sometimes useful to know is the ratio of weight average molecular weight to number average molecular weight (M_w/M_n) or polydispersity. This value is often used to represent the spread of molecular weights although it cannot provide any information about unusually high or low molecular weight tails, which might be significant [74]. Typical values for polymers may vary from 5 – 50 although if it is equal to one, then all chains will be the same length [154].

A fairly accurate way of determining molecular weight distribution of a polymer is by Gel Permeation Chromatography (GPC). This technique passes a solution of the polymer through a column packed with a gel of uniform and known pore size, the principle being that chains of differing length will behave differently. The smaller molecules can diffuse freely into the pores of the gel and are therefore retarded in their passage through the column, while the larger chains are not delayed as such and so emerge first from the column. A detector such as an infrared detector will monitor the polymer content of the discharge from the column, at a fixed frequency and produce a chromatogram of the various fractions identified [63].

The molecular weight of a polymer is a very important and useful piece of information to know. The molecular weight of a polymer has an influence on many properties including tensile strength and stiffness, impact toughness, viscosity and T_g [64,130]. In general an increase in molecular weight will influence tensile and impact strength. Experimentally a proportional relationship has been established between the viscosity of a linear polymer and M_w [147, 148, 154, 155]. For a low M_w the relationship is [148]

$$\eta \propto M_w \qquad \text{Equation 2.12}$$

However above a critical chain length (M_w^c) the relationship between M_w and η becomes [147, 148, 154, 155]

$$\eta \propto M_w^{3.4} \qquad \text{Equation 2.13}$$

where M_w^c is the point at which chain entanglements form [154], and can differ between polymer types. The T_g of a polymer is affected by M_n. At a M_n, the T_g of a polymer increases as M_n increases. However on reaching a critical size of M_n, the T_g of a polymer becomes independent and remains constant to further increases to M_n [147, 149]

A low molecular weight is often the reason given for premature failure of a plastics component. In reality this could be the original length of the plastic chain as low molecular weight polymers are easier to thermally process. However it could also be due to a break down of polymer chains during its service life. Factors that affect molecular weight include thermal degradation by subjecting the polymer to an excessively severe thermal treatment, exposure to a chemical environment causing decomposition, and insufficient stabilizer against UV degradation for example [63] (See Section 2.6.5 Polymer Degradation).

2.7.6 Plastics Microscopy

The microstructure of engineering plastics and resins is mainly determined by the manufacturing process. Plastics produced by processes such as extrusion and injection and compression moulding can be evaluated by microscopy techniques in order to determine their structure and evaluate an understanding of the structure – property relations [156]. Many polymers are single phase materials that do not have discernable second phase structures of different chemical composition, even if they are semi-crystalline, i.e. contain both amorphous and crystalline regions. While much information can be obtained by microscopy of crystalline thermoplastics, a microstructural study of a single phase amorphous material will not be able to reveal any information of much practical use as there are no contrasting regions. Some polymer blends that mix well can also produce a single phase material, which although can produce a wide range of mechanical properties, will be difficult to study microstructurally due to the miscibility of the blend. PS-PPO is an example of such a blend [156].

Most polymer blends, as well as block and graft copolymers, are however multiphase materials. Mictrostructual observations will be more useful as the structure is more complex than single-phase polymers, which means that there is a distribution of various phases to describe, as well as their internal structure. A highly commercial set of multiphase polymer systems are the toughened, high impact or impact modified polymers such as HIPS, ABS and SBS. These are combinations of polymers containing dispersed elastomer rubber particles in a continuous matrix that is usually a glassy amorphous thermoplastic. The size, distribution, composition and compatibility of the rubber particles all influence the mechanical properties of the engineering resin [156] and also provide a contrast with which to study the microstructure.

A wide range of microscopy techniques can be applied to characterise engineering resins and plastics. The most common techniques include light microscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Because of the resolution limitation of light microscopy and the relative complexity of obtaining samples for TEM, the SEM has been widely employed in the microscopical study of polymers, and especially polymer blends [107]. The principle behind the SEM is that the specimen is examined by scanning a finely focused electron beam across the sample surface. The electrons emitted from the specimen are detected and amplified and the signal is then used in the image forming process. The only requirement for sample preparation is that the sample must be conductive. For polymers, an electrically conductive layer such as gold (preferably), or carbon, can be provided by coating or sputtering a thin layer of metal onto the sample.

Two types of contrast are available in the SEM image; compositional contrast and topographical contrast. Compositional contrast uses backscattered electrons that have been elastically scattered by the nuclei in the sample. Thus the intensity of backscattered electrons is decided by the sample composition. However as most polymers are composed of low atomic number elements, there will be little variation in electron density between one polymer and another. Compositional contrast of polymers is therefore generally poor [107], although this method can be fairly useful in detecting the presence of additives and fillers that contain higher atomic number elements, such as bromine for example. However compositional contrast can be used with samples that have been selectively stained, usually by heavy metal oxides such as OsO_4 and RuO_4, which provide contrast in certain areas and especially enhances compositional contrast between phases [107].

Topographical contrast of a specimen is mainly due to secondary electrons which are the electrons emitted from the sample with an energy below 50eV. As this energy is low, the secondary electron signal only comes from a region close to the surface [107]. As topographic contrast depends greatly on surface texture, techniques such as chemical or plasma etching or cryogenic fracture are often used to generate different surface textures between phases in order to enhance the topographic contrast. Cryogenic fracture of a multiphase polymer blend can be used to create fracture surfaces with high roughness in order to obtain information on the bulk or interior structure. In preparation for a cryogenic fracture surface of a two phase polymer blend the operation temperature will ideally be selected to be lower than the T_g of one component but higher than the T_g of the other. This is to create two distinct phases of fracture, one brittle and the other more ductile according to whether the component is in a glassy or plastic state. The polymer will be held at the selected temperature for a period of time and then fast fractured immediately. SEM observation on the fracture surface should be able to disclose the two phases of the blend quite clearly [107]. However, it must be noted that it may not always be possible to enhance the phases of all polymer blends as some will have similar T_g values. Although, as well as contrasting polymer blends, this technique can be useful with impact modified polymers containing rubber or elastomer particles. SEM images may show debonding between phases as particles are pulled away from the matrix.

CHAPTER 3:

IDENTIFICATION ANALYSIS – EXPERIMENTAL PROCEDURE

3.1 MATERIALS FOR ANALYSIS

One of the main problems that recyclers face when dealing the housings from computer equipment is that of correctly identifying the plastic type. Previous work [17] found that more than five different plastic types were used in computer equipment housings. If these waste housings were recycled without sufficient sorting the eventual product would most likely be a low quality recyclate, that would be of no use in any high grade applications such as that of its initial life. The accuracy of the identification of plastics is therefore an important part of a recycling process.

New European legislation is now placing even greater demands on the identification of plastics and it is now necessary to be able to identify and separate plastics containing certain brominated flame retardants from those that do not. If this identification cannot be performed to 100% accuracy, it will have to be assumed that all such plastic waste may contain these hazardous additives and so recycling would be impossible. The aim of this part of the project is to evaluate the capabilities of current available plastics identification systems whilst ascertaining any needs that have not been fulfilled. Samples used were supplied by PMI (Wales) Ltd, in the form of one hundred circular disc shaped specimens of approximately 60mm diameter, that were taken from a range of redundant computer equipment. These samples were a good representation of the proportions of the different plastics used in computer equipment and were used, and identified, in a previous project [17] using FTIR spectroscopy to identify the plastic type, and X-ray microanalysis to identify the presence of flame retardants and other additives.

3.2 FURTHER CHARACTERISATION OF FTIR SPECTROSCOPY AND X-RAY MICROANALYSIS OF PLASTICS

3.2.1 Characterisation of Peaks in FTIR Spectra of Plastics

FTIR spectroscopy is a method of vibrational spectroscopy that detects molecular photon transitions resulting from atomic vibrations. Each group of atoms vibrates at a frequency characteristic of their molecular structure and is affected by the presence of other atoms close by, which means that each molecule has its own distinct set of resonance vibrations. As each polymer compound has its own distinct molecular structure, no two polymers will have the same set of vibrational frequencies and intensities on exposure to radiation, and each polymer will therefore exhibit a unique infrared spectrum.

In order to more fully understand the collection of FTIR spectra that had been assembled for the one hundred samples studied in a previous project, the infrared spectrum of each polymer type was analysed. The main peaks exhibited on each polymer spectrum were characterised according to the molecular structure of the polymer type and designated a molecular bond type such as 'C – C' for example. The frequency for each characteristic bond was determined by studying and comparing the different bond types and frequencies from several reference books [157-160].

3.2.2 Analysis of Flame Retardant Plastics Using FTIR Spectra

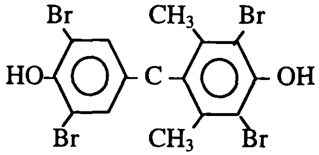
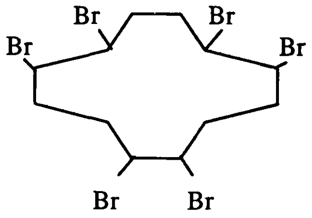
In order to ascertain the possibility as to whether flame retardants may be detected by the characterisation of peaks on an infrared spectrum, each sample previously used for FTIR analysis [17] was reanalysed for flame retardants. This analysis concentrated on peaks for halogenated flame retardants and was accomplished by focussing on the lower end of the spectrum, from wavenumber 1400 – 650 cm^{-1}, as this is where halogenated compounds are more likely to exhibit peaks.

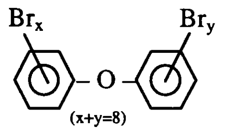
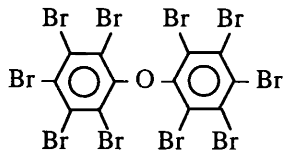
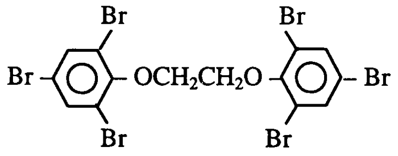
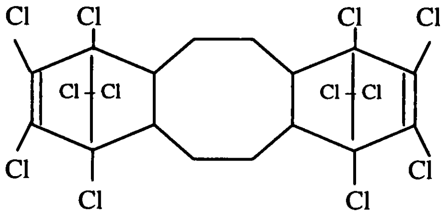
Peaks for the different compounds were characterised on the basis of deduction by comparing the spectra of samples that had been elementally characterised by X-ray microanalysis. Comparisons were made between samples that contained different combinations of non polymeric elements, such as those containing just Br, those containing just Cl, those containing both Br and Cl, and samples that did not appear to contain any detectable additives. Characterisation of this sort was attempted for each plastic type, although some plastic types were more difficult due to small sample numbers.

3.2.3 Analysis of Infrared Spectra of Commercially Available Flame Retardants

In order to try and confirm the results for the above study, infrared spectra of several commercially available flame retardants were obtained from GLCC (Great Lakes Chemical Company) and Oxychem®. Table 3.1 gives a summary of each flame retardant compound including chemical structure, commercial name and recommended uses. The infrared spectrum from each flame retardant was analysed in an attempt to match the main peaks from the actual flame retardant with peaks suspected to be due to flame retardants in the FTIR spectra of the previously analysed samples.

Table 3.1 List of flame retardant compounds used for infrared spectral analysis

Flame Retardant	**Commercial Name**	**Chemical Structure**	**Recommended Uses in**
Antimony Trioxide	Thermo-guard ® S Antimony Oxide	Sb_2O_3	only in conjunc-tion with Cl or Br FR's
Tetrabromobisphenol A	Great Lakes BA-59P		PC, ABS, HIPS
Phenoxy-terminated carbonate oligomer of Tetrabromobisphenol A	Great Lakes BC-52HP	Unavailable	PC, ABS, ABS/PC, SAN, PET, PBT
Phenoxy-terminated carbonate oligomer of Tetrabromobisphenol A	Great Lakes BC-58	Unavailable	PC, ABS, ABS/PC, SAN, PET, PBT
Hexabromo-cyclododecane	Great Lakes CD-75P		General thermoplastics especially styrenic based resin systems

Octabromodiphenyl Oxide	Great Lakes DE-79		ABS, nylon, thermo-plastic elastomers, polyolefins
Decabromodiphenyl Oxide	Great Lakes DE-83R		HIPS, PBT, nylon, PP, LDPE
Bis(Tribromo-phenoxy)ethane	Great Lakes FF-680		HIPS, ABS, PC
1,2,3,4,7,8,9,10,13,13, 14,14-dodecachloro-1,4,4a,5,6,6a,7,10,10a, 11,12,12a-dodecahydro-1,4,7,10-dimethanodibenzo (a,e) cyclooctene	Dechlorane Plus	$C_{18}H_{12}Cl_{12}$ 	ABS, PBT, PE, PP, PU, SBR

3.3 COMPARISON OF RAPID PLASTICS IDENTIFICATION TECHNIQUES

The importance of accurate plastics identification has already been emphasised and an accurate, as well as rapid, system is key to breaking down technical and economic barriers that impede a recycling process. As there is quite a range of plastic types used in computer equipment housings, the simpler separation and sorting methods that work well for packaging waste are unsuitable and even some systems involving NIR (near infrared) spectroscopy are not able to identify dark coloured plastics. Therefore research was conducted into finding commercially available rapid plastics identification methods that were more suited for plastics from computer equipment, and as a result several companies were contacted.

From these contacts, four different systems were tested using the one hundred samples previously identified [17] using FTIR spectroscopy and x-ray microanalysis. Each rapid identification system was assessed on the accuracy of identifying the different plastic types as well as the possibility of detecting flame retardant additives and results were compared with those of slower but accurate laboratory systems i.e. FTIR spectroscopy and x-ray microanalysis. The main aim of this part of the study is to assess the current state of plastics identification technology, whilst identifying areas for improvement in order to help progress available technology in this area, which in turn should improve recycling activities of plastics from waste electrical and electronic equipment.

3.3.1 Repeating FTIR and X-ray Microanalysis From a Previous Study

Of the one hundred plastics used for this study, certain samples were subjected to a repeat of identification experiments using FTIR spectroscopy and X-ray microanalysis. Reasons for repeating previous work was to; a) Verify the accuracy of results from this work, and b) To investigate any discrepancies between these results and comparisons with other identification techniques from previous work [17] and the studies as described below.

Fourier transform infrared spectroscopy was undertaken at the former Welsh Technology Centre at Corus Steelworks Port Talbot, using a Perkin Elmer System 2000 Fourier Transform Infrared spectrometer. This type of spectrometer used was a attenuated total reflection (ATR) method, where a crystal was placed in almost direct contact with the sample and an IR beam reflected from the surface. Samples tested had previously been identified as Acrylic or PMMA. No sample preparation was needed and the resulting spectra was compiled from the average of thirty scans in total.

Elemental analysis was carried out on several samples using a SEM with an Oxford Instruments EDX (Energy Dispersive X-ray) Spectroscopy Micro-Analyser. Samples used had been previously prepared by cutting a small piece of each sample (approximately 3mm^2) from each plastic disc, attaching it to an aluminium stub and subsequently coating it with a layer of gold using a vapour deposition technique. Prepared samples were then positioned in a Jeol JSM-35c SEM and exposed to an electron beam accelerated to 1-50keV. The x-ray photons emitted from the sample were detected using an energy dispersive detector, and the elemental composition was analysed using the EDX software linked to the detector.

3.3.2 P/ID22

The P/ID22 is a compact benchtop analyser that was developed by Bruker Optics Ltd (Figure 3.1). It is a mid infrared spectrometer, which means that it can identify dark coloured plastics and was probably designed with the automotive industry in mind, although it could be used for WEEE quite easily. Sample preparation requires only that the sample is free from contaminants as it is not able to scan through layers of paint, dirt or other coatings. Identification involves holding an object against the measurement cone (Figure 3.2) and pressing the foot pedal to begin measurement. In total it takes about four seconds to both scan the object and find the best match for the spectrum from those stored in the system database. It is also possible to create additional reference databases, which would make it easier to adapt the system to specific needs such as plastics from waste computer housings or automotive plastics for example.

The set of samples for identification were taken to the UK office for Bruker Optics Ltd and were tested using the P/ID22 and identified using the basic plastics reference library. In order to test the capabilities of the programmable database, a representative library was set up, from the one hundred samples being tested, of several different plastic types including plastics with and without flame retardant additives. A selection of samples were then retested and identified using the new database.

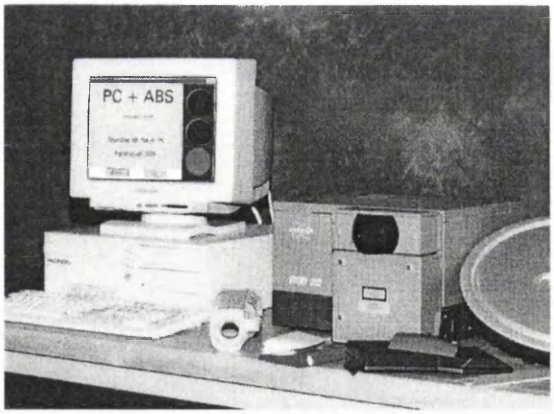


Figure 3.1 The P/ID 22 Mid-infrared Spectrometer

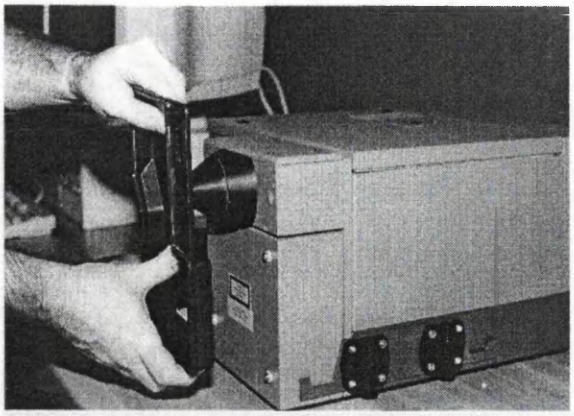


Figure 3.2 Sample measurement of the P/ID 22 Mid-infrared Spectrometer

3.3.3 Polyana

The Polyana is an MIR spectrometer that was developed by Peter Walker Systems in conjunction with the Wolfson Electrostatics Centre at Southampton University and Ford. The original purpose of the Polyana was for identifying automotive plastics, so the main reference spectra in the library database are for such plastic types.

The identification method of the Polyana is fairly similar to the P/ID22 in that a sample is held against the measuring cone (See Figure 3.3). The system takes

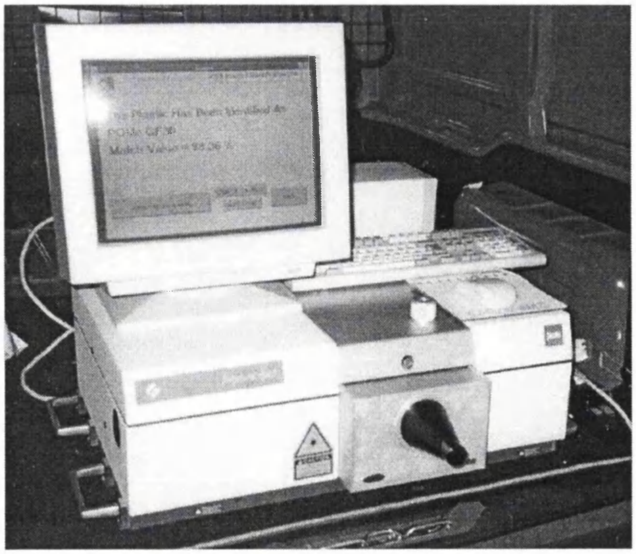


Figure 3.3 Image of the Polyana Mid-Infrared Spectrometer

approximately ten seconds to scan the sample and find a match for the spectrum from the reference database. For this study, the one hundred samples were tested on the Polyana based at Southampton University. Prior to this visit, the Polyana had been used to identify the casings of waste computers and a reference library has been set up for this purpose. Sample requirements included a shiny and contaminant free surface.

3.3.4 SSS2

The SSS2 is a sliding spark spectrometer that can be used for identifying electronic and automotive waste plastics. It was developed by AGR GmbH and is a portable hand-held spectrometer (Figure 3.4) that enables the identification of plastics without prior sample preparation. Any surface contaminants may be removed by pre-sparking. The principle of this method is the thermal vaporization of a small amount of the plastic surface using a train of defined high-current sliding sparks. The vaporised particles that are in the spark plasma are then atomised and activated to emit radiation, which is detected and characterised according to the spectral library.

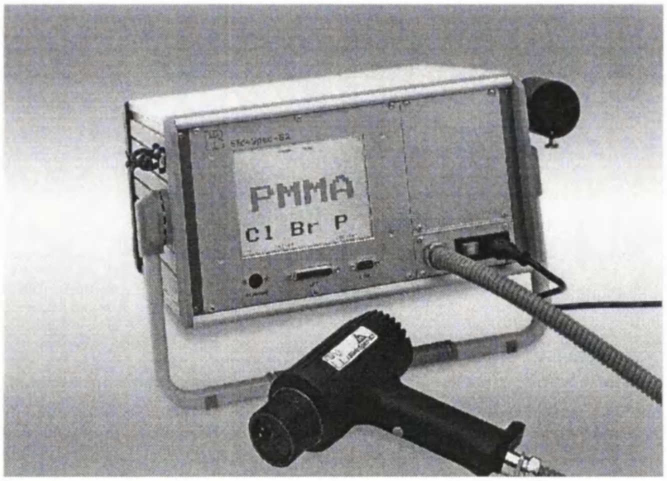


Figure 3.4 The SSS2 Sliding Spark Spectrometer

The SSS2 is said to be able to detect heavy metal containing additives, as well as halogenated flame retardants, and the system may also be calibrated to specific plastic types. Plastic identification involves simply pressing the sparking head onto the sample and pressing start on the pistol grip. Measuring time has been given as one second and is unaffected by the colour of the sample. As there was no branch of AGR in the UK, samples were sent to the company in Germany to be tested for identification and elemental analysis.

3.3.5 mIRo Spectrometer

The mIRo is a mobile hand-held near infrared optic that was designed by IoSys (Individual Optic Systems) for the rapid identification of recycled plastics. It looks very similar to the SSS2 (Figure 3.5), as it was designed by the same person and sample measurement is obtained in the same way of pressing the measuring head onto the sample and pushing the start button. However, instead of emitting a series of sparks, the polymer sample is instead radiated with infrared light and the light reflected is analysed using a near infrared detector array. Again, sample measurement is said to take one second for the result to be displayed on the screen. The system is programmable and could probably be trained to recognise different grades of plastics. It is claimed that the mIRo is able to identify such polymers from household, automotive and electronic waste regardless of colour, and requires no sample preparation. Again, as there is no branch of IoSys in the UK samples were sent away to be tested for identification.

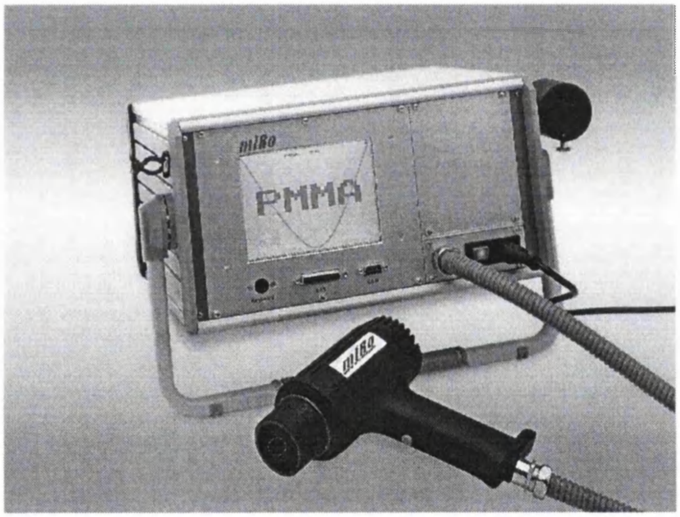


Figure 3.5 The mIRo Near Infrared Spectrometer

CHAPTER 4:

IDENTIFICATION ANALYSIS – EXPERIMENTAL RESULTS AND DISCUSSION

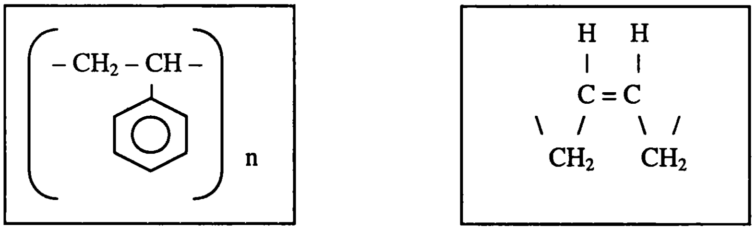
4.1 CHARACTERISATION OF PEAKS IN FTIR SPECTRA OF PLASTICS

The main peaks of the FTIR spectrum of each polymer type used in computer equipment housings were analysed in order to determine which molecular vibrations caused which peaks on each spectrum. Polymer types analysed were HIPS, ABS, PPO, PC, PVC, PP and PMMA. The purpose behind this part of the study is to contribute to the improvement of rapid plastics identification systems, by testing the presence or absence of certain peaks, rather than comparing whole spectra.

4.1.1 High Impact Polystyrene

The structure of high impact polystyrene is made up of polystyrene chains with polybutadiene rubber as shown in Figure 4.1. The bonds that will show distinct peaks in the infrared spectrum of HIPS are mainly C – H, C – C, C = C, aromatic–CH and aromatic bonds from the benzene ring in PS. Figure 4.2 is the FTIR spectrum for HIPS. The main peaks from this spectrum are approximately at wavenumbers 1600, 1492, 1452, 1370, 1069, 1027, 965, 910, 841, 752 and 696 cm^{-1}. Peaks above approximately $2300cm^{-1}$ can be distorted by moisture in the atmosphere around the sample and are generally not used to characterise a plastic unless they are very clear.

Interpretation of each peak is found in Table 4.1. The notations next to some peaks describe the types of peaks such as (b) broad, (m) medium, (s) strong, (vs) very strong.



(a) (b)

Figure 4.1 Repeat structures of (a) Polystyrene molecule and (b) cis-1-4 polybutadiene rubber, both which make up the structure of HIPS.

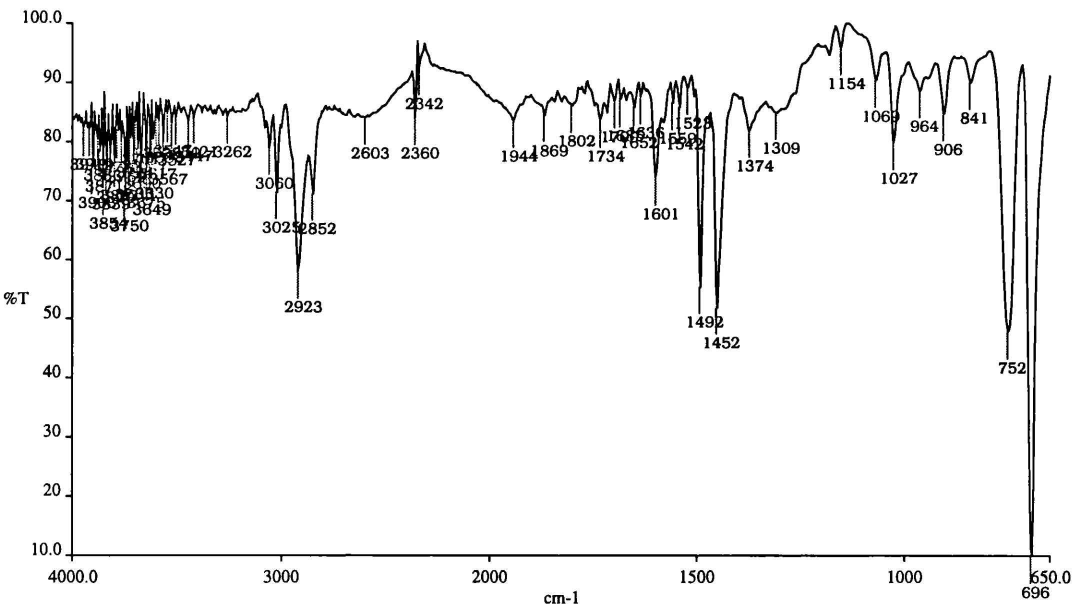


Figure 4.2 The FTIR spectrum of HIPS

From Table 4.1, it can be seen that some structures, such as the aromatics for example, are responsible for more than one peak. The benzene molecule has a more complex bonding system within a molecule than other C–H structures and so the different bonds between C–H and C–C atoms vibrate at more than one different frequency, such as 1600, 1492, 1452, 1069, 841, 752 and 696 cm^{-1}. Where the benzene ring is bonded to the rest of the styrene molecule will have an effect on the frequency of the connecting bond, as well as the surrounding bonds. This may explain why many peaks on the HIPS spectrum appear to be due to the aromatic structure. The carbon – carbon double bond in butadiene also appears to contribute to several peaks although many overlap with those from PS and only the peak at 1370 cm^{-1} appears to be solely from the carbon – carbon double bond in butadiene.

Table 4.1 Interpretation of Peaks for the FTIR spectrum of HIPS

Peak (cm^{-1})	Assignment	Reference
1600 (m)	Aromatic and C=C	[159]
1492 (s)	Aromatic	[159]
1452 (s)	Aromatic and C–CH_2–C from styrene	[159]
1370 (b)	C=C butadiene	[158]
1069	Aromatic or the C=C bond in butadiene	[158]
1027 (m)	Probably due to the butadiene CH_2–CH=CH bonds	[158]
965 (vs)	CH_2–CH	[158]
906 (s)	C–H modes of vinyl group, probably from butadiene.	[159]
841	Probably CH_2–CH in styrene and butadiene Or aromatic	[158] [157]
752 (vs)	C–H modes of aromatic ring	[157], [159]
696 (vs)	C–H modes of aromatic ring	[157], [159]

4.1.2 Acrylonitrile – Butadiene – Styrene

ABS is a two-phase co-polymer with a basic structure that is made up of the same compounds as HIPS, with the addition of acrylonitrile CH_2=CH–C≡N. The main peaks are expected to be similar to those of HIPS, however the presence of acrylonitrile should cause some variation, especially with the triple C≡N bond, enabling the distinction of FTIR spectra between the two polymer types. Figure 4.3 shows the FTIR spectrum for ABS highlighting the main peaks. The main peaks from this spectrum are seen as 2236, 1600, 1492, 1449, 1362, 1026, 965, 910, 758 and 696 cm^{-1}. The interpretation of peaks from the FTIR spectrum of ABS can be found in Table 4.2. From the ABS spectrum in Figure 4.3 and interpretation in Table 4.2, ABS appears to have a similar spectrum to HIPS (Figure 4.2), with the exception of the additional peak at 2236, which is due to the triple nitrile bond (C≡N). There is also a slight change to the HIPS peak at 1370, which appears as a broader peak at 1362 cm^{-1} on ABS.

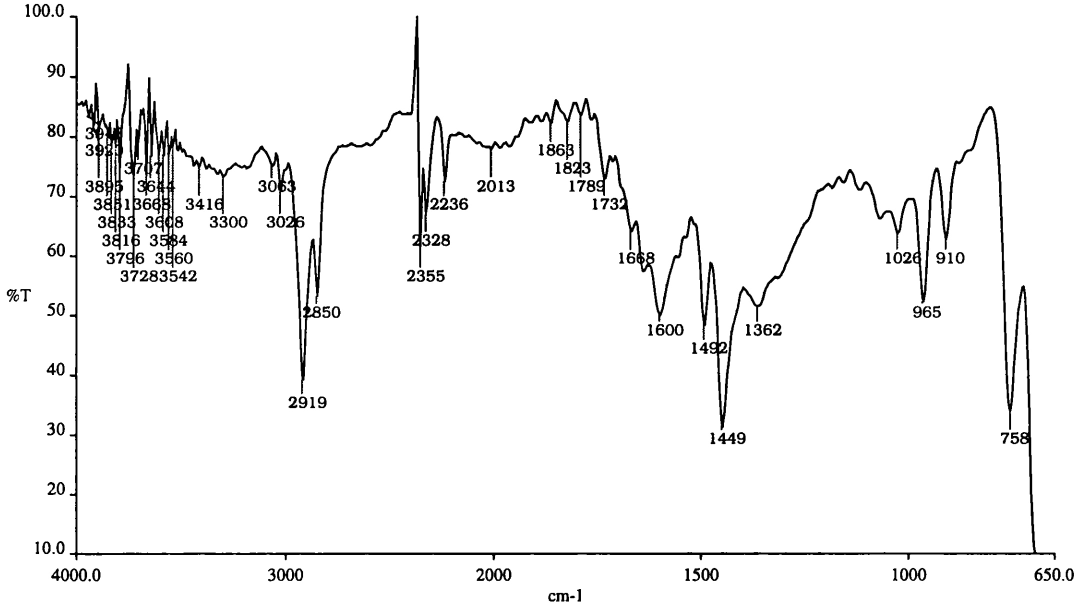


Figure 4.3 The FTIR spectrum of ABS

Table 4.2 Interpretation of Peaks for the FTIR spectrum of ABS

Peak (cm^{-1})	Assignment	Reference
2236	–C≡N	[157], [158]
1600 (m)	Aromatic and C=C	[159]
1492 (s)	Aromatic	[159]
1449 (s)	Aromatic and C–CH_2–C from styrene	[159]
1362 (b)	CH2=CH from butadiene	[158]
1069	Aromatic or the C=C bond in butadiene	[158]
1026 (m)	Probably due to the butadiene CH_2–CH=CH bonds	[158]
965 (vs)	CH_2–CH	[158]
910 (s)	C–H modes of vinyl group, probably from butadiene.	[159]
758 (vs)	C–H modes of aromatic ring	[157], [159]
696 (vs)	C–H modes of aromatic ring	[157], [159]

4.1.3 Polyphenylene Oxide

The structure of PPO is shown in Figure 4.4 and the main bonds in this structure will be aromatic, aromatic–O, or C–O–C, aromatic–C and CH_3. The FTIR spectrum of PPO is found in Figure 4.5. This spectrum is actually PPO Noryl, so it may contain an amount of HIPS or PS, which may be the cause of some peaks. The main peaks are at 1600, 1489, 1468, 1452, 1378, 1304, 1185, 1070, 1020, 958, 907, 856 and 752 cm^{-1}.

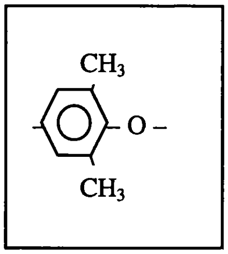


Figure 4.4 Structure of the PPO repeat molecule

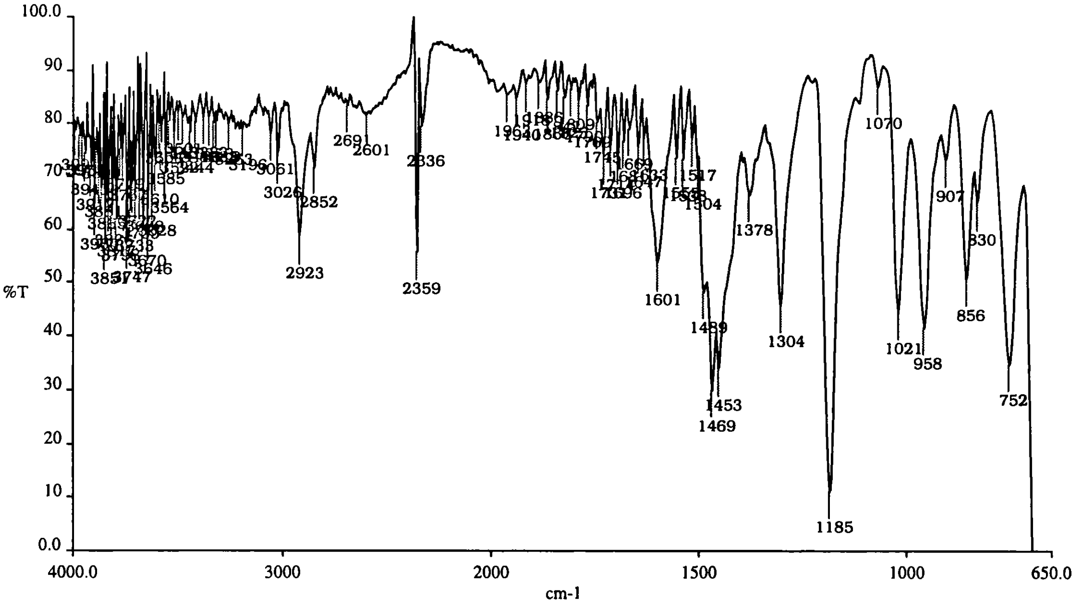


Figure 4.5 The FTIR spectrum of PPO

The interpretation of these peaks can be found in Table 4.3. From this table, it appears that many of the peaks from the PPO spectrum are due to the benzene ring, as in HIPS and ABS. The CH_3 bonds also cause several peaks including the triplet between 1500-1400 cm^{-1}. The C–O bonds, due to oxygen connecting benzene rings, appear to be responsible for a couple of fairly prominent peaks including the really strong peak at 1185 cm^{-1}. On comparison with a FTIR spectrum of pure PPO [136], it was found that peaks at 1070 cm^{-1} and 907 cm^{-1} were absent. These two peaks are therefore most likely to be from HIPS, which is commonly blended with PPO to create the engineering blend Noryl.

Table 4.3 Interpretation of Peaks for the FTIR spectrum of PPO

Peak (cm^{-1})	Assignment	Reference
1600	Aromatic	[157]
1489	CH_3	[157]
1468	CH_3	[157], [160]
1452	Aromatic and CH_3	[157]
1378	CH_3	[160]
1304 (m)	C–O	[157]
1185 (s)	C–O	[157]
1070	Aromatic or the C=C bond in butadiene	[158]
1021	Aromatic – CH_3	[158]
958 (m)	C – H modes	[159]
907	C–H modes of vinyl group (probably from butadiene)	[159]
856	Aromatic	[157]
752	Aromatic	[157]

4.1.4 Polycarbonate

The structure of PC is more complex than the plastics looked at so far. From the structure of the PC repeat unit in Figure 4.6, it can be seen that there will be many different types of bonds that will produce quite a varied range of peaks on the FTIR spectrum. The FTIR spectrum of PC is shown in Figure 4.7. The main peaks appear to be at wavelengths 1769, 1503, 1221, 1188, 1159, 1079, 1012, 885, 827 and 765 cm^{-1}. Table 4.4 is a summary of the interpretation of these peaks. Peaks around 1800-1700 cm^{-1} are believed to be the C=O bond of the ester group, which is fairly prominent at 1770 cm^{-1}. There is also a range of fairly strong peaks between 1300 and 1100 cm^{-1}, which are from the C–O bonds and could account for any of the peaks in the triple peak of the PC spectrum. However this triple could also be due to the molecular group CH_3–C–CH_3, situated between the two benzene rings, which are also responsible for peaks at 1080, 1012 and 885 cm^{-1}. Peak 1221 cm^{-1} could be from para-substituted benzenes i.e. a benzene ring bonded to two other atoms at opposite sides, as is the case for the peak at 827 cm^{-1}. The peak at 1503 cm^{-1} is likely to be from the benzene/C(CH_3) bonds, while that at 765 cm^{-1} is probably due to the CH_3 group frequency.

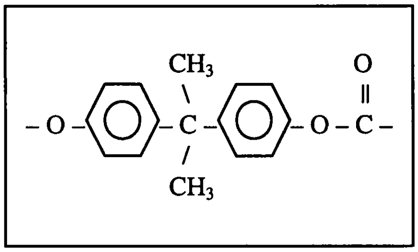


Figure 4.6 Structure of the PC repeat unit

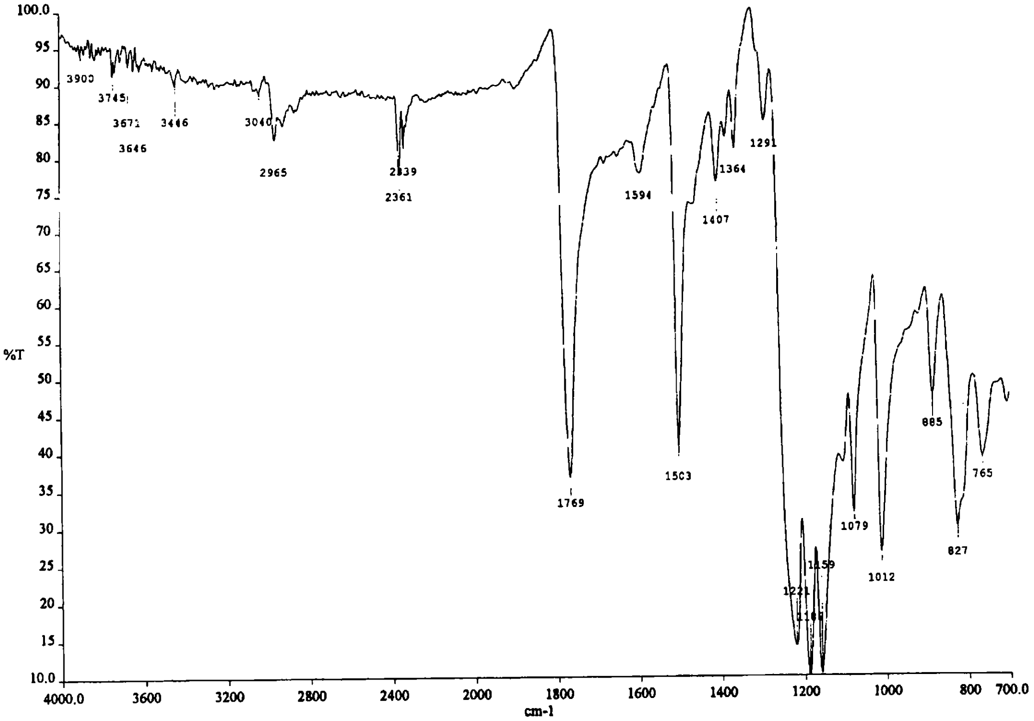


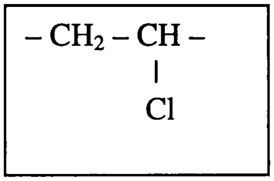
Figure 4.7 FTIR spectrum of Polycarbonate

Table 4.4 Interpretation of Peaks for the FTIR spectrum of PC

Peak (cm^{-1})	Assignment	Reference
1769	C=O	[157], [160]
1503	Benzene –C(CH_3) Or Para substituted benzene	[158] [160]
1221	C–O Or CH_3–C–CH_3 Or Para substituted benzene	[157] [158] [160]
1188	C–O Or CH_3–C–CH_3	[157] [158]
1159	C–O Or CH_3–C–CH_3	[157] [158]
1080	CH_3–C–CH_3	[158]
1012	CH_3–C–CH_3 Or Para substituted benzene	[158] [160]
885	CH_3–C–CH_3	[158]
827	Para substituted benzene	[157], [160]
765	CH_3	[158]

4.1.5 Poly-Vinyl-Chloride

Compared with all of the plastic types looked at so far, PVC appears to have the simplest structure as seen in Figure 4.8. Bonds will be mainly CH_2, CH, C–Cl and C–C. The main peaks seen on the FTIR spectrum of PVC (Figure 4.9) are at 1730, 1427, 1328, 1251, 1097, 965, 698. From Table 4.5 it can be seen that the FTIR spectrum for PVC appears to be fairly simple, as is the structure of the repeat molecule. The bonding between CH_2–CH on the main polymer chain exhibits a very strong peak at 964 cm^{-1}, while the bond with Cl such as C or CH is responsible for several strong peaks at 1427, 1251, 1097 and 698 cm^{-1}. The peak at 1328 cm^{-1} was attributed to the C–H bond, which is a bond type that should be present in pretty much all polymers although, when more than one H atom is present, this changes the frequency.



$$-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-$$

Figure 4.8 Structure of the PVC repeat unit

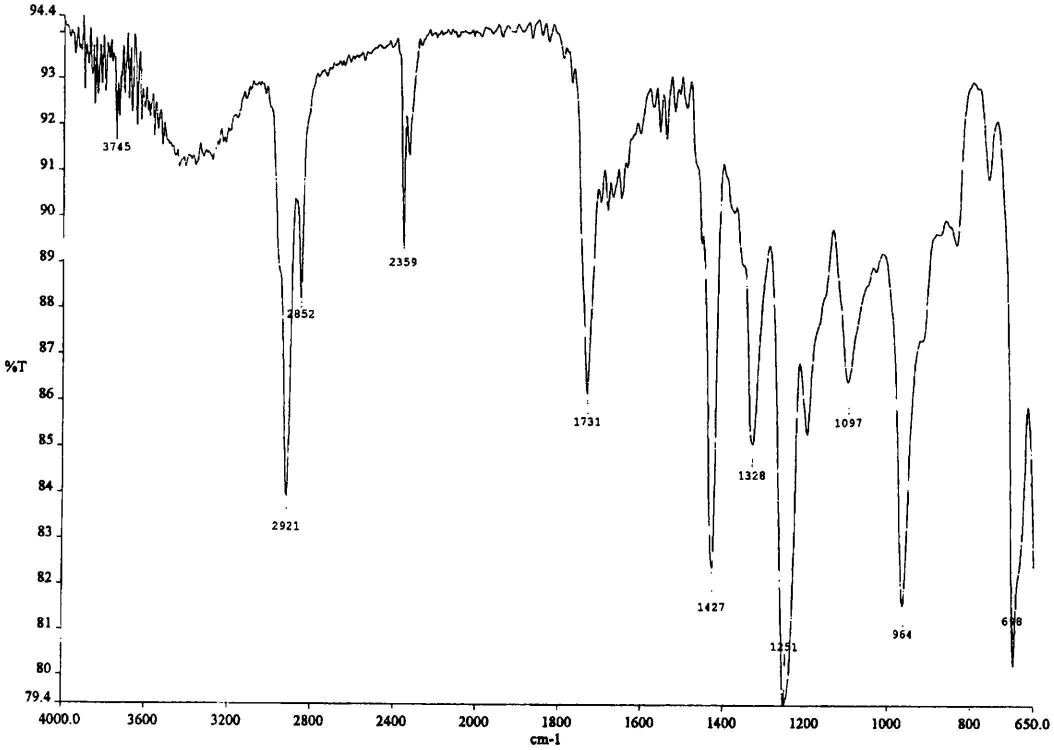


Figure 4.9 FTIR spectrum of PVC

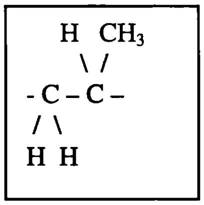
One prominent peak (1730 cm^{-1}) could not be identified to correspond with any of the molecular groups of the PVC structure and on comparison with a spectrum of pure PVC [161], this peak was absent. Due to the instability of the PVC structure during processing, fairly large quantities of additives are usually added to PVC, and it will be rare to find processed PVC in its pure form. Therefore, it is more than likely that these unidentified peaks will be due to additives such as thermal stabilisers or plasticizers of some kind. The vast majority of plasticizers in PVC are organic esters. However as the exact compounds are unknown, it was not possible to establish the exact type of molecular group that would have caused this peak. The double bond C=O is strong around the frequency of 1730 cm^{-1} [160], and therefore it is possible that this could be caused by an ester based plasticizer. Although this peak at 1730 cm^{-1} does not therefore appear to be from PVC itself, it has so far appeared on the FTIR spectrum of all samples containing PVC that were from disused housings from computer equipment, indicating that it is likely to be present in PVC collectable from waste computer housings.

Table 4.5 Interpretation of Peaks for the FTIR spectrum of PVC

Peak (cm^{-1})	Bond Type	Reference
1730	Additive? Maybe C=O	[160]
1427 (m)	CH–Cl	[160]
1328	C–H	[157], [160]
1251 (s)	CH–Cl	[160]
1097	C – Cl	[160]
964 (vs)	CH_2–CH	[158]
698 (s)	C–Cl	[160]

4.1.6 Polypropylene

The structure of the repeat molecule of PP is found in Figure 4.10. The main bonds appear to be combinations of CH, CH_2, CH_3 and C–C. The FTIR spectrum from all previous plastics looked at frequencies approximately below 2000 cm^{-1} as there did not appear to be many discernable peaks at higher frequencies. However the PP spectrum in Figure 4.11 shows an extremely prominent quadruple group of peaks between 3200 and 2800 cm^{-1} that cannot be disregarded. Other main peaks include 1454, 1375, 1165, 997, 972 and 840 cm^{-1}. From Table 4.6 it appears that most peaks are due to combinations of C and H on the carbon backbone of PP according to the structure of the polymer chain. However, the strong quadruple of peaks between 3200 and 2800 cm^{-1} are instead due to CH_2 and CH_3 alkane groups, although it is very difficult to tell which peaks are due to which group of bonds as the frequencies all overlap.



$$-\mathrm{CH_2}-\mathrm{CH}(\mathrm{CH_3})-$$

Figure 4.10 Structure of the PP repeat unit

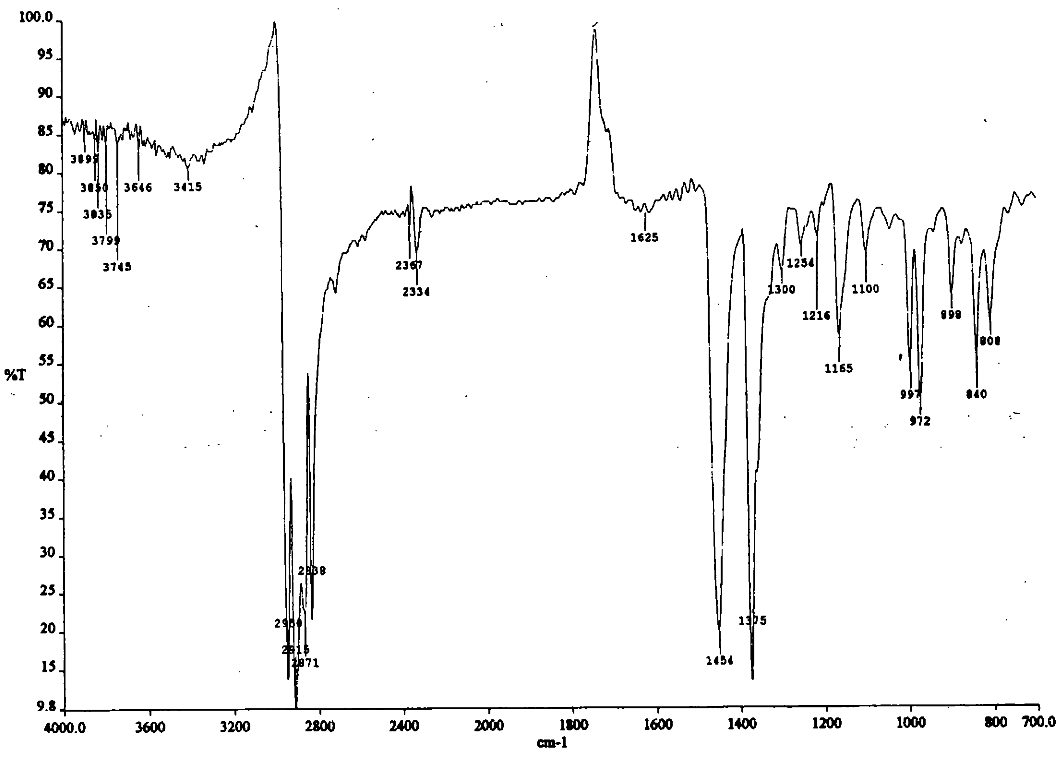


Figure 4.11 FTIR spectrum of PP

Table 4.6 Interpretation of Peaks for the FTIR spectrum of PP

Peak (cm^{-1})	Bond Type	Reference
2950	CH_3 and CH_2	[160]
2915	CH_3 and CH_2	[160]
2871	CH_3 and CH_2	[160]
2838	CH_3 and CH_2	[160]
1454	CH_3 or $C–CH_2–C$ CH_3CH_2	[160] [157]
1375	CH_3 CH_3CH_2	[160] [157]
1165	$CH_3–C–$	[158]
997	$CH_2–CH–CH_3$	[158]
972	$CH_2–CH$	[158]
840	$CH_2–CH$	[158]

4.1.7 Poly-Methyl-Methacrylate

The structure of the repeat molecule of PMMA in Figure 4.12 appears to be fairly complex and has quite a variety of different bond types. The main peaks as seen on the FTIR spectrum in Figure 4.13 are at 2991, 2947, 1724, 1438, 1385, 1239, 1142, 983, 841 and 750 cm^{-1}. Again the peaks between 3200 and 2800 cm^{-1} are so clear, they were included in the analysis in Table 4.7 and are due to the CH_2 and CH_3 group bonds, as are peaks at 1239, 983, 841 and 750 cm^{-1}. The most prominent peak at 1724 cm^{-1} is due to a carbonyl grouping and is likely to be due to the double C=O bond, whereas other carbonyl group peaks at 1438 and 1385 cm^{-1} are probably due to the O–CH_3 part of the group.

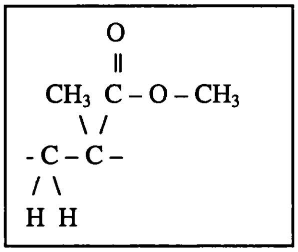


Figure 4.12 Structure of the PMMA repeat molecule

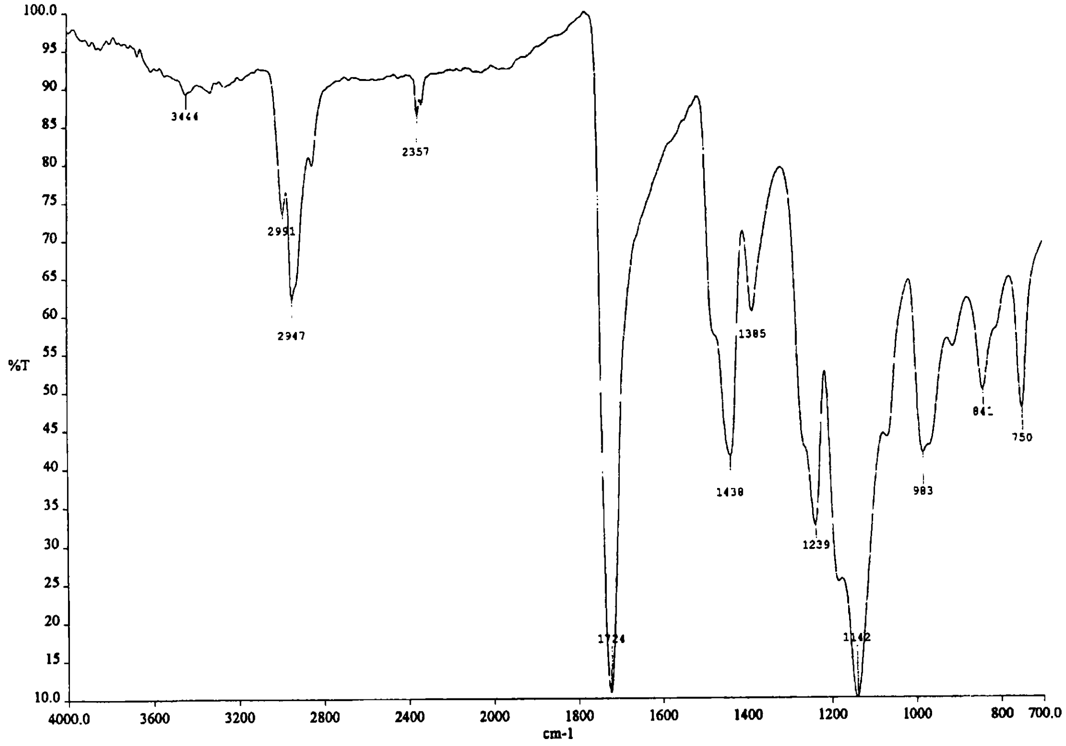


Figure 4.13 FTIR spectrum of PMMA

Table 4.7 Interpretation of Peaks for the FTIR spectrum of PMMA

Peak (cm^{-1})	Bond Type	Reference
2991	CH_3 and CH_2 or $C–CH_2–C$	[160]
2947 (m)	CH_3 and CH_2 or $C–CH_2–C$	[160]
1724 (vs)	C–CO–O–C	[157], [158], [160]
1438 (s)	$O=C–O–CH_3$ or $O–CH_3$	[160]
1385 (m)	$O=C–O–CH_3$	[160]
1239 (s)	$CH_2–C(CH_3)–$ Or C–O stretch	[158] [157]
1142 (vs)	C–O stretch	[157]
983 (b)	$CH_3–C–CH_2$	[158]
841	CH_2	[160]
750	CH_3	[158]

4.1.8 Discussion

From the FTIR spectra analysed in this study, it has been found to be fairly difficult to ascertain the exact wavenumber of each different bond type. Instead it has only been possible to establish several possible frequencies from different atomic groupings within a polymer molecule. This is due to the limited amount of information available, as the references used mainly provided the FTIR frequencies of commonly grouped atoms, and not always for individual bonds. However, as the purpose of this study was to improve understanding of the FTIR spectra of the different plastic types this was, on the whole, fairly successful. It has been seen that from the molecular differences between each polymer structure, the FTIR spectrum will show the presence or absence of peaks not only according to the distinct vibrational frequencies of the different bond types, but also according to the group of nearby atoms. Figure 4.14 is a flow chart showing a possible way of quickly identifying different plastic types used in housings for computer equipment using a simple process of elimination of prominent peaks from each plastic type. Many plastics identification systems distinguish each plastic by matching the whole spectrum of a sample with those stored on a reference database. By applying the flow chart in Figure 4.14 into a software programme, this could change the way a plastic is identified, by matching a few of the main peaks rather than the whole spectrum. Such a programme could contribute to the improvement of rapid plastics identification systems including those analysed in Section 4.4.

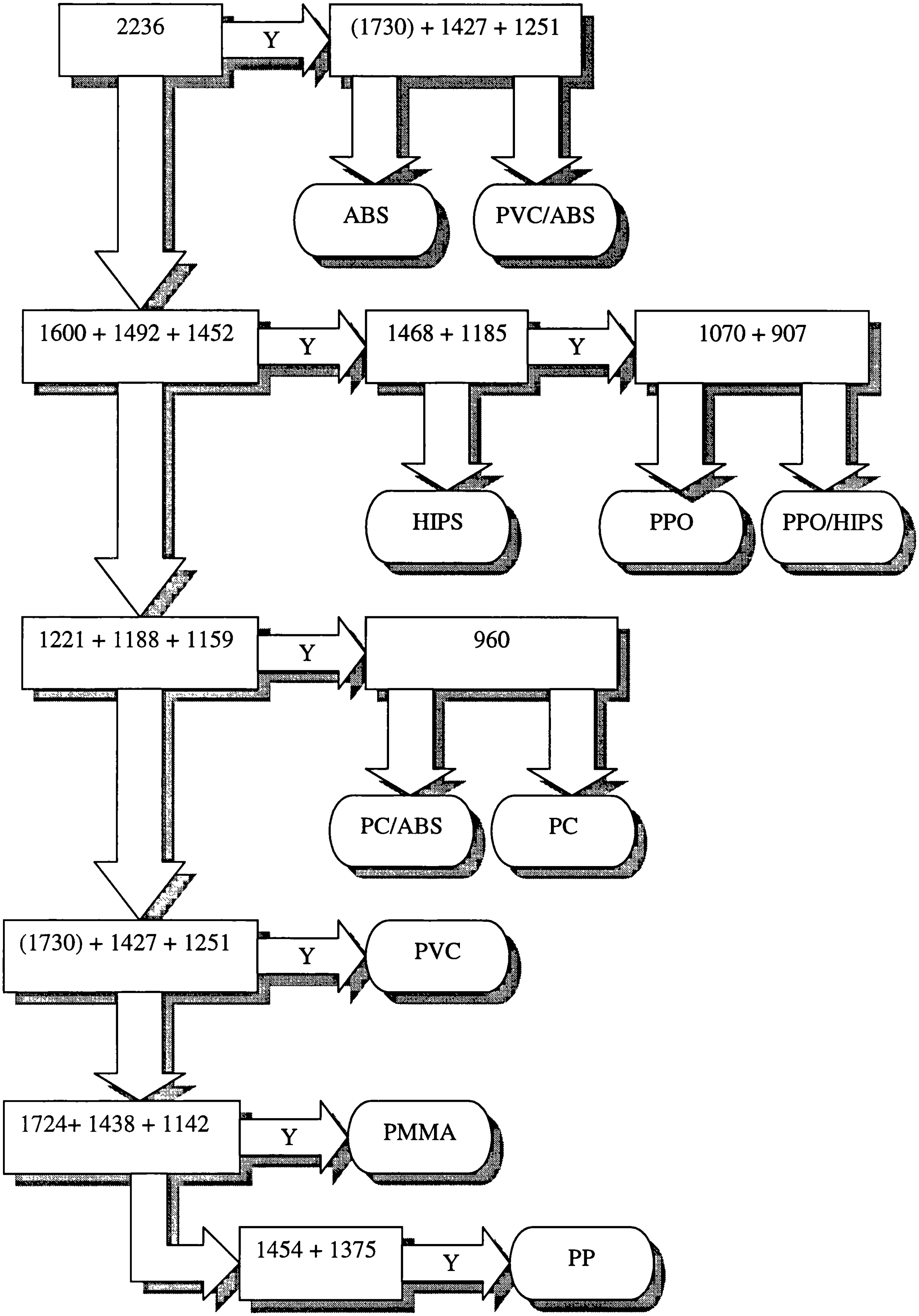


Figure 4.14 Flow chart showing a programme that could be used to rapidly identify a plastic from computer housings, by using the most prominent peaks from an FTIR spectrum

4.2 ANALYSIS OF FLAME RETARDANT PLASTICS USING FTIR SPECTRA

The purpose behind this study was to see if infrared spectroscopy could be used to detect and identify flame retardants in plastics. The flame retardants looked for in the infrared spectra were of the halogenated types, such as bromine and chlorine based and also the synergist antimony (Sb). Infrared spectra of plastics containing these types of flame retardants that had been previously detected using x-ray microanalysis in previous work [17], were compared with those of plastics that did not appear to contain any flame retardants. The FTIR spectra of the plastic types analysed for flame retardant detection includes ABS, HIPS, PPO and PC/ABS.

4.2.1 Acrylonitrile-Butadiene-Styrene

There were several different combinations of additive elements detected by x-ray microanalysis in ABS. The samples were split into those that were ABS with no other elements, ABS+Ti, ABS+Br+Sb+Ti, ABS+Cl+Sb+Ti and ABS+Br+Cl+Sb+Ti. The main peaks seen between 1400 – 650 cm^{-1} for each of these sample groups are listed in Table 4.8. The figure in brackets by each heading is the number of samples that were available for each combination of additives. The main peaks of ABS identified in the previous section are at 1362, 1069, 1026, 965, 910, 758 and 699 cm^{-1}. However, on studying the isolated FTIR spectrum of ABS in more detail (Figure 4.15), other peaks have appeared in every ABS combination that were not apparent on the whole spectrum of ABS at 1315, 1181 and 1155 cm^{-1}. All peaks that are only due to ABS appear on Table 4.8 in bold. From Table 4.8, it can be seen that there are virtually no differences between samples of ABS containing no additives and ABS+Ti, although ABS has a peak at 1272 cm^{-1}, and ABS+Ti has instead a peak at 1260 cm^{-1}. This peak displacement could possibly be an effect of the presence of TiO_2, however the FTIR of TiO_2 is almost featureless in the FTIR region 1400 – 650 cm^{-1} (Figure 4.16) and has no nearby molecular frequency that could displace the 1272 cm^{-1} ABS peak.

There appear to be several peaks that are present in the samples of ABS containing flame retardants that are not in ABS or ABS+Ti. From these peaks, it could be logical to deduce that peaks due to Br will be present in both

ABS+Br+Sb+Ti and ABS+Br+Cl+Sb+Ti. Peaks exclusive to Cl will be present in both ABS+Cl+Sb+Ti and ABS+Br+Cl+Sb+Ti, and peaks from Sb will be in all combinations.

Table 4.8 Main peaks in all ABS combinations between 1400 – 650 cm^{-1}

ABS (3)	ABS + Ti (12)	ABS + Br, Sb, Ti (4)	ABS + Cl, Sb, Ti (5)	ABS + Br, Cl, Sb, Ti (16)
		1393	1393	1393
		1370	1372	1371
1362	**1360**	**1360**	**1360**	**1360**
		1336	1335	1336
1315	**1315**	**1315**	**1316**	**1316**
1272				1270
	1260	1252	1256	1245
		1197	1197	1197
1181	**1181**	**1183**	**1183**	**1182**
1155	**1155**	**1156**	**1155**	**1156**
		1127		1128
		1107	1100	1100
1069	**1068**	**1066**	**1069**	**1066**
			1048	1049
1028	**1028**	**1028**	**1027**	**1028**
		1004		1004
966	**965**	**965**	**966**	**966**
910	**910**	**910**	**910**	**910**
		870		871
845	845		844	
759	**758**	**758**	**758**	**758**
		740		740
699	**699**	**699**	**699**	**699**

From Table 4.8 there appear to be several peaks that are present in all flame retarded ABS and are probably related to the presence of Sb. These peaks are at 1393, 1371, 1336, 1197 and 1100 cm^{-1}. There seems to be just one peak exclusive to Cl at 1048 cm^{-1}, which is present in just ABS+Cl+Sb+Ti and ABS+Br+Cl+Sb+Ti, although the peak at 1256 cm^{-1} for ABS+Cl+Sb+Ti could also be a variation on the 1252 cm^{-1} peak due to the presence of Cl. The peaks of all ABS combinations around this frequency appear to be slightly different and each combination of additives appears to have some effect, which is seen by a change in the frequency especially when compared with ABS.

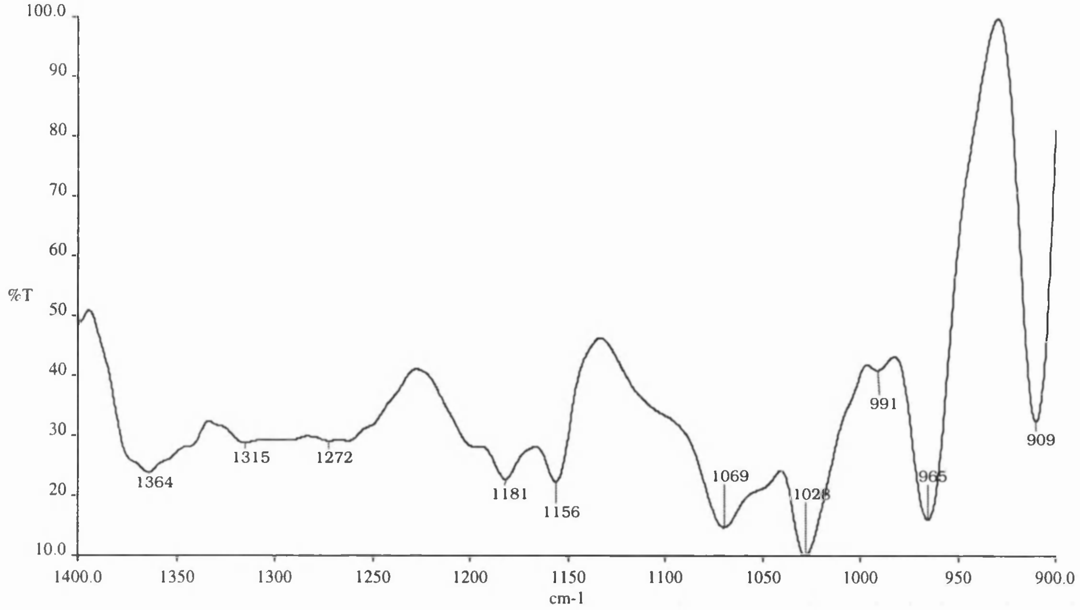


Figure 4.15 ABS Spectrum Between 1400 – 650 cm^{-1}

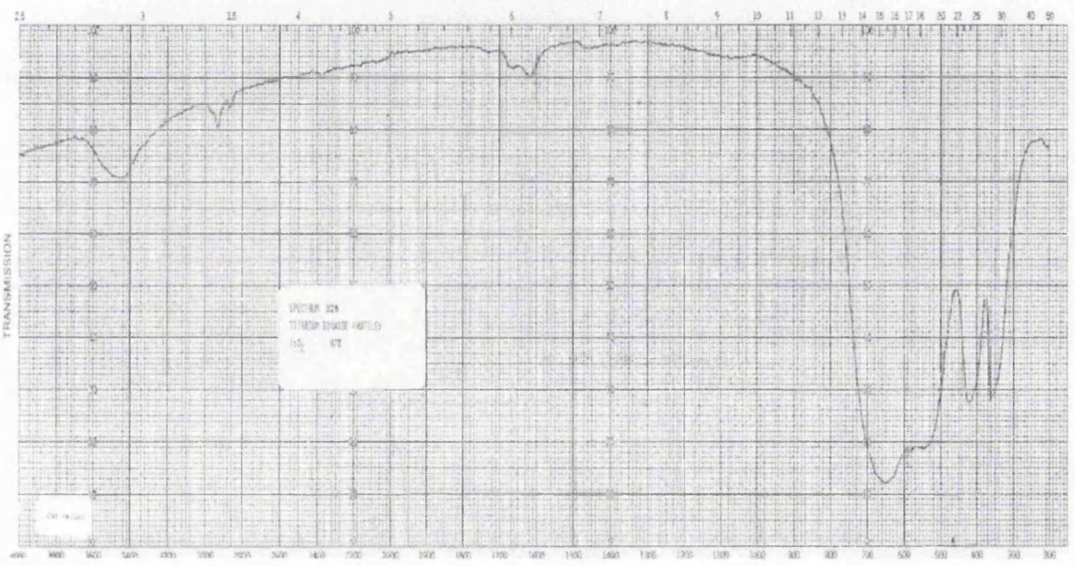
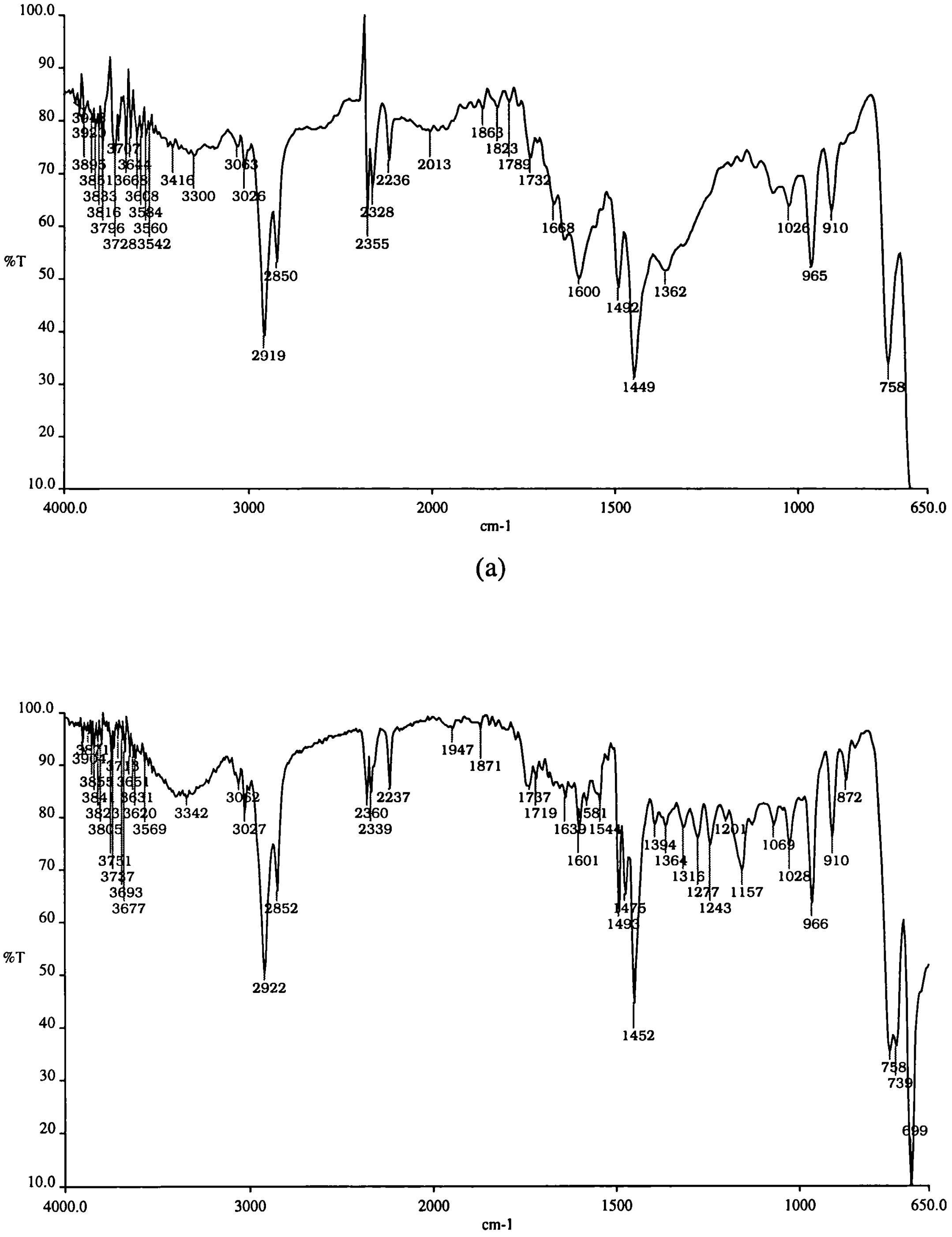


Figure 4.16 FTIR spectrum of TiO_2 [162]

For ABS+Br+Cl+Sb+Ti, there are actually two peaks displayed around this frequency, with a higher one at 1270 cm^{-1} that is comparable to that of ABS and a lower peak at 1245 cm^{-1}. Another peak that changes due to flame retardants is that at 844 cm^{-1} in ABS, ABS+Ti and ABS+Cl+Sb+Ti, which changes to a higher frequency of 870 cm^{-1} in all samples containing Br. Peaks exclusive to Br have been deduced as 1127, 1004 and 740 cm^{-1} as seen in Table 4.8. These peaks are only present in ABS+Br+Sb+Ti and ABS+Br+Cl+Sb+Ti. The Br peak at 740 cm^{-1} appears to be especially important as it creates a double peak with the ABS peak at 758 cm^{-1}. The intensity of this peak is sufficiently strong that it can be easily seen on a spectrum covering the usual wavenumber range of 4000 – 640 cm^{-1} as shown in Figure 4.17. This means that it could be considered as a suitable reference peak indicating the presence of bromine for an automated identification system.



(a)

(b)

Figure 4.17 Comparison of the 740 and 758 cm^{-1} peaks in the spectra of
(a) ABS and (b) ABS with Br, Cl, Sb, Ti

4.2.2 High Impact Polystyrene

The various combinations of additives in HIPS were fairly difficult to analyse due to the small numbers of samples found within each combination. Such combinations of additives can be found in Table 4.9 as HIPS, HIPS+Ti, HIPS+Br+Ti, HIPS+Br+Fe+Ti, HIPS+Br+Cl+Fe+Ti and HIPS+Br+Sb+Ti. The number of samples for each combination is in brackets by the heading.

Table 4.9 Main peaks in all HIPS combinations between 1400 – 650 cm^{-1}

HIPS (3)	HIPS+Ti (9)	HIPS+Br+Ti (1)	HIPS+Br+Fe+Ti (2)	HIPS+Br+Cl+ Fe+Ti (1)	HIPS+Br+Sb+Ti (1)
			1392	1391	1395
1370	**1370**	**1373**			**1377**
			1352	1352	
					1343
	1326		1323	1322	1323
	1311	1312		1315	1315
	1279			1260	1271
			1232	1230	
1181	**1180**	**1181**	**1181**	**1180**	**1181**
1154	**1154**	**1154**	**1154**	**1154**	**1160**
					1076
1068	**1068**	**1068**	**1068**	**1068**	**1068**
			1047	1050	
1027	**1027**	**1027**	**1027**	**1027**	**1027**
		979			979
964	**964**	**965**	**965**	**965**	**964**
905	**905**	**906**	**905**	**906**	**906**
840	**841**	**841**	**841**		**841**
752	**751**	**752**	**748**	**751**	**747**
695	**696**	**696**	**696**	**696**	**696**

The main peaks identified for HIPS from the previous section between 1400–650 cm^{-1} are at 1370, 1154, 1069, 1027, 965, 905, 841, 752 and 696 cm^{-1}. An additional peak, which is not apparent on the full spectrum of HIPS can be seen in the reduced spectrum in Figure 4.18 at 1181cm^{-1}. The main peaks for HIPS are in bold in Table 4.9. From this Table, it appears that there are a couple of peaks present in HIPS+Ti that are absent in HIPS with no addititives. These are at 1326 and 1311cm^{-1} and the peak at 1279 cm^{-1} is also present in about half the HIPS+Ti spectra. However it must remembered that the FTIR spsectrum of TiO_2 in Figure 4.16 shows no peaks in the region being studied and such peaks cannot be due to the presence of TiO_2. However due to the small numbers of HIPS spectra it is unclear whether the difference of two to three peaks is representative between HIPS and HIPS+Ti or whether it is due to the sensitivity of the FTIR spectrometer.

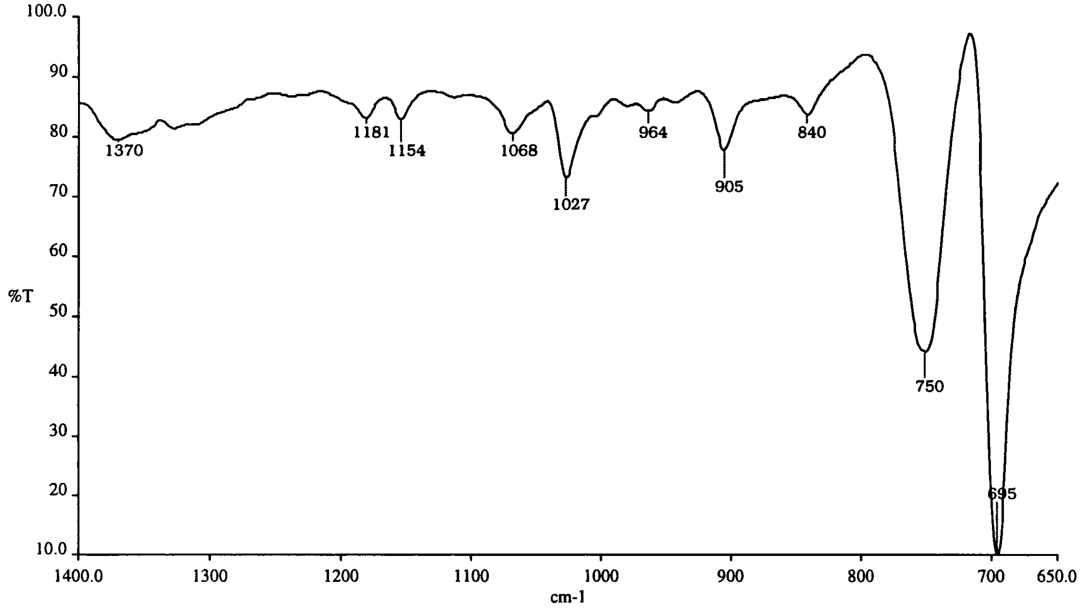


Figure 4.18 HIPS Spectrum Between 1400 – 650 cm^{-1}

From Table 4.9, the peak at 1392 cm^{-1} could be due to Br as is it present in most combinations containing Br, however it does not appear in the spectrum for HIPS+Br+Ti. The two combinations containing Fe appear to displace the HIPS peak at 1372 cm^{-1} to a lower frequency of 1352 cm^{-1}. Peaks at 1230 and approximately 1047 cm^{-1} also appear to be exclusively in both combinations of samples containing Fe and in no other type. The peaks at 1343 and 1076 cm^{-1} only appear on the spectrum for HIPS+Br+Sb+Ti and could be due to Sb as this is not present in any other sample. The spectrum for HIPS+Br+Ti does not display the peak at 1279 cm^{-1} like most other spectra, although HIPS+Br+Fe+Ti is missing this peak too, including the peak at 1312 cm^{-1}. The spectrum of HIPS+Br+Cl+Fe+Ti is also missing a couple of fundamental HIPS peaks at 841 and 748 cm^{-1} and it is unclear why this would happen. The peak at 979cm^{-1} was initially though to be the only peak that could be attributed to bonds with Br, however it is only present in two of the four combinations containing Br. The two combinations not displaying this peak both contain Fe and it is possible that the presence of Fe has the effect of displacing this peak as happened with other peaks.

Many of the deductions made from studying the spectra of HIPS are inconclusive, which is generally down to the small numbers of spectra representing each combination of additives. The FTIR spectra studied are not always one hundred percent clear and by studying just one spectrum per group of additives is relying solely on the accuracy of that spectrum. If just one peak is not as clear as it could be, or if the spectrometer used does not run as well on one day as it could, then this could give misleading information for that spectrum. It is therefore not possible to fully conclude the observations made above unless further studies can be made with a larger number of spectra for each combination of additives within HIPS.

4.2.3 Polypheneylene Oxide

The various combinations of additives in PPO are found in Table 4.10 with the number of spectra for each group in brackets by the heading. Combinations of PPO with various additives are PPO+Ti, PPO+P+Ti, PPO+Cl+P+Ti and PPO+Br+Ti. The main peaks identified for PPO in Section 4.1 between 1400 and 650 cm^{-1} are at 1378, 1304, 1185, 1020, 957, 856 and 752 cm^{-1}, however on studying the reduced spectrum of PPO (Figure 4.19), more peaks are apparent at 1110, 1070, 907 (clearer on some spectra than others) and 830 cm^{-1}.

Table 4.10 Main peaks in all PPO combinations between 1400 – 650 cm^{-1}

PPO+Ti (1)	PPO+P+Ti (13)	PPO+Cl+P+Ti (1)	PPO+Br+Ti (1)
1378	1377	1379	1377
1304	1304	1304	1304
1185	1185	1184	1184
1110	1127	1129	1228
			1113
1070	1070	1072	1070
1021	1020	1019	1021
		1000	
959	958	959	958
907	906	905	906
857	856	857	856
830	831	830	830
752	752	753	751
699	699	699	699

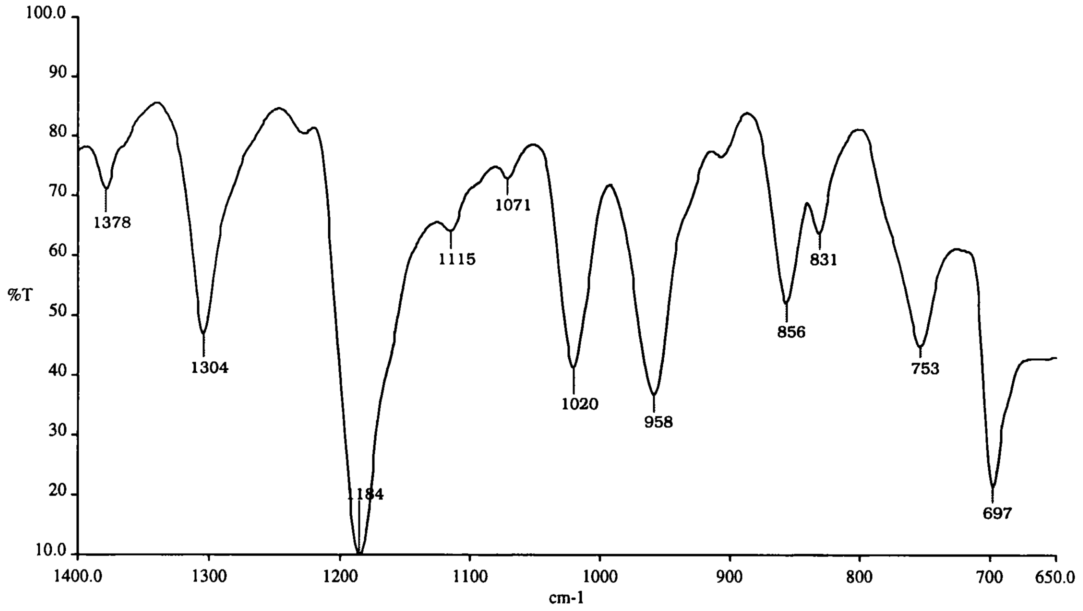


Figure 4.19 PPO Spectrum Between 1400 – 650 cm^{-1}

From Table 4.10, it can be seen that there are no apparent differences between peaks of PPO+Ti and PPO+P+Ti. A possible explanation for this occurrence could be that peaks due to bonds with P are not in this region of the FTIR spectrum. From the other combinations of flame retardants, the peak due to Br in PPO appears to be at 1113 cm^{-1}, while the only differing peak due to the presence of Cl in PPO is found at 1000 cm^{-1}. While these results have been nice and simple to work out, they are quite distinct from what was found for halogenated ABS. From the results for ABS, it was found that the peak at 1113 cm^{-1} was common to all halogenated flame retardant systems and was concluded to be due to Sb, however this element is not actually present in PPO. The peak at 1004 cm^{-1} in ABS was also deduced as being due to Br, which is quite different to the results for PPO, which have pointed to the nearest frequency to this peak as being due to Cl. However, it has to be realised that the molecular structures of PPO and ABS are quite different, which is seen by their distinct FTIR spectra. The differences between structures in these plastics may have an effect on the vibrational peaks of other molecules, such as flame retardants, present in the plastics. Such flame retardant molecules could therefore exhibit different frequencies in individual plastics and so such results between plastic types should not really be compared. Again due to the small numbers of spectra available for each combination of flame retardants in PPO, these results can only be considered as speculative.

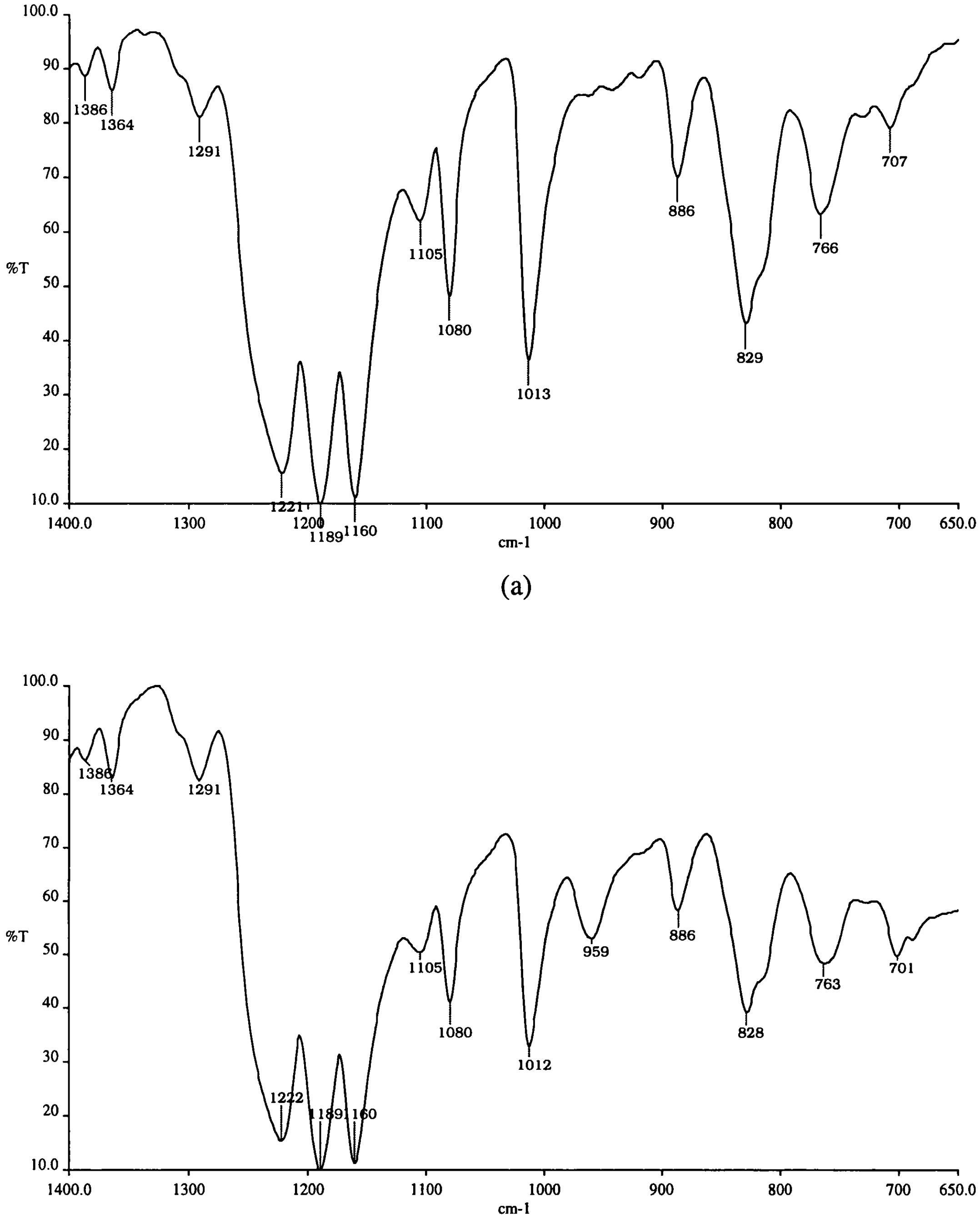
4.2.4 Polycarbonate / Acrylonitrile-Butadiene-Styrene

The various combinations of additives in PC/ABS are found in Table 4.11 with the number of spectra for each group in brackets by the heading. Combinations of PC and ABS with various additives are PC, PC/ABS+Ti, PC/ABS+P+Ti, PC/ABS+Br+Ti and PC/ABS+Br+Cl+Sb+Ti. The main peaks identified in Section 4.1 for PC between 1400 and 650 cm^{-1} are at 1221, 1188, 1159, 1080, 1012, 885 and 765 cm^{-1}. Previous studies [17] found that for the PC/ABS blend, the only indication of the presence of ABS was the peak at 959 cm^{-1}, which can be seen in Figure 4.20. This is present in all of the groups in Table 4.11 with the exception of PC. On studying the reduced spectrum of PC in Figure 4.20(a), quite a few more peaks become apparent for PC and PC/ABS at 1387, 1364, 1291, 1105, 829 and 707 cm^{-1}.

Table 4.11 Main peaks in all PC and PC/ABS combinations between 1400 – 650 cm^{-1}

PC (1)	PC/ABS+Ti (1)	PC/ABS+P+Ti (5)	PC/ABS+Br+Ti (1)	PC/ABS+Br+Cl+Sb+Ti (1)
1387	1387	1387	1386	1392
1364	1364	1364	1364	1353
1291	1291	1293	1292	1278
1221	1221	1223	1223	1230
1189	1189	1190	1190	1194
1160	1160	1160	1161	1163
1105	1105	1105	1105	1106
1080	1080	1080	1080	1071
1013	1013	1012	1013	1015
	959	959	958	965
				910
886	886	887	887	886
829	828	828	829	834
766	763	764	758	757
				739
707	701	700	700	700

From Table 4.11, it can be seen that PC/ABS+P+Ti do not appear to have any additional peaks than those already displayed by PC/ABS. This is also the case for the group PC/ABS+Br+Ti. The previous section on PPO found that the additives



(a)

(b)

Figure 4.20 Comparison of Spectrum Between 1400 – 650 cm^{-1} of (a) PC and (b) PC/ABS (note the only peak for ABS at 959cm^{-1})

based on P did not show any additional peaks, and it was thought that maybe bonds with P did not vibrate at frequencies in this part of the FTIR spectrum being studied. The absence of any additional peaks in PC/ABS from Br could be due to the amount of peaks that are already present in PC/ABS due to the more complex structure of PC.

These peaks could coincide with the frequencies of the vibrational bonds due to Br flame retardants.

The only difference between the spectra of PC/ABS is the group of PC/ABS+Br+Cl+Sb+Ti, which actually display two additional peaks at 910 and 739 cm^{-1}. From the interpretation of the different vibrational frequencies in Section 4.1, it was found that the peak at 910 cm^{-1} is common to ABS and is believed to be from the C–H bonds from butadiene. However, as only one peak common to ABS actually shows up on the spectrum of PC/ABS, it is probably unlikely that an ABS peak would appear with this combination of additives and not in all PC/ABS blends. The peak at 910 cm^{-1} is more than likely to be due to Cl or Sb, as neither of these elements were present in any of the other PC/ABS groups.

Although the 739 cm^{-1} peak does not show up on the FTIR spectrum for PC/ABS+Br+Ti, it is thought highly possible that this peak is due to Br. The results for ABS found that the presence of Br created a double peak with the one at 757cm^{-1}, which can also be seen quite clearly from the spectrum of this PC/ABS blend in Figure 4.21. The difference between the PC/ABS combination PC/ABS+Br+Cl+Sb+Ti and the previous group with Br, is the absence of Sb in PC/ABS+Br+Ti. Therefore it is probable that the presence of Br will only display the doublet peak at 740 cm^{-1} if combined with Sb, and plastics that contain Br without Sb may be harder to detect.

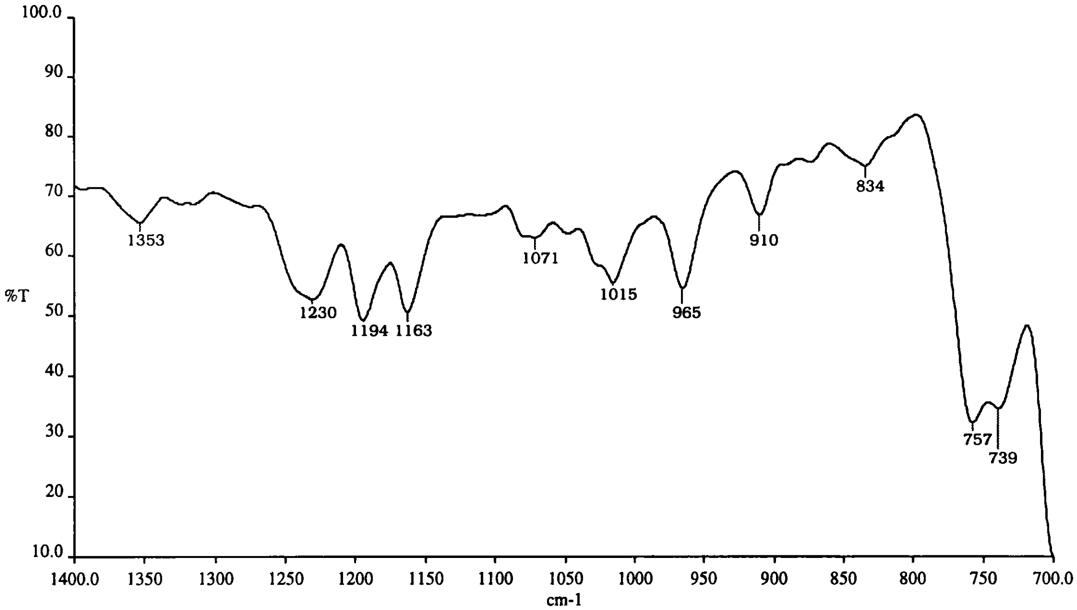


Figure 4.21 Spectrum of PC/ABS+Br+Cl+Sb+Ti Between 1400 – 650 cm^{-1}

4.2.5 Discussion

On the whole, it has been fairly difficult to determine which peaks on the FTIR spectrum of a plastic are due to the presence of flame retardants and other additives because of the limited number of spectra available on most combinations of plastics and flame retardants examined. The only plastic type that had a representative number of spectra for each combination of additives was ABS. From these spectra it was found that peaks due to the presence of Sb were at 1393, 1371, 1336, 1197 and 1100 cm^{-1}, whereas the peak at 1048 cm^{-1} appears to be due to Cl. Peaks exclusive to Br have been deduced as 1127, 1004 and 740 cm^{-1}, with the 740 cm^{-1} peak being the most prominent as it causes a doublet with the ABS peak at 758 cm^{-1}, which can be seen quite clearly on a full size spectrum of ABS. This doublet was also present in flame retarded PC/ABS, however it is thought to be present only if the Br is present with Sb. The results from studying the FTIR spectra of HIPS must remain inconclusive due to the various different combinations of additives that had insufficient representative spectra. The same must be said about combinations of PPO as PPO+P+Ti was the only combination with sufficient number of spectra, despite the other combinations being easy to evaluate. The presence of Br and Cl producing peaks at 1113 and 1000 cm^{-1} respectively and P showing no characteristic peaks in the 1400 – 650 cm^{-1} FTIR region were not sufficiently represented to verify such assumptions. A way of trying to verify the above results could be to compare the peaks thought to be due to certain flame retardants with the FTIR spectra of different types of flame retardants commonly used in the plastic studied for this project. However it is possible that the FTIR spectrum of an isolated flame retardant could differ from that of a flame retardant within a plastic.

4.3 ANALYSIS OF INFRARED SPECTRA OF COMMERCIAL FLAME RETARDANTS

In the previous section, ABS was the only plastic type that had sufficient numbers of samples for each different combination of flame retardants. This was therefore the only plastic type for which suitable comparisons could be made between spectra in order to determine a way of detecting the presence of flame retardants by using the FTIR spectrum alone. This section will therefore compare the results from just ABS with infrared spectra from several commercial flame retardants in order to try and verify these results.

The infrared spectra provided by Great Lakes Chemical Company, of several different flame retardants, were studied including antimony trioxide and brominated and chlorinated flame retardants. Table 4.12 is a summary of the main peaks from the spectra of each compound and each starred (*) compound has been recommended as suitable for use in ABS. The structure and other information on each compound can be found in Table 3.1 in the previous chapter. It may be useful to compare Table 4.12. with the main peaks for all additive combinations of ABS in Table 4.8. Using the results from Table 4.8, the peaks highlighted in bold type in Table 4.12 are at the same frequency as some of the peaks from ABS. As these peaks are present on the infrared spectrum of ABS, they will be useless for flame retardant detection. On Table 4.12, the coloured peaks are those that were also found in the FTIR spectrum of ABS samples in the previous section. Peaks highlighted in red were attributed to Brominated compounds, while green is thought to be from Chlorinated compounds. All peaks highlighted in blue are suspected as being from antimony trioxide because they are present in all flame retarded ABS samples, whereas peaks left in normal black type are from each individual flame retardant and do not correspond with any of the results in the previous section.

From Table 4.12, it can be seen that Antimony trioxide (Sb_2O_3) exhibits very few peaks on the IR spectrum as a single compound. Several peaks were thought to be due to Sb in ABS in the previous section because they had been present in all Br and Cl combinations of flame retardants. These were at 1393, 1371, 1336, 1197 and 1100 cm^{-1}. However not one of these have appeared on the IR spectrum of Sb_2O_3, although the peak at 1090 cm^{-1} is fairly close. These peaks do however, appear in all

Table 4.12 Main peaks from infrared spectra of commercial halogenated flame retardants

Antimony trioxide*	BA-59P*	BC-52HP*	BC-58*	CD-75P*	DE-79*	DE-83R	FF-680*	Dechlorane Plus*
	1400	1400	1400		1400			
	1372						1378	1379
				1363				
	1322			1327	1332	1336	1343	1340
				1315				
	1275			**1281**	**1295**			**1280**
	1255	**1236**	**1227**	**1254**	**1227**		**1254**	
		1200	1201					
	1181			**1181**				
	1163							**1170**
	1141				1145		1136	
		1109		1109				1100
1090			1081		1080	1072		1080
					1063	**1069**	**1063**	
		1054	1045	1042	1036			
		1000		1000			1000	1000
	934			**976**		**964**		**950**
				910	**910**			**910**
	872	890	872	885	849	873	860	870
				856				
				818			824	830
	781			772				785
		763	**750**		**754**	**764**		**760**
745							745	
	727	720				728		
	708			709	709			715
				694				
				670		673	672	678
	654				636			
618	618	636		618		619		
	581			582			572	

KEY

Black Bold Type = ABS	Blue = Sb in ABS
Red = Br in ABS	Black = peaks from the commercial spectra
Green = Cl in ABS	

of the halogenated flame retardants, with compounds such as Dechlorane Plus, BC-52HP and BA-59P exhibiting at least three peaks out of five, although no single compound contains all five peaks. It is highly likely that the peaks thought to be due to Sb_2O_3 from the previous results are incorrect, and are more likely to be due to both Br and Cl based compounds as the spectra of both types of flame retardant exhibit some of these peaks. Only a combination of Dechlorane Plus with either brominated compounds BC-52HP or BC-58 would show all five peaks present, which cannot explain the presence of any of these peaks when there is just a Br or Cl based flame retardant present without the other.

Out of the three peaks that do appear to be present in Sb_2O_3, only one appears to correspond with any of the peaks highlighted from ABS, which is at 745 cm^{-1}. From the previous section, the peak at 740 cm^{-1} was thought to be fairly important as this peak caused a doublet with the ABS 758 cm^{-1} peak, which was fairly prominent even on the full size spectrum. This peak was initially thought to be due to a Brominated flame retardant as it was present only in combinations of Br and Sb compounds and not ABS with Cl and Sb compounds without Br (Table 4.9). However in Table 4.12, it appears that only one Br flame retardant (FF-680) exhibits a peak at 745 cm^{-1}, although other compounds display one at approximately 760 cm^{-1}. From the results for PC/ABS (Table 4.11 in the previous section), the 740 cm^{-1} peak was only present for the combination PC/ABS+Br+Cl+Sb+Ti and was not actually present in the group PC/ABS+Br+Ti. Initially, it was thought that this peak was probably due to Br compounds combined with Sb. However, as this peak was absent in the group PC/ABS+Br+Ti, and from studying the spectra from flame retardants it is now thought more than likely to be due to Sb_2O_3 and not any of the Br flame retardants. This point is strengthened by the IR spectrum of Sb_2O_3, which is shown in Figure 4.22. From this spectrum it can be seen that despite only displaying very few peaks, the intensity of the peak at 745 cm^{-1} is very strong.

The peak at approximately 1255 cm^{-1} was present in all ABS combinations except the one that did not contain Ti. Although it could appear to be due to a Ti compound, the FTIR spectrum of TiO_2 (Figure 4.16), a common white pigment, shows very few peaks and probably has very little effect on the FTIR spectrum of plastics. Some of the brominated compounds also contain the 1255 cm^{-1} peak at a medium to strong intensity, which will probably not replace the assumption that this peak is mainly from Ti, although a spectrum of TiO_2 would probably need to be studied to verify this conclusion. The peak previously thought to be due to Cl in ABS at approximately 1048 cm^{-1} is not actually present in the spectrum of Dechlorane Plus, neither is there another peak close-by that could have been slightly displaced when blended with ABS, although there are a few Br compounds that appear to display a similar peak.

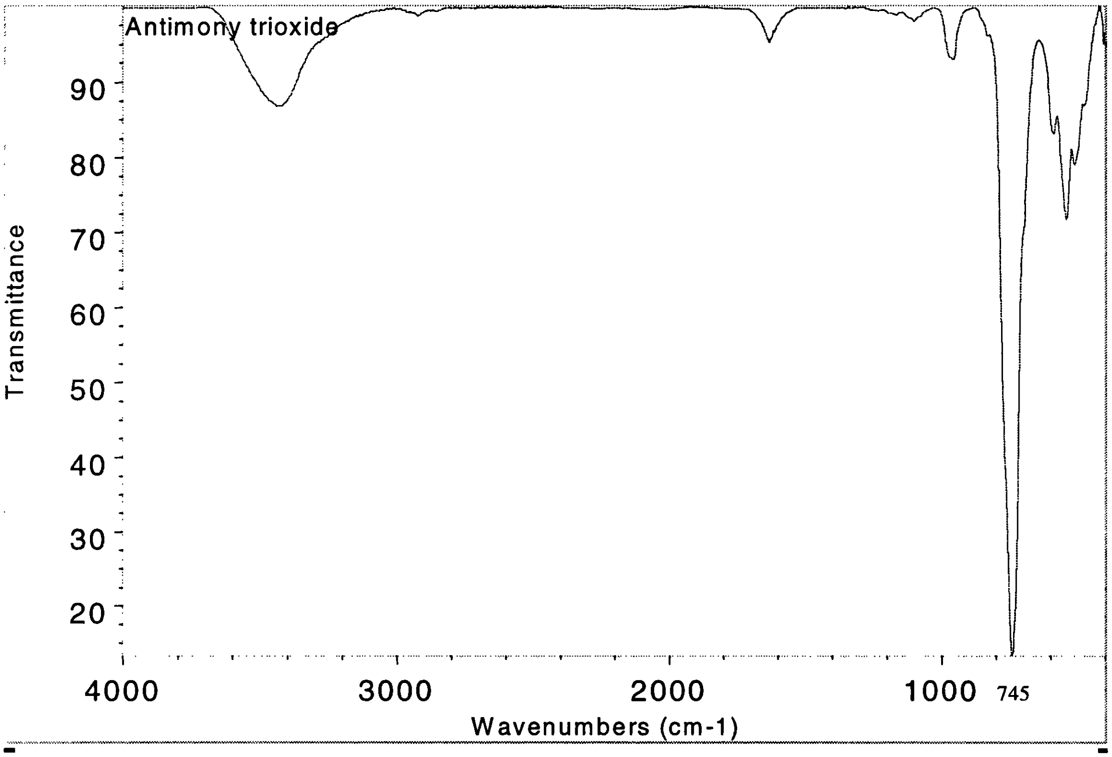


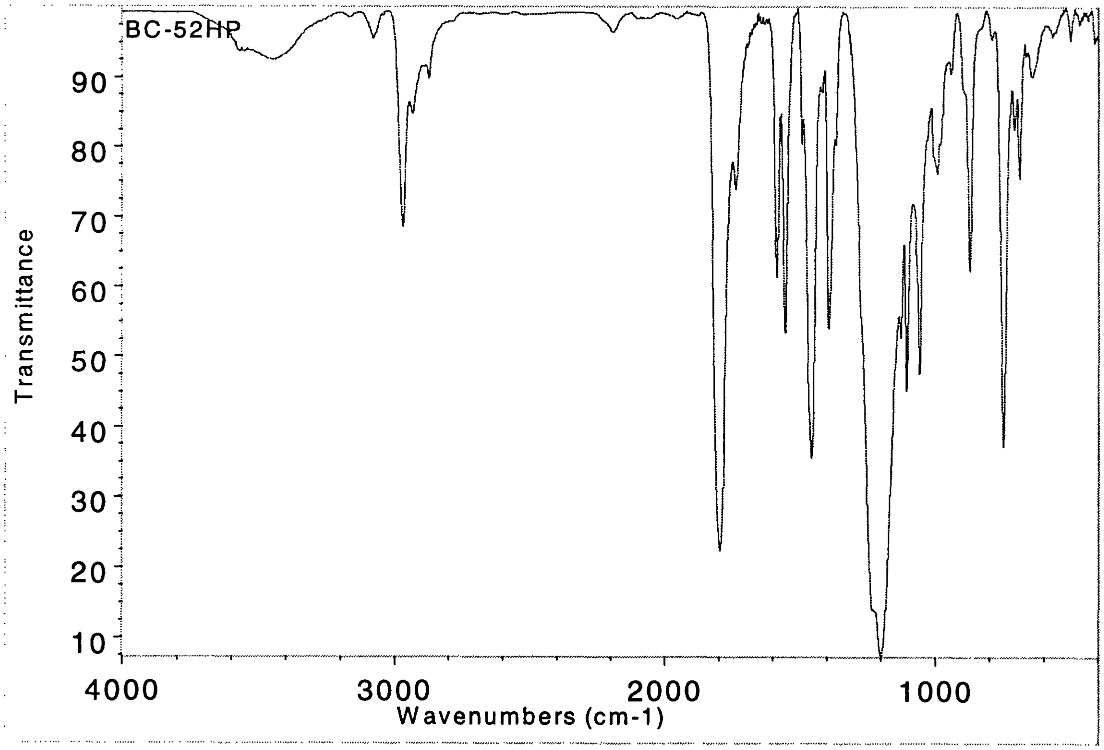
Figure 4.22 IR spectrum for Antimony Trioxide

In Table 4.8, four peaks were construed to be due to a Br compound at approximately 1128, 1004, 871 and 740 cm^{-1}. From Table 4.12 it can be seen that all Br flame retardants have a peak approximate to 871 cm^{-1} as does Dechlorane Plus, which also has the peak approximate to 1004 cm^{-1}, while only half of the Br compounds exhibit this one. Just two compounds FF-680 and DE-79 exhibited peaks at 745 cm^{-1}, which was the nearest approximation to 740 cm^{-1}, although the peak intensity for both was medium and narrow and not quite as prominent as the same peak displayed by Antimony Trioxide. None of the flame retardants appeared to exhibit the peak at 1128 cm^{-1}, although the compound FF-680 had the closest peak to this at 1136 cm^{-1}, which makes this compound appear to be the most compatible with the results from the previous section.

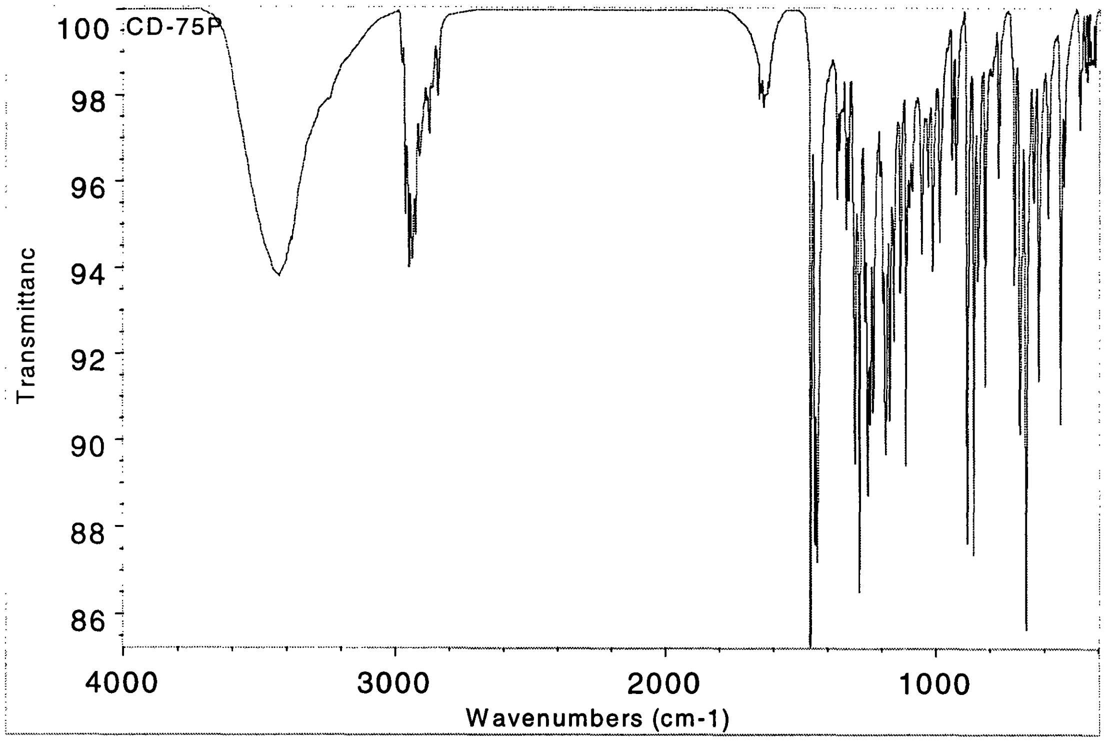
From Table 4.12, it can also be seen that there are several peaks for each compound that are not highlighted in any way, as they did not appear in any of the spectra for ABS. Peaks below about 700 cm^{-1} can be dismissed as there are no data to compare them with because the ABS spectra were not able to show peaks much lower than this. Peaks above 700 cm^{-1} tend to be common to individual compounds and are not present in more than two or three flame retardants at the most, and they may not be prominent enough when mixed with ABS. However it was very useful to search the IR spectra of ABS in the 1400-650 cm^{-1} region of the spectrum as most of the prominent peaks from all of the flame retardant spectra studied were displayed in this region. This is illustrated in Figure 4.23, which shows a selection of spectra from some of the brominated flame retardant compounds studied in this section.

From studying IR spectra of different flame retardants it appears that the most important peak is at 740 cm^{-1}. In the previous section, this peak was thought to be due to a Br compound, however these studies have revealed that it is more likely to be due to Sb_2O_3, as this compound displays a very strong peak near this frequency on the IR spectrum. However it is still unknown why this peak did not occur in the ABS samples containing Cl+Sb+Ti with no Br. A possible explanation could be that the 745 cm^{-1} peak from Sb_2O_3 is slightly displaced when with a chlorinated flame retardant, to a frequency similar to a peak in ABS.

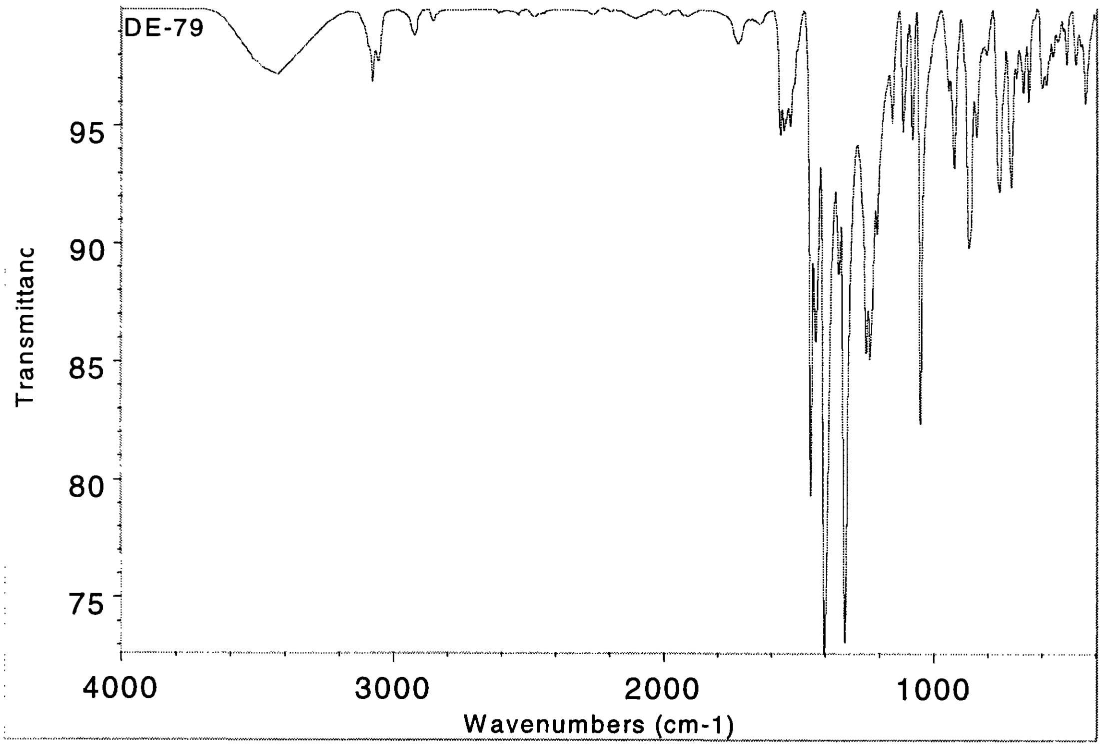
It appears as though a peak identifying the presence of Br is more likely to be found at 841 cm^{-1}, although this peak is also present in Dechlorane Plus. It is also possible that many of the ABS samples studied in the previous section contained the compound FF-680, as the spectrum of this compound appeared to be the most compatible with results from the previous section. However it must be remembered that just a small selection of flame retardants have been studied in this project. There are many more different flame retardants containing Br and many with Cl that can be used in combination together and, unless the exact compound is known, it is quite difficult to ascertain the correct combination of flame retardants just by comparison of peaks from a flame retarded plastic with those of flame retardant compounds. It is equally difficult to determine the proportion of flame retardants in a plastic by studying an FTIR spectrum. Previous work by Eisenreich et al [95] on the detection of flame retardants in plastics using laser break down spectroscopy actually found that



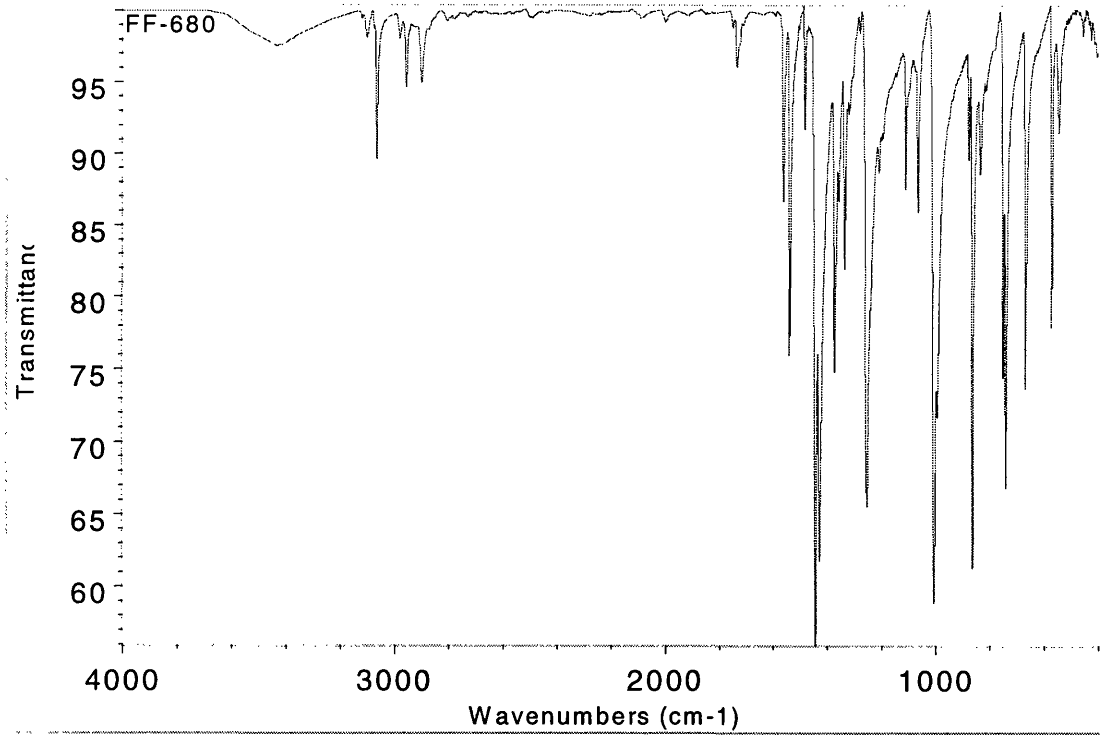
(a) Phenoxy-terminated carbonate oligomer of Tetrabromobisphenol A



(b) Hexabromo-cyclododecane



(c) Octabromodiphenyl Oxide



(d) Bis(Tribromo-phenoxy)ethane

Figure 4.23 A seclection of infrared spectra of brominated flame retardant compounds the brominated flame retardants tested did not yield a specific fingerprint on the spectrum of PE and were therefore unable to be detected. However the synergist antimony trioxide, which is almost always present with Br, did show significant peaks on the PE spectrum, thus drawing the conclusion that Sb_2O_3 could be used as a tracer for brominated flame retardants. As Sb_2O_3 could be clearly identified, this was indirect proof of the presence of a brominated flame retardant. This theory could be adapted to the present study where the peak at 740 cm^{-1} (that distinctly appeared on the FTIR spectrum of flame retarded ABS) found to be from Sb_2O_3, could also be used as an indirect indicator to the presence of a brominated flame retardant. However if a brominated flame retardant was present in a plastic without Sb_2O_3, as with some samples, then it would go undetected, which means that this method of indirect detection is not an exact guarantee as to the presence of Br based flame retardants. Also the Sb_2O_3 peak at 740 cm^{-1} has only been confirmed to occur in ABS and PC/ABS, which leaves out other plastic types from such an assumption such as with HIPS.

Under the most recent European recycling legislation, the directive on the Restriction of the Use of Certain Hazardous Substances in Electrical and Electronic Equipment (RoHS) has required the phasing out of polybrominated biphenyls (PBB's) and some polybrominated diphenyl ethers (PBDE's). Penta-BDE's are currently being phased out however, although not yet banned from use at present, Octa-BDE and Deca-BDE are currently under assessment [52]. The IR spectrum of each of these compounds have been studied in this section (Octa-BDE is DE-79 and Deca-BDE is DE-83R). If these compounds are to be phased out, it would be useful if they could be identified in a plastic by a characteristic IR frequency. However by comparing common peaks with other flame retardants in Table 4.12, there does not appear to be any peak frequency specific to either compound that is not shared by others. This could mean that if such flame retardants are banned from use, then all brominated plastics will have to be separated unless there is a way of distinguishing the different flame retardant types.

Although it has been very useful to study the spectra of such flame retardants, it is quite possible that when actually blended with a polymer, the infrared frequencies from these compounds may be affected by molecular vibrations of the constituent plastic. This could displace the frequency of peaks from the infrared spectrum of an isolated flame retardant to other frequencies, some of which may even overlap those of the constituent polymer. The extent of this may not be obvious on the spectrum of a flame retarded plastic. Also, the incorporation of flame retardants into different plastic types could also cause different degrees of overlap / shifting of the peaks. To fully explore this, the IR spectra of all combinations of plastics, with known flame retardants, would need to be compared. This is a huge task, and when considering the results from this section, this would probably not yield any single peaks that could be used unambiguously.

Therefore the results from this part of the study must be considered as purely speculative as there are too many unknown factors to attribute each flame retardant to certain peaks on an IR spectrum of a polymer. This leads to the only conclusion that can be drawn from this study, which is that infrared spectroscopy in the current state of technology cannot be used to determine the content of flame retardants in a plastic and must therefore be combined with other methods in order to ensure accurate detection.

4.4 COMPARISON OF RAPID PLASTICS IDENTIFICATION TECHNIQUES

4.4.1 FTIR and X-ray Microanalysis

The selection of samples that were tested further using FTIR spectroscopy had previously been identified as acrylic or PMMA [17]. However, on comparison with results from other identification systems in previous work [17], and results from this section, it appeared that none of the other systems were able to properly identify acrylic or PMMA and usually identified such samples as HIPS or PS. So, on retesting, both sides of each sample were tested. The FTIR results from retesting samples are found in Table 4.13.

Table 4.13 Comparison of FTIR results from initial tests and retests of Acrylic Samples.

Sample	**Previous FTIR Results [17]**	**Other identification Results [17]**	**FTIR Results**
6	Acrylic	PS	(a) Acrylic (b) HIPS
7	PMMA	PS	(a) PMMA (b) HIPS
31	Acrylic	PS	(a) HIPS (b) Acrylic
37	Acrylic	PS	(a) Acrylic (b) HIPS
47	PMMA	PMMA	PMMA

From testing both sides of the samples, it was found that they were actually double sided plastics, one side was HIPS and the other side was an acrylic. The differences between the FTIR spectra of both sides of sample 6(a) and 6(b) are compared in Figures 4.24 and 4.25 This explains why these results never seemed to agree with other identification systems, as all results were technically right. It also highlights an important feature of computer housing materials in that some are double sided. As only a selection of samples were tested further, it is possible that there may be others and as such samples cannot be detected visually, the thickness of each plastic layer is not known. This raises the additional points to consider as to what

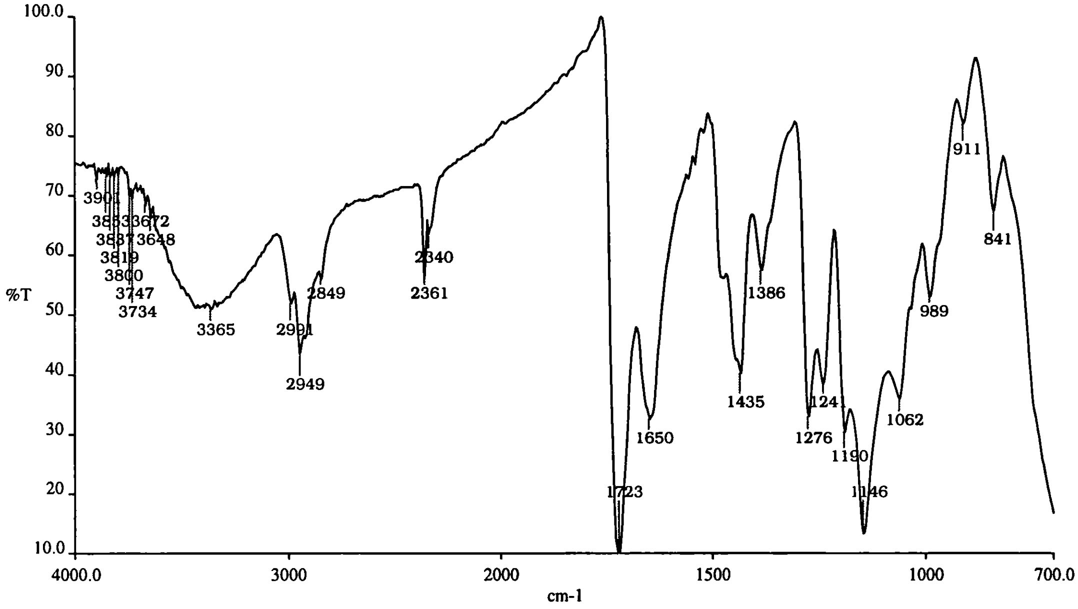


Figure 4.24 FTIR Spectra of Sample 6(a) – Acrylic

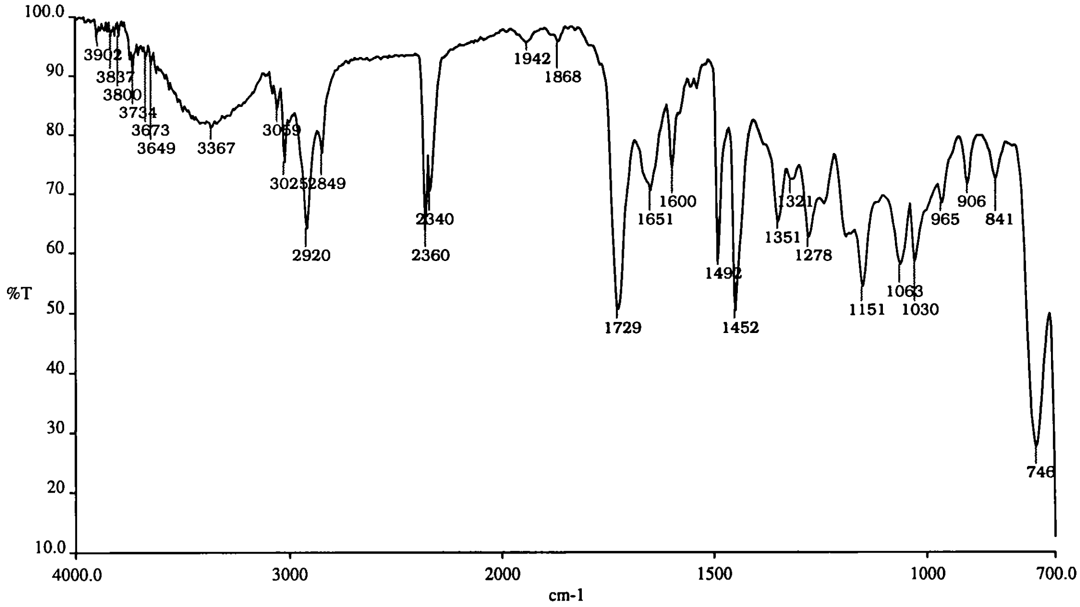


Figure 4.25 FTIR Spectra of Sample 6(b) – HIPS

proportion of equipment housing actually consists of two different plastics and therefore what the implications for recycling would be.

Further tests on samples using elemental analysis resulted mainly in PPO and PC/ABS, with a few HIPS and ABS samples that showed the presence of unexpected elements. The main reason for further analysis is that results from other work ([17] and further into Section 4.4) detected the presence of phosphorous (P) in samples of PPO and PC/ABS that had not been detected in an earlier study using elemental analysis. The elemental energies detected from each sample were studied and compared with those of samples that did not appear to contain any non-polymeric elements. Examples of these energy spectra are found in Figure 4.26. Figure 4.26a shows the elemental spectrum of sample 78, which is ABS with no apparent flame retardant. Elemental analysis detects the electrons of an element and emits a peak for each electron in each shell (such as k, l, m etc) at different frequencies. Hydrogen is generally too light an element to be detected by this method and carbon appears at a fairly low energy. Therefore the only additional detectable element seen on this spectrum is that of gold (Au), which is due to the gold coating on the plastic for conductivity purposes and is present on every sample. It was found that the peaks kαP and kβP, at 2.0 keV and 2.14 keV respectively, have similar energies to those of peaks mαAu and mβAu (2.123 keV and 2.205 keV respectively). The notations 'm' and 'k' refer to the atomic shells from which the measured photon energy originated from due to electron movement, with α and β referring to different electrons from the same atomic shell. Although P appears to display a distinct kα peak as seen in Figure 4.26b (sample 77), most samples were not so easy to define as the P peaks usually appeared as slight shoulders on the Au peaks as seen in Figure 4.26c (sample 76). These shoulders on the mAu peaks initially went unnoticed, as the previous analysis [17] was mainly speculative, with no preconceptions as to which elements to expect at the time of examination. The presence of P only became apparent on comparing the different elemental spectra as shown in Figure 4.26. P was found to be present in almost all of the PPO and PC/ABS samples that were retested and these results are shown in Table 4.14.

From Table 4.14, it appears that the unusual combinations of elements found in some ABS and HIPS samples are mainly due to the possibility of dust contamination despite efforts to keep samples contaminate free. This seems to be

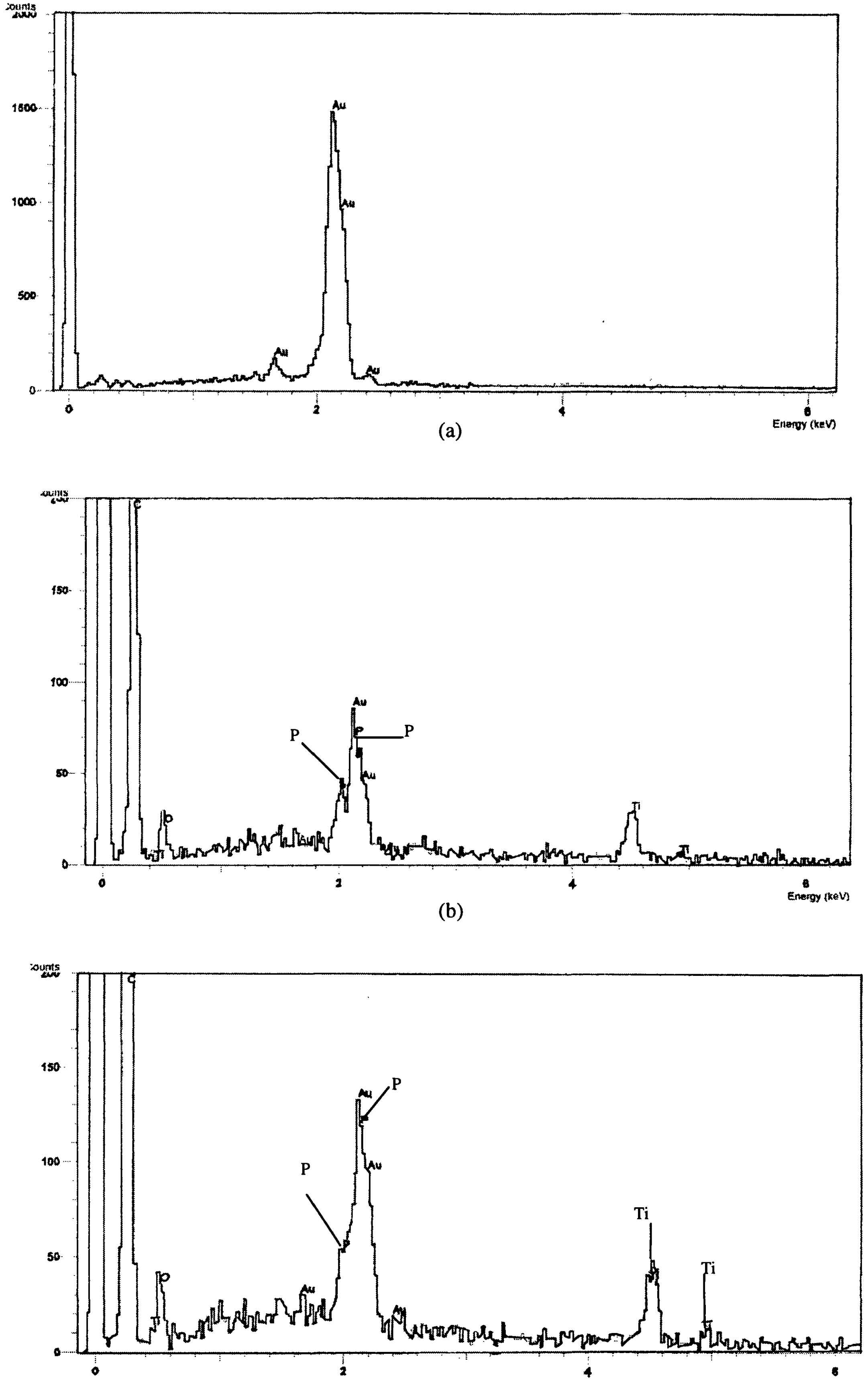


Figure 4.26 Elemental analysis spectra of (a) ABS with no additives, showing only the Au coating (b) PPO showing P as a separate peak to Au, plus Ti (c) PPO showing P as a shoulder on the Au peak, plus Ti

case for sample #50, which appears to contain just Br and Ti following the second examination and although sample #59 is thought to contain a lot less elements than previously thought, it is still unusual in that it contains Ba, S and Ti, as the Ba and S could be barium sulphate ($BaSO_4$), which is white pigment and not a flame retardant [105]. Sample #90 is a typical combination of a halogenated flame retardant system and was retested to verify the accuracy of the previous results.

Table 4.14 Retested results from elemental X-ray microanalysis

Sample	**FTIR Identification**	**Previous Elemental Analysis [17]**	**Elemental Analysis**
2	PPO	Br, Ti	Br, Ti
14	PPO	Ti	Ti
15	PPO	Cl, P, Si, Ti	Cl, P, Ti
27	PC/ABS	Ti	P, Ti
29	PC/ABS	Ti	P, Ti
50	HIPS	Al, Br, Ca, Ti	Br, Ti
52	PC/ABS	Ti	P, Ti
55	PC/ABS	Ti	P, Ti
59	ABS	Ba, Ca, Fe, Mg, S, Si, Ti	Ba, S, Ti
61	PC/ABS	Al, Ti	Br, Ti
62	PPO	Al, Ti	P, Ti
63	PPO	Al, Si, Ti	Al, P, Si, Ti
72	PPO	Ti	P, Ti
74	PPO	Ti	P, Ti
76	PPO	Al, Ti	P, Ti
77	PPO	Ti	P, Ti
79	PC/ABS	Al, Ti	P, Ti
83	PPO	Ti	P, Ti
87	PPO	Si, Ti	P, Ti
88	PPO	P, Si, Ti	P, Ti
89	PPO	Al, P, Ti	P, Ti
90	ABS	Br, Cl, Sb, Ti	Br, Cl, Sb, Ti

From Table 4.14 it can be seen that the majority of PPO and PC/ABS do appear to contain a phosphoric flame retardant. Phosphoric flame retardants are of the char formation type and when used in styrenic plastics, they are usually more effective in combination with other flame retardants. One approach to flame retardancy is to add a more fire resistant polymer. PPO also has char formation properties, and a common combination would be PS with PPO and triaryl phosphate [62]. This suggests that the PPO samples in Table 4.14 are blends with PS or HIPS and a phosphorous flame retardant. A common flame retardant used with PC/ABS blends is triphenyl phosphate, which is likely to be what was detected. However it must be noted that these assumptions can only be speculative as this method of element detection can only suggest which elements are present and cannot define the makeup of actual compounds.

4.4.2 P/ID22

The results from testing one hundred samples taken from various computer equipment housings on each commercial rapid plastics identification systems can be found in Table 4.15. Comparisons can be made with the two laboratory methods that were initially used and results from repeat testing as discussed above have also been incorporated into this table.

From Table 4.15, it was found that the P/ID22 showed 66/100 samples in agreement with the FTIR analysis however, it was not able to identify any additives present in the samples. There were generally no problems in identifying HIPS, PC/ABS and PP apart from the occasional mistakes such as samples #69, which identified HIPS as PMMA (which could actually be a double-sided sample) and #18 where only the ABS component of PC/ABS was identified, although this did not happen again. PPO was identified as PPE+SB, which is basically German notation and means the same as PPO. All PPO samples were consistently identified this way, so there were no problems there. There were also no problems with sample colour and dark coloured samples were analysed successfully.

The P/ID22 was not able to identify any of the ABS/PVC blends and generally would identify one part of the blend but not be completely sure about it. The main reason for this inaccuracy was found to be because there was no spectrum for ABS/PVC in the library database of the P/ID22, which means that it was possible to identify ABS or PVC but not both together. If this factor was taken into account then the P/ID22 would be seen as being 66/92 or 72% in agreement with the FTIR results, which is slightly more accurate.

Initially, there was thought to be a problem in identifying acrylic as these samples were identified as HIPS. However from retesting the acrylic samples using FTIR spectroscopy, it was found that they were actually double sided, one side being

Table 4.15 Comparison of laboratory based plastics identification techniques with commercially available rapid plastics identification systems

Sample	FTIR	X-RAY	PID/22	Polyana analysis		SSS2	IoSys Analysis	
	Spectroscopy	MICROANALYSIS	Results	Material	Second	Results	mIRo result	comments
				Identification	Choice			
1	HIPS	Br, Cl, Fe, Ti	HIPS	HIPS		PS+Br	PS	
2	PPO	Br, Ti	PPE+SB	PS-fr		ABS+Br	ABS	
3	HIPS	Br, Fe, Ti	PMMA(rough)HIPS(smooth)	HIPS		PS+Br	PS	
4	ABS	Br, Cl, Sb, Ti	SAN	ABS/PPO		ABS+Br	ABS	
5	PVC	Ti	PVC	PVC		PVC	PVC	
6a	acrylic	Br, Sb, Ti	ASA or ABS?	U-nmd		PS+Cl+Br	PS	
6b	HIPS							
7a	PMMA	Al, Fe, Ti	HIPS	(a) U-nss		PS+Br	PS	
7b	HIPS			(b) HIPS				
8	ABS	Cl, Sb, Ti	ABS	HIPS		PVC	PVCA	
9	HIPS	Ti	HIPS	HIPS		PS	PS	
10	ABS		SAN	HIPS		PS	PS	
11	ABS	Br, Cl, Sb, Ti	ABS	HIPS		ABS+Br	ABS	
12	ABS	Br, Cl, Sb, Ti	SAN	HIPS		ABS+Br	ABS	
13	ABS	Cl, Sb, Ti	HIPS or ABS?	HIPS		PVC	PVCA	
14	PPO	Ti	PPE+SB	PS-fr		PPO	PS	
15	PPO	Cl, P, Ti	PPE+SB	PS-fr		PPO+P	PPO	
16	ABS	Br, Cl, Sb,	SAN	HIPS		PVC	PVCA	
17	ABS	Br, Cl, Sb, Ti	ABS	HIPS		ABS+Br	ABS	
18	PC/ABS	Br, Cl, Sb, Ti	ABS	HIPS		ABS+Br	ABS	
19	HIPS	Ti	HIPS	HIPS		PS	./.	black
20	ABS	Br, Cl, Sb, Ti	ABS	HIPS		ABS+Br	ABS	
21	ABS	Br, Cl, Sb, Ti	ABS	HIPS		ABS+Br	ABS	
22	HIPS	Ti	SB	HIPS		PS	PS	

23	HIPS	Ti	HIPS	U-nss		PS	PS	
24	HIPS	Al, Ti	HIPS	HIPS		PS	PS	
25	ABS	Ti	SB or SAN or HIPS?	HIPS		ABS	ABS	
26	ABS	Br, Cl, Sb, Ti	ABS	U-nss		ABS+Br	ABS	
27	PC/ABS	P, Ti	PC+ABS	PC/ABS		PCA+P	PCA	
28	ABS	Ti	ABS	HIPS		ABS	ABS	
29	PC/ABS	P, Ti	PC+ABS	PC/ABS		PCA+P	PCA	
30	ABS	Mg, Ti	ABS	U-nss		ABS	ABS	
31a	HIPS	Al, Fe, Ti						
31b	acrylic		PMMA	U-nmd		PS	PS	
32	ABS/PVC	Sn, Ti	ASA or ABS or PVC?	PVC		PVC	PVC	
33	ABS/PVC	Sn, Ti	ABS or ASA	ABS		PVC	PVC	
34	ABS	Br, Cl, Sb, Ti	SAN or ABS?	ABS		PS+Br	ABS	
35	ABS	Br,Sb	ABS	HIPS		./.	ABS	
36	ABS	Br, Cl, Sb, Ti	ABS	U-nss		./.	ABS	
37a	acrylic	Br, Fe, Ti	HIPS/PMMA 2sides	U-nmd		PS+Br	PS	
37b	HIPS							
38	HIPS	Ti	HIPS	HIPS		PS	PS	
39	HIPS	Br, Fe, Ti	PMMA(2sides?)	U-nss		./.	PS	
40	PC/ABS	Ti	PC+ABS	PC/ABS		PCA	PCA	
41	PC		PC	PC/ABS		PC	PC	
42	ABS		ABS	HIPS		ABS	./.	black
43	ABS	Cl, Sb, Ti	ABS	HIPS		PVC	PVCA	
44	ABS		HIPS or SAN?	HIPS		ABS	./.	black
45	ABS	Cl, Sb, Ti	SAN	HIPS		PVC	PVCA	
46	ABS	Cl, Sb, Ti	SAN	HIPS		PVC	PVCA	
47	PMMA		PMMA	PMMA		PMMA	PMMA	
48	HIPS		PS	HIPS		PS	PS	

49	HIPS		HIPS	HIPS		PS	./.	black
50	HIPS	Br, Ti	HIPS	U-nss		PS	PS	
51	ABS	Ti	SAN	HIPS		ABS	ABS	
52	PC/ABS	P, Ti	PC+ABS	PC/ABS		PCA+P	PCA	
53	ABS/PVC	Ti	ABS	HIPS		PVC	PVC	
54	ABS	Ti	ABS	HIPS		ABS	ABS	
55	PC/ABS	P, Ti	PC+ABS	PC/ABS		PCA+P	PCA	
56	ABS	Ti	SAN or SB?	HIPS		ABS	ABS	
57	ABS	Ti	SB or SAN or HIPS?	HIPS		ABS	ABS	
58	ABS	Ti	ABS	HIPS		ABS	./.	too dark
59	ABS	Ba, S, Ti	SAN	HIPS		ABS+Br	./.	coated
60	ABS	Br, Cl, Sb, Ti	SAN or HIPS or ABS?	HIPS	ABS	ABS+Br	ABS	
61	PC/ABS	Br, Ti	PC+ABS	PC/ABS		PCA+P+Br	PCA	
62	PPO	P, Ti	PPE+SB	PS-fr		PPO+P	PPO	
63	PPO	Al, P, Si, Ti	PPE+SB	PS-fr		PPO+P	PPO	
64	ABS/PVC	Sn, Ti	ABS	U-nss		PVC	PVC	
65	ABS	Br, Sb, Ti	ABS	HIPS	ABS	ABS+Br	ABS	
66	ABS	Br, Sb, Ti	SAN	ABS		ABS+Br	ABS	
67	HIPS	Ti	HIPS	HIPS		PS	PS	
68	ABS	Ti	ABS	HIPS	ABS	ABS	ABS	
69	HIPS	Ti	HIPS	HIPS		PS	PS	
70	ABS/PVC	Sn, Ti	ABS	ABS		PVC	PVC	
71	ABS	Ti	SAN	HIPS	ABS	ABS	ABS	
72	PPO	P, Ti	PPE+SB	PS-fr		PPO+P	PPO	
73	ABS	Br, Cl, Sb, Ti	ABS	ABS/PPO		ABS+Br	ABS	
74	PPO	P, Ti	PPE+SB	PS-fr		PCA+P	ABS	
75	HIPS	Ti	HIPS	HIPS		PS	PS	
76	PPO	P, Ti	PPE+SB	PS-fr		PPO+P	PPO	

77	PPO	P, Ti	PPE+SB	PS-fr		PCA+P	PPO	
78	ABS	Ti	SAN	HIPS	ABS	ABS	ABS	
79	PC/ABS	P, Ti	PC+ABS	PC/ABS		PCA+P	PCA	
80	ABS	Ti	SAN or ABS or SB?	HIPS	ABS	ABS	ABS	
81	PPO	Ti	PPE+SB	PS-fr		PPO+P	PPO	
82	ABS	Ti	HIPS	HIPS	ABS	ABS	ABS	
83	PPO	P, Ti	PPE+SB	PS-fr		PPO+P	PPO	
84	ABS	Br, Sb, Ti	SAN	HIPS	ABS	ABS+Br	ABS	
85	HIPS	Br, Sb, Ti	SAN or HIPS?	HIPS		ABS+Br	ABS	
86	ABS/PVC	Sn, Ti	ABS	HIPS	ABS/HIPS/PVC	PVC	PVC	
87	PPO	P, Ti	PPE+SB	PS-fr		PPO+P	PPO	
88	PPO	P, Ti	PPE+SB	PS-fr		PPO+P	PPO	
89	PPO	P, Ti	PPE+SB	PS-fr		PCA+P	PPO	
90	ABS	Br, Cl, Sb, Ti	ABS	U-nss		ABS+Br	ABS	
91	ABS	Ti	ABS	HIPS	ABS	ABS	ABS	
92	ABS/PVC	Sn, Ti	ABS	HIPS	ABS	PVC	PVCA	
93	ABS	Br, Cl, Sb, Ti	ABS	HIPS	ABS	ABS+Br	ABS	
94	ABS	Br, Cl, Sb, Ti	ABS	HIPS	ABS	ABS+Br	ABS	
95	ABS	Br, Cl, Sb, Ti	ABS	HIPS	ABS	ABS+Br	ABS	
96	ABS	Ti	ABS	HIPS	ABS	ABS	ABS	
97	ABS	Br, Cl, Sb, Ti	ABS	HIPS		ABS+Br	ABS	
98	ABS	Br, Cl, Sb, Ti	ABS	HIPS		ABS+Br	ABS	
99	ABS/PVC	Sn, Ti	ABS	U-nss		PVC	PVC	
100	PP		PP	PP		PP	PPO	

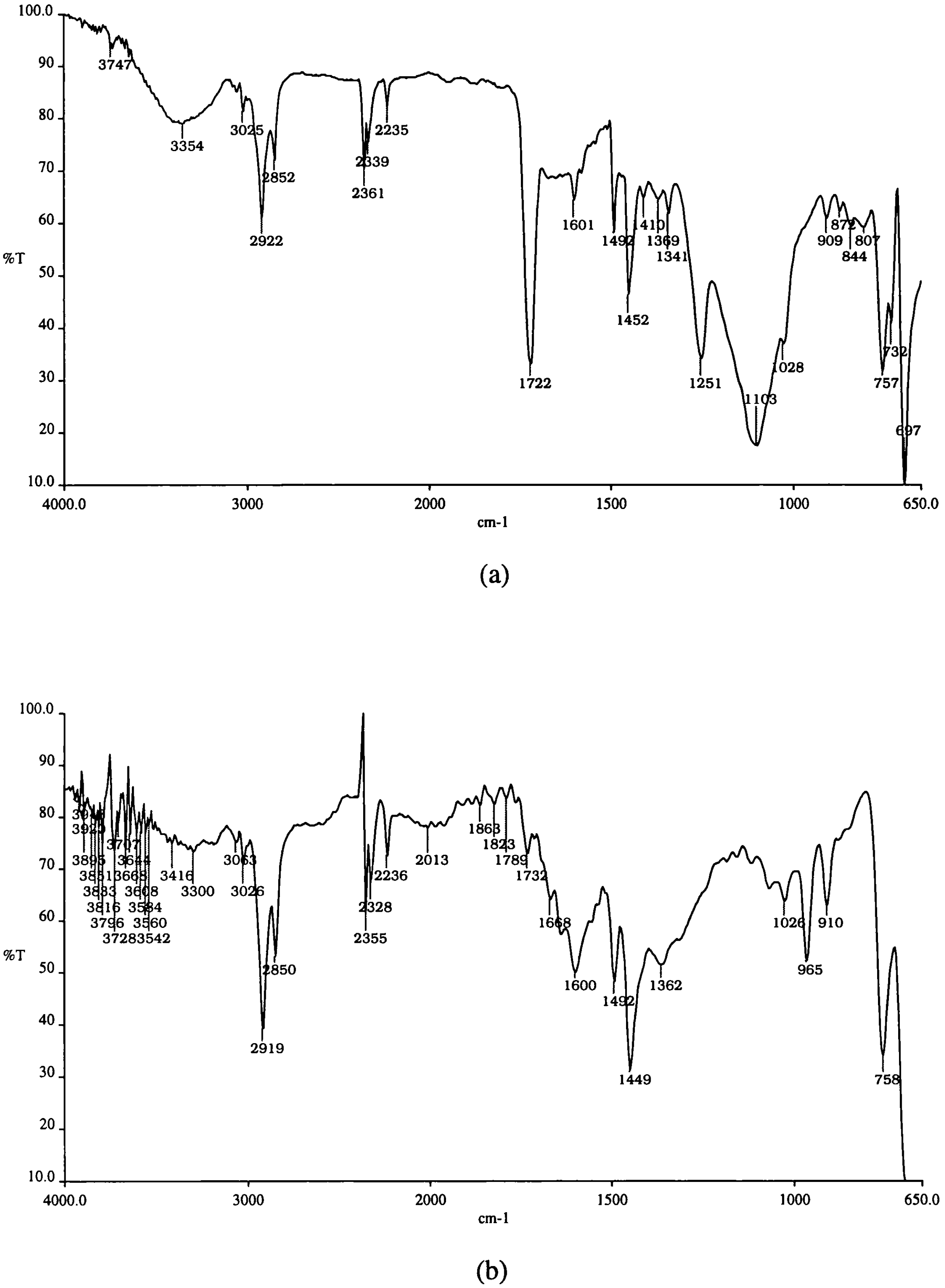
U-nss=unidentified, no smooth side

U-nmd=unidentified, no matching data

HIPS and the other acrylic so that all identifications had been correct, and only differed according to which side had been identified. The main inaccuracy with the P/ID22 was due to the identification of ABS for which only 25/46 ABS samples were identified correctly. The incorrect samples were mostly identified either as SAN (styrene-acrylonitrile), with a few as HIPS and SB.

In order to try and understand why many ABS samples were identified as SAN, the FTIR spectrum of SAN was compared with that of ABS in Figure 4.27. From section 4.1, the FTIR spectra of HIPS and ABS have been found very similar with the main differing peak present only in ABS being at 2236 cm^{-1}, which is due to the nitrile bond. The spectra of ABS and SAN also appear to have many common peaks including the nitrile peak at 2236 as well as 1492 and 1452 cm^{-1}. However major differences include the small peak at 1732 cm^{-1} of ABS which appears a little lower in SAN at 1722 cm^{-1} and is very strong. The 1600 cm^{-1} peak in SAN is fairly small but is strong in ABS and SAN has a very broad triple peak at 1251, 1103 and 1028 cm^{-1}, which is not present in ABS apart from a small peak at 1026 cm^{-1}. From Figure 4.27 the differences between the two spectra are fairly obvious. However as the P/ID22 is a mid infrared spectrometer, it may not focus on peaks over the entire infrared region as does FTIR spectroscopy. One method to try to improve the accuracy of ABS detection would be to fine tune the detection equipment into better differentiating between the two spectra. The flow chart in Figure 4.14 in Section 4.1 shows a way of quickly identifying different plastic types using a simple process of elimination of prominent peaks from the FTIR spectrum of each plastic type. This could possibly be adapted for an identification process such as the P/ID22, and to try to define more differences between ABS and SAN, the flow chart could be adapted to that shown in Figure 4.28. Another simpler solution would be to exclude the spectrum for SAN from the library of reference spectra from the database that is used to match the material being identified, although this is not a suggestion to improve the system, but is more a way of removing the problem.

The library of reference spectra on the P/ID22 database at the time of testing was just a general selection of polymers and was not specifically adapted for detecting plastics from waste computer equipment. This is why ABS/PVC samples were not identified as there was no such reference spectrum on the database. This is also why there was no differentiation between flame retarded and non-flame retarded plastics, as there were no differentiating spectra on the library database. However, the type of



(a)

(b)

Figure 4.27 Comparison of FTIR spectra for (a) SAN and (b) ABS software used to analyse the spectrum from each sample tested was such that the database of reference spectra is able to be adapted to specific needs such as automotive plastics or electrical and electronic plastics for example. In order to test the capabilities of the programmable database and to overcome some of the inaccuracies due to insufficient library data, a representative library was set up using a selection of the samples that were being tested. The types of samples used for the library are found in Table 4.16.

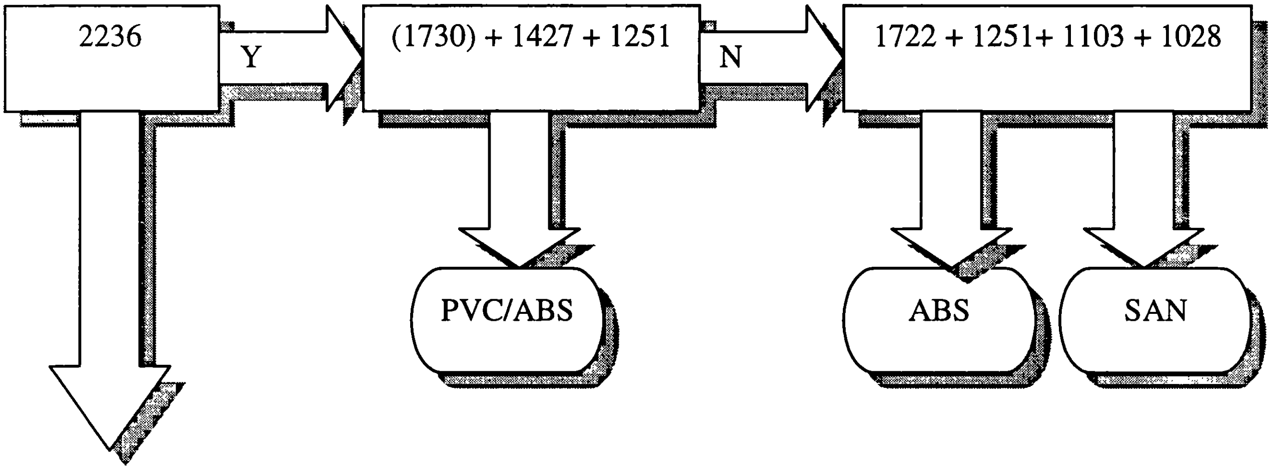


Figure 4.28 Amendment to the flow chart in Figure 4.14 to include differentiation between ABS and SAN

Either one, two or three samples were used to create the library database for different combinations of flame retarded ABS and HIPS, as well as ABS/PVC, depending on how many samples were available for each combination. Then a selection from each sample type were retested and identified using the new spectrum library. Results are found in Table 4.17. On displaying results from a scan, the P/ID22 usually displays the spectrum of the most positive match from the database, but information regarding the second most positive match and others can also be accessed. The first two choices for each sample tested are displayed in order to see if they would automatically be matched with the two reference spectra for each material type on the database. For some samples that did not successfully match on the first two choices, a third was looked at. From the table of results, just one sample of HIPS was tested.

Table 4.16 Samples used for an adapted library of spectra from computer equipment for the P/ID22

SAMPLE LIBRARY	
Material	**Sample**
HIPS	19
	38
HIPS+Br+Cl	1
ABS	10
	28
ABS+Br	35
ABS+Cl	43
	46
ABS+Br+Cl	4
	12
	21
ABS/PVC	86
	92

Table 4.17 Results from retesting samples on the P/ID22 using a specially created spectrum library

LIBRARY TEST				
Sample	**Material**	**1st choice**	**2nd choice**	**3rd choice**
50	**HIPS+Br**	38 (HIPS)	19 (HIPS)	1 (HIPS+Br+Cl)
30	**ABS**	28 (ABS)	10 (ABS)	
42	**ABS**	10 (ABS)	28 (ABS)	
32	**ABS/PVC**	86 (ABS/PVC)	92 (ABS/PVC)	43 (ABS+Cl)
33	**ABS/PVC**	4 (ABS+Br+Cl)	92 (ABS/PVC)	86 (ABS/PVC)
53	**ABS/PVC**	92 (ABS/PVC)	86 (ABS/PVC)	
64	ABS/PVC	86 (ABS/PVC)	46 (ABS+Cl)	
70	**ABS/PVC**	86 (ABS/PVC)	92 (ABS/PVC)	
66	**ABS+Br**	4 (ABS+Br+Cl)	35 (ABS+Br)	
11	**ABS+Br+Cl**	35 (ABS+Br)	12 (ABS+Br+Cl)	
16	**ABS+Br+Cl**	46 (ABS+Cl)	43 (ABS+Cl)	35 (ABS+Br)
17	**ABS+Br+Cl**	43 (ABS+Cl)	46 (ABS+Cl)	
20	**ABS+Br+Cl**	43 (ABS+Cl)	43 (ABS+Cl)	35 (ABS+Br)
26	**ABS+Br+Cl**	46 (ABS+Cl)	43 (ABS+Cl)	
13	**ABS+Cl**	43 (ABS+Cl)	46 (ABS+Cl)	

As very few inaccuracies had been found with the identification of HIPS, there was no need to see if it would still be identified correctly and so it was instead tested for the detection of Br. From the previous section, it was found that there were few samples of flame retarded HIPS. For this experiment sample #50 was retested, which is HIPS flame retarded with a Br compound. The first two choices from testing were the HIPS samples but not flame retarded HIPS. This could be due to the library spectrum as there was only one sample of flame retarded HIPS with Br and Cl, so the presence of Cl in the library spectrum could have caused enough difference for it to not be the best match. For samples of non-flame retarded ABS, there appear to be no problem whatsoever in finding the most positively matching spectra. The same can be said for ABS/PVC, with the exception of just one sample that did not match on the first choice, but did on the second. This goes to show that the P/ID22 is capable of identifying ABS/PVC, but just needed the appropriate spectrum in the database.

Although each sample using the new library database was correctly identified by plastic type, except one sample of ABS/PVC, when trying to differentiate between flame retarded and non-flame retarded ABS, the P/ID22 was not so successful. All flame retarded ABS samples, apart from one, were identified as containing Cl, which for most cases was true as many samples did contain Cl, however for ABS+Br+Cl, the Br flame retardant was not detected. The one sample only detected Br for the initial choice, but the gave a correct analysis for the second choice. The sample ABS+Br was identified as containing Br and Cl, despite the absence of Cl and only correctly matched the spectrum on the second choice. However the correct analysis of a sample on the second choice is not the desired result, because when identifying an unknown plastic, the system operator will most likely take the first analysis as being correct. The correct analysis of ABS+Cl from the first choice could just be a coincidence as Cl was detected in all flame retarded ABS.

On the whole the results from creating a new library database were fairly positive and it appears that previous identification problems initially highlighted may be overcome just by tailoring the library database of spectrum for the P/ID22 to the specific needs of the application. Had all samples been retested using the new database, this could probably see an increase in the accuracy of identifying the different plastic types to more than 90%. The detection of flame retardants in the plastics tested was not accurate, which allows the same conclusion to be drawn from the previous section, that IR spectroscopy is not one hundred percent accurate for flame retardant identification by any means.

4.4.3 Polyana

The Polyana did not appear to do as well as the P/ID22 and only agreed on 24/100 samples with the FTIR results, seen in Table 4.15. One of the main requirements for testing on the Polyana is a smooth shiny surface. All of the samples tested are from various computer equipment housings and therefore some samples had rough matt surfaces on both sides from which the Polyana was not able to take a scan. This led to ten samples that were unable to be identified due to surface texture. There was no reference spectrum for acrylic, which can explain why the double-sided acrylic/HIPS samples were unable to be identified. This was also the reason why the ABS/PVC samples were not identified. Taking into account the amount of samples that were not identified due to surface texture and lack of library spectra, the amount of samples that should have been identified would be about 80. So for identifying 24 out of a possible 80 samples leaves the Polyana at 30% accuracy, which is still very low.

The Polyana did not appear to have any problems in identifying HIPS and PC/ABS, and correctly identified most of these sample types. PPO however, was consistently identified as flame retarded polystyrene (PS-fr). When considering that the PPO samples are most likely to be Noryl or another modified PPO (a blend of PPO and PS or HIPS), and that the modified PPO samples generally contain P, which is a known flame retardant for PPO, and that the PPO and P could also be used as a flame retardant system for PS or HIPS, then the Polyana is technically right. It is also highly likely that there was no spectrum in the library database for PPO. However, unless the operator knows that PPO or Noryl will consistently be identified as PS-fr, then this plastic type will be mis-identified. If including the results for PPO as being correctly identified, then the Polyana could be said to have been in agreement with FTIR results for 38/80 or 48%.

So although the lack of suitable reference spectra contributes to some inaccuracy in the Polyana, the main problem appears to be with the identification of ABS. For some reason the Polyana had trouble identifying ABS and most of the time identified it as HIPS. However, it did get a few ABS samples right, which means that it has the potential, although there was no trend in these samples i.e. types of flame retardants present etc. ABS and HIPS do have fairly similar FTIR spectra, which could mean that they are also fairly difficult to differentiate using MIR. One way of differentiating between results of ABS and HIPS was through manipulation of the data that involved smoothing the curve of the spectrum just scanned. If the sample was actually ABS then the spectrometer would change the most positive match to ABS and if it was actually HIPS then it would remain as HIPS. However, this kind of data manipulation is time consuming and would not at all be practical for use as a rapid plastics identification system in a recycling sorting process.

From all of the samples tested, the Polyana did not identify flame retarded plastics. Although the library database is supposed to be able to distinguish HIPS from HIPS-fr and ABS from ABS-fr for example, this did not occur, except in the case of PPO. However, as seen in Table 4.15, there are quite a few different combinations of flame retardants, especially in the case of ABS and HIPS, and as it was not known which flame retardants were in the reference spectra, they might not be the same combinations as in the samples being tested.

Unfortunately at the time of testing it was not possible to set up a new reference library of spectra using some of the samples that had been tested. However, apart from problems with being unable to identify non-smooth or shiny surfaces, one of the main problems encountered with the Polyana was due to the lack of suitable reference spectra in the library database, which can only be solved by improving this library or adapting a new database to conform to the needs of the plastic types being tested. The other main problem is being able to distinguish between HIPS and ABS. However, as there is a manual way of further manipulating the results, maybe this problem could be overcome by automating this type of data manipulation when scanning an object. Although the Polyana did not initially appear to be very accurate in rapid plastics identification, there is a lot potential for improvement that does not appear to be impossible to achieve. Although the Polyana was designed several years ago, the person who designed it has unfortunately retired and further developments to this system have stopped. However, the Wolfson Electrostatics Centre at Southampton University are currently applying for funding to continue improving this system.

4.4.4 SSS2

The SSS2 was found to agree on the identification of 72/100 when compared with the FTIR analysis, which can be seen in Table 4.15. There are generally no problems in detecting ABS, HIPS, PPO and PC/ABS, however the SSS2 occasionally gets them mixed up, which is the main inaccuracy with this identification system and is said to occur due to the similarities of the spectra of HIPS, ABS and PPO. HIPS is consistently identified as PS, which is probably not that important, although it is probably useful to realise the difference in notation. The SSS2 was initially thought to have a problem in identifying acrylic as only the PMMA sample was identified correctly. However, as further FTIR studies have shown, all acrylic samples are actually double sided with the other side being HIPS and it appears that all double sided samples were tested on the HIPS side only.

The SSS2 did not identify any of the ABS/PVC samples correctly as all ABS/PVC samples were identified as PVC. Some ABS samples that contained Cl as a flame retardant were also identified as PVC and usually occurred when there was no Br present as seen in samples 8, 13, 43, 45 and 46. The way to rectify this is apparently a case of adjusting the limit of chlorine detection on the spectrometer, although this type of inaccuracy could be considered as unimportant if the only concern is to separate out any PVC containing plastic. However, being able to correctly identify ABS samples that contain Cl without Br as ABS and not PVC is probably more important and would only serve to increase the accuracy of the system.

The main advantage to the SSS2 is that it also has the ability to detect the presence of flame retardants and other additives present in a plastic. From Table 4.15 the SSS2 can be seen to agree with 92/100 when compared with the results from x-ray microanalysis. This is a very high level of accuracy. The SSS2 can be set to focus on certain elements rather than analysing everything and this can be seen in Table 4.15, where most element detection was for Br, Cl and P. Sb and Ti were not detected, although the SSS2 could probably be set to detect these and other elements if desired. As legislation on WEEE is stipulating the separation of plastics containing Br flame retardants, it may seem that it is becoming extremely important to be able to identify Br in a plastic more than any other additive. Although the SSS2 identified Cl in some plastics, it actually missed out most Cl containing samples and the high level of element detection is merited only on its ability to detect Br, which is very accurate.

Therefore, in order to improve on the identification of plastics, it seems that the SSS2 needs to be able to better distinguish between ABS, HIPS and PPO, which is probably down to further programming or fine-tuning the neural network. However, the SSS2 is very accurate in detecting additives, especially Br, and it is currently better at additive detection than it is at identification of plastics.

4.4.5 mIRo mobile NIR system

When looking at the initial results in Table 4.15, the mIRo appears to be the most accurate identification system out of all systems tested with 76/100 samples being matched with the FTIR results. However, like the other identification systems based on infrared spectroscopy, the mIRo was not able to detect additives such as flame retardants. Like the SSS2, all HIPS samples were identified as PS and it is most probable that there is no spectrum of HIPS on the library database. There appears to be no problems in identifying PC/ABS, however the mIRo did occasionally mix up the identifications of ABS, HIPS and PPO. This did seem to be less frequently than any of the other systems tested, and as the spectra of the three plastic types are fairly similar, the only way to overcome this problem would probably be through fine-tuning the neural network of the spectrometer. However, if blends of these plastics are found to be compatible in the mechanical recycling part of this project, then this may not actually be too big a problem. Sample 100, which is PP, was identified as PPO. The spectra of these two plastics are very distinct and so it was wondered if this results was a typing error, or whether there was a genuine problem in identifying this sample as all other systems had no problem with this one. The same results were found for the double-sided acrylic/HIPS samples as before in that it appears that only the HIPS sides appear to have been tested, although there is not likely to be too much of a problem in identifying this plastic type as sample 47 was correctly identified as PMMA.

Again like the SSS2, there was a problem in identifying ABS/PVC, and such samples were usually identified as PVC, with the exception of sample 92 that was identified correctly, showing that there is the potential to identify this plastic type. This may not be a bad thing if it is undesirable to recycle PVC with other plastics due to the low degradation temperatures of PVC, however some samples of ABS were also identified as PVCA (mIRo notation for ABS/PVC). It was found that all of these samples contained Cl as a flame retardant, although if the Cl tolerances on the spectrometer can be lowered, this could ensure correct analysis of all ABS/PVC and ABS+Cl samples, which could increase the accuracy of the system to 89/100.

One of the main inabilities of a near infrared identification system is that such spectrometers are not able to identify black coloured plastics. This is because the black pigment used in dark coloured plastic (usually carbon black) is a strong absorber in the NIR region and produces a featureless spectra. The mIRo is no exception, and despite claims that identification could be made regardless of colour, was not able to identify any of the dark and black samples that were among this selection. There isn't really any way for the mIRo to overcome this, and such samples would have to be identified by another system. Therefore when looking at the results in Table 4.15, by not including that the mIRo cannot identify due to colour, the initial accuracy of the mIRo becomes 76/94, which is 80%. If the Cl tolerances on the spectrometer are lowered to ensure correct identification of ABS/PVC and ABS+Cl, or this is considered as an unimportant inaccuracy, then the mIRo could potentially be considered as 95% accurate.

4.4.6 Discussion

As it has been seen from the results in this section, it appears that all commercially available rapid plastics identification systems shown in this study have need of some adjustment in order to increase identification accuracy. A main issue appears to be due to the need for tailoring the reference library database to better suit the types of plastics more common to the electrical and electronic sector. However systems such as the Polyana and the SSS2 will also need some kind of fine-tuning to enable them to better distinguish between the spectra of ABS and HIPS and PPO. One way could be to change the actual identification process of the identification systems. Rather than matching the whole spectra of a plastic from those stored in a reference library, an identification system could instead be programmed to look for the presence or absence of specific peaks. The flow chart already illustrated in Figure 4.14 is one possible suggestion, which, if used as a programme in an identification system, could significantly improve accuracy for plastics from electrical and electronic equipment. If a system is required to identify waste plastics from another source such as automotive waste, then a programme such as the flow chart in Figure 4.14 could be adapted to incorporate the different plastics used in this sector. While the mIRo appears to be more accurate at plastics identification, the limitations of NIR means that it cannot identify dark coloured plastics due to the strong absorbance of dark pigments in the NIR region. As dark or black colours are being used more and more for monitor and other computer equipment casings, the ability of a system to identify such plastics will probably become more of a requirement in the near future. Just like the MIR systems, the mIRo does not appear to be able to detect additives such as flame retardants, which serves to illustrate the conclusion from the previous section that IR spectroscopy at the present time is not able to detect the presence of additives in a plastic.

The only system that was able to successfully and consistently detect the presence of flame retardants is the SSS2. The SSS2 is not as accurate in plastics identification as that which could potentially be reached by the infrared systems, however it has been proved excellent at detecting flame retardant additives such as Br-based compounds. This is due to slight differences in sampling which penetrates the sample slightly deeper than IR methods.

In conclusion, it appears that the most accurate way of identifying plastics from waste computer equipment and detecting additives including Br flame retardants is through a combination of identification techniques such as an IR system and the SSS2. The infrared system, such as one of the systems described above would be accurate in identifying plastics, ideally including dark coloured ones, once improvements have been made including adaptations to electrical and electronic plastics. The SSS2 would therefore be most useful in detecting flame retardants and could also identify dark coloured plastics if paired with a NIR system. Currently such systems are being developed. The Fraunhofer Institute of Technology is incorporating a NIR spectrometer with a LBDS (Laser break down spectrometer) [85], while Individual Optical Systems [163] is combining a NIR spectrometer with the SSS2. While the NIR spectrometers will be used to identify plastics, the LBDS and SSS2 can identify black samples and also detect the presence of additives such as fillers and flame retardants. From the results above it appears that at the present time there is still need for some improvement and fine-tuning in order to increase the accuracy of such systems to over 90%. However, such systems do have the potential to overcome many of the identification barriers facing recyclers of plastics waste from the electrical and electronic sector, which can only serve to decrease separation costs, improve recyclate quality and contribute towards recycling and recovery targets imposed by WEEE and RoHS directives.

CHAPTER 5:

RECYCLING PLASTICS – EXPERIMENTAL PROCEDURE

5.1 MATERIALS FOR RECYCLING

When recycling plastics, it is important to be able to understand the effects that a recycling process will have on the mechanical properties of recyclate. As most of the identification methods described previously are not one hundred percent accurate there will always be the possibility of a small proportion of another plastic being present. The purpose of this part of the project is to analyse the effects of not only a recycling process, but also of blends of recycled plastics.

Previous work into this subject [17] concluded that the proportion of different plastics types used to house computer equipment were as follows; ABS 45%, HIPS 21%, PC/ABS blend 15%, PPO 9%, ABS/PVC blend 7%, PC 1%, PVC 1%, Acrylic, PMMA and PP 1% together. This previous work looked at the effects of recycling and blending ABS and HIPS, as they are the two most widely used materials in casings for computer equipment. For the present study, as well as continuing research on ABS and HIPS, studies were also conducted into PPO and PC/ABS as well as combinations of blends of all four plastics. As these are the four materials most used as housings for computer equipment, the proportion of these four plastics comprises of a weighted proportion of approximately 90%, thus accounting for a significant amount of this type of waste.

The waste plastics used for the recycling part of this project were obtained from local recycling companies. PMI (Wales) Ltd, a prominent computer recycling company in Britain, donated a substantial amount of ABS, HIPS and PPO, in the form of pieces of plastics approximately 20mm X 50mm originating from various housings for computer equipment such as monitor casings. However, it was at the time difficult to acquire sufficient amounts of PC/ABS blend from this source, and an equivalent grade of used PC/ABS blend was provided by "4 The Environment (4TE)", a plastics recycling company. Also samples were made using virgin materials in order to observe any differences between recycled plastics and virgin plastics. Virgin plastics used were injection moulding grades of ABS from Bayer and HIPS from BP. It must be noted that the plastic PPO is rarely processed in its pure form due to high processing temperatures, and is commonly blended with PS, which reduces such temperatures. Therefore the PPO supplied by PMI is more than likely to be Noryl or a blend of PS and PPO from another manufacturer and as the exact manufacturer and grade is not known, the phrase 'modified PPO' (or mPPO) will be used to incorporate the grade of PPO used in this project.

In previous work [17] the recycling process was carried out under laboratory conditions using laboratory scale processing equipment. However there is a possibility that these results could differ slightly from what would actually occur during a commercial process due to differences in the scale of equipment used. Therefore the recycling process for this project was carried out using commercial scale equipment in order to obtain results as realistic as possible and also to see if these results differ in any way from previous results.

5.2 RECYCLING PROCESS

The recycling process used in this project is illustrated in Figure 5.1, where X indicates the steps of the recycling process undertaken by each plastic. The process followed a typical mechanical recycling process consisting of size reduction, blending, extrusion, re-granulation and injection moulding, although not all batches of plastics were extruded and the virgin plastics only needed injection moulding.

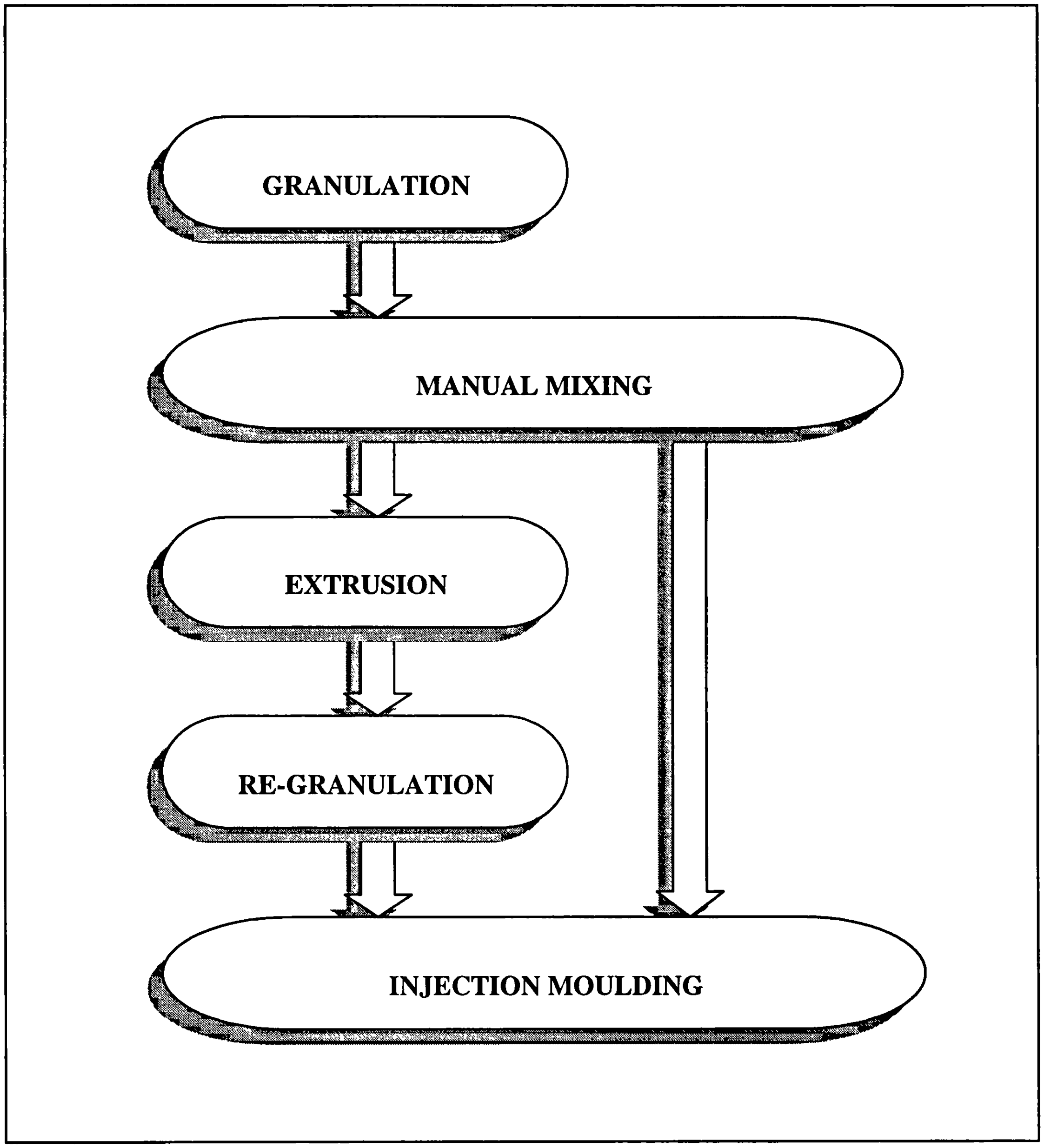


Figure 5.1 Flow chart of the mechanical recycling process used for this project using commercial scale equipment.

5.2.1 Granulation and Blending

All plastics used in this project were initially granulated using a large industrial granulator at 4TE. The plastics used were reduced from pieces of about 20mm X 50mm to granules approximately 2mm X 5mm. The granulated material was subsequently weighed and separated into batches weighing 2.5 kg. All blends were weighed according to the proportions given in Table 5.1 and hand shaken in order to ensure a more even mix before any thermal processing occurred. Four batches, one of each plastic being studied, were set aside for injection moulding into samples without any further processing. This was to determine the effects of the additional thermal processing that was required for the mixtures of plastics. Without this, it would not be possible to separate any effects of the mixing, rather than the additional processing.

5.2.2 Extrusion and Re-granulation

Thermal mixing of the recycled plastics was carried out using a small single screw extruder with a cavity transfer mixer that was produced by RAPRA Technology Ltd. As processing temperatures for each of the four plastics varies, extrusion temperatures were estimated according to each blend proportion based on polymer melt processing temperatures shown in Table 5.2. With a small amount of trial and error, the polymer blends were extruded at the temperatures shown in Table 5.3.

Each batch was processed at a speed of 70 rpm and the initial 0.5kg of plastic extruded was used for purging the extruder so that the final extruded plastic was not contaminated by the previous batch. The most difficult batches to process were the ABS – PC/ABS blends. For example with the 90%ABS / 10% PC/ABS blend it was found that at 220°C, the PC/ABS didn't melt fully, yet the ABS constituent would degrade on raising the temperature to 230°C, therefore the best processing temperature for this blend was found to be at 225°C. Also the PC/ABS was prone to absorbing moisture from the atmosphere, despite efforts to dry it out and keep it covered, which happened frequently throughout the whole recycling process.

Following extrusion, each batch was dried out in a drying room and re-granulated into a more processable size using a small Spruemaster granulater, as there were no automatic cutting or compounding facilities with the extruder. In order to reduce moisture in the material that could have been picked up from the extrusion or granulation process as well as exposure to the air, the batches were further dried in a

Table 5.1 List of virgin and recycled plastics, blend proportions and mechanical recycling process for each batch

Material	Batch name	Mechanical Recycling Process Components			
		Granulation	Extrusion	Re-granulation	Injection Moulding
Virgin Plastics					
ABS	VA				X
HIPS	VH				X
Recycled Plastics					
ABS	RA	X			X
ABS	RAE	X	X	X	X
HIPS	RH	X			X
HIPS	RHE	X	X	X	X
MPPO	RP	X			X
MPPO	RPE	X	X	X	X
PC/ABS	RPC	X			X
PC/ABS	RPCE	X	X	X	X
Plastics Blends					
% HIPS/% ABS					
10 HIPS/90 ABS	1H9A	X	X	X	X
50 HIPS/50 ABS	5HA	X	X	X	X
90 HIPS/10 ABS	9H1A	X	X	X	X
% HIPS/% mPPO					
10 HIPS/90 mPPO	1H9P	X	X	X	X
50 HIPS/50 mPPO	5HP	X	X	X	X
90 HIPS/10 mPPO	9H1P	X	X	X	X
% PC/ABS/% ABS					
10 PC-ABS/90 ABS	1PC9A	X	X	X	X
50 PC-ABS/50 ABS	5PCA	X	X	X	X
90 PC-ABS/10 ABS	9PC1A	X	X	X	X
Equal blend of all plastics					
25 ABS/ 25 HIPS/ 25 PPO/ 25 PC-ABS	25AHPPC	X	X	X	X

Table 5.2 Melt Processing Temperatures of Polymers [64]

Polymer	Melt Temperature (°C)
ABS	240
PS	200
PPO	280
PC	300

Table 5.3 Processing temperatures for extrusion and injection moulding of virgin, recycled and blends of plastics.

Material Batch Name	Extrusion Temperature (°C)	Injection Moulding Temperature (°C)
VA	N/A	200
VH	N/A	180
RA	N/A	220
RAE	230	220
RH	N/A	210
RHE	200	200
RP	N/A	280
RPE	240	240
RPC	N/A	280
RPCE	245	260
1H9A	225	220
5HA	220	210
9H1A	215	200
1H9P	260	260
5HP	240	230
9H1P	220	210
1PC9A	225	220
5PCA	240	240
9PC1A	250	240
25AHPPC	230	230

Gallenkemp OV-440 oven at 60°C for ABS, HIPS and mPPO, and at 100°C for PC/ABS for twenty-four hours before further processing.

5.2.3 Injection Moulding and Production of Samples

The final part of the process was injection moulding into samples. The injection moulder used was a Negri Bossi NB 62, 10 Press, 32mm diameter screw Injection Moulder, which was based at Merthyr Tydfil College of Further Education. Each batch of material was injection moulded at the processing temperatures defined in Table 5.3 at a speed of 40% and a pressure of 120 bar followed by a holding pressure of 2 bar for one second. The mould produced two dog bone shaped tensile test pieces as shown in Figure 5.2. The mould temperature was fixed at 60°C during injecting, and was subsequently cooled by a water cooling system for 20s before samples were ejected.

The amount of material available for injection moulding was approximately 2kg for extruded batches and 2.5kg for non-extruded batches. The first kilogram of each batch was used for purging the machine. This material was run through the machine without making any samples. Once the machine was purged the samples were injection moulded out of the remaining material and samples were made from forty shots, producing eighty samples in all. Samples from the initial twenty shots were also discarded as a continuation of purging, so that the specimens used for testing would be the best quality and uncontaminated. These initial shots were also used to find the best processing temperatures for each batch, leaving a total of forty specimen per batch for testing.

As previously stated, the test samples produced were dog bone shaped for tensile testing. The dimensions of the test pieces were such that it would be possible to convert them into appropriately sized samples for other tests such as impact testing, DMTA, and viscosity measurements (see Figure 5.2) in accordance with international standard ISO 3167:2002 [164].

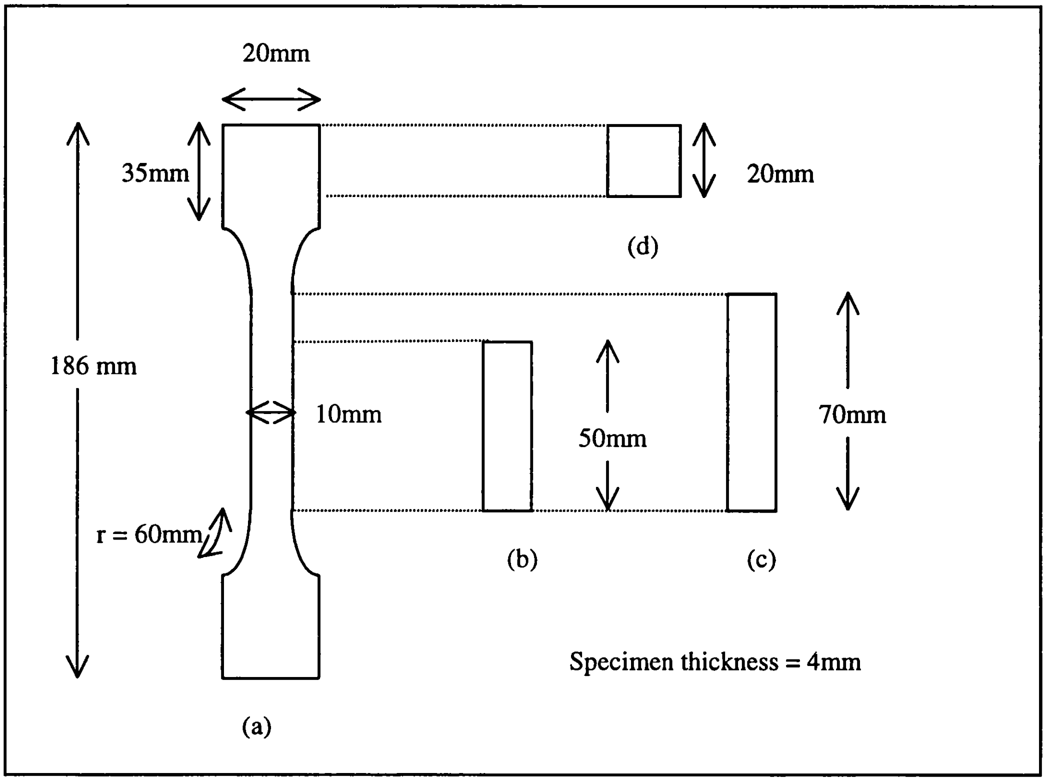


Figure 5.2 Injection moulded sample geometry showing (a) dog bone shaped tensile test piece (b) DMTA test piece (c) Impact test piece (d) Viscosity test piece.

5.3 TESTING METHODS

5.3.1 Tensile Testing

Tensile tests were performed using a Hounsfield H25K-S Benchtop Testing Machine with a Hounsfield 500LC Laser Extensometer as shown in Figure 5.3. The laser extensometer was used in order to obtain more accurate strain measurements as it monitored extension between two points on the sample gauge length, thus being unaffected by any movement of the crosshead on the testing machine.

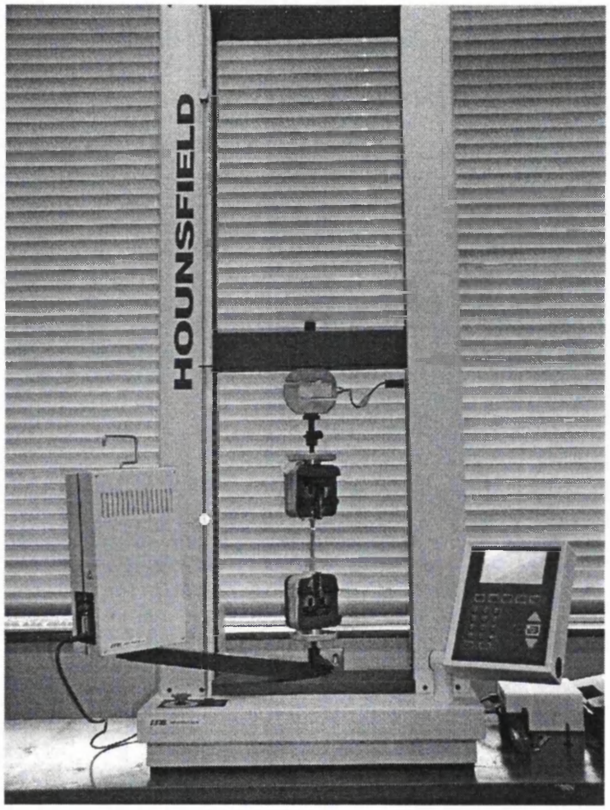


Figure 5.3 Image of a Hounsfield Tensometer showing the set up for Tensile test with a laser extensometer

Samples used for testing were injection-moulded dog bone shaped test pieces, illustrated in Figure 5.2. Ten samples were tested per batch of material in order to produce sufficient data representative of that material. Tests were carried out at room temperature under a crosshead speed of 5mm/min using a load cell of 2500N maximum load. Prior to loading, the gauge length of each sample was smoothed, in case of possible defects, using P320 followed by P1200 fine metallographic grinding paper. Reflective tape approximately 1.5 mm thick was attached to the gauge length of each sample approximately 60mm apart, which acted as reference points for the laser extensometer. The exact distance between each piece of reflective tape and the width and thickness of the gauge length were measured with callipers and recorded for future analysis of results. A sample was then loaded into the testing machine ready for testing.

As part of the test programming options, the tensile strength of each sample was automatically calculated and the extension at failure was also displayed. Data from each test was saved as load and extension. These data were converted into stress and strain using the following equations;

$$\sigma = \frac{F}{A} \qquad \varepsilon = \frac{e_x}{l_o}$$

Where

σ = stress

F = force

A = cross sectional area of sample.

ε = strain

e_x = extension

l_o = original gauge length

The tensile strength and strain to failure were easily obtained from the data provided by the laser extensometer software. Plotting a stress/strain graph and taking the gradient of the initial elastic part of the slope obtained the tensile modulus as described in Section 2.7.1.

5.3.1.1 Comparisons With Previous Data

Since the tensile tests carried out in this project differed from previous work [17], due to the use of the laser extensometer, additional tensile tests were carried out on recycled HIPS and ABS, using the same Hounsfield H25K-S Benchtop Testing Machine but using the cross-head movement to measure the sample extension. Results were calculated using the same equations as before and compared with previous work as well as results taken from tensile tests as described above.

5.3.2 Impact Testing

Izod impact tests were carried out on samples using a Ray Ran Universal Pendulum Impact System designed for various geometries such as Izod, Charpy and Tension (See Figure 5.4). Tests were performed at room temperature using both hammer sizes (0.4528 kg and 1.811 kg) over a range of hammer velocities from 2.8 –

3.8 ms^{-1}, causing samples to be subjected to energy between 2.93 – 13.07 Joules depending on the material. Prior to testing, the system was calibrated by conducting an impact test with no sample present. Once calibrated, a sample was loaded and impacted with the pendulum hammer. Samples used were un-notched gauge lengths cut from injection moulded tensile test pieces as shown in Figure 5.2 and ten impact tests were conducted for each material type. The impact energy absorbed by each sample was recorded by the impact tester as impact strength in kJ/m^2.

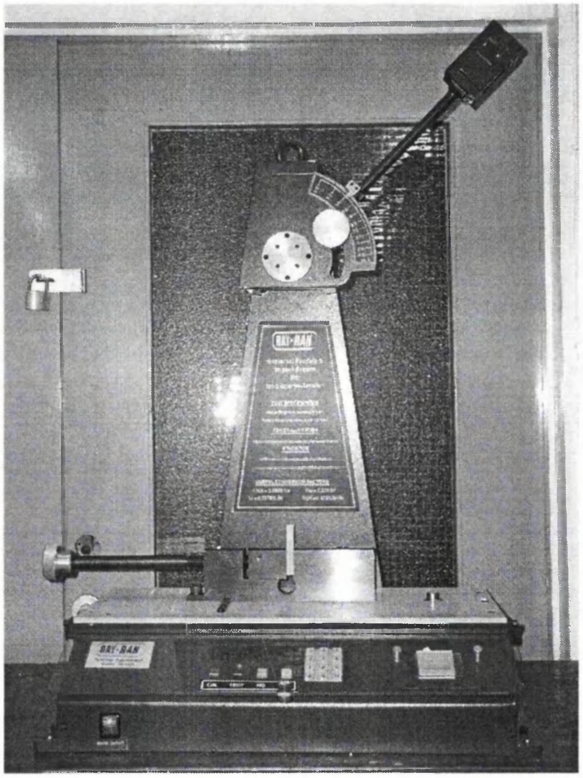


Figure 5.4 Image of a Ray Ran Universal Pendulum Impact System for Izod – Charpy – Tension, showing the set up for an Izod Impact Test

5.3.3 Dynamic Mechanical Thermal Analysis

Dynamic mechanical thermal analysis was performed on all batches of plastics using a Rheometric Scientific Dynamic Mechanical Thermal Analyser MK III. This allows measurements of the dynamic (complex) modulus at various frequencies and temperatures. Tests were run using a combined head with a large frame for dual cantilever bending at a frequency of 1Hz, with an amplitude of 20μm, and a clamping torque of 30Nm. The temperature range was started from 50 °C to 150 °C, which increased at a rate of 1 °C/min. The test set up is shown in Figure 5.5.

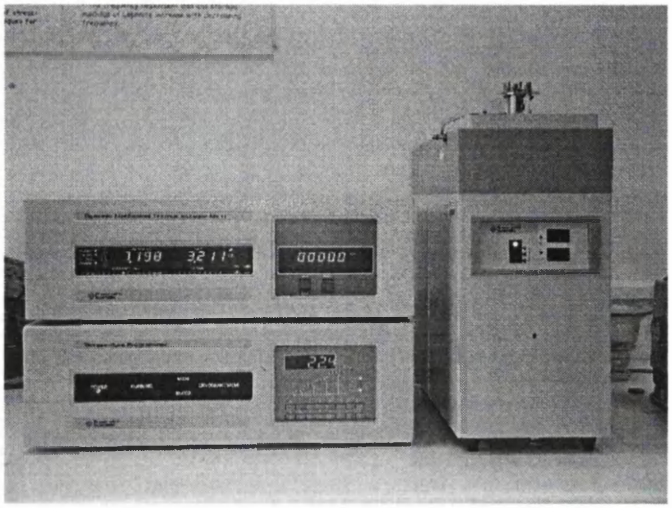


Figure 5.5 Image showing the test set up for Dynamic Mechanical Thermal Analysis

Samples were cut from injection moulded tensile test pieces as shown in Figure 5.2 and two tests were run for each plastic and blend type. Results from these tests were plotted as the log of the elastic modulus (logE) and the damping or loss tangent (tanδ) as a function of temperature. From these results the glass transition temperature (T_g) of each material was taken as the temperature at the maximum level of damping (i.e. the tanδ peak) reached by each material.

5.3.4 Viscosity Measurements

The viscosity of each material was measured using a Rheometrics ARES (Advanced Rheometer and Expansion System) Controlled Strain Rheometer. Tests were run using 25mm diameter parallel plate tool geometry with a gap of 3mm between the plates. Test temperatures were over a range of 200 – 300 °C and were controlled by an external oven as shown in Figure 5.6.

Two types of tests were performed. Initial tests were Steady Shear Rate Sweep Tests and were performed at 200 °C only. Materials tested using this method included virgin and recycled HIPS and ABS and their blends as well as other blends containing 90% of these materials. The other test performed was a Temperature Sweep at a Constant Shear Rate of $10^{-2}s^{-1}$ over a temperature range of 200 – 300 °C.

These tests were carried out on recycled mPPO and PC/ABS and blends containing 25% or more of these materials.

Samples for these tests were cut from the ends of the injection moulded dog bone test pieces shown in Figure 5.2. The sample size was $20mm^2$ and 4mm thick. This was initially too small for the tool geometry of 2.5mm diameter. Therefore in order to obtain the right size and shape, the sample was placed in-between previously heated plates and heated by covering with the external oven. As the sample reached 200 °C and therefore became more processable, the initial gap of 4mm between plates was reduced to 3mm, thus causing the sample to expand and cover the tool geometry. On reaching the 3mm gap, the oven was opened and any excess material was scraped from around the tool geometry. Testing began a few moments later, as soon as the sample reached temperature on closing the oven. Results were measured as Viscosity, η (Pa-s) and were compared at 200 °C for all materials and also over a range of temperatures for blends of mPPO and PC/ABS.

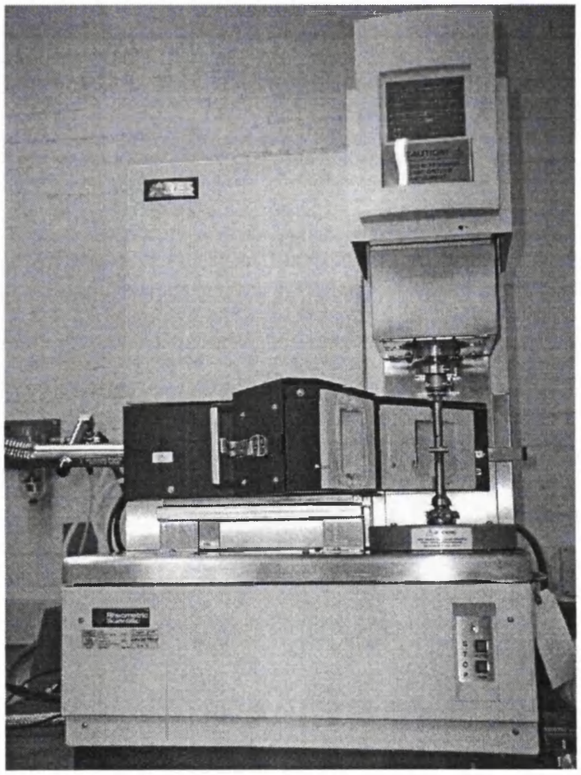


Figure 5.6 Image of a Rheometrics ARES Controlled Strain Rheometer, showing the set up for Viscosity Testing

5.3.5 Molecular Weight Measurements

Experiments to measure the molecular weight of each plastic and blend type were carried out at RAPRA Technology Ltd, who used the method of Gel Permeation Chromatography with chloroform as a solvent. Samples tested were of each plastic and blend type and were collected at various stages of the recycling process in order to see changes to molecular weight not only from blending, but also from the different stages of the recycling process.

Table 5.4 is a list of the samples sent to RAPRA Technology Ltd for molecular weight analysis. As the GPC system used for this work was calibrated with polystyrene, the given results are expressed as 'polystyrene equivalent' molecular weights and there is the possibility that they may differ from the actual molecular weights of the samples. Results used are the weighted average molecular weight and are comparing differences between different stages of a recycling process as well as variations between blends of materials.

Table 5.4 List of samples collected at various stages of the recycling process, for molecular weight experiments

Material	Before Thermal processing	After Extrusion	After Injection Moulding
ABS – RA	X	—	X
ABS – RAE	—	X	X
HIPS – VH	X	—	X
HIPS – RH	X	—	X
HIPS – RHE	—	X	X
mPPO – RP	X	—	X
mPPO – RPE	—	X	X
PC/ABS – RPC	X		X
PC/ABS – RPCE	—	X	X
HIPS/ABS – 1H9A	—	—	X
HIPS/ABS – 5HA	—	X	X
HIPS/ABS – 9H1A	—	—	X
HIPS/mPPO – 1H9P	—	—	X
HIPS/mPPO – 5HP	—	X	X
HIPS/mPPO – 9H1P	—	—	X
ABS/PC/ABS – 1PC9A	—	—	X
ABS/PC/ABS – 5PCA	—	X	X
ABS/PC/ABS – 9PC1A	—	—	X
25% ABS/HIPS/mPPO/PC/ABS	—	X	X

5.3.6 Microscopy of Plastics

5.3.6.1 Bulk Microscopy of Recycled Plastics

Bulk microscopy of recycled and blended plastics was carried out in order to observe any differences of the microstructure between the four recycled plastics and 25% and 50% blends. The plastics studied are listed in Table 5.5. Sample preparation involved cooling samples to –196°C in liquid nitrogen prior to impact testing. This created a very brittle fracture surface, with the aim of fracturing round any particles within the plastic matrix rather than fracturing through them.

The selected fracture surfaces were lightly coated in gold under vacuum conditions and were then examined using a Phillips XL 30 CP (Control Pressure) SEM (scanning electron microscope). Imaging was carried out using secondary electrons. Although the morphology of plastics are often studied using transmission electron microscopy techniques, both time and equipment constraints meant that it was more appropriate to use a SEM for this study.

Table 5.5 List of samples for bulk microscopy and fracture surface imaging.

Samples for Bulk Microscopy	Samples for Fracture Surface Imaging
ABS – RA	ABS – VA ABS – RA ABS – RAE
HIPS – RH	HIPS – VH HIPS – RH HIPS – RHE
mPPO – RP	mPPO – RP mPPO – RPE
PC/ABS – RPC	PC/ABS – RPC PC/ABS – RPCE
Blends – 5HA – 5HP – 5PCA – 25AHPPC	Blends – 5HA – 5HP – 5PCA – 25AHPPC

5.3.6.2 Fracture Surface Imaging

Specimens from either tensile or impact tests were selected for fracture analysis from virgin and recycled plastics and 25% and 50% blends as listed in Table 5.5. Macro images were taken using NIKON Coolpix 950 digital camera with adaptor and close-up shots were taken also using the above camera with a MEIJI stereo-microscope. The images were processed using Microsoft Photo Editor Software.

CHAPTER 6:
RECYCLING PLASTICS – EXPERIMENTAL RESULTS

6.1 TENSILE TESTING

Information obtained from tensile testing using a laser extensometer was in the form of a curve showing load versus extension. This information was converted into stress / strain curves for each test, using measurements of the gauge length geometry and the formulae described in Chapter 5. Figures 6.1 – 6.2 show typical stress / strain curves for different plastic types and blends tested for this project.

Looking at Figure 6.1, the curves for modified PPO (mPPO) and HIPS are very similar, in that plastic deformation occurs on reaching a yield stress, which is seen as a peak on the stress level, which then decreases suddenly as necking commences. As deformation continues, the stress then starts to increase due to orientation stiffening. As these plastics are capable of high levels of strain, the stress usually continues to increase with failure occurring at a stress higher than the yield stress. All blends of HIPS and mPPO behaved in this manner, although stress and strain levels varied. With ABS however, yielding starts to occur following elastic deformation until the ultimate tensile stress is reached. The stress then decreases rapidly and then more slowly as strain continues and then more rapidly again just before failure occurs, so that this part of the curve appears to shoulder. Strains to failure are a lot lower than for HIPS and mPPO. Blends of HIPS and ABS tend to portray characteristic curves of the two, according to the blend proportion. For example, the curve for the blend 5HA (50% HIPS and 50% ABS) as seen in Figure

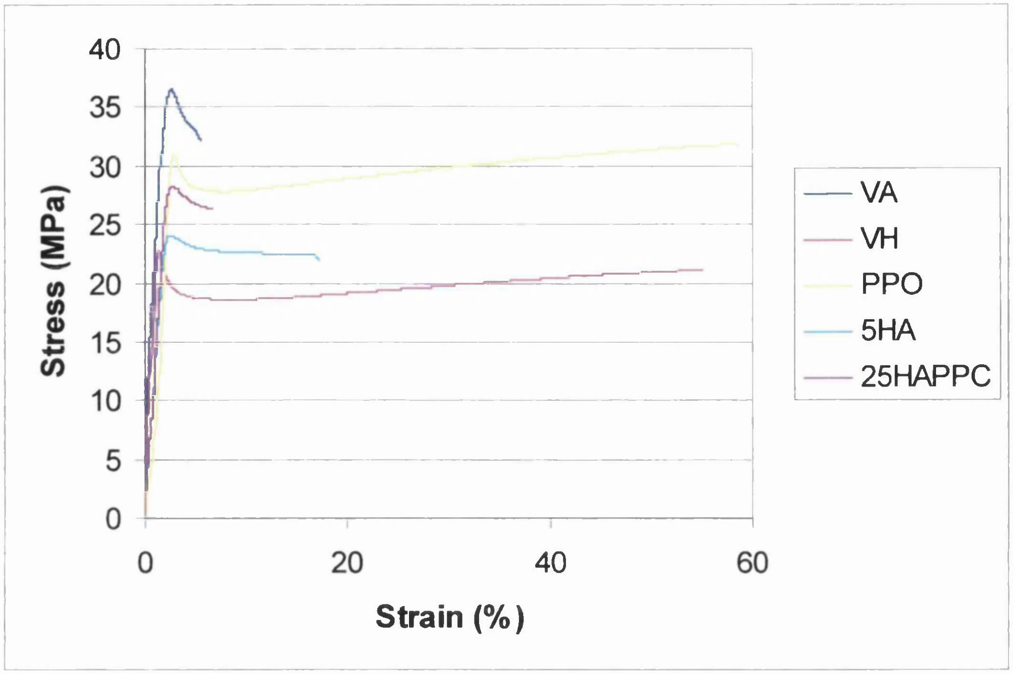


Figure 6.1 Typical Stress strain curves of HIPS, ABS, mPPO and selected blends of these plastics.

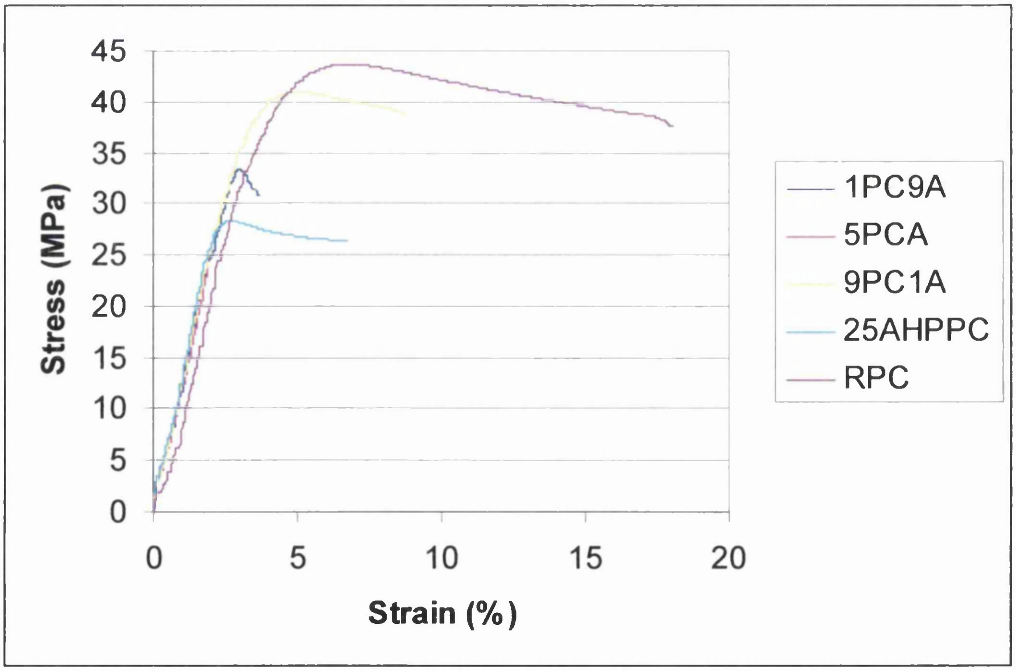


Figure 6.2 Typical Stress strain curves of PC/ABS and blends with ABS.

6.1 appears to be more ductile than ABS, but less than HIPS, displaying a curve approximately halfway between the two.

Figure 6.2 displays the stress / strain curves of PC/ABS and blends of PC/ABS and ABS, as they were all quite distinct. The blends 1PC9A and 9PC1A do actually appear to display curves rather similar to their main constituent. However the 50% blend, instead of being a mixture of the two, produces a completely brittle stress strain curve (close to a straight line), showing no yield whatsoever. The stress at failure is the ultimate tensile stress. The blend of all four plastics (25AHPPC) is present in both figures and appears to display a curve different from all plastics types, yet with similarities to each of them. This curve displays neither the highest nor the lowest tensile strength and is neither the most nor the least ductile.

From each stress / strain curve, information that can be extracted includes tensile strength, strain to failure and tensile modulus, which was taken as the gradient from the initial steep part of each curve.

6.1.1 Tensile Strength

6.1.1.1 Recycled ABS, HIPS, mPPO, PC/ABS

Figures 6.3 – 6.6 compare tensile strengths of recycled and virgin plastics of all four plastic types studied in this project. All error bars on these figures are standard deviations of at least ten samples, and apply to all other results in this chapter unless stated otherwise.

Due to the presence of voids found on fracture surfaces of ABS samples VA and RA, the measured tensile strengths for these plastics may not be accurate values. The tensile strengths for these two plastic types appear in Figure 6.3, but this is just for general comparison with RAE and so should not be taken as particularly significant. Results for RAE are a good representation for recycled ABS as no voids were found in samples

The tensile strength of HIPS decreased, due to recycling, from 22.4 MPa (±0.4) for VH to 18.7 MPa (±0.4) for RH (Figure 6.4). Differences between RH and RHE are so small (0.7 MPa) that it appears that the effect of extrusion on the tensile strength of recycled HIPS is negligible. Extrusion as part of a recycling process also causes no significant changes to tensile strengths of recycled mPPO and PC/ABS as

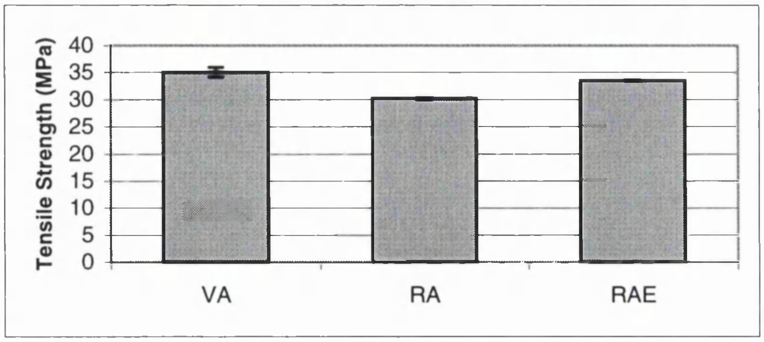


Figure 6.3 Histogram showing the tensile strengths of virgin, recycled and recycled – extruded ABS

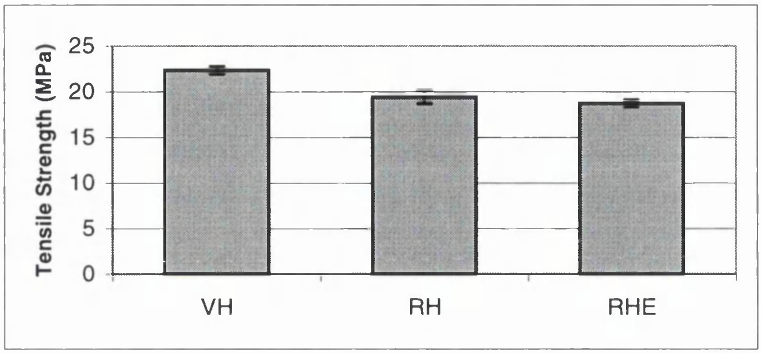


Figure 6.4 Histogram showing the tensile strengths of virgin, recycled and recycled – extruded HIPS

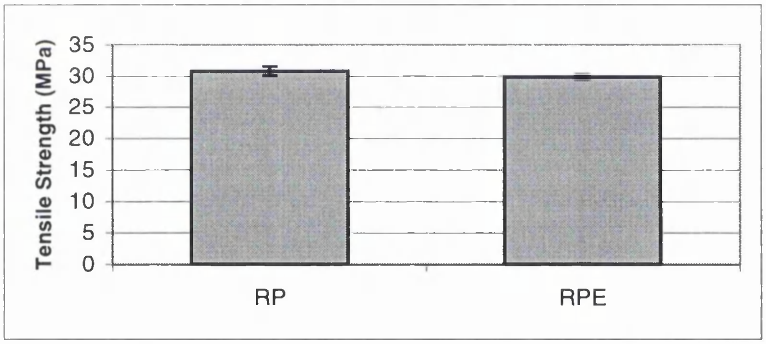


Figure 6.5 Histogram showing the tensile strengths of recycled and recycled – extruded mPPO

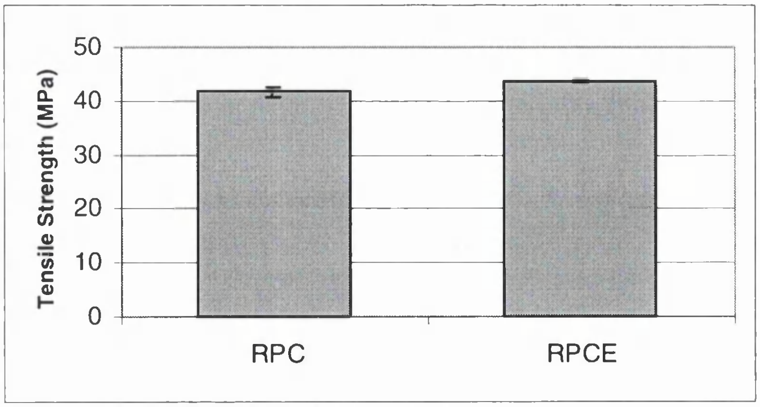


Figure 6.6 Histogram showing the tensile strengths of recycled and recycled – extruded PC/ABS

seen in Figures 6.5 and 6.6 respectively. Results for RPC an RPCE are the average of five samples, due to the presence of voids in some samples, the results of which were discounted.

6.1.1.2 Blends of ABS, HIPS, mPPO and PC/ABS

Figure 6.7 shows the tensile strengths of recycled and extruded ABS, HIPS and their blends. From this histogram, it can be seen that an addition of 10% ABS into HIPS and vice versa has little effect on the tensile strength and both 9H1A and 1H9A display strengths comparable with their main plastic type. The blend containing equal amounts of ABS and HIPS has a tensile strength of 24.0 MPa (±0.2), which is more or less between those of recycled ABS and HIPS. This is what could be expected according to a linear law of mixtures.

Tensile strengths for HIPS / mPPO blends are shown in Figure 6.8. The tensile strength of each 10/90 blend appears to fall slightly when compared with their main constituent, however the range of scatter is sufficient that such differences are negligible. The 50% blend displays a tensile strength of 25.5 MPa (±1), which is slightly higher than the linear average between recycled HIPS and mPPO. This indicates that the addition of mPPO in HIPS after a certain proportion is beneficial to strength, although an increasing amount of HIPS in mPPO is not considered too detrimental to the tensile strength of mPPO.

Blending small proportions of ABS into PC/ABS has no effect on tensile strength as shown in Figure 6.9. However the 50% blend of the two plastics, exhibits a tensile strength of 24.5 MPa (±1.6), which is considerably lower than both recycled ABS (33.0 MPa ±0.3) and PC/ABS (41.0 MPa ±3.1). Therefore, as the proportion of each of these plastics in the other increases, the tensile strength will remain unaffected until a critical proportion is reached and will then decrease quite significantly.

The blend of recycled plastics that contains equal proportions of ABS, HIPS, mPPO and PC/ABS is compared with the tensile strengths of its constituent plastics in Figure 6.10. From this figure it can be seen that the 25% blend displays a tensile strength of 27.9 MPa (±0.2). This is neither the highest nor the lowest tensile strength and is just slightly below the average tensile strength (31.4 MPa) of the four plastics.

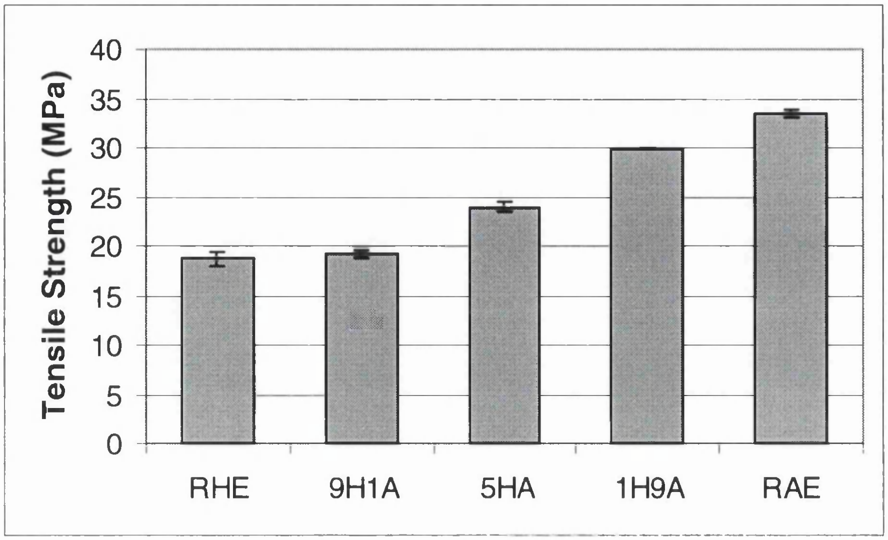


Figure 6.7 Histogram showing the tensile strengths of blends of recycled ABS and HIPS.

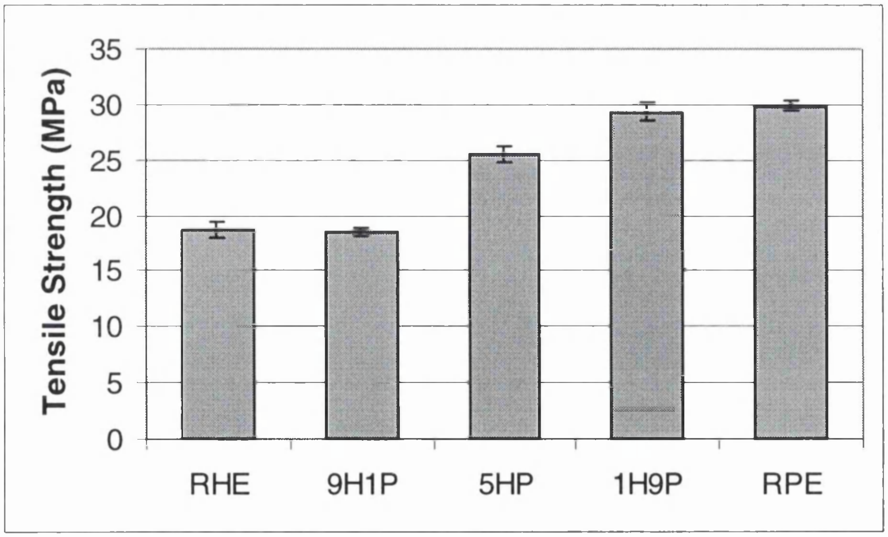


Figure 6.8 Histogram showing the tensile strengths of blends of recycled HIPS and mPPO.

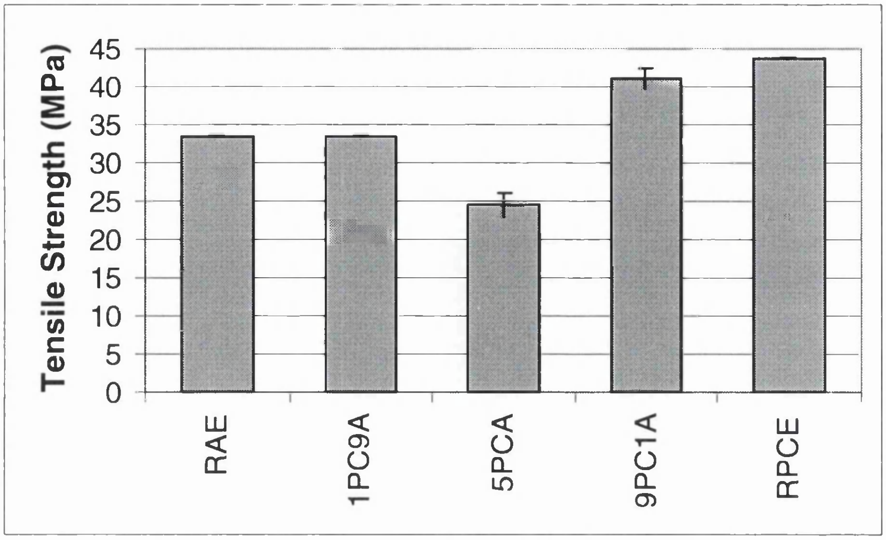


Figure 6.9 Histogram showing the tensile strengths of blends of recycled ABS and PC/ABS.

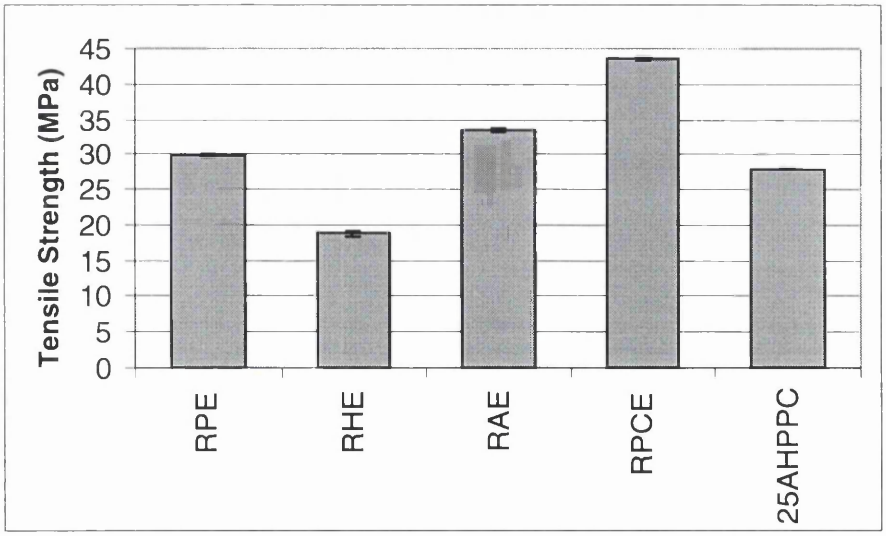


Figure 6.10 Histogram comparing the tensile strengths of recycled ABS, HIPS, mPPO and PC/ABS with a 25% blend of these plastics.

6.1.1.3 Comparison between a commercial scale recycling process with a laboratory scale recycling process.

Figure 6.11 is a histogram comparing tensile strengths of samples of recycled ABS and HIPS and their blends made for this project using commercial scale equipment and samples made under laboratory conditions for previous work [17]. From this comparison it appears that samples manufactured in laboratory conditions display a higher tensile strength than those made using commercial equipment. The greatest differences were seen in RHE and 9H1A, where the commercial results were up to 10 MPa lower than the laboratory results. However despite such differences between sets of results, the overall effects of blending and recycling HIPS and ABS are the same for each recycling process.

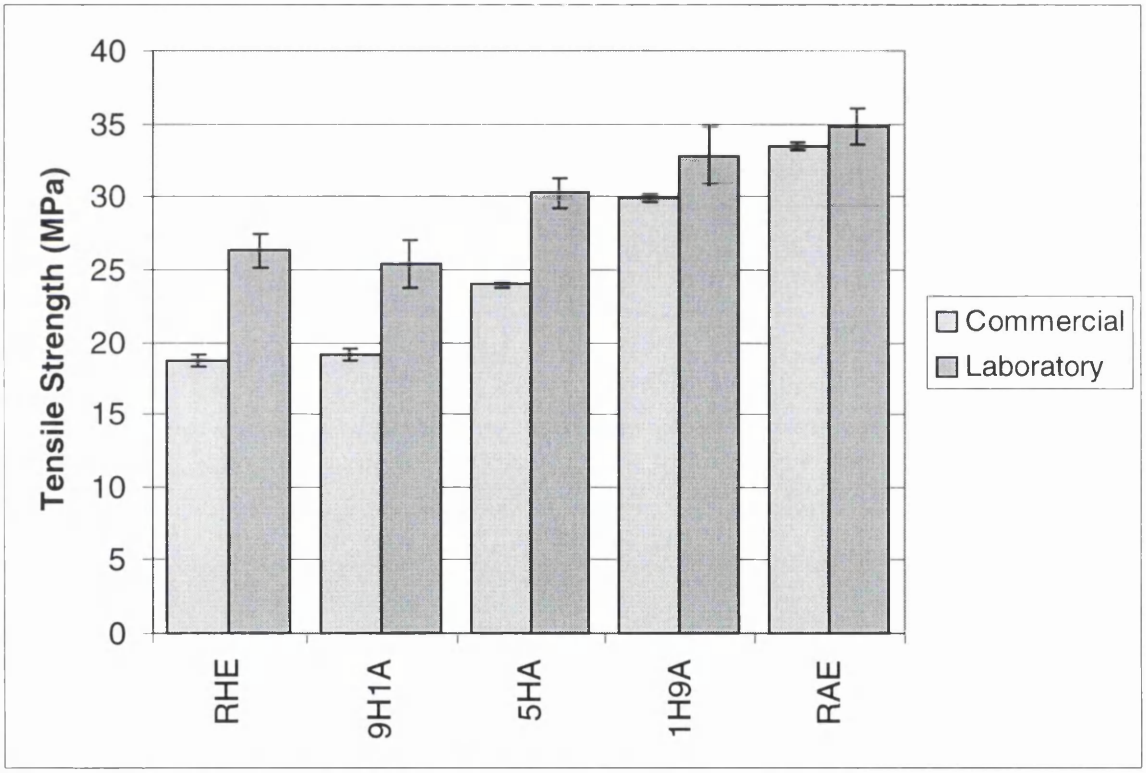


Figure 6.11 Histogram comparing the tensile strengths of various recycled ABS and HIPS and their blends, the samples from which were recycled using laboratory and commercial scale processing conditions.

6.1.2 Strain to Failure

6.1.2.1 Recycled ABS, HIPS, mPPO, PC/ABS

The strains to failure of the ABS, HIPS, mPPO and PC/ABS obtained for this study are illustrated in Figures 6.12 to 6.15 respectively. From Figure 6.12 the strain to failure of RAE at 12.9% (±6.6) is more than double those of the other ABS samples, despite a large range of scatter. This is more than likely to be due to the voids present in samples of VA and RA. Therefore it has not been possible to make a comparison between the different recycling processes on ABS as these samples will have failed prematurely due to the load being supported by a smaller cross sectional area. Throughout testing, most ABS samples exhibited bands of stress whitening along the gauge length, due to shear yielding. Failure occurred as localised yielding along one of these bands developed a crack that propagated through the sample.

The strains to failure of virgin and recycled HIPS decreased as the plastic underwent thermal processing (Figure 6.13). VH exhibited the highest strain to failure at 50.6% (±11.7), which decreased to 36.4% (±12.5) (RH) following the initial recycling process. This was then reduced to 23.9% (±8.2) after the plastic was subjected to extrusion as well as injection moulding (RHE). This could be due to thermal and/or mechanical degradation, which could occur during each stage of the recycling process, thus causing a breakdown of the length of the polymer chains and therefore affecting the ductility of the material. This could also be what caused the strain to failure of mPPO to decrease by 8.7% to 44.3% (±9.4) for RPE, due to the additional extrusion process not experienced by RP (Figure 6.14).

For recycled PC/ABS (Figure 6.15), the addition of the extrusion process has very little influence on ductility and the strain to failure of RPCE at 31.2% (±17.0) is just slightly lower than RPC at 34.2% (±12.3). The level of scatter from these results is sufficient that any changes to ductility due to extrusion are negligible. Results were from an average of five samples due some samples being discounted due to air bubbles. It can be also noted that this was the only plastic type that exhibited apparent necking of samples during yielding.

6.1.2.2 Blends of ABS, HIPS, mPPO and PC/ABS

Figure 6.16 shows the histogram of strains to failure of ABS, HIPS and their blends. Despite a small improvement being seen when blending a small amount of

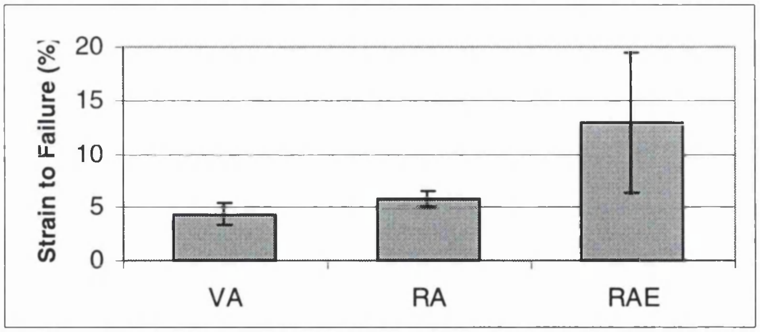


Figure 6.12 Histogram showing the strains to failure of virgin, recycled and recycled – extruded ABS

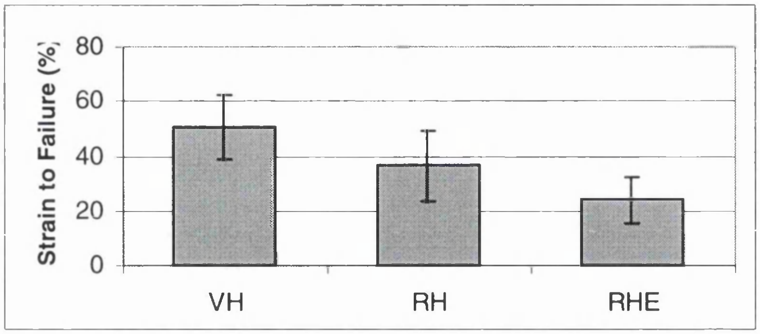


Figure 6.13 Histogram showing the strains to failure of virgin, recycled and recycled – extruded HIPS

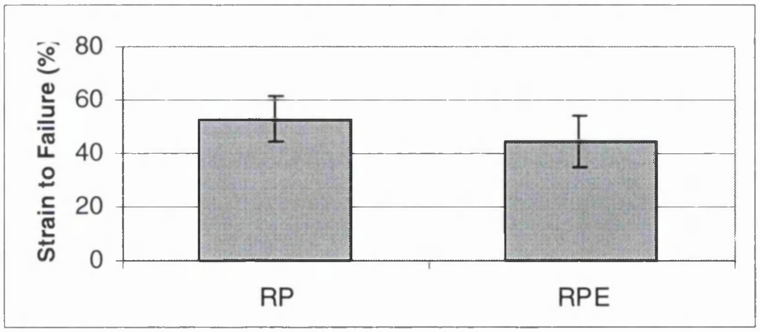


Figure 6.14 Histogram showing the strains to failure of recycled and recycled – extruded mPPO

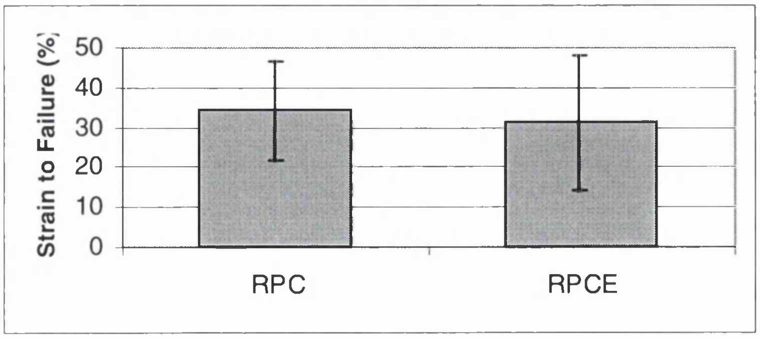


Figure 6.15 Histogram showing the strains to failure of recycled and recycled – extruded PC/ABS

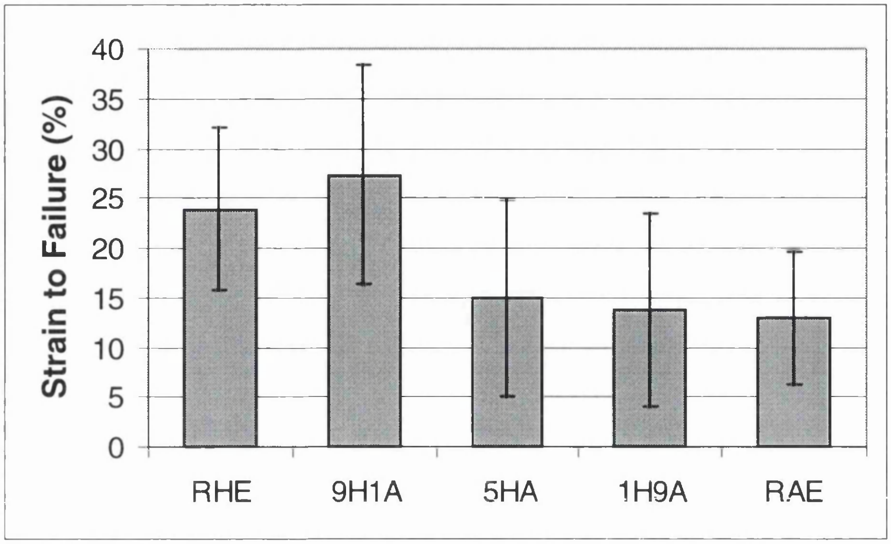


Figure 6.16 Histogram showing the strains to failure of blends of recycled ABS and HIPS.

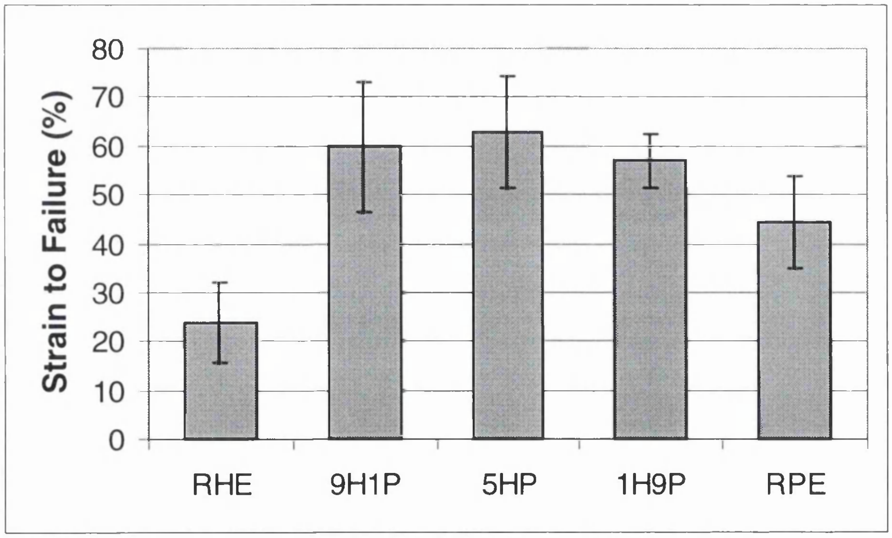


Figure 6.17 Histogram showing the strains to failure of blends of recycled HIPS and mPPO.

ABS into HIPS, the effects of blending ABS with HIPS appear to be negligible at all proportions tested due to the large range of scatter from results. For blends of HIPS and mPPO however, just a small addition of mPPO into HIPS dramatically increases the strain to failure with 9H1P at 59.7% (±13.4) being more than double that of RHE (Figure 6.17). The same behaviour is also observed when just a small amount (10%) of HIPS is added to mPPO. The strain to failure to significantly increases to 57.0% (±5.6), which more than restores the ductility in mPPO that is lost due to the extrusion process during recycling. The 50% blend displays the highest strain to failure at 62.8% (±11.6), however this increase is negligible due to the range of scatter displayed by these results. Therefore it seems that any combination of recycled HIPS/mPPO blends is favourable to ductility.

Blending ABS and PC/ABS significantly decreases strain to failure at all blend proportions as seen in Figure 6.18. At 3.8% (±0.4) and 8.4% (±3.2) the strains to failure of 1PC9A and 9PC1A respectively, are reduced to approximately one quarter that of their main constituents. The strain to failure of the blend 5PCA sees an even further reduction to a low of 2.1% (±0.5). There is no overlapping of scatter for any results.

Figure 6.19 compares the strains to failure of ABS, HIPS, mPPO and PC/ABS with a blend of 25% of all four plastics. From this histogram it can be seen that the blending of all four plastics only serves to reduce the strain to failure rather dramatically to 7.2% (±1.5). This is far lower than the average strain to failure of all four plastics of 28.1%, which could indicate the incompatibility of such a blend.

6.1.2.3 Comparison between a commercial scale recycling process with a laboratory scale recycling process.

The histogram in Figure 6.20 shows the strains to failure of recycled ABS and HIPS and their blends, comparing samples made from commercial and laboratory scale recycling processes. From this histogram it can be seen that the strains to failure of samples made on a commercial scale are considerably higher than the laboratory scale samples. The data for RH is not shown in Figure 6.20, as comparisons are only being made with materials from the same recycling process. However it can be noted that the differences between RH and RHE for both lab and commercial scale recycling processes are the same, in that the strain to failure of RH is significantly higher than for RHE by the same amount for each processing scale. This suggests that the

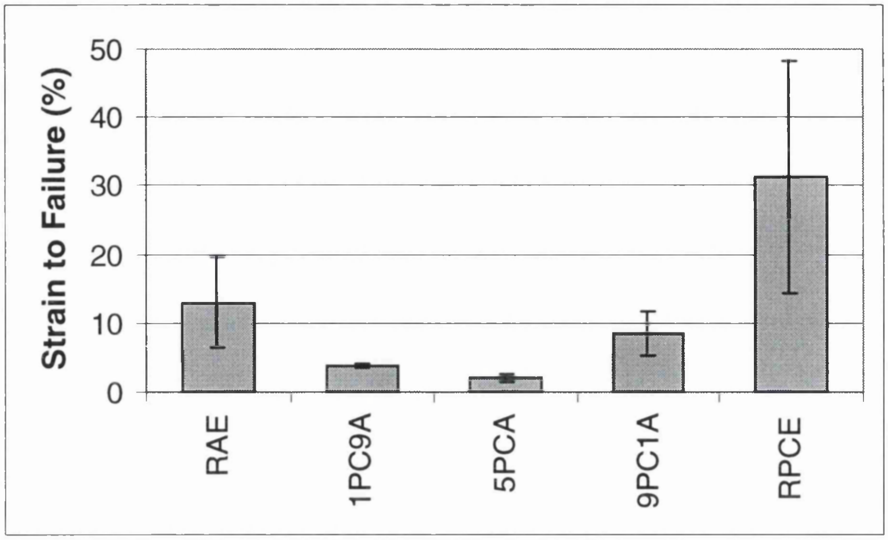


Figure 6.18 Histogram showing the strains to failure of blends of recycled ABS and PC/ABS.

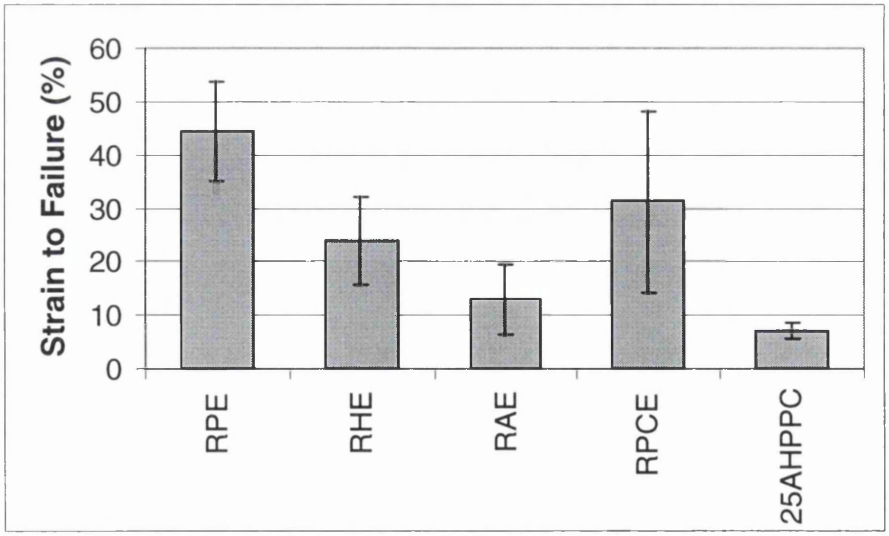


Figure 6.19 Histogram comparing the strains to failure of recycled ABS, HIPS, mPPO and PC/ABS with a 25% blend of these plastics.

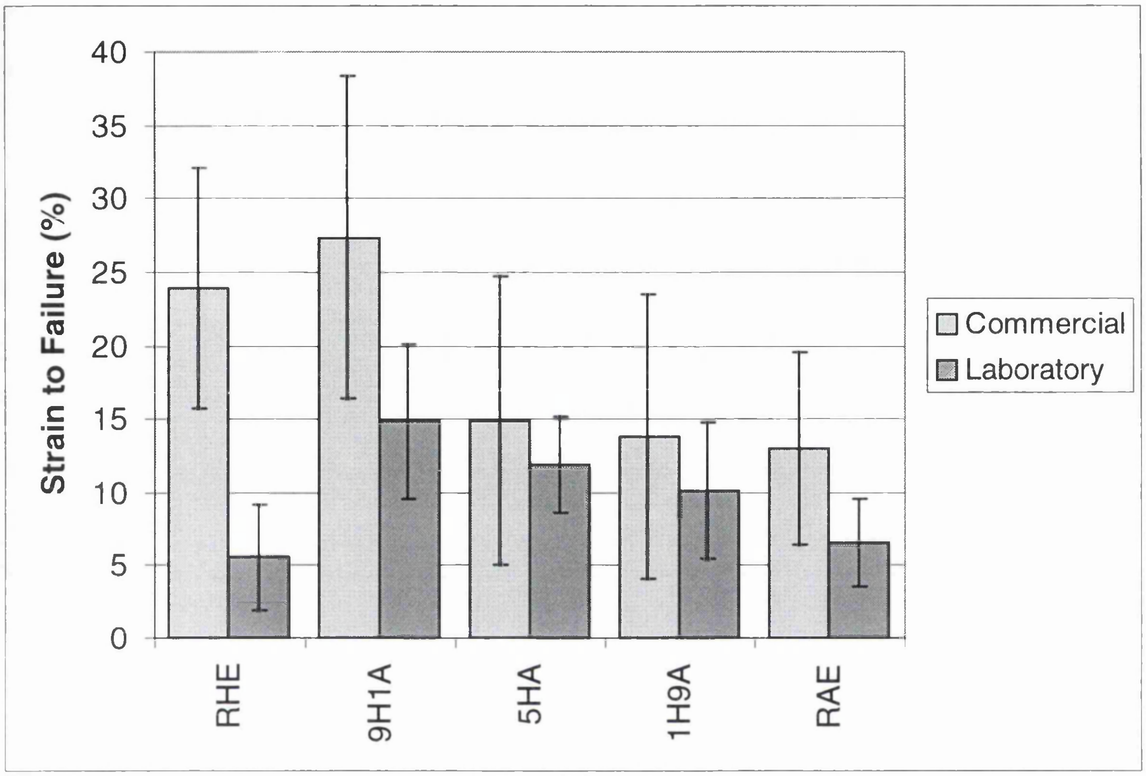


Figure 6.20 Histogram comparing the strains to failure of various recycled ABS and HIPS and their blends, the samples from which were recycled using laboratory and commercial scale processing conditions.

extrusion and torque rheometer processes had the same effects on this plastic type. Therefore the major differences in results could be due to the geometry or scale of the injection moulders or thermal mixers used.

For both scales of recycling processes, similar trends were observed in the strains to failure as a result of blending the two plastics, in that despite a small improvement being seen when blending a small amount of ABS into HIPS, the overall effects of blending ABS with HIPS appear to be negligible at all proportions tested due to the large range of scatter from results

Due to such differences between the strains to failure of commercial and laboratory samples, additional tensile tests were carried out on commercially made samples of RAE, RH and RHE using just the crosshead movement of the Hounsfield Tensometer to record strains to failure. This was just a precautionary check on the measurement procedures already used. These results displayed strains to failure higher than the laboratory results shown in Figure 6.20, but lower than commercial results with the laser extensometer. This shows that while there is still a difference in evels of strain to failure between laboratory and commercially produced samples, there are differences between results for testing methods with and without the laser extensometer. However, while the effects between recycling processes are still the same for all types of testing, the main observation is that the laser extensometer records higher strains than those from the crosshead movement, which will have an effect on the tensile modulus.

6.1.3 Tensile Modulus

6.1.3.1 Recycled ABS, HIPS, mPPO, PC/ABS

Figures 6.21 – 6.24 show the tensile moduli calculated from stress / strain curves of ABS, HIPS, mPPO and PC/ABS respectively. Although the tensile strength and strain to failure results for VA and RA were not included, due to air bubbles on fracture surfaces, the tensile modulus would probably not be as affected by voids in samples. Results suggest that the tensile moduli of VA and RA are likely to be similar to RAE as seen in Figure 6.21. This is not the case for HIPS (Figure 6.22), which shows a reduction in material stiffness following recycling, as VH at 1570 MPa (±110), is significantly higher than RH and RHE. The extrusion process appears to have no further effect on the tensile modulus as there is no significant difference between results for RH and RHE.

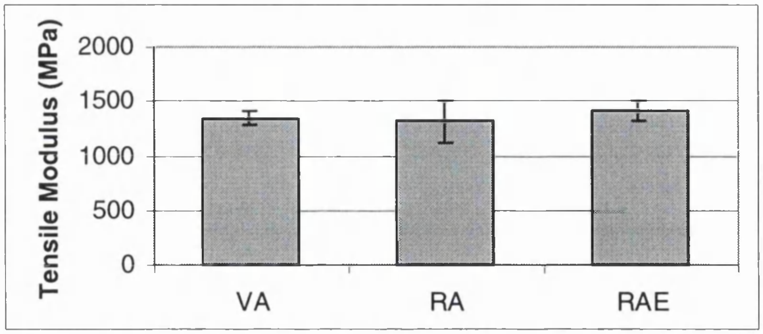


Figure 6.21 Histogram showing the tensile moduli of virgin, recycled and recycled – extruded ABS

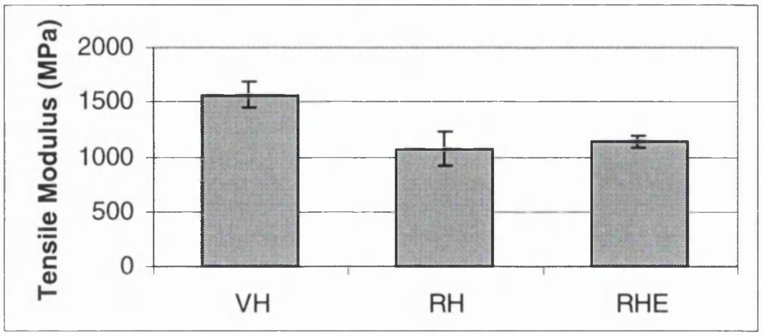


Figure 6.22 Histogram showing the tensile moduli of virgin, recycled and recycled – extruded HIPS

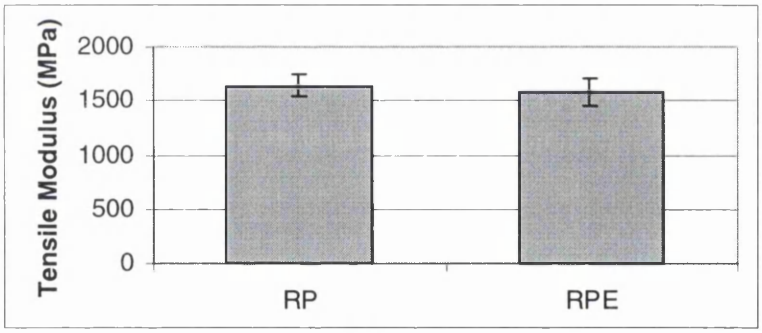


Figure 6.23 Histogram showing the tensile moduli of recycled and recycled – extruded mPPO

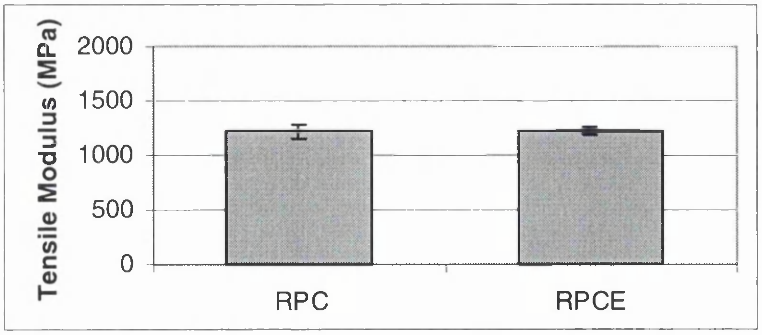


Figure 6.24 Histogram showing the tensile moduli of recycled and recycled – extruded PC/ABS

There is also little difference between results for both types of recycled mPPO and PC/ABS (Figures 6.23 and 6.24 respectively), showing that the extrusion process has negligible effects on the stiffnesses of these materials. This is probably not too surprising seeing as the extrusion process also had little or no effect on the tensile strengths and strains to failure of these two materials.

6.1.3.2 Blends of ABS, HIPS, PPO and PC/ABS

Figure 6.25 compares the tensile moduli of recycled ABS, HIPS and their blends. The pattern emerging appears to be a steady increase of the tensile modulus of HIPS due to recycling, which continues as ABS is added. Considering the range of scatter of these results, the increase in tensile modulus is said to be generally between those of RAE and RHE if considering a linear law of mixtures. This indicates that blending has no further effect on the tensile modulus of ABS and HIPS than already seen from recycling. This can also be said for blends of HIPS and mPPO, where changes to the tensile modulus with blend proportion follow a similar pattern (Figure 6.26).

For blends of ABS and PC/ABS (shown in Figure 6.27), the blending of 10% PC/ABS into ABS and vice versa has little effect on the tensile modulus with such blends representing more or less the same level of stiffness as their main constituent plastic. The blend, 5PCA sees a rise in tensile modulus to a high of 1560 MPa (±150), which is slightly more than both recycled RAE and RPCE. This result is closer to that of RAE, than RPCE, indicating the possibility that there is a critical level of ABS in PC/ABS and vice versa that has to be reached before any significant change to material stiffness occurs.

The histogram in Figure 6.28 compares the tensile moduli of a blend of 25% ABS, HIPS, PPO and PC/ABS with those of its four constituents. At 1400 MPa (±190) the 25% blend is just above the average stiffness of all four plastic types (1340 MPa) and is most comparable to the stiffness of ABS.

6.1.3.3 Comparison between a commercial scale recycling process with a laboratory scale recycling process.

Figure 6.29 compares the tensile modulus of recycled ABS and HIPS and their blends, using samples made from commercial and laboratory scale recycling processes. For both scales of processing the trend is the same in that effects of

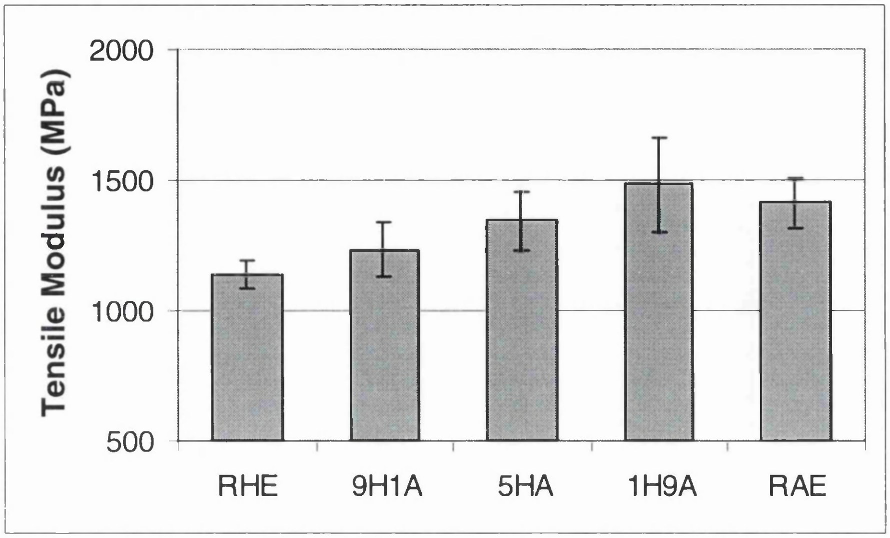


Figure 6.25 Histogram showing the tensile moduli of blends of recycled ABS and HIPS.

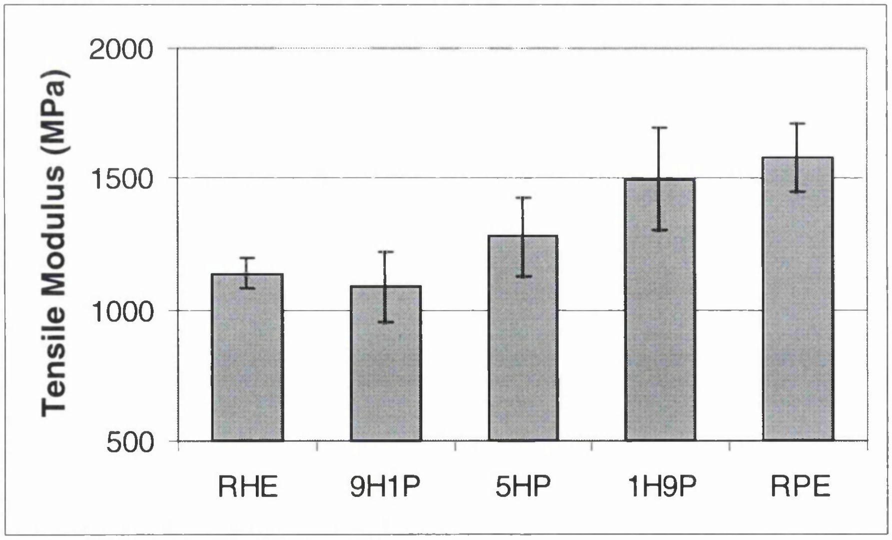


Figure 6.26 Histogram showing the tensile moduli of blends of recycled HIPS and mPPO.

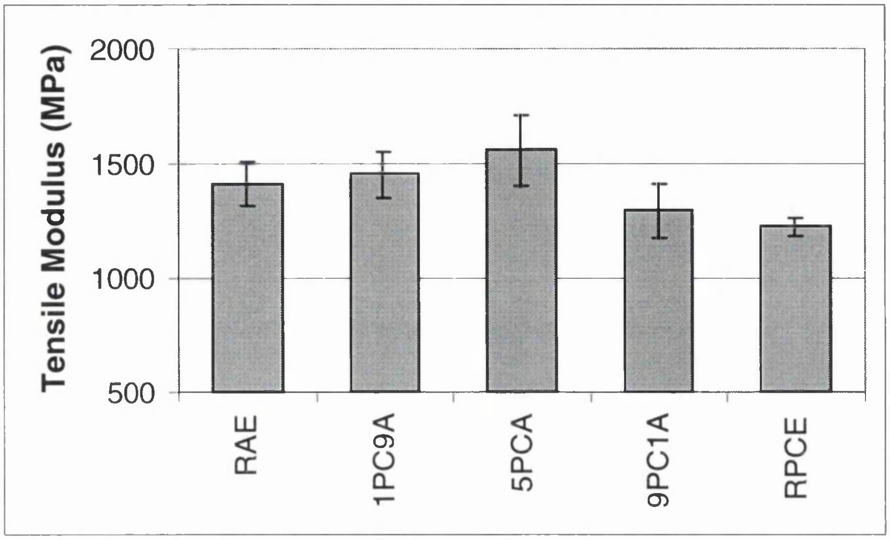


Figure 6.27 Histogram showing the tensile moduli of blends of recycled ABS and PC/ABS.

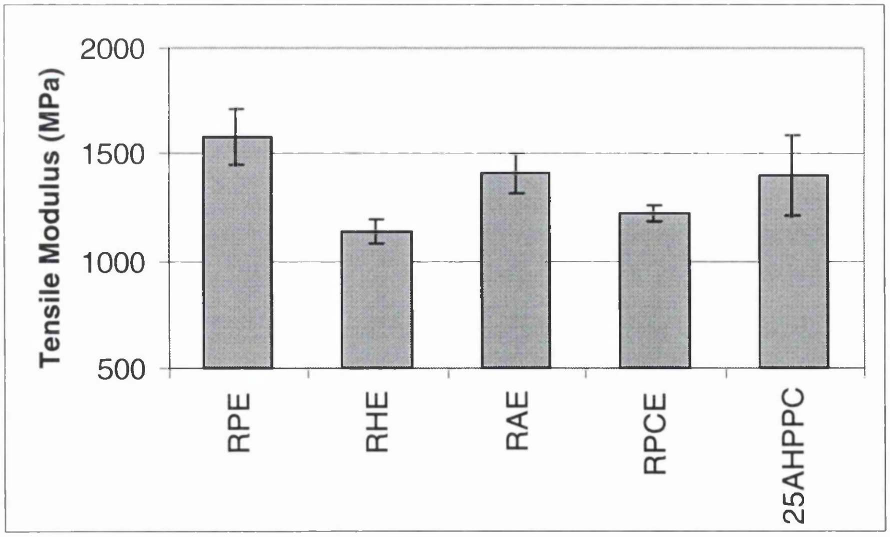


Figure 6.28 Histogram comparing the tensile moduli of recycled ABS, HIPS, mPPO and PC/ABS with a 25% blend of these plastics.

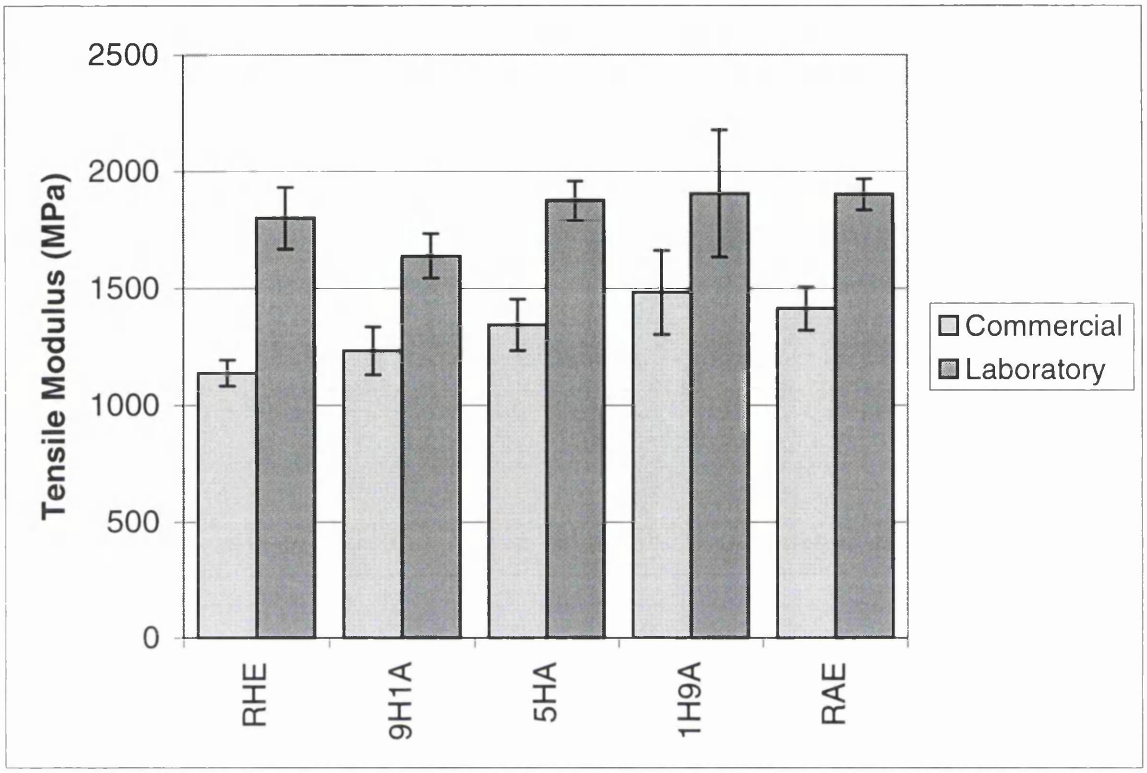


Figure 6.29 Histogram comparing the tensile moduli of various recycled ABS and HIPS and their blends, the samples from which were recycled using laboratory and commercial scale processing conditions.

blending on tensile strength are no more than those seen from recycling and results are more or less in accordance with a linear law of mixtures. However each set of results display different levels of stiffness, the laboratory made samples displaying much higher levels of stiffness than commercially processed samples. The laboratory scale samples exhibit moduli between 1400–1900 MPa whereas those of the commercially processed samples are much lower between 1000–1400 MPa.

Due to such large differences between each set of results, samples of recycled ABS and HIPS, processed on a commercial scale, were tested as already mentioned using the crosshead movement of the Hounsfield tensometer to record results. This was the same method previously used for the laboratory samples, and was done to see if there would be any differences between results from these and samples tested with the laser extensometer. Tensile moduli were calculated using the gradient of the proportional part of the stress/strain curve. As found with the strain to failure, the commercial samples tested using the crosshead movement of the Hounsfield tensometer with no extensometer, displayed a higher tensile modulus than the original commercial samples that were tested with the laser extensometer. However these results were still significantly lower than moduli exhibited by the laboratory samples. This indicates definite differences in stiffness between scales of recycling and such variances in results are not solely due to different testing techniques.

6.2 IMPACT TESTING

6.2.1 Recycled ABS, HIPS, mPPO, PC/ABS

The average impact strengths of virgin and recycled ABS, HIPS, mPPO and PC/ABS are displayed as histograms in Figures 6.30 – 6.33 respectively. Although the tensile results for VA and RA could not be counted due to air bubbles at fractures surfaces, there were some impact samples that did not show voids on fracture surfaces. Therefore results for VA and RA are the average impact strengths from 4 and 6 tests respectively. Looking at Figure 6.30, the impact strength of ABS is reduced by 12 kJm^{-2} to 43 kJm^{-2} (±4) for RA following recycling. The range of scatter for the RAE results indicates that the additional processing does not have any further significant effects on impact strength than those already seen. Changes to the impact strength of HIPS due to the different recycling processes also appear to be of little significance when considering the range of scatter from these results (Figure 6.31).

The two different recycling processes do appear to have a greater effect on the impact strength of mPPO, despite a slight overlap of the scatter margin as seen in Figure 6.32. As a result of the extrusion process the impact strength of RPE falls approximately 14 kJm^{-2} from that of RP at 70 kJm^{-2} (±7). While the impact strength of RPCE increases by almost the same amount that RPE was decreased, the impact strengths of recycled PC/ABS are notably higher than all other plastic types tested, and so the proportion of change is actually less. Coupled with the large range of scatter from both PC/ABS results, any differences between RPC and RPCE are negligible. The results for RPC and RPCE are both the average of five impact tests as other samples exhibited voids at fracture surfaces and were not included.

6.2.2 Blends of ABS, HIPS, mPPO and PC/ABS

As the full recycling process slightly decreases the impact strength of HIPS, blending with a small amount of ABS decreases impact strength even more so. In Figure 6.34 the blend 9H1A saw a decrease in impact strength by 8 kJm^{-2} to 27 kJm^{-2} (±8), however, further blending up to a proportion of 50% ABS had no subsequent effect and the impact strength remained the same. Blending 10% HIPS into ABS is also detrimental to impact strength. The impact strength of the blend 1H9A fell 11 kJm^{-2} to 37 kJm^{-2} (±6) when compared with RAE and the blend 5HA had a much lower impact strength by 10 kJm^{-2}.

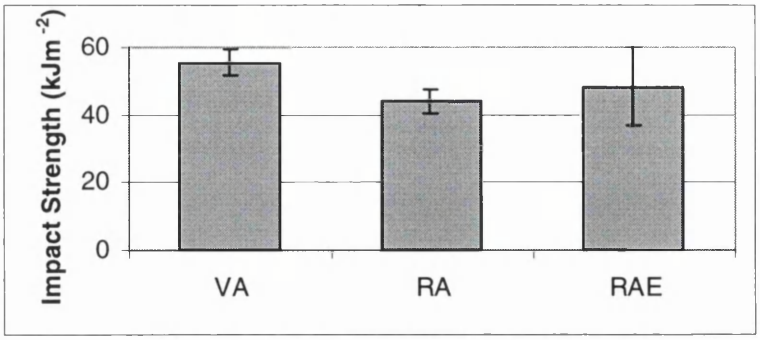


Figure 6.30 Histogram showing the impact strengths of virgin, recycled and recycled – extruded ABS

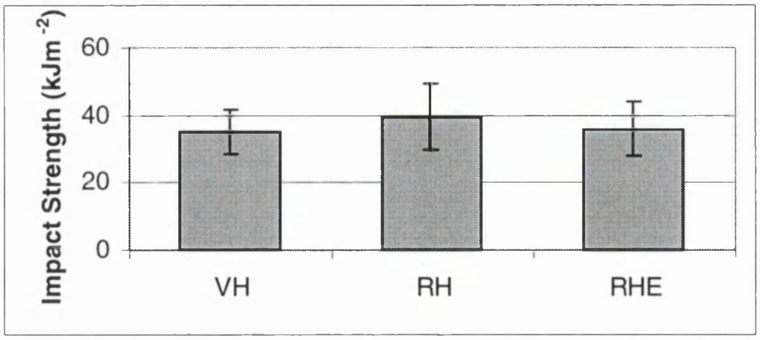


Figure 6.31 Histogram showing the impact strengths of virgin, recycled and recycled – extruded HIPS

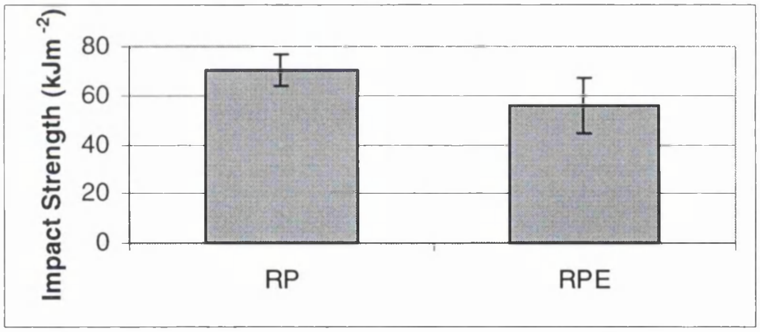


Figure 6.32 Histogram showing the impact strengths of recycled and recycled – extruded mPPO

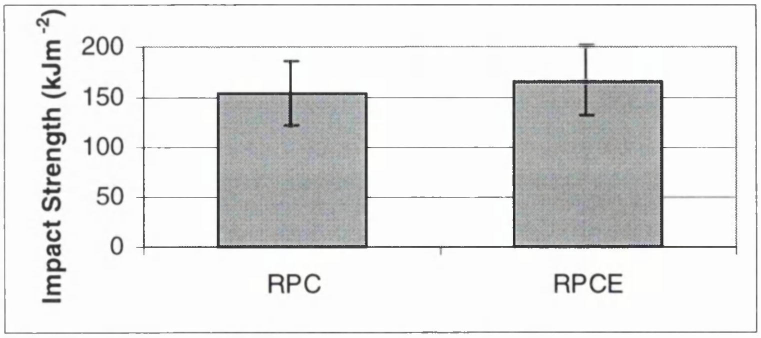


Figure 6.33 Histogram showing the impact strengths of recycled and recycled – extruded PC/ABS

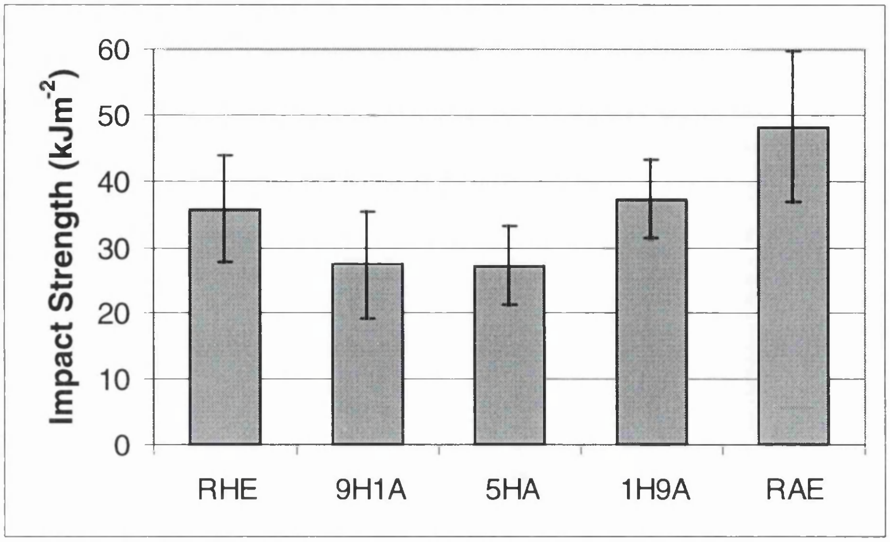


Figure 6.34 Histogram showing the impact strengths of blends of recycled ABS and HIPS.

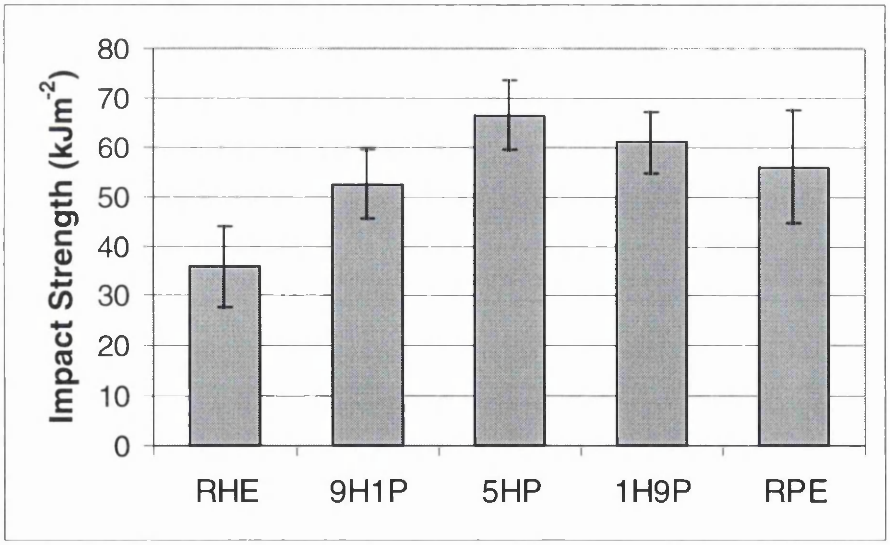


Figure 6.35 Histogram showing the impact strengths of blends of recycled HIPS and mPPO.

The blending of mPPO into HIPS and HIPS into mPPO has beneficial effect on both plastics, which can be viewed as excellent impact modification (Figure 6.35). The largest relative effect is seen between RHE at 36 kJm^{-2} (±8) and 9H1P where the impact strength increases to 52 kJm^{-2} (±7). However, this is not the highest impact strength and the increase of the proportion of mPPO up to 50% gives a further increase in the impact strength to a maximum value of 67 kJm^{-2} (±7), which is almost double that of RHE. Blending HIPS into mPPO also increases impact strength at all proportions. However it must be noted that despite the favourable effects of blending these two plastics, the impact strength of RP at 70 kJm^{-2} (±6) (see Figure 6.32) is still greater than 5HP so the total impact strength that was lost due to extrusion is not fully restored.

Just as with strain to failure, blending ABS and PC/ABS, is significantly detrimental to impact strength (see Figure 6.36). The blend 1PC9A decreases by 13 kJm^{-2} to 35.6 kJm^{-2} (±12) compared with RAE and just a small proportion of ABS in PC/ABS catastrophically reduces the impact strength of 9PC1A by more than half that of RPCE. Both plastics in equal amounts see an incredible reduction of impact strength to a low of 6.5 kJm^{-2} (±1), which is just an eighth of RAE and less than 4% that of RPCE.

The effect of blending the four main plastics, ABS, HIPS, mPPO and PC/ABS is also fairly detrimental to impact strength as seen in Figure 6.37. Here the 25% blend has an impact strength considerably lower than all four constituent plastics. At a level of 13.5 kJm^{-2} (±1.7), this is less than half the impact strength of HIPS, which has the lowest of the four plastic types studied.

6.2.3 Comparison between a commercial scale recycling process with a laboratory scale recycling process.

Figure 6.38 compares impact strengths from laboratory and commercial scale recycling processes of ABS, HIPS and their blends. Commercially produced samples generally exhibited higher impact strengths than the laboratory made samples. For both scales of production the impact strength of HIPS decreased on blending with 10% ABS. Increasing the ABS content up to 50% caused no further changes than those already brought about by recycling. When adding HIPS to ABS, the commercially produced results showed a continual decrease with an increase in the HIPS content up to 50%. The laboratory results instead showed a slight increase in

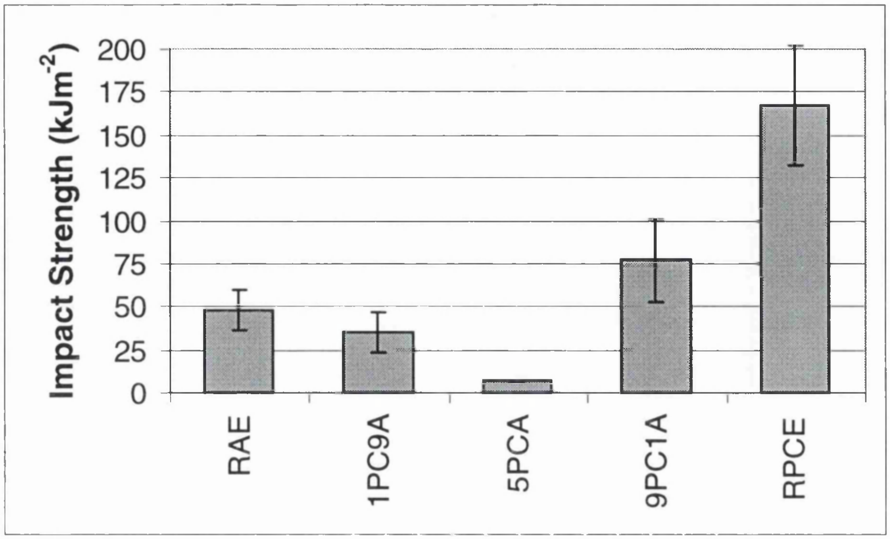


Figure 6.36 Histogram showing the impact strengths of blends of recycled ABS and PC/ABS.

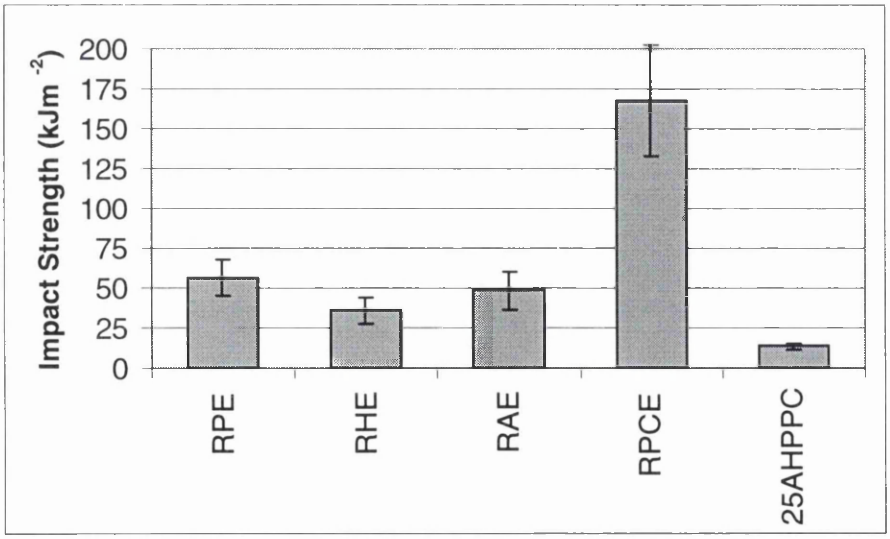


Figure 6.37 Histogram comparing the impact strengths of recycled ABS, HIPS, PPO and PC/ABS with a 25% blend of these plastics.

impact strength for the blend 1H9A, although this increase is probably small enough and sufficiently within the scatter range that it can be considered negligible. For both sets of results, the impact strength decreased as the HIPS content approached 50%.

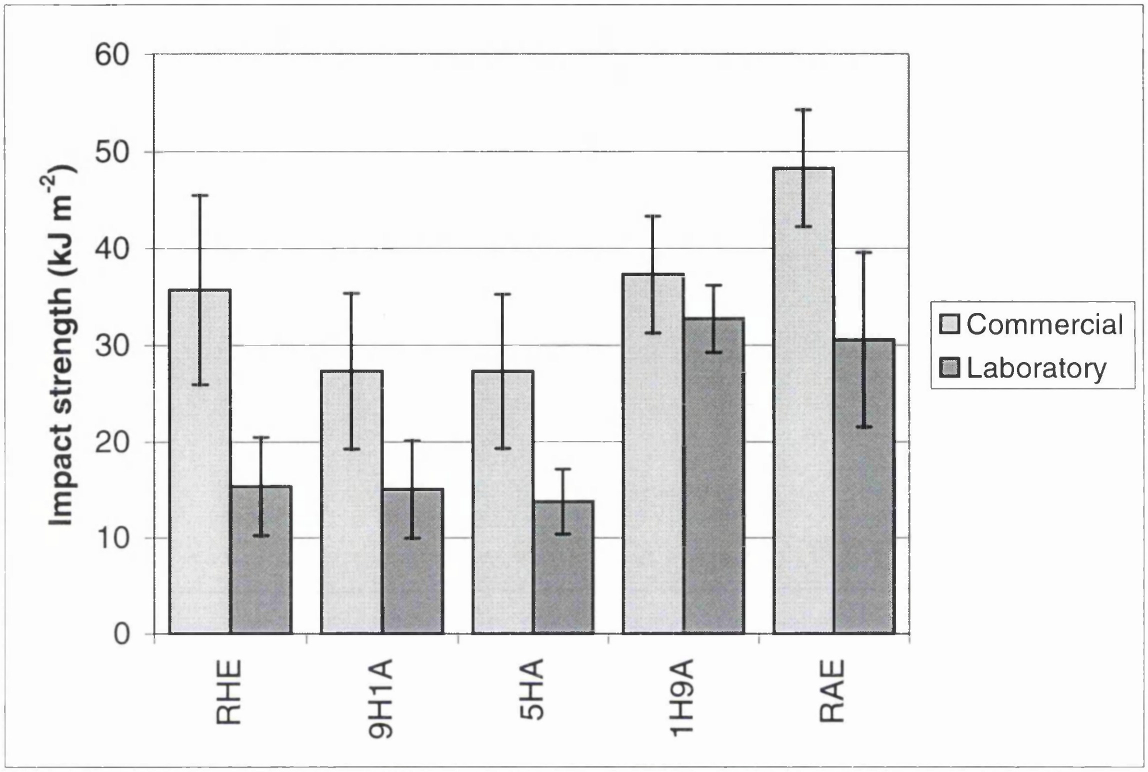


Figure 6.38 Histogram comparing the impact strengths of various recycled ABS and HIPS and their blends, the samples from which were recycled using laboratory and commercial scale processing conditions.

6.3 DYNAMIC MECHANICAL THERMAL ANALYSIS

Results obtained from DMTA experiments are in the format of the elastic modulus (E') and the bending loss tangent or damping (tanδ) (the proportion of energy lost during each bending cycle) as a function of temperature. Figure 6.39 shows the DMTA results for recycled ABS. This is representative of results obtained for a single phase plastic such as ABS, HIPS, mPPO and the majority of blends.

The elastic modulus (E') or stiffness of the plastic is relatively constant at lower temperatures. At the lower tempearathres the plastic is in a state of a glassy solid and the level of damping (tanδ), which is very low, is also relatively constant so the plastic is able to elastically recover. As the temperature increases, E' starts to decrease as parts of the plastic begin to become flexible as opposed to rigid. This is seen as a gradual increase to tanδ, as the plastic begins to dissipate energy that was previously recovered elastically. As the temperature tends towards the glass transition region, the stiffness of the material drops rapidly as the polymer chains become more flexible and easier to bend or deform. This causes tanδ to increase rapidly as the change from a glassy solid to a viscous material causes an increasing amount of energy to be lost. The highest proportion of energy is lost at the glass transition temperature (T_g), which is seen by a peak of tanδ. This is probably the point at which chain flexibility is changing most rapidly, and the tanδ peak coincides approximately with the inflexion of the modulus curve (see Figure 6.39).

As the temperature increases exceeding the T_g, the material becomes more viscous than elastic. The elastic modulus starts to decrease more gradually and at the same time, the tanδ, having reached the maximum, also starts to decrease, initially quite rapidly, and then more slowly but to a level higher than at the lower temperatures. The decrease of tanδ occurs as less energy is now required to bend the material and therefore less energy is lost.

Figure 6.40 is a graph of the DMTA results obtained for PC/ABS. This is representative of a two-phase immiscible blend, where the glass transitions for each component are analysed separately and the T_g's for each component are easily discernable as two distinct peaks on the tanδ curve. These peaks coincide with the two inflexions that can be seen on the E' curve. If the T_g's for each plastic had been closer, it would be more difficult to discern each one as the tanδ curves would

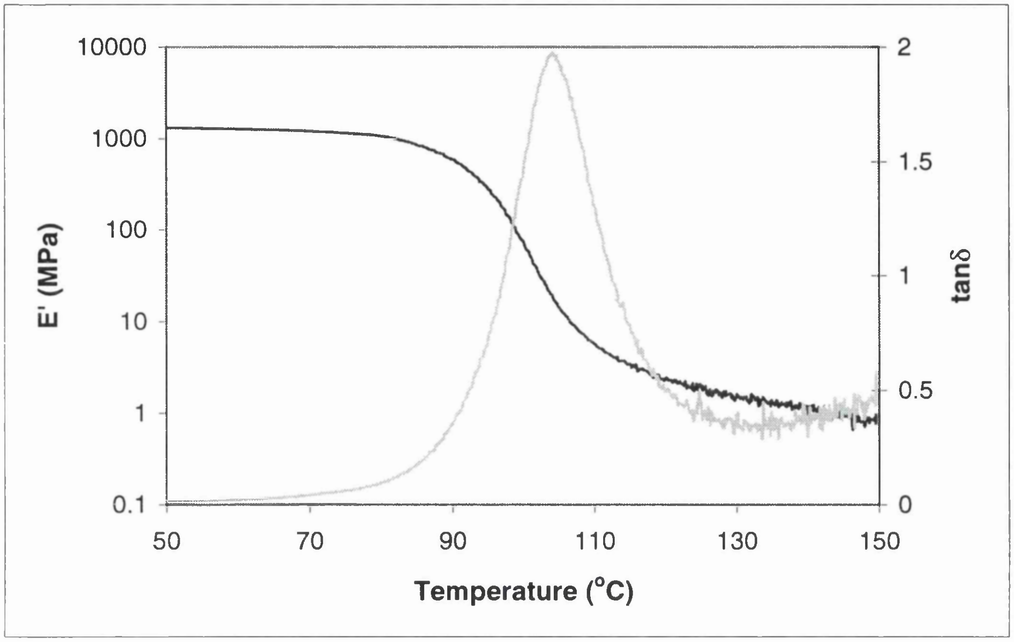


Figure 6.39 Graph showing the results obtained from DMTA testing of recycled ABS

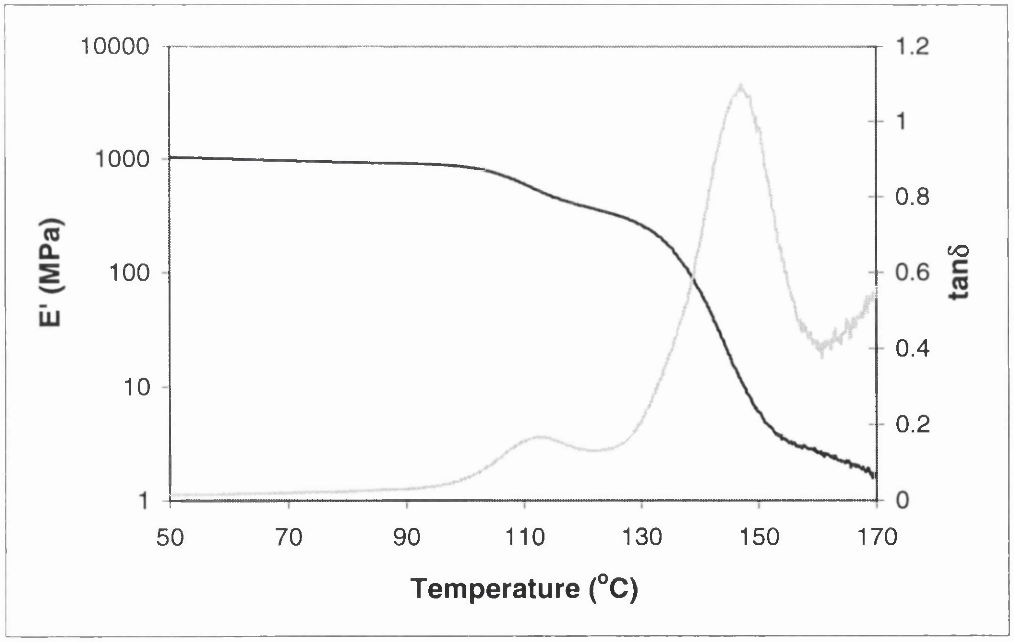


Figure 6.40 Graph showing the results obtained from DMTA testing of recycled PC/ABS.

overlap. However this may be indicated by the tanδ curve, which would most probably show a peak a lot broader than a single phase polymer.

Glass transition temperatures for each plastic type tested for this project were measured from the peak of the damping tanδ obtained from DMTA results and are the average of two tests. The following is a comparison of the data obtained.

6.3.1 Recycled ABS, HIPS, mPPO, PC/ABS

The glass transition temperatures (T_g) of virgin and recycled ABS, HIPS, mPPO and PC/ABS, extracted from the results of DMTA tests are displayed in Figures 6.41 – 6.44 respectively. From Figure 6.41 it appears as though recycling could lower the T_g of ABS as that of RA at 103.9°C is considerably lower than VA. However it must be noted that the VA used for this work may not necessarily be exactly the same grade as the recycled ABS and therefore may differ in some properties. Further recycling has negligible effects on the T_g of RAE.

Changes to the T_g of HIPS also appear to be minor as seen in Figure 6.42 and at 108.6°C, the T_g of VH is just one degree less than that of RH. Further recycling has no effect and the T_g's of RH and RHE are the same. This is the same for recycled mPPO (Figure 6.43), and the difference between T_g's of RP (118.4°C) and RPE (118.6°C) is too small to be significant.

Results for PC/ABS are a little different than for the other plastics in that there are actually two sets of glass transition temperatures in these results, one for the ABS part and the other for the PC part of the blend (Figure 6.44). For RPC, $T_{g\text{-low}}$ at 113°C is considerably lower than $T_{g\text{-high}}$, which is at 145.5°C. Further recycling has no more significant effects on either T_g.

6.3.2 Blends of ABS, HIPS, mPPO and PC/ABS

When considering two different plastic types of different T_g, it could be expected that when blended together the T_g of the blend if homogeneous, would be at a temperature between those of the constituent plastics, according to blend proportions. This would be a miscible blend as an immiscible blend would still show a different T_g for each constituent.

The histogram in Figure 6.45 compares the T_g's of ABS, HIPS and their blends. The difference in T_g between ABS and HIPS is about 5°C, with HIPS

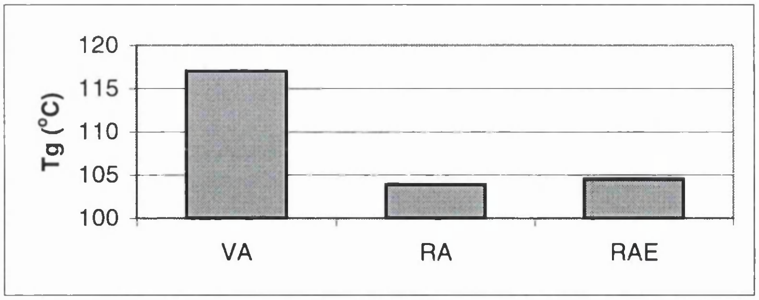


Figure 6.41 Histogram showing the glass transition temperatures of virgin, recycled and recycled – extruded ABS

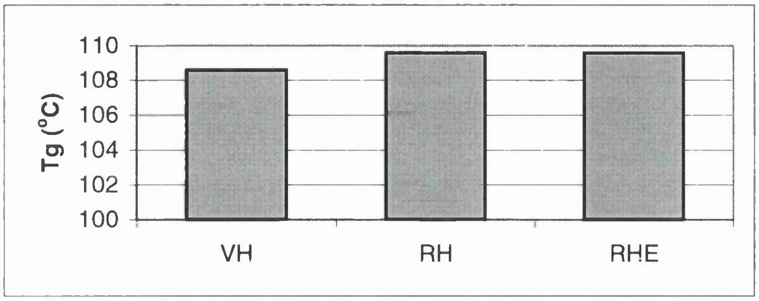


Figure 6.42 Histogram showing the glass transition temperatures of virgin, recycled and recycled – extruded HIPS

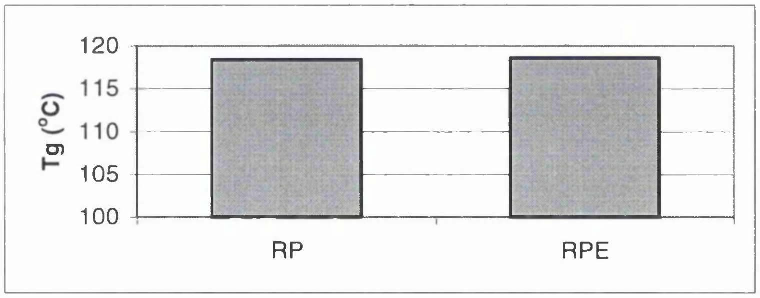


Figure 6.43 Histogram showing the glass transition temperatures of recycled and recycled – extruded mPPO

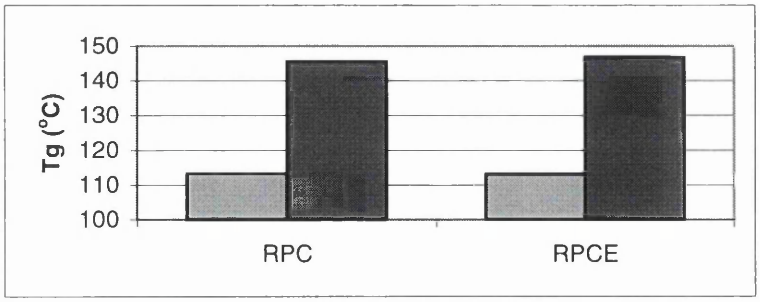


Figure 6.44 Histogram showing the glass transition temperatures of recycled and recycled – extruded PC/ABS

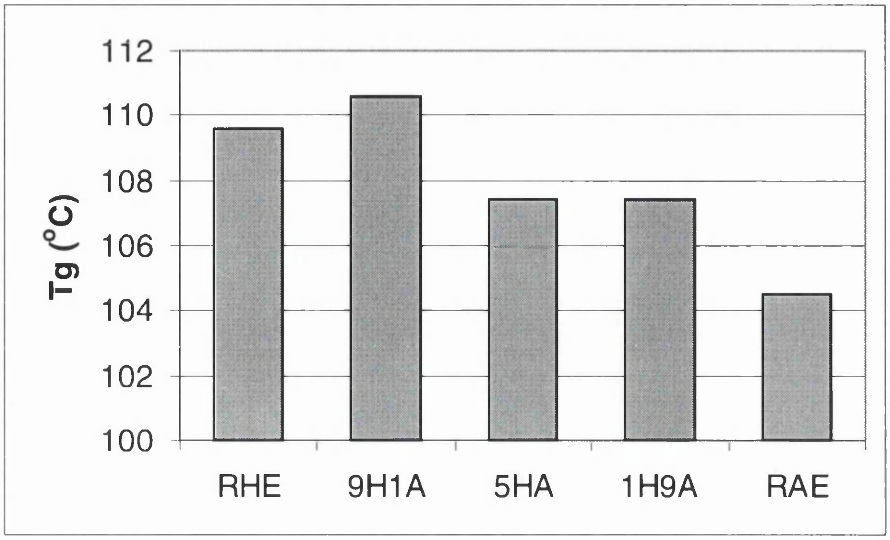


Figure 6.45 Histogram showing the glass transition temperatures of blends of recycled ABS and HIPS.

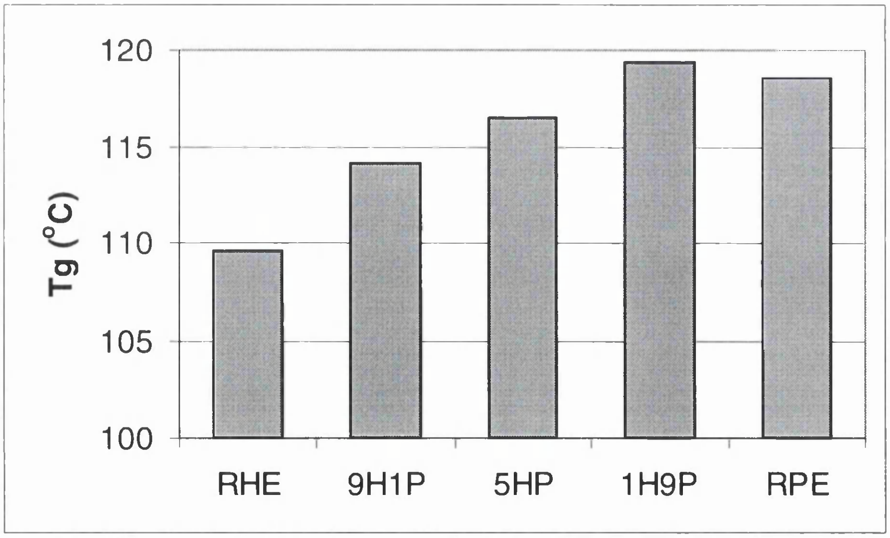


Figure 6.46 Histogram showing the glass transition temperatures of blends of recycled HIPS and mPPO.

displaying the higher value. This is not a large difference and therefore the effect of blending the two plastics would not be inducing a large change to T_g at any blend proportion. From these results the effect of blending 10% HIPS into ABS does increase the T_g by a few degrees up to 107.4°C. This is probably a little higher than expected, as proportionally the T_g is now closer to that of HIPS than of ABS however, a further increase in the HIPS content to 50%, sees no further change and the T_g remains the same. What is fairly unexpected however, is that on blending 10% ABS with HIPS the T_g increases to 110.6°C, which is a degree higher than RHE, instead of decreasing to a temperature between ABS and HIPS as would be expected, although the difference of just one degree can be considered negligible. There is no broadening of the tanδ peak for any blend indicating that these two plastics mixed sufficiently at all proportions.

A similar pattern can also be seen in the HIPS/mPPO blends in Figure 6.46. The difference between T_g's of HIPS and mPPO is 9°C, the higher value being mPPO. Blending just 10% mPPO into HIPS, increases the T_g to 114.1°C, which is at a temperature halfway between the T_g's of the constituent plastics, instead of being at a temperature closer to that of RHE as would be expected. An increase in the mPPO content to 50% continues to increase the T_g up to 116.5°C. The blend 1H9P has a slightly higher T_g than RPE although as this is less than one degree Celsius, this can be considered negligible. Again there is no broadening of the tanδ curves indicating the miscibility of these two plastics.

Blending ABS with PC/ABS appears to have different effects on T_g's due to the double T_g's displayed by PC/ABS as opposed to the single T_g for ABS (Figure 6.47). Adding 10% PC/ABS to ABS has no significant effects on T_g compared with RAE and the blend 1PC9A has a single T_g value. Blending PC/ABS with a small proportion of ABS still produces two distinct T_g's and while there is no change to $T_{g\text{-low}}$, the higher temperature peak decreases by about three degrees to 142.7°C. On increasing the proportion of ABS to 50%, there are no longer two values for T_g but a single value at 116.5°C. This is only slightly higher than $T_{g\text{-low}}$, as opposed to being more proportionally in-between the higher and lower T_g's. This could be due to a higher proportion of ABS than PC in this blend. It is also unclear as to when the transition from a double to a single glass transition temperature occurs i.e. whether the $T_{g\text{-high}}$ for PC/ABS decreases gradually as the ABS content increases or whether there

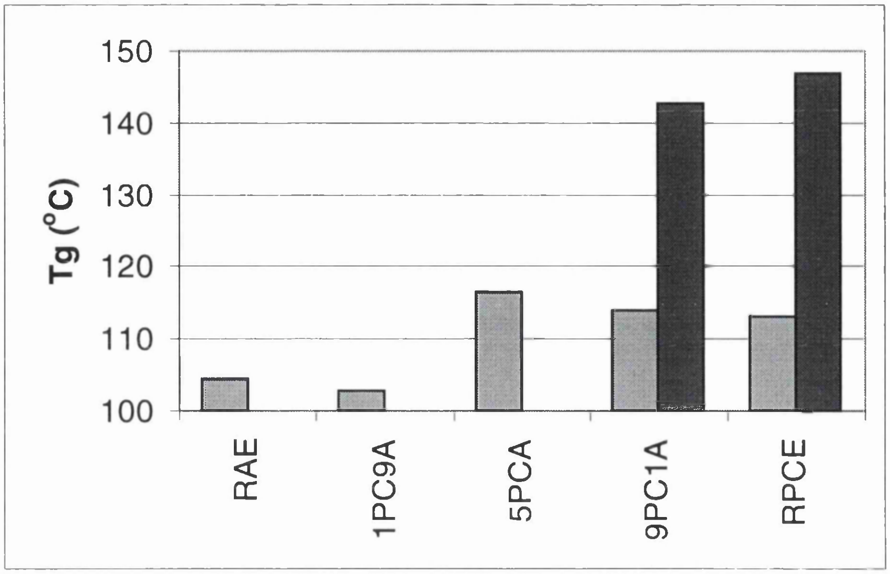


Figure 6.47 Histogram showing the glass transition temperatures of blends of recycled ABS and PC/ABS.

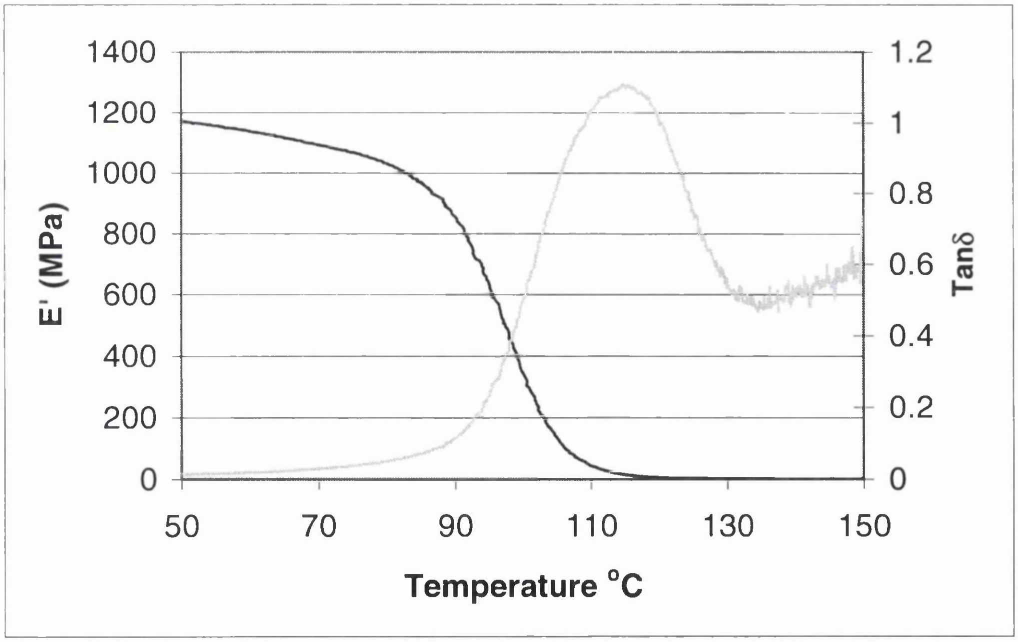


Figure 6.48 Graph showing the results from a DMTA test of the recycled blend 5PCA

is a critical amount of ABS that suddenly changes the T_g from two temperatures to a single T_g. The tanδ peak for 5PCA can be seen in Figure 6.48 and although it is clearly a single peak, it is broader, than those of its constituent peaks in Figures 6.39 and 6.40. This could suggest more than one T_g, due to phase separation in the structure, but would be difficult to detect due to overlapping of the tanδ curves.

Figure 6.49 compares the T_g's of each of the four plastics being studied with an equal blend of them all. A concern with blending so many different plastics could be total immiscibility that would be seen in DMTA results as several different tanδ peaks or one very broad one. However the tanδ peak for 25AHPPC is fairly narrow, especially when compared to that of 5PCA, indicating that the four plastics mixed well enough to produce a single T_g. While this suggests a miscible blend, it may not necessarily be a compatible blend, which will be apparent in other measured properties. At 118°C, the T_g of the 25% blend is more or less the same as that of mPPO and is the same as an average T_g of all four constituent plastics.

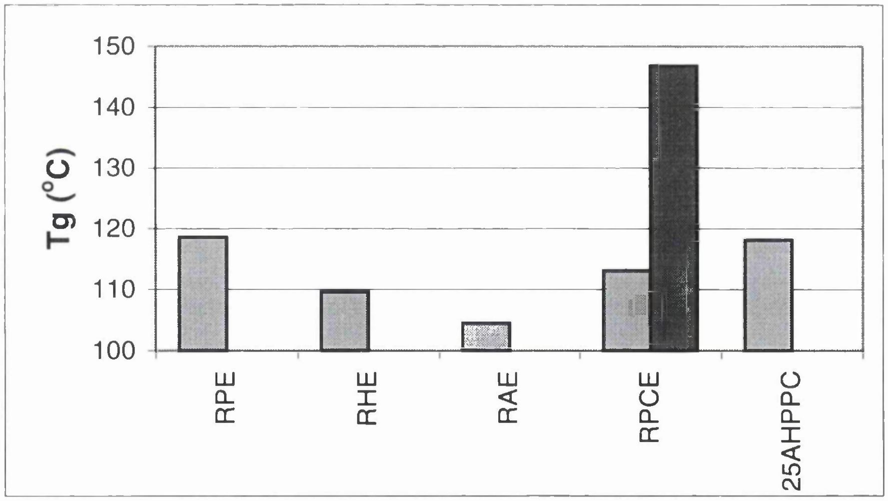


Figure 6.49 Histogram comparing the glass transition temperatures of recycled ABS, HIPS, mPPO and PC/ABS with a 25% blend of these plastics.

6.3.3 Comparison between a commercial scale recycling process with a laboratory scale recycling process.

Figure 6.50 Compares the T_g's of ABS, HIPS and their blends between two commercial and labaoratory scales of recycling processes. For both sets of results changes to T_g values are negligible and are more or less due to differences in blend proportions. The main difference between results is that the laboratory scale results are all several degrees lower than the commercial scale results. A simple explanation for this could be the position of the thermocouple within the heated zone of the DMTA. For example, some commercially recycled samples that were tested with the thermocouple near the bottom of the oven showed T_g's that were significantly lower than other samples that were tested with the thermocouple placed next to the sample as shown in Table 6.1. From this table, the T_g values obtained from different thermocouple placings show differences of approximately 16°C on average. Whereas the difference between T_g results of laboratory and commercial samples in Figure are approximately 6°C. Results from experiments with the thermocouple next to the sample are the most representative of the sample temperature and not different parts of the oven. Therefore it is possible that the laboratory recycled samples could have been tested with the thermocouple in a different place, although not necessarily at the bottom of the furnace.

Table 6.1 Table showing T_g's of various plastics comparing temperatures obtained at different positions of the thermocouple in the furnace of the DMTA

Material	T_g with thermocouple at bottom of furnace (°C)	T_g with thermocouple next to sample (°C)
RA	90	104
RH	95	110
RP	103	118
RPC	96 / 127	113 / 146

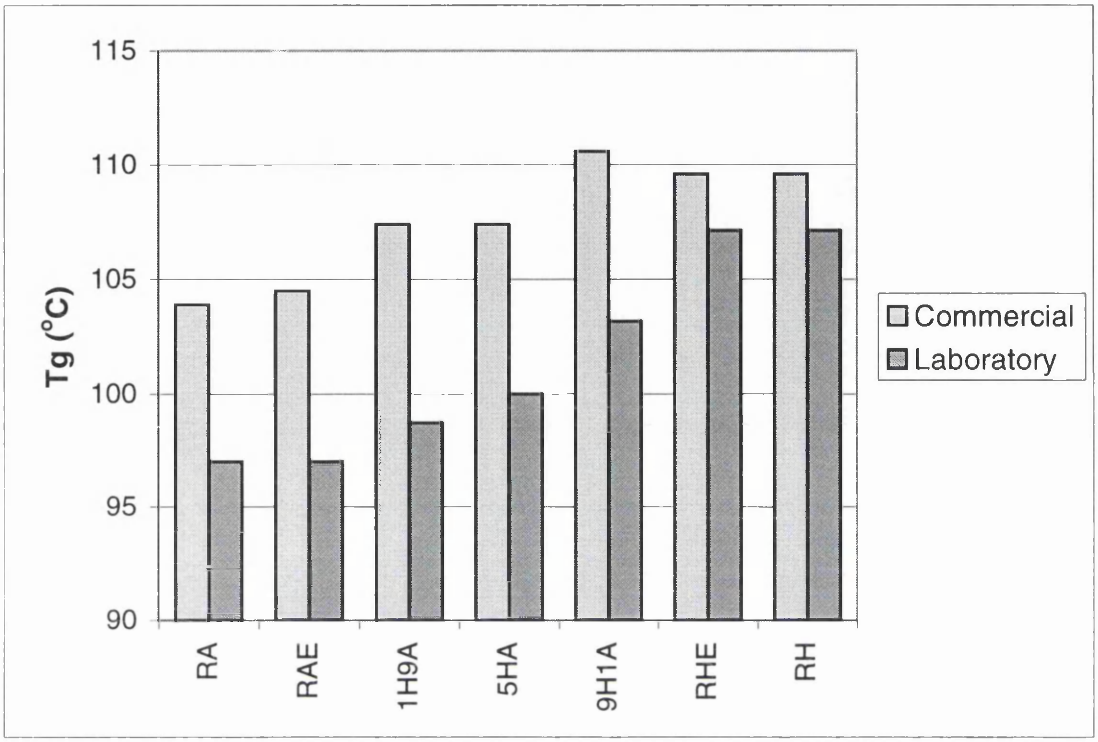


Figure 6.50 Histogram comparing the glass transition temperatures of various recycled ABS and HIPS and their blends, the samples from which were recycled using laboratory and commercial scale processing conditions.

6.4 VISCOSITY MEASUREMENTS

There were two types of results obtained from viscosity measurements;

(1) Steady Shear Rate Sweep Tests, which were performed at 200 °C

(2) Temperature Sweep at a Constant Shear Rate of $10^{-2}s^{-1}$, which were carried out over a temperature range of 200 – 300 °C.

Figure 6.51 shows typical results obtained from a steady shear rate sweep test of recycled HIPS and shows shear stress (τ) and viscosity (η) plotted against shear strain rate ($\dot{\gamma}\, s^{-1}$). At very low strain rates, τ appears to be increasing in a linear fashion, which means that η is constant, and is known as Newtonian behaviour. As $\dot{\gamma}$ tends towards $1s^{-1}$, the behaviour of the plastic changes and τ continues to increase, while η decreases. This is known as Pseudoplasticity and is a common response in polymer melts.

As $\dot{\gamma}$ continues to increase, both η and τ decrease, however, readings for the higher strain rates become erratic and viscosity measurements are not usually taken at such high strain rates. Conversely, in a realistic situation such as, an extrusion or injection moulding process, the strain rate could be around the order of 10^3 – 10^5 s^{-1} and so it could actually be useful to take viscosity measurements at such strain rates. However for this project viscosity measurements were taken at lower strain rates in the Newtonian region in order to make viable comparisons between the different plastic types and blends used for this study. The temperature sweep tests were carried out at a constant shear rate of $10^{-2}s^{-1}$, because as seen in Figure 6.51, it can be seen that this rate is in the Newtonian region. This was the case for all polymers tested, before the pseudoplastic behaviour occurred. Repeat tests found the accuracy of the viscometer to be about ±10%.

6.4.1 Recycled ABS, HIPS, mPPO, PC/ABS

The viscosities of recycled and virgin ABS, HIPS PPO and PC/ABS, measured at 200 °C and taken as the average of two tests, are shown in are Figures 6.52 – 6.55 respectively. From Figure 6.52, it is seen that there is no change to the viscosity of ABS due to the initial recycling process, as VA and RA have the same viscosities of 12.2 kPa.s (±10%). There is a difference however following the second recycling process and the viscosity of RAE at 8.4 kPa.s (±10%) is considerably lower.

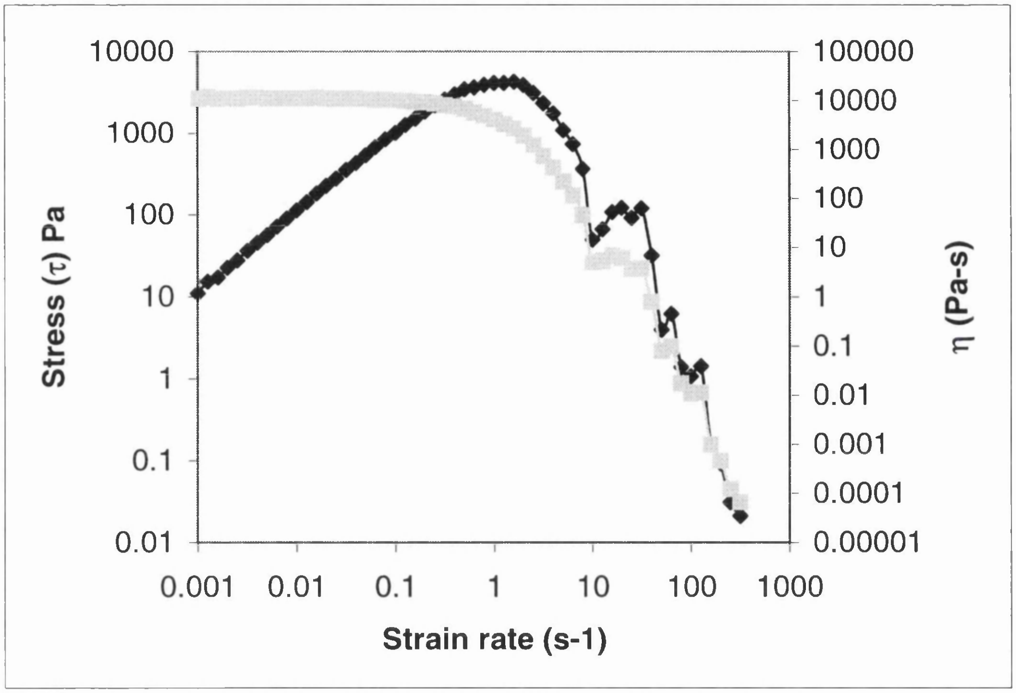


Figure 6.51 Shear stress and viscosity of HIPS plotted against shear strain rate at a constant temperature of 200°C

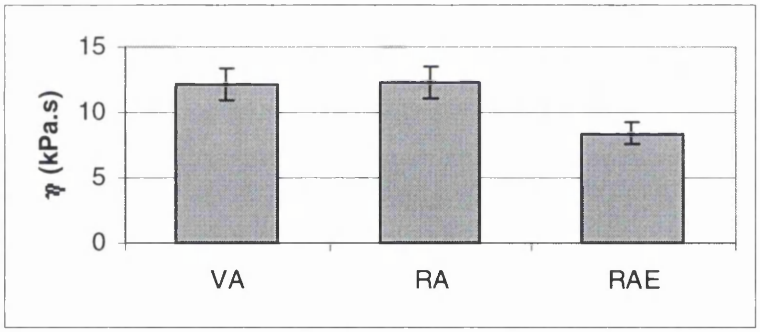


Figure 6.52 Histogram showing the viscosity at 200°C of virgin, recycled and recycled – extruded ABS

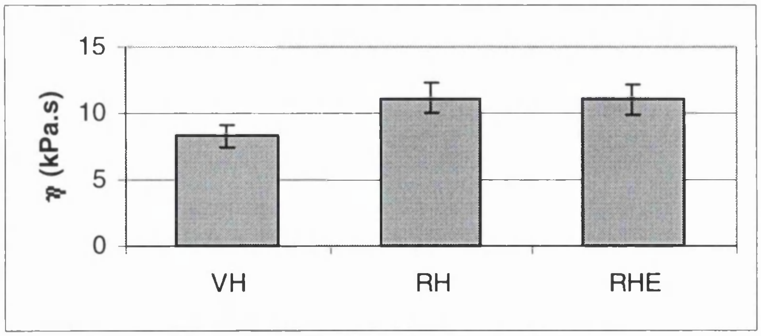


Figure 6.53 Histogram showing the viscosity at 200°C of virgin, recycled and recycled – extruded HIPS

The effects of recycling are different for HIPS as seen in Figure 6.53 and the viscosity of RH at 11.1 kPa.s (±10%) is almost 3 kPa.s more than that of VH. There is no further change to the viscosity of RHE indicating that extrusion has no further effect on the viscosity of HIPS.

The viscosities of recycled mPPO (Figure 6.54) are considerably higher than those exhibited by ABS and HIPS, which could probably be expected at the test temperature of 200°C due to differences between processing temperatures. Changes to the viscosities of mPPO due to differences in processing are negligible.

Figure 6.55 shows a considerable increase in the viscosity of PC/ABS following the second recycling process to 20.2 kPa.s (±10%), which is almost 6 kPa.s higher than RPC. This is a significant increase, as at 14.1 kPa.s (±10%), the viscosity of RPC is well below the margin of error of RPCE

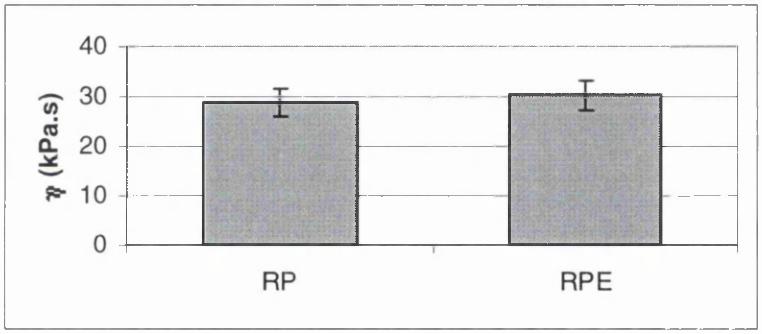


Figure 6.54 Histogram showing the viscosity at 200°C of recycled and recycled – extruded mPPO

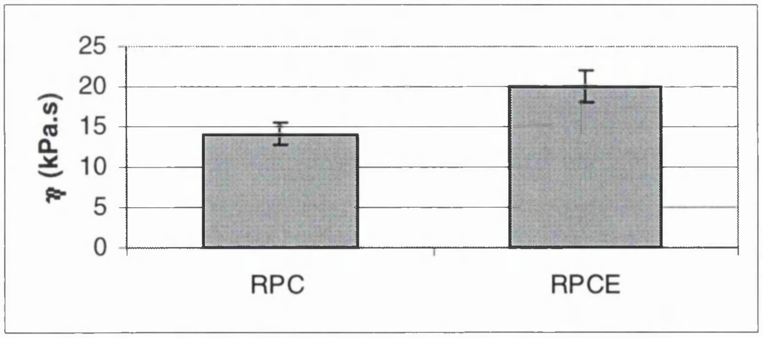


Figure 6.55 Histogram showing the viscosity at 200°C of recycled and recycled – extruded PC/ABS

6.4.2 Blends of ABS, HIPS, mPPO and PC/ABS

From Figure 6.56, it is seen that the blending of 10% ABS into HIPS has a negligible effect on viscosity at 200°C and at 11.4 kPa.s (±10%), the blend 9H1A is well within the accuracy margin of RHE. Blending 10% HIPS with ABS appears to noticeably increase the viscosity to 12.1 kPa.s (±10%) when compared with RAE. However the viscosity of 1PC9A is similar to the viscosity of RA (Figure 6.52), which could be an indication that the viscosity of RAE is possibly lower than would be expected, however several repeat tests have not shown any difference to this result. The blend 5HA displays the lowest viscosity at 10.0 kPa.s (±10%), which can be considered prominent although there is slight overlapping of accuracy margins with other blends.

The blends of HIPS and mPPO were subjected to temperature sweep tests as opposed to steady shear rate sweep tests, with the exception of 9H1P, in order to observe viscosities at their processing temperatures. From the graph in Figure 6.57 it can be seen that RP, RPE and 1H9P have similar viscosities at the start temperature of 200°C, with that of 5HP being slightly lower. As the temperature increases, the viscosities of all of the blends show an initial rapid decrease, which becomes less rapid as the temperature continues to rise, the blend viscosities tending towards similar values. At 280°C viscosities are lowest for all blends and as the temperature continues to increase, the viscosities also increase. This is probably an effect of degradation and possible crosslinking of polymer chains, which occur due to exposure to elevated temperatures and mechanical processes for periods of time and can cause the material to be less processable. Also shown in Figure 6.57 is the temperature sweep of the blend 25AHPPC, which is plotted here as it contains 25% mPPO. This blend appears to approximately follow the trend of the mPPO blends up until 230°C, after which the viscosity seems to increase slightly, again probably due to crosslinking or degradation of one or more of the components.

The viscosities of the HIPS/mPPO blends at 200°C are compared in Figure 6.58. From this histogram it appears as though the addition of 10% HIPS in mPPO and 10% mPPO into HIPS has no effect on viscosity and 9H1P and 1H9P have the same viscosities as their main constituent. What is interesting to see however, is the viscosity of 5HP, which at 26.5 kPa.s (±10%) is within the accuracy margins of the mPPO based blends but is much higher than the viscosities of the HIPS based blends.

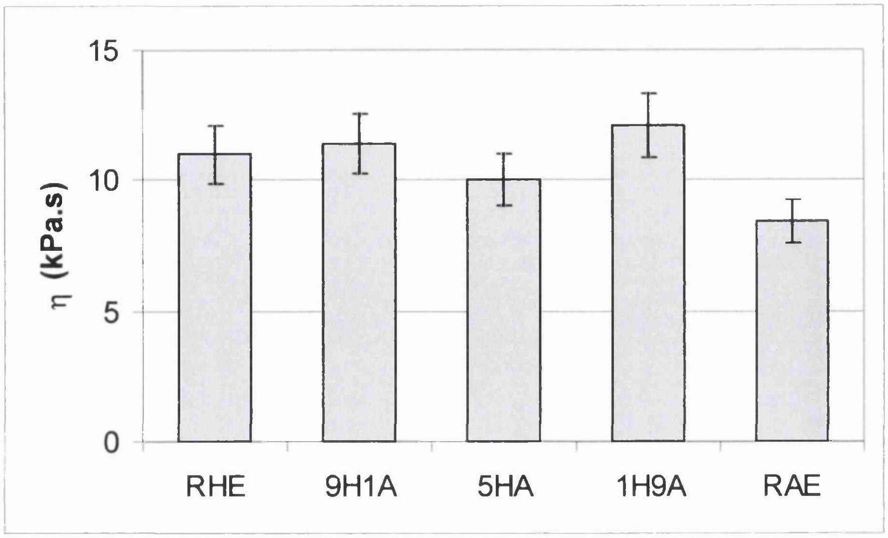


Figure 6.56 Histogram showing the viscosities at 200°C of blends of recycled ABS and HIPS.

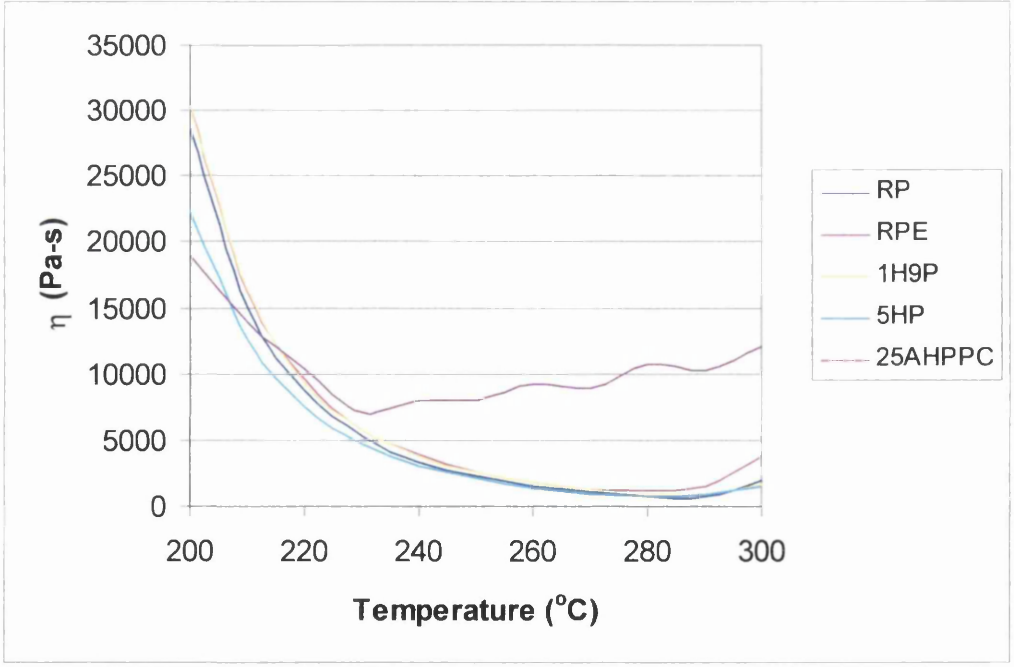


Figure 6.57 Graph showing Temperature Sweep tests for HIPS/mPPO blends at a constant shear rate of $10^{-2}s^{-1}$, over a temperature range of 200 – 300 °C.

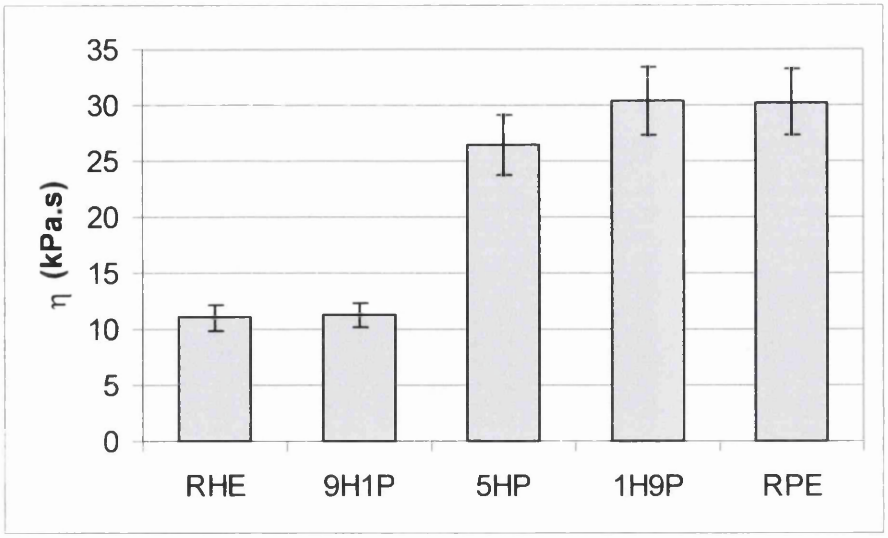


Figure 6.58 Histogram showing the viscosities at 200°C of blends of recycled HIPS and mPPO.

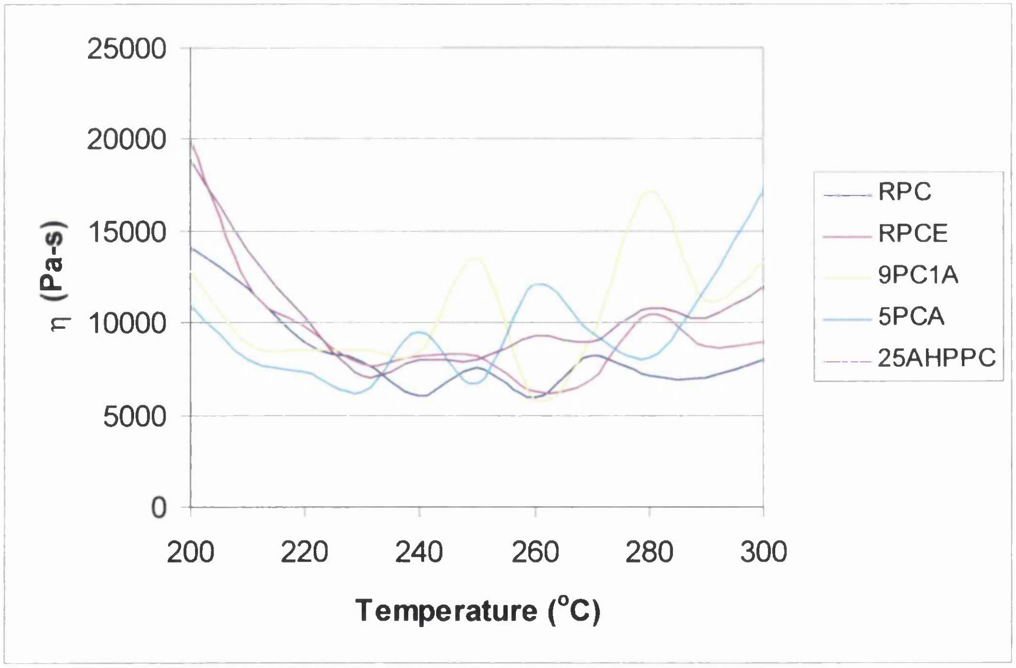


Figure 6.59 Graph showing Temperature Sweep tests for ABS/PC/ABS blends at a constant shear rate of $10^{-2}s^{-1}$, over a temperature range of 200 – 300 °C.

Temperature sweep tests were also carried out on blends of ABS with PC/ABS, with the exception of 1PC9A, and are compared in Figure 6.59. These results are also compared with the temperature sweep of the blend 25AHPPC. From this graph, it can be seen that the initial viscosities of RPC, 9PC1A and 5PCA at 200°C are fairly close and that of RPCE is significantly higher. As the temperature increases, the viscosities of each blend and recycled plastic decreases and at 230°C they all appear to have viscosities fairly close together. At temperatures above 230°C however, the only consistent behaviour is that all blends give erratic results as the temperature increases, the biggest differences being seen in the 9PC1A and 5PCA blends. This is likely to be due to the thermal degradation of the ABS component, at temperatures above its thermal processing conditions.

Figure 6.60 compares the viscosities of ABS and PC/ABS blends at 200°C. From this histogram it appears that all three ABS/(PC/ABS) blends exhibit viscosities between 11-13 kPa-s which is actually comparable to the viscosity of RA. Although the blend 9PC1A, at a viscosity of 12.9 kPa-s (±10%), is well below the viscosity of RPCE, it does actually overlap accuracy margins with RPC. Therefore as the results of these blends appear to be comparable with RA and RPC, the viscosities of RAE and RPCE do appear to be slightly unexpected and RAE has an unexpectedly low viscosity at this temperature, whereas RPCE appears to be unexpectedly high.

Figure 6.61 compares the viscosities of recycled ABS, HIPS, mPPO and PC/ABS with an equal blend of the four plastics. There appears to be quite a difference between the highest and lowest viscosities at 200°C, RPE exhibiting the highest viscosity and RAE the lowest. This is probably due the difference between processing temperatures. The viscosity of the 25AHPPC blend is more comparable to RPCE and at 19.0 kPa-s (±10%), this is slightly higher than the average viscosity (17.4 kPa-s) of all four plastic types.

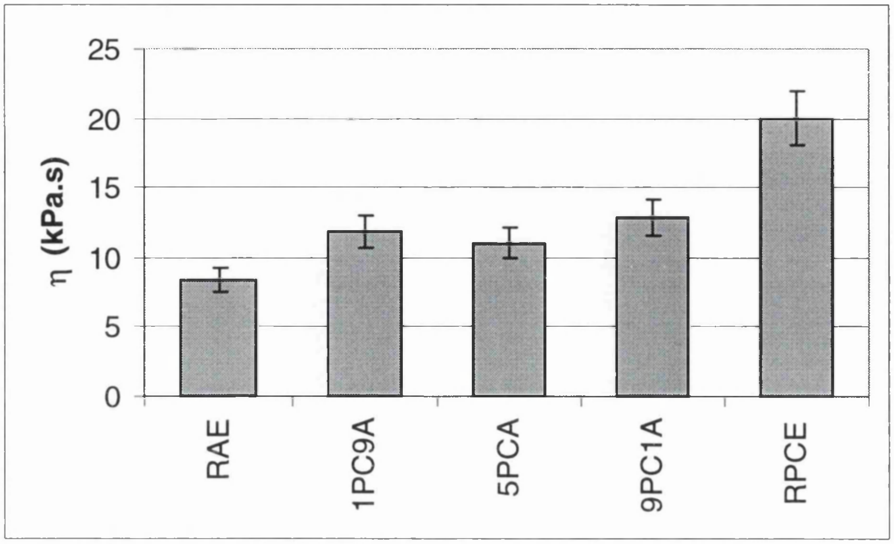


Figure 6.60 Histogram showing the viscosities at 200°C of blends of recycled ABS and PC/ABS.

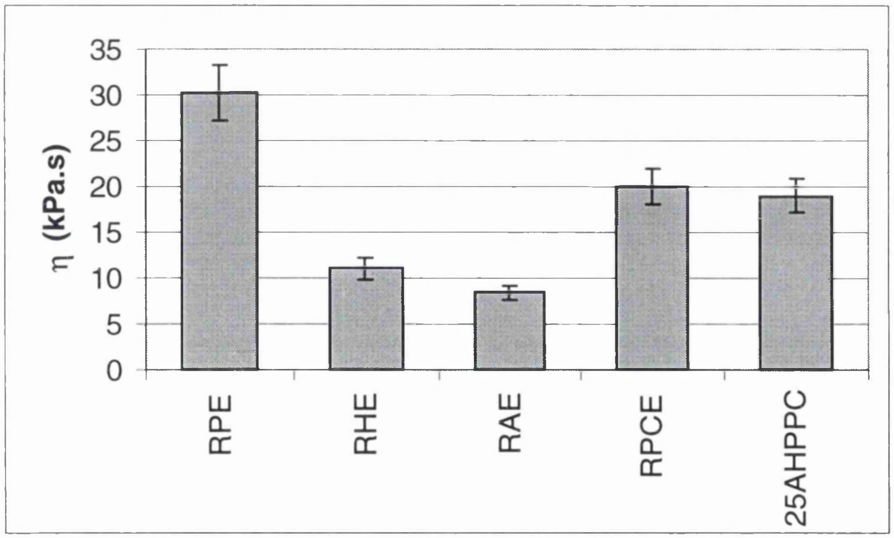


Figure 6.61 Histogram comparing the viscosities at 200°C of recycled ABS, HIPS, mPPO and PC/ABS with a 25% blend of these plastics.

6.5 MOLECULAR WEIGHT

For all plastics and blends tested, the gel permeation chromatography (GPC) produced molecular weight values for M_w M_n and polydispersity for each stage of the recycling process. All values were expressed as 'polystyrene equivalent' because the GPC system used by RAPRA Technology Ltd, was calibrated with polystyrene. Both M_w and M_n have an effect on various properties. M_n has more effect on the T_g and tensile strength whereas M_w has more effect on the viscosity and impact strength. Because the plastics and blends tested have not shown a great deal of change to the tensile strengths and because the T_g is only affected at very low values of M_n the results for M_n were not compared. However as there were more changes to impact strength and viscosity it was deemed more appropriate to compare values of M_w.

The weight average molecular weight (M_w) results are tabulated in Table 6.2 in order to compare any differences between the several stages of the recycling process, as well as any variations between the plastic blends. All results are the average of two tests and differences between results have enabled an accuracy range of ±2,000 to be determined.

Table 6.2 Weight average molecular weight of ABS, HIPS, mPPO, PC/ABS and their blends, from various stages of the recycling process.

Molecular Weight (Mw)				
Material	UPR	IM	Ex	Ex + IM
ABS	124,000	125,000	126,000	125,000
HIPS	172,500	181,500	183,500	180,500
mPPO	150,000	138,000	141,500	136,500
PC/ABS	61,000	53,500	61,200	57,150
9H1A				178,000
5HA			163,000	159,000
1H9A				134,000
9H1P				163,500
5HP			154,500	151,000
1H9P				141,000
1PC9A				114,500
5PCA			75,900	77,300
9PC1A				53,350
25AHPPC			118,500	125,000

The abbreviations from the table headings, which are used on the histograms in the subsequent section, are as follows:

UPR	Unprocessed Recyclate i.e. before or after granulation.
Ex	Extrusion i.e. following this process.
IM	Injection Moulded i.e. following granulation with no other processing.
Ex+IM	Extrusion and Injection Moulding i.e. the final product of all blends and some of the component plastics.

Processing details can be found in Section 5.2.

6.5.1 Recycled ABS, HIPS, mPPO, PC/ABS

The average weight molecular weight (M_w) of recycled ABS, HIPS, mPPO and PC/ABS were compared at different stages of the recycling process and are illustrated as histograms in Figures 6.62 – 6.65 respectively. The molecular weight distributions are found in Figures 6.66 – 6.69 respectively. Figure 6.62 shows that as all M_w results for ABS throughout the recycling process are within the calculated accuracy of ±2,000 the differences between results are considered insignificant. This can be confirmed by the M_w distributions for ABS in Figure 6.66, which shows little difference between molecular weight distributions for all stages of recycling

In Figure 6.63, the M_w of the recycled HIPS are compared with that of injection moulded virgin HIPS. From this histogram it can be seen that V-HIPS at 217,250 is considerably higher than the recycled HIPS. The M_w distributions in Figure 6.67 show that the virgin HIPS has a smaller proportion of lower molecular weight chains and more higher molecular weight chains. This could either be because the virgin HIPS is a different grade to the recylate, or it could be due to a breakdown of polymer chains of the recycled HIPS during the product lifetime and/or recycling process. UPR-HIPS exhibits the lowest M_w at 172,500 and has a narrower distribution curve. The M_w of the Ex-HIPS was the highest at 183,500, and although molecular weights for both injection moulded samples are lower than Ex-HIPS, they are at levels within the region of scatter and further changes are therefore not significant. The distribution curves at each process stage are similar (Figure 6.67) and display a slight shoulder towards the lower M_w chains, with a wider curve than for UPR-HIPS that includes a higher proportion of the higher molecular weight chains. This indicates that the increase in molecular weight of all processed recylate is due to

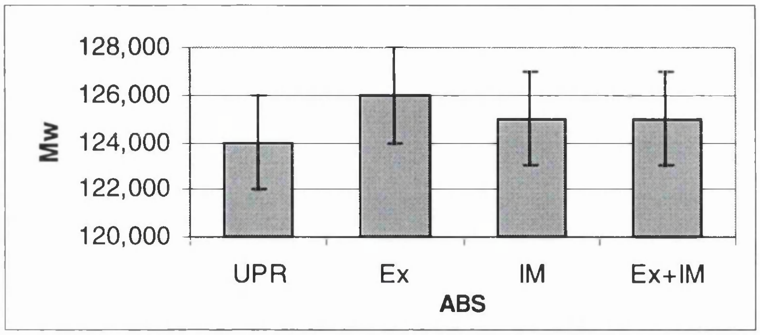


Figure 6.62 Histogram showing the molecular weights of recycled ABS at various processing stages

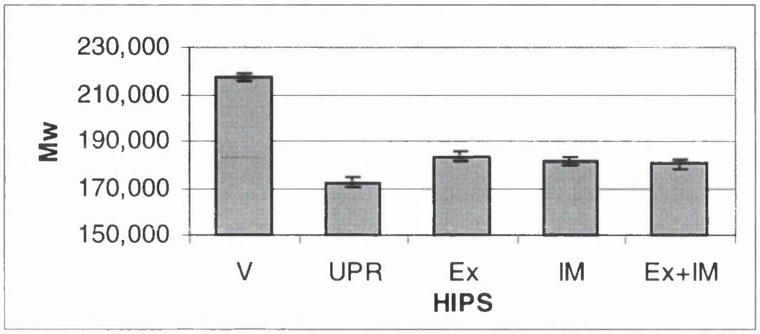


Figure 6.63 Histogram showing the weight average molecular weights of virgin and recycled HIPS at various processing stages

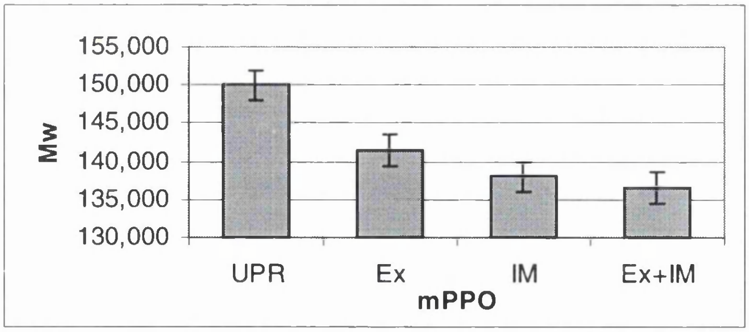


Figure 6.64 Histogram showing the weight average molecular weights of recycled mPPO at various processing stages

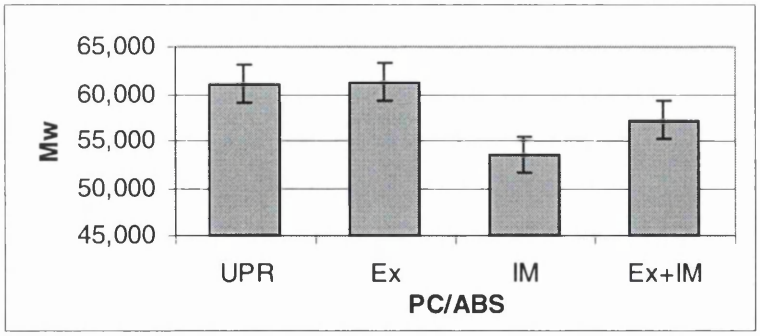


Figure 6.65 Histogram showing the weight average molecular weights of recycled PC/ABS at various processing stages

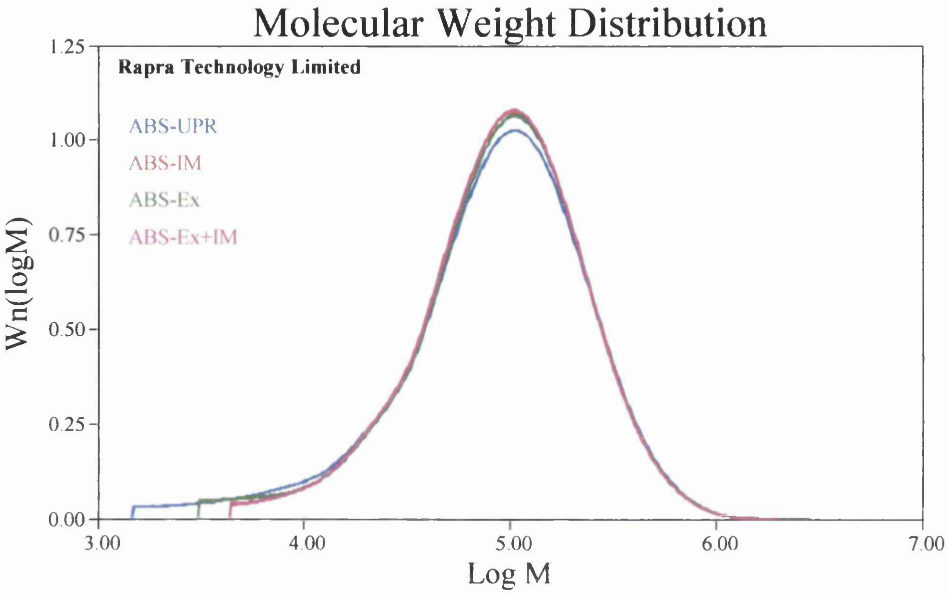


Figure 6.66 M_w distribution for ABS

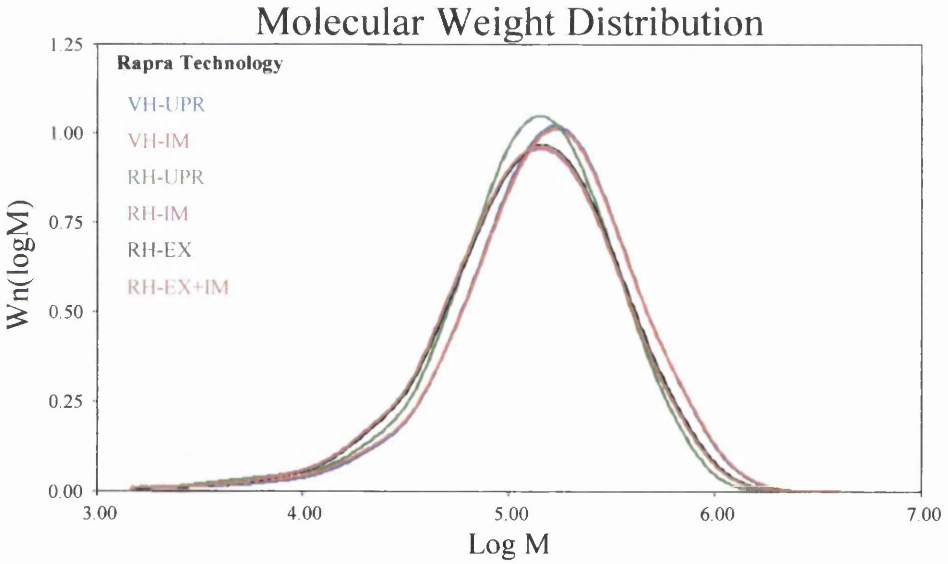


Figure 6.67 M_w distribution for HIPS

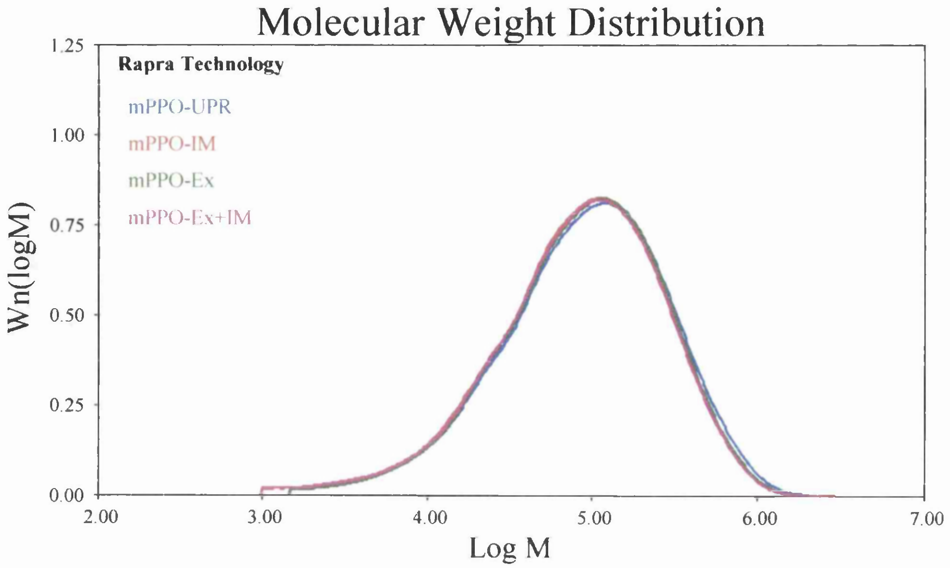


Figure 6.68 M_w distribution for mPPO

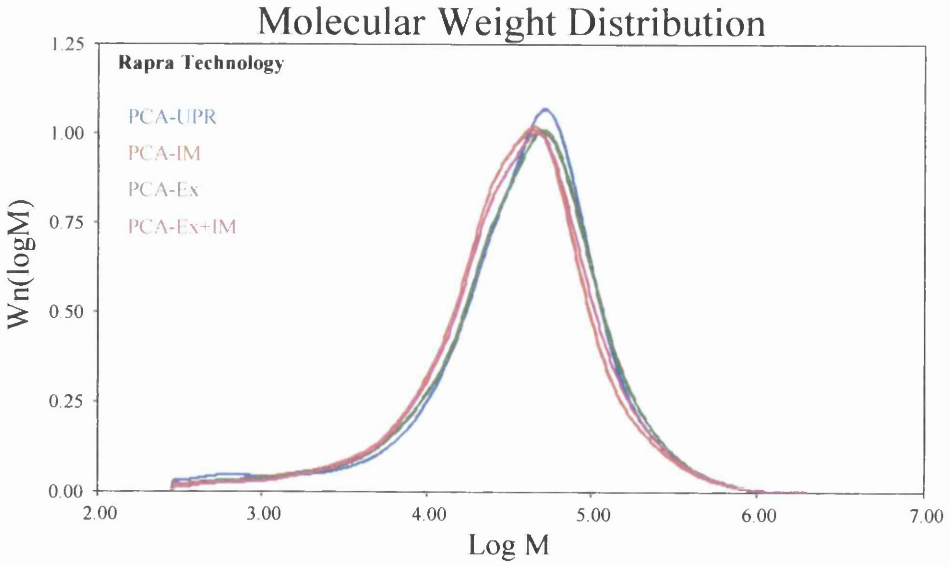


Figure 6.69 M_w distribution for PC/ABS

an amount of chain scission and cross-linking reactions and that the extent to which the material is thermally processed has negligible effects on this.

In Figure 6.64, the differences in M_w between the various processing stages of recycled mPPO appear to behave as what would be expected from continual thermal degradation throughout processing. UPR-mPPO actually exhibits the highest M_w of 150,000 and following the extrusion process the M_w falls to 141,500. The M_w of IM-mPPO at 138,000 is again considerably lower than that of Ex-mPPO, indicating that the injection moulding process was quite harsh to the material compared with the extrusion process. The M_w of Ex+IM-mPPO instead of being the same as IM-mPPO, as occurred with other plastics, is actually lower by 1,500, although this difference is sufficiently small to be considered negligible. This can be confirmed by studying the molecular weight distribution for mPPO (Figure 6.68), where although each curve appears to show the same distribution, there is a very slight shift of each curve to the left following each stage of the recycling process that would result in a progressively lower M_w.

For PC/ABS the extrusion process did not have any effect on M_w (Figure 6.65) and Ex-PC/ABS is almost the same as that of UPR-PC/ABS at 61,000. The distribution curve in Figure 6.69 shows that UPR and Ex have similar distribution curves, although that of UPR is slightly narrower, suggesting the possibility of chain scission and crosslinking during extrusion. Injection moulding had more of an effect on M_w in that the M_w of both IM and Ex+IM PC/ABS were significantly lower although that of Ex+IM-PC/ABS at 57,150 was still significantly higher than IM-PC/ABS (53,500). From the M_w distributions in Figure 6.69, the curves for both injection moulded samples displayed a shoulder to the left of the peak showing an increase of the proportion of chains of that molecular weight. Each curve also shifted towards the left when compared with UPR and Ex PC/ABS indicating the effect of chain scission, although this effect was less for Ex+IM suggesting that the extrusion process either reduced the extent of thermal degradation or promoted a small amount of crosslinking.

6.5.2 Blends of ABS, HIPS, mPPO and PC/ABS

The weight average molecular weights of blends of ABS, HIPS, mPPO and PC/ABS are compared by using results from Ex+IM as this was the only stage of the process that molecular weight experiments were conducted for all blends and recyclate (Figures 6.70-73). The distribution charts for each blend can be found in Figures 6.74-77. Any M_w values not compared in these histograms can be found in Table 6.4.

Figure 6.70 compares M_w of blends of ABS and HIPS from the Ex+IM stage of the recycling process. The effects of blending on M_w appear to approximately follow a linear law of mixtures with the Mw of the 90/10 blends showing significant changes but being close to their main constituent. The 50% blend displays a M_w of 159,000, which is almost in the middle of RAE and RHE. The differences between molecular weights of the HIPS/ABS blends can be seen quite clearly on the distribution chart in Figure 6.74. The blend 1H9A has a narrower distribution and lower overall molecular weight while 9H1A is of broader distribution and higher molecular weight, and 5HA is somewhat between the two.

The weight average molecular weights of blends of HIPS and mPPO are shown in Figure 6.71. At 141,000 the M_w of the blend 1H9P shows an increase that is more or less proportionally between those of RHE and RPE according to a linear law of mixtures. However the blending of mPPO into HIPS appears to reduce M_w by more than is proportional and at 163,500, the M_w of 9H1P is lower than what could be expected from a linear law of mixtures. The same can be said of the blend 5HP, which at 151,000 displays a M_w that is also less than proportionally in-between molecular weights of the two blends. Therefore it appears that the presence of mPPO in HIPS has a noticeable effect of lowering molecular weight. This can be seen in the molecular weight distributions in Figure 6.75, as all blends exhibit a slight shoulder towards the lower molecular weight, which is characteristic of mPPO as seen in Figure 6.68. This indicates an increase in the proportion of lower molecular weight chains and becomes stronger with an increase in the mPPO content.

Blending a small proportion of PC/ABS with ABS has the effect of lowering the M_w of the blend 1PC9A to 114,500, which when compared with that of RAE, is an almost proportional decrease according to a linear law of mixtures (Figure 6.72). Blending 10% ABS into PC/ABS also reduces M_w, and the blend 9PC1A exhibits a M_w of 53,350. This is contrary to what was expected, as this value is not between the molecular weights of its constituents. The M_w of 5PCA at 77,300 is also lower than what could be expected when considering a linear law of mixtures, and is closer to the M_w of RPCE than RAE, instead of being proportionally between the two. From the distributions in Figure 6.76, 1PC9A has a narrower distribution with a slight lower

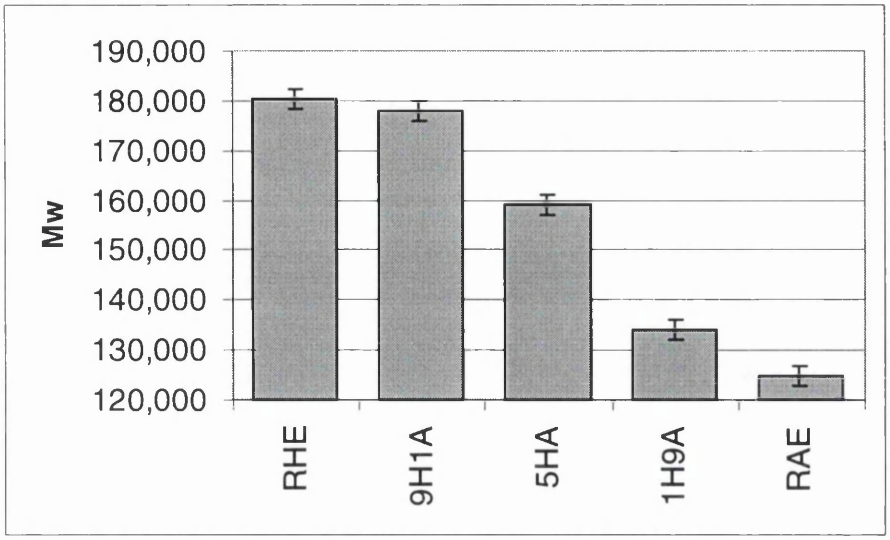


Figure 6.70 Histogram showing the weight average molecular weights of blends of recycled ABS and HIPS.

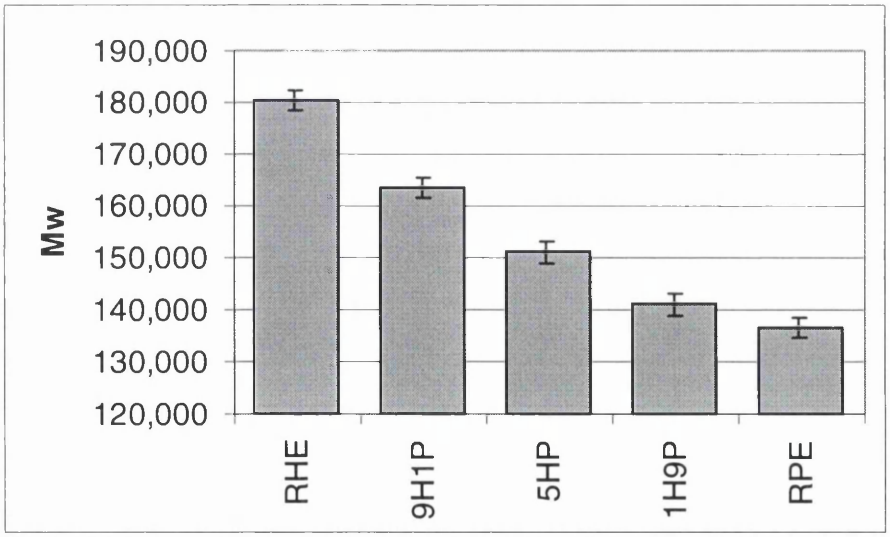


Figure 6.71 Histogram showing the weight average molecular weights of blends of recycled HIPS and mPPO.

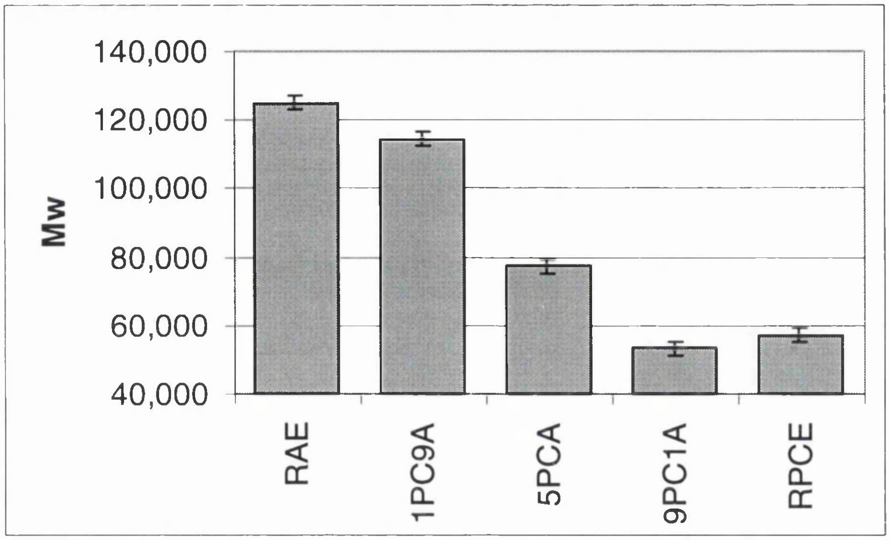


Figure 6.72 Histogram showing the weight average molecular weights of blends of recycled ABS and PC/ABS.

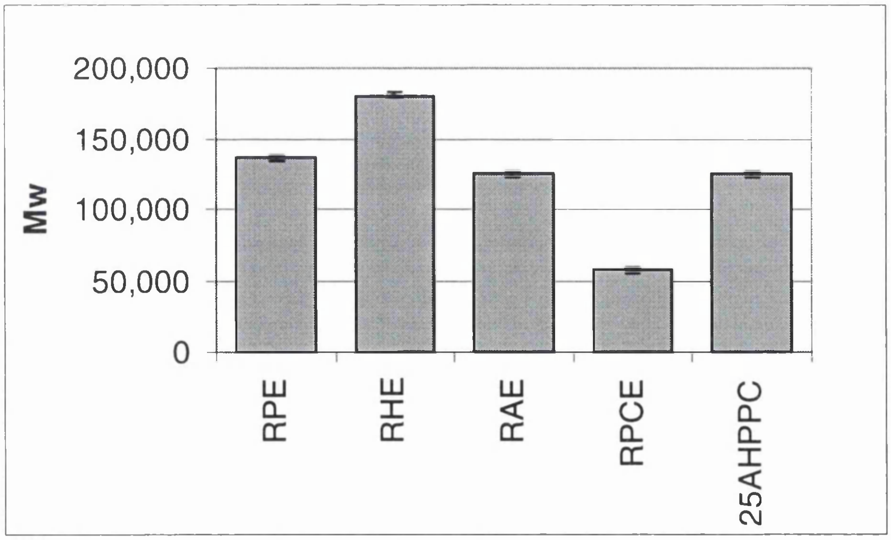


Figure 6.73 Histogram comparing the weight average molecular weights of recycled ABS, HIPS, mPPO and PC/ABS with a 25% blend of these plastics.

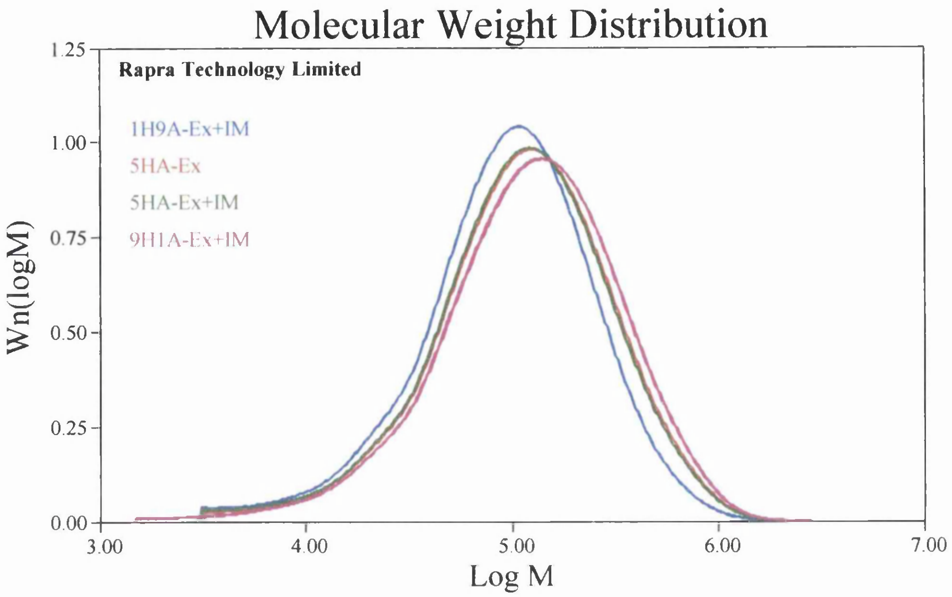


Figure 6.74 M_w distribution for blends of HIPS and ABS

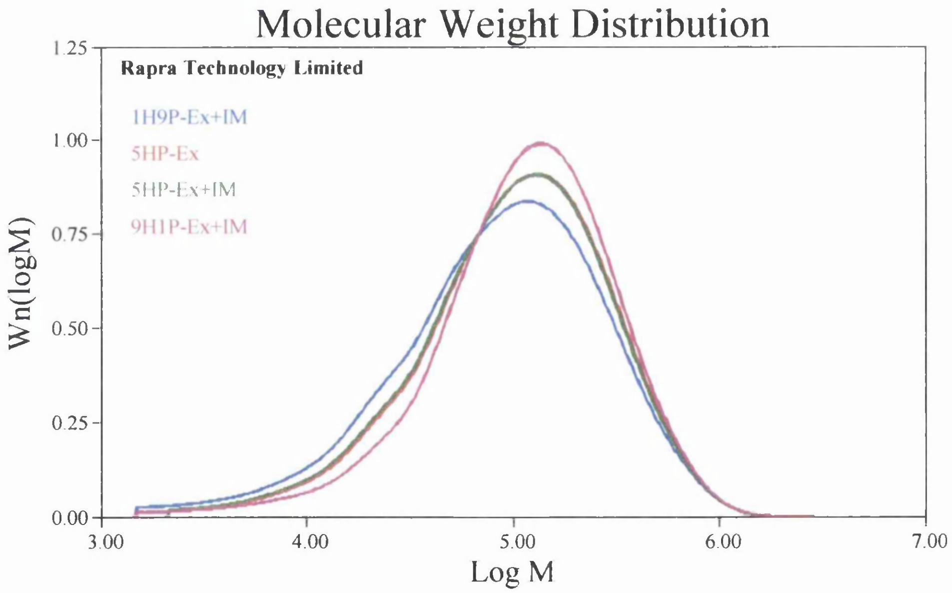


Figure 6.75 M_w distribution for blends of HIPS and mPPO

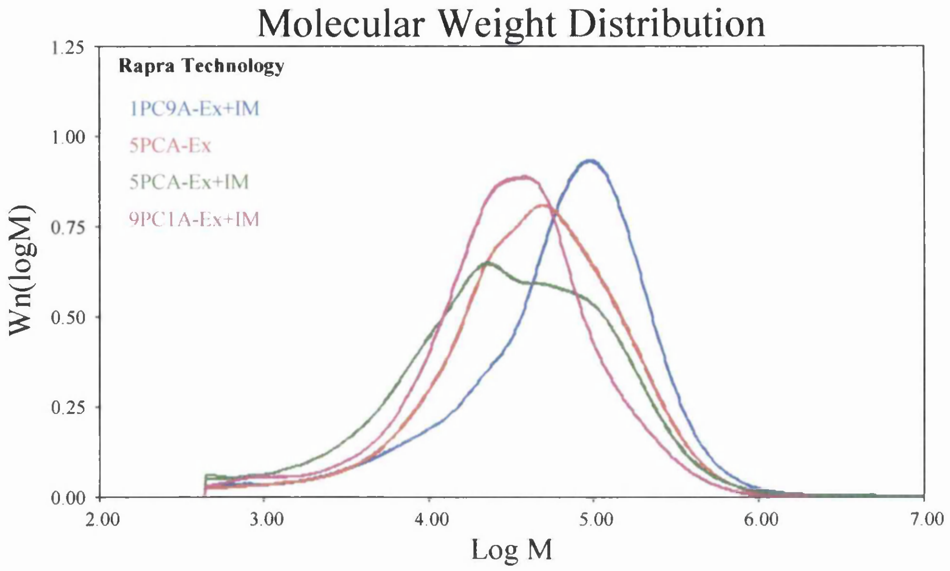


Figure 6.76 M_w distribution for blends of ABS and PC/ABS

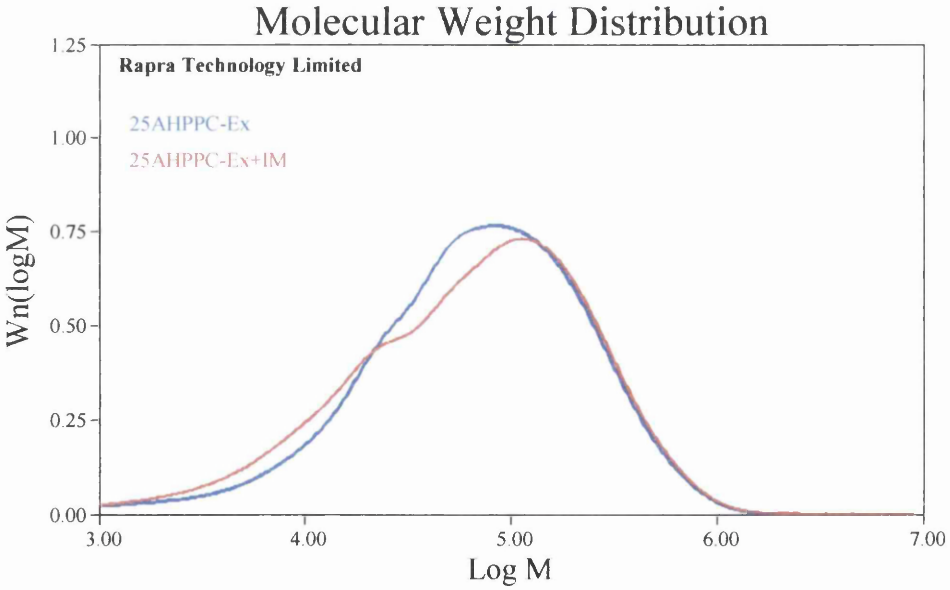


Figure 6.77 M_w distribution for a blend of ABS, HIPS, mPPO and PC/ABS

molecular weight shoulder but a significantly higher molecular weight peak. The blend 9PC1A has a wider distribution but much lower molecular weight. The blend 5PCA appears to show distinct distributions for the Ex and Ex+IM stages of the process. 5PCA-Ex has a major peak of high molecular weight with a low molecular weight shoulder while 5PCA-Ex+IM has a lower molecular weight peak with a high molecular weight shoulder indicating the possibility of some chain scission. However these distributions are broad enough that the differences between M_w values are negligible. In any case, it seems that blending ABS into PC/ABS has a detrimental effect on the molecular weight, whereas blending a small amount of PC/ABS into ABS does not have any further effect than from blending.

The weight average molecular weights of ABS, HIPS, mPPO and PC/ABS taken from the processing stage Ex+IM are compared with that of a 25% blend of the four plastics in Figure 6.73. From this figure it can be seen that the 25% blend displays neither the highest nor the lowest M_w and at 125,000 it is actually equal to that of RAE. This is also more or less equal to the average M_w of the four constituent plastics. The molecular weight distributions of 25AHPPC following extrusion and then injection moulding are shown in Figure 6.77 and appear very similar in the high molecular weight region of the distribution. The observed differences are in the lower molecular weight region with Ex+IM displaying a prominent shoulder, indicating possible chain scission, which is probably due to the breakdown of some components but not all.

6.6 MICROSCOPY OF PLASTICS

6.6.1 Bulk Microscopy of Recycled Plastics

6.6.1.1 Recycled ABS, HIPS, mPPO, PC/ABS

A SEM image of the cold fracture surface of recycled ABS is shown in Figure 6.78. From this image, it can be seen that the overall fracture surface was not entirely flat but appears to cover several different planes. However, the topography of the actual planes appears fairly flat and relatively smooth with a fair amount of micro-cracks over the surface. There are not too many prominent features, indicating that the structure of ABS is fairly well dispersed, although the surface does appear to be pitted in places indicating the debonding of particles within the matrix, which would appear on the opposite fracture surface. The particles that experienced debonding instead of fracture, which are probably the butadiene rubber phase, are not too well defined on this fracture surface so the most prominent are indicated with short arrows. The micro-cracks are likely to be crazes as ABS deforms by both shear yielding and crazing mechanisms. Shear bands are not visible in the SEM image, however the micro-cracks or crazes that are usually initiated and terminated between two butadiene particles, are highlighted by the longer arrows.

Figure 6.79 is a SEM image showing a cold fracture of recycled HIPS. From this image, the surface appears to be more or less in the same plane however the surface topography does not look entirely flat but exhibits ridges. The actual surface can only be described as ‘bobbly’, i.e. has the appearance of lots of small round particles or granules packed together. There are regions with quite a few micro-cracks, especially to the top left of the image (arrows (a)) that are probably crazing between particles. There are several debonding sites (arrow (b)) that can be seen throughout the surface, however they are quite small when compared with those seen on the previous image of ABS. The matching particles are highlighted by arrow (c), and can be seen as dispersed all over the surface. These particles appear much lighter than the rest of the surface and are thought to be the impact modifiying butadiene rubber that does not compatibly blend with the PS matrix. Another prominent feature is the geometric looking shapes towards the top right of the surface (arrow (d)). These particles are probably the colourant titanium dioxide (TiO_2) and are probably responsible for the larger crater-like pull out sites towards the top centre of the image (arrow (e)).

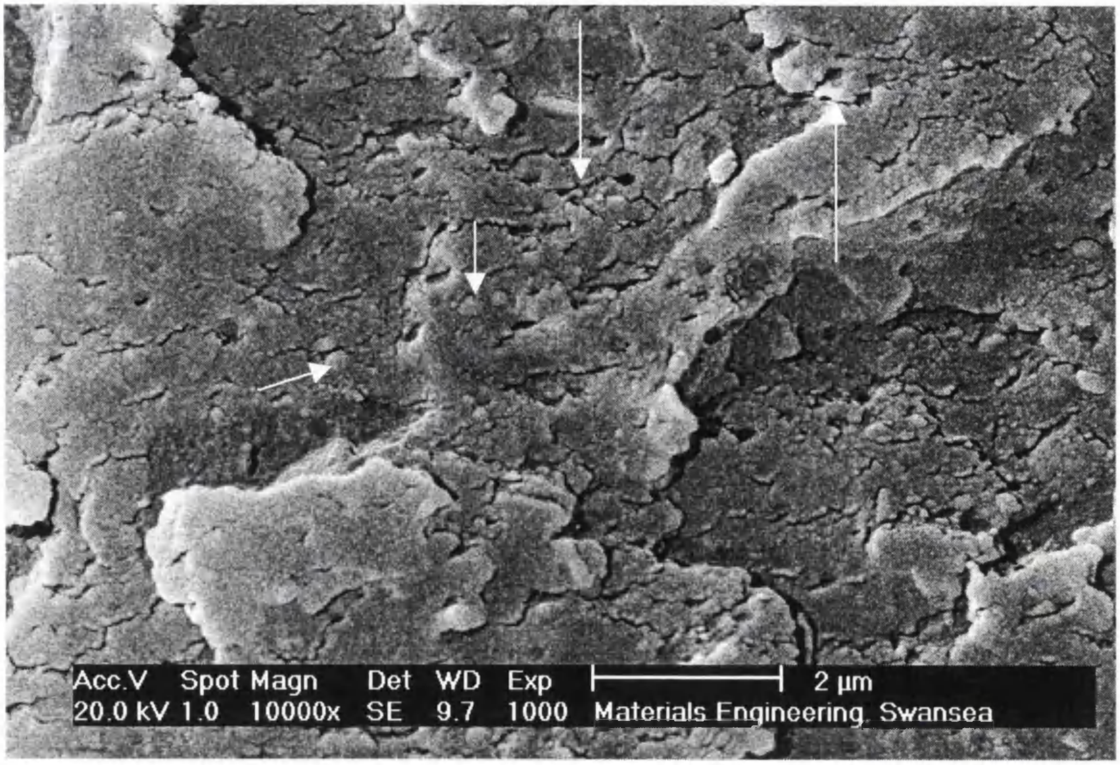


Figure 6.78 SEM image of a very brittle fracture surface of recycled ABS at magnification x10,000

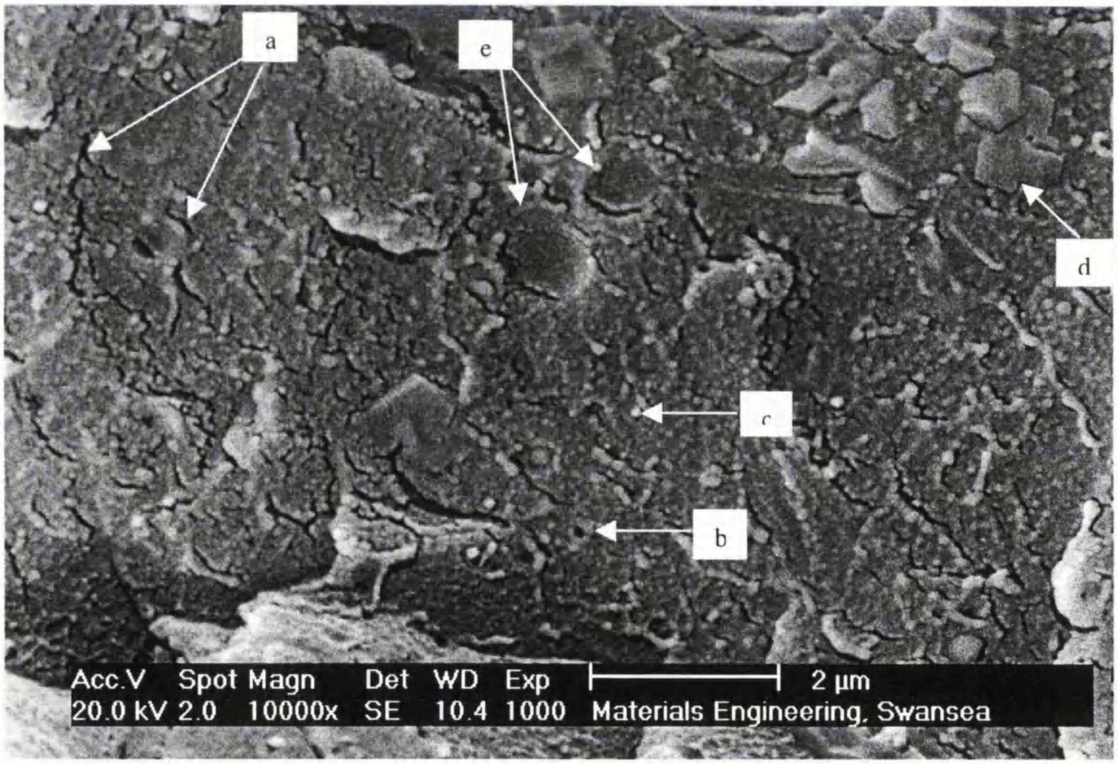


Figure 6.79 SEM image of a very brittle fracture surface of recycled HIPS at magnification x10,000

The fracture surface of mPPO is quite different as seen Figure 6.80. The structure is fairly prominent and appears to be mostly made up of debonding sites (longer arrows) of different sizes and round particles (shorter arrows), some within these sites. The topography appears to be more or less on the same plane. While many grades of modified PPO are blended with PS into a single phase that would be difficult to visually distinguish by scanning electron microscopy, the particles seen in Figure 6.80 suggest a blend of PPO and HIPS. The particles are likely to be the butadiene rubber component from HIPS, which will form a separate phase.

Figure 6.81 is a cold brittle fracture surface of recycled PC/ABS blend. The main surface seems to be multi-planar although appearing fairly flat on each plane. The main features of this surface are the debonding sites (longer arrows) on the topography and the fairly uniform round particles (shorter arrows) that are dispersed all over the surface within the matrix. These are probably the impact modifying particles form the ABS part of the blend, although they appear to be larger than those seen in the ABS sample.

6.6.1.2 Blends of ABS, HIPS, mPPO and PC/ABS

Figure 6.82 shows a cold brittle fracture surface of a recycled 50% HIPS/ABS blend. When compared with the bulk surfaces of its constituent plastics, the topography of this blend appears to show fewer and smaller features. The surface appears multi-planar, which is probably an effect of shear yielding. The appearance is less granular than HIPS but less smooth than ABS. There are some debonding sites (longer arrow) and a few round shaped particles (short arrow) situated within the matrix but the concentration of these is fairly low. However they are certainly what appears to be impact modifying rubbery particles present as is probably the case for the larger particle situated in the centre of the image. The general appearance shows a good deal of compatibility, but the fine surface ridges maybe suggest a small scale segregation of phases.

The features on the bulk fracture surface of the blend 5HP in Figure 6.83 also seem somewhat reduced compared with the constituent images, which could be an indication of blend compatibility. The topography appears a little flatter and the ridges that stood out on the image of PPO (Figure 6.80) are less prominent. The main features are smaller round particles (short arrow) within the matrix with empty debonding sites (longer arrow) where the particle is on the opposite fracture surface.

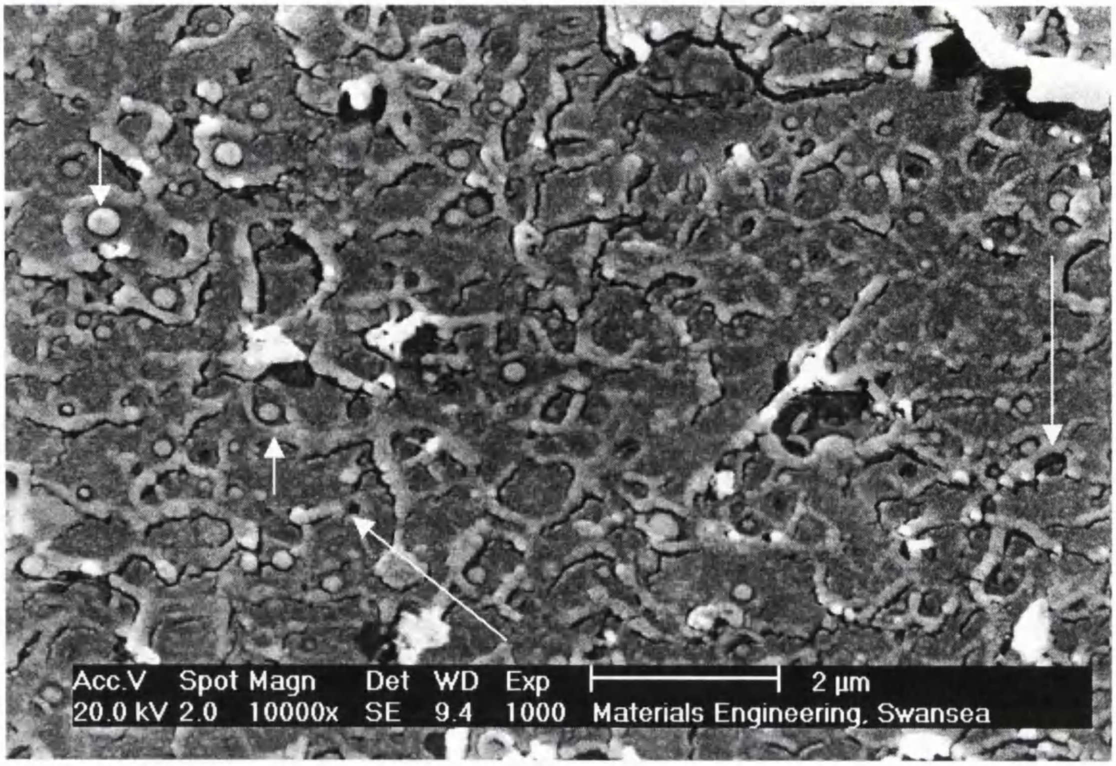


Figure 6.80 SEM image of a very brittle fracture surface of recycled mPPO at magnification x10,000

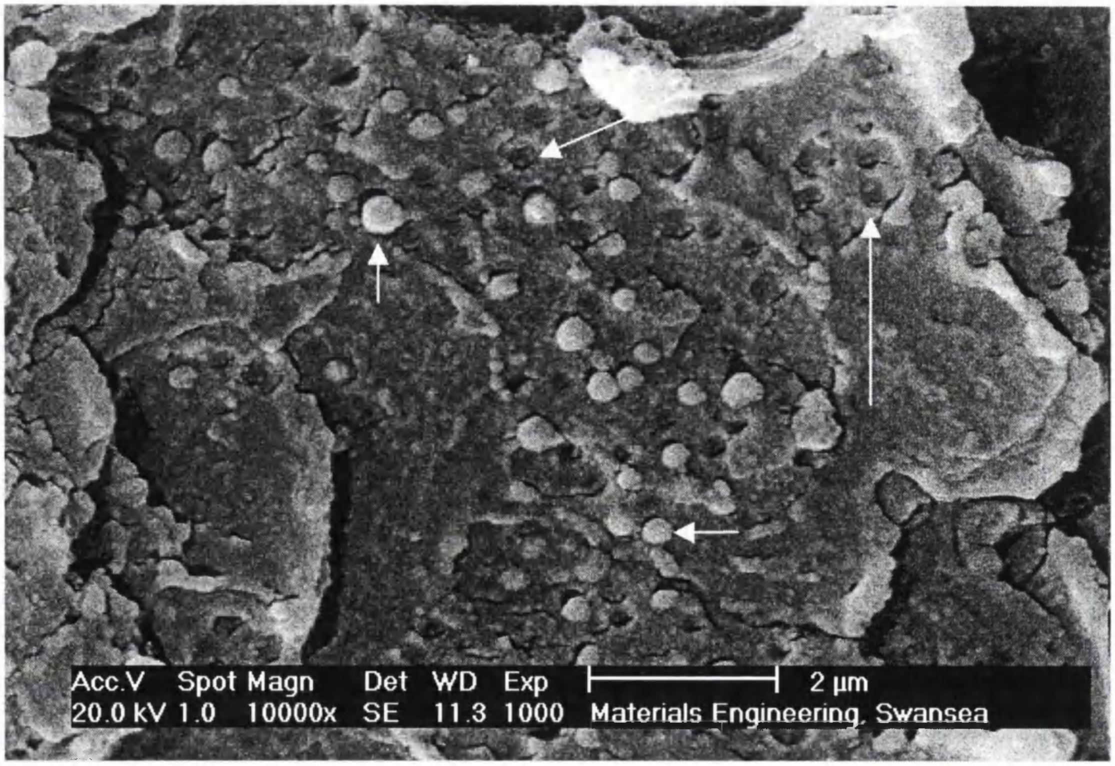


Figure 6.81 SEM image of a very brittle fracture surface of recycled PC/ABS blend at magnification x10,000

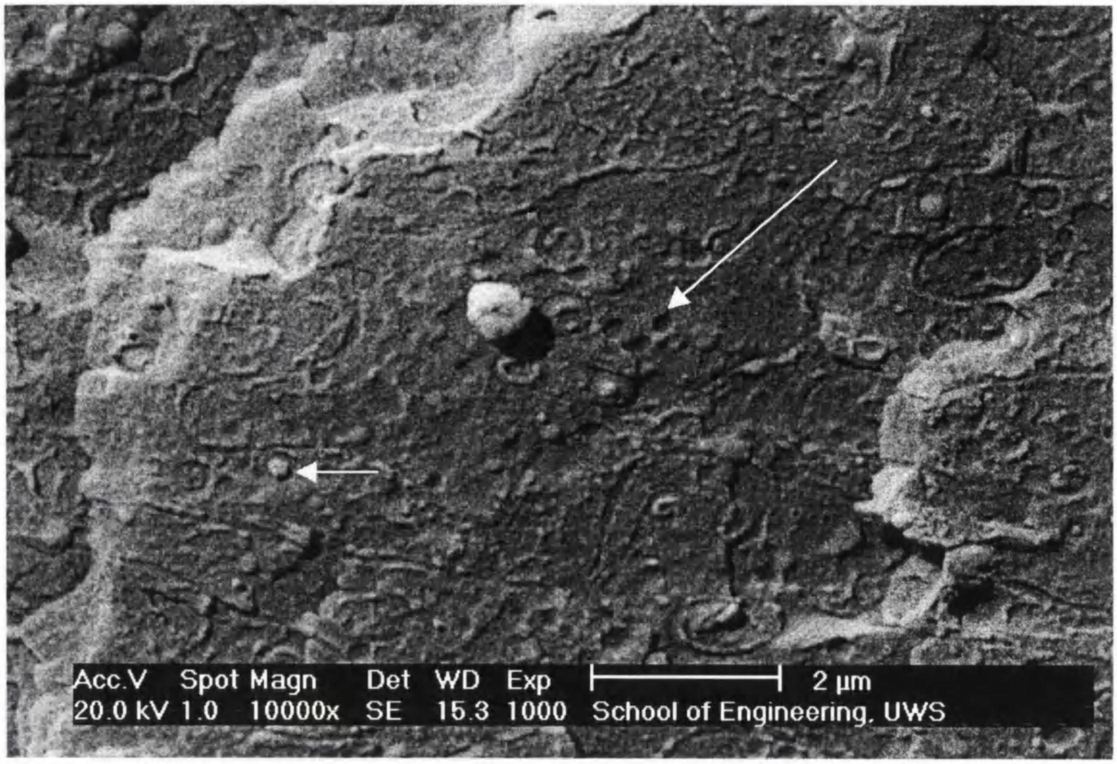


Figure 6.82 SEM image of a very brittle fracture surface of a recycled 50% HIPS/ABS blend at magnification x10,000

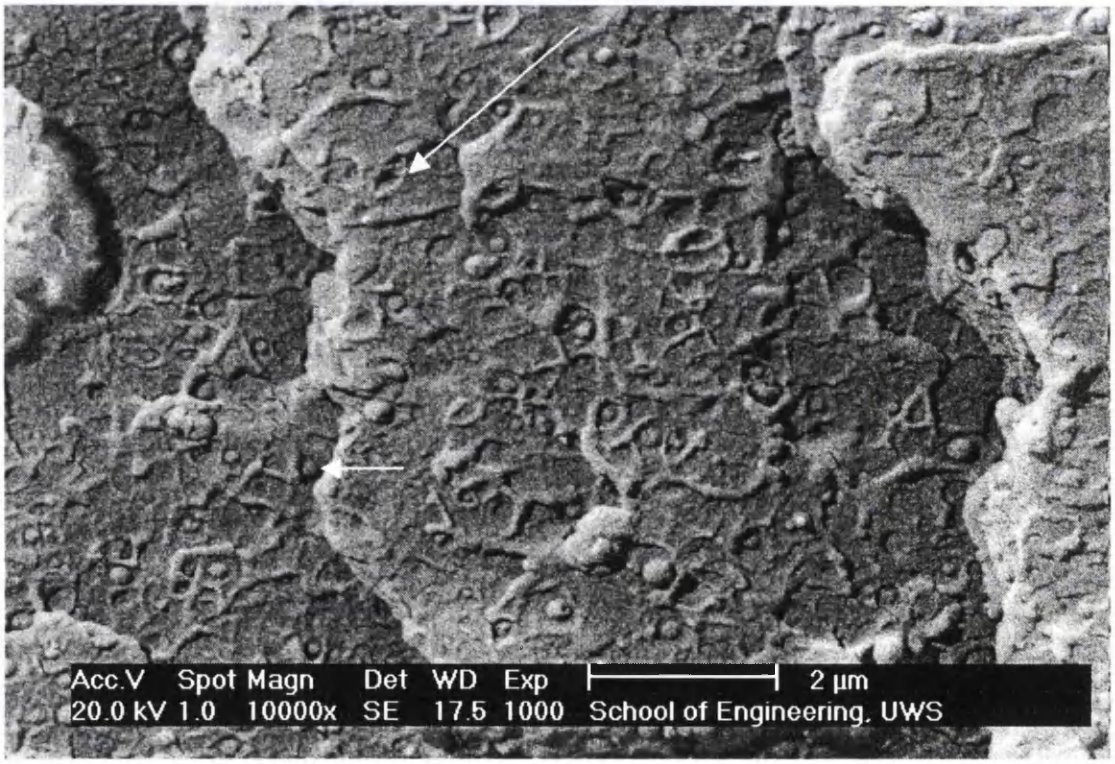


Figure 6.83 SEM image of a very brittle fracture surface of a recycled 50% HIPS/mPPO blend at magnification x10,000

Figure 6.84 is the bulk fracture of a recycled blend of 50% ABS with PC/ABS. The image shows a multi-planar surface, characteristic of both ABS and PC/ABS (Figures 6.78 and 6.81), that is also smooth looking, which is characteristic of ABS. There are no micro-cracks as in ABS and although there is the appearance of some particles (short arrow) and debonding sites (longer arrow), they are more thinly dispersed and there are fewer than the blend PC/ABS.

The bulk fracture surface of the blend containing 25% of recycled ABS, HIPS, mPPO and PC/ABS (Figure 6.85) does not appear to resemble that of any of the constituents. The topography is fairly rough and multi-planar, and looks to show grooves that resemble jigsaw pieces, although this is probably the contrast between planes. There are a few particles (short arrow) that appear to sit within the matrix and a few debonding sites (longer arrow) can also be seen. It would seem that there is maybe a very small-scale segregation of different phases, but impact modifying particles also seem to be present.

6.6.2 Fracture Surface Imaging

Images were taken of fracture surfaces from tensile and impact testing of various samples of the four plastic types used in this work as well as from some of the blends of these plastics. These images were studied in an attempt to better understand possible reasons behind any anomalies in results from experiments, or to show what occurred normally within the material as a result of testing to failure. As all images were taken following testing, the cross sectional fracture surface for each plastic will have undergone some deformation from a rectangular cross-section to a more concave shape.

6.6.2.1 Recycled ABS, HIPS, mPPO, PC/ABS

Figure 6.86 displays various fracture surfaces of VA, RA and RAE. Image (a) shows a typical tensile fracture surface of VA. Tensile results were discounted due to such voids being present. Image (b) is a typical impact fracture surface of VA that failed under normal conditions with no large voids or defects. The fracture surface appearance is relatively smooth, although there is more than one fracture plane indicating that micro-voids or inclusions as seen to the right of each plane probably had a role in crack propagation. A fairly low strain to failure indicates brittle fracture. Image (c) shows failure due to impact of RA. What is interesting to note is

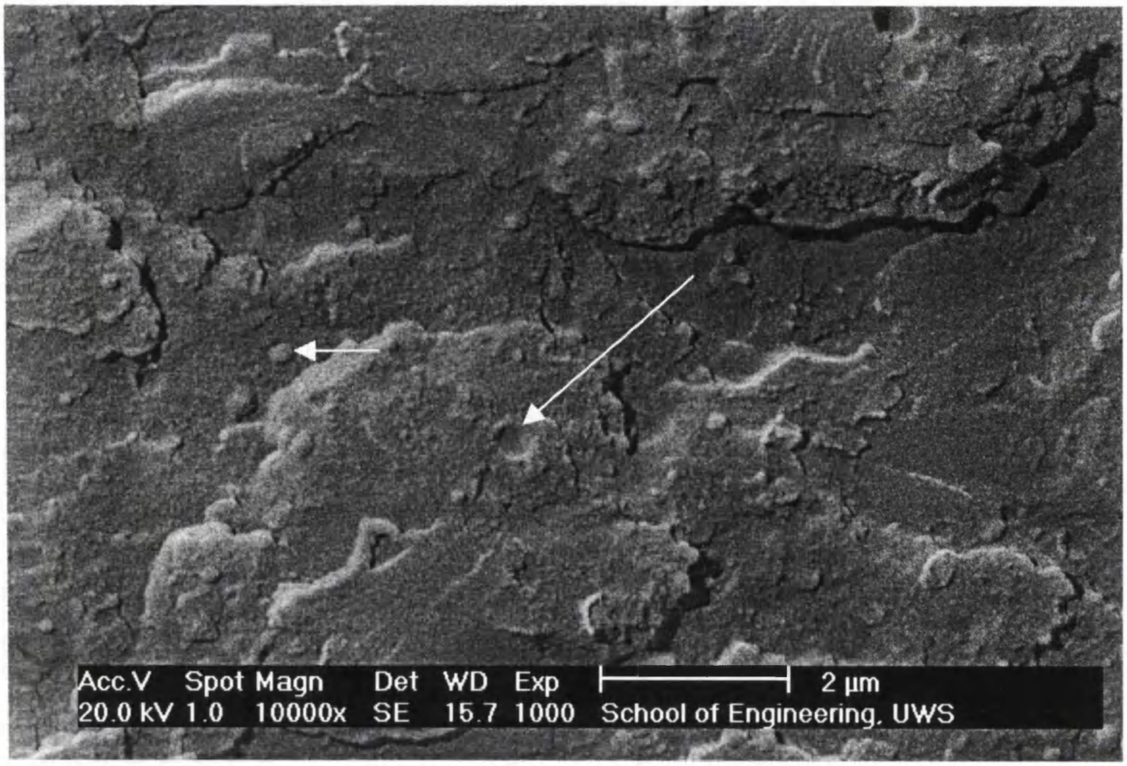


Figure 6.84 SEM image of a very brittle fracture surface of a recycled 50% ABS/PC/ABS bend at magnification x10,000

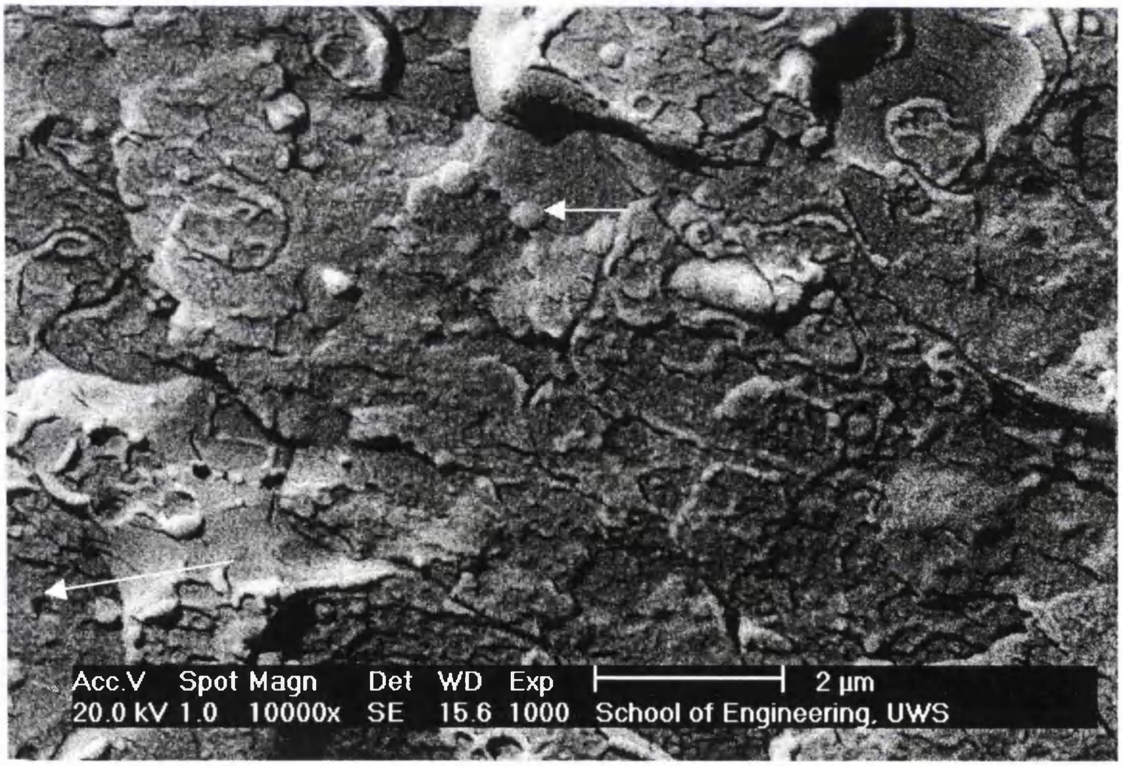
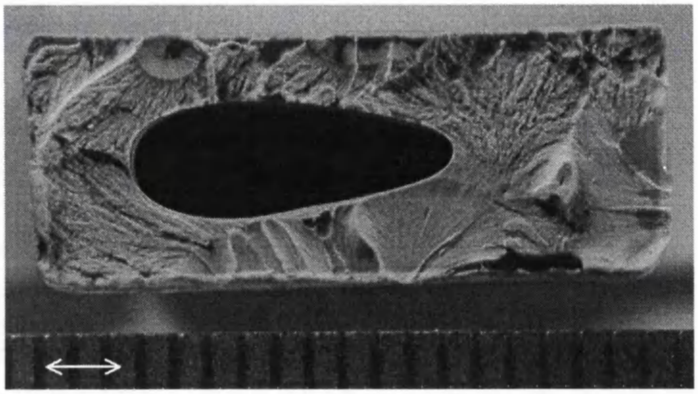
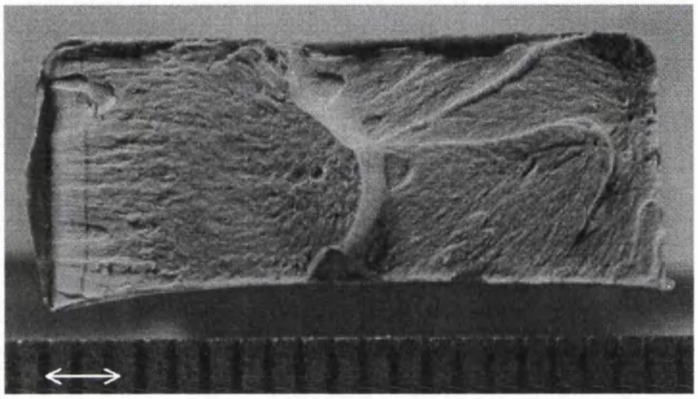


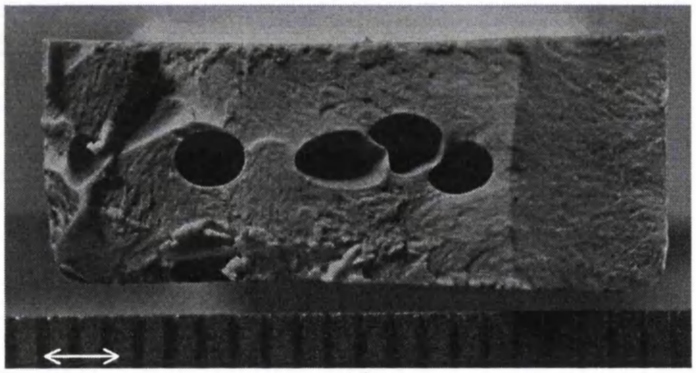
Figure 6.85 SEM image of a very brittle fracture surface of a blend containing 25% recycled ABS, HIPS, mPPO and PC/ABS at magnification x10,000

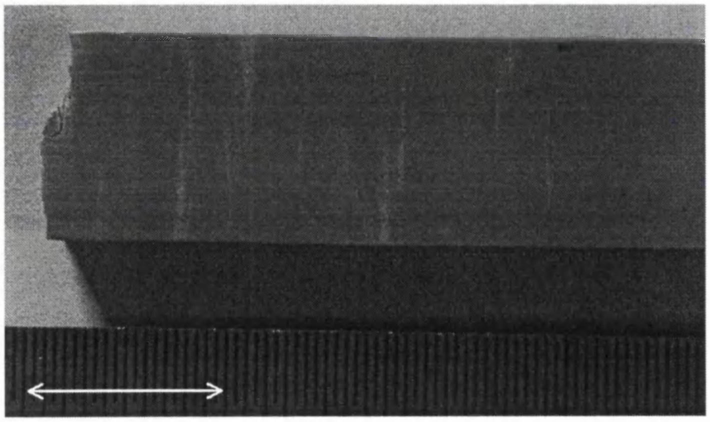


(a)



(b)


(c)



(d)

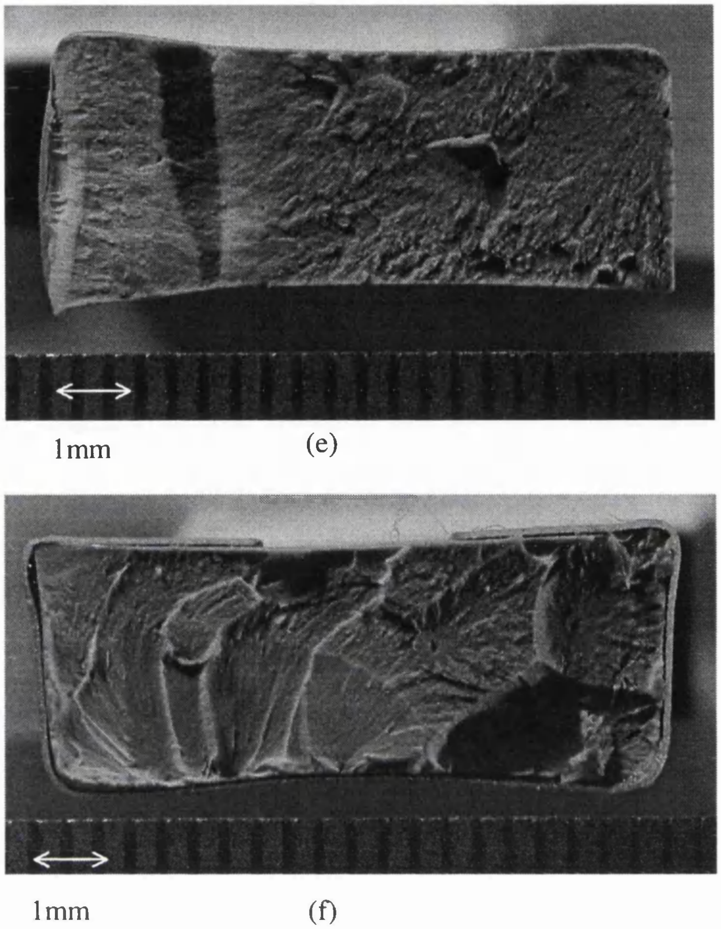


Figure 6.86 Tensile and impact fracture surface images of (a) VA tensile fracture showing void (b) typical impact fracture of VA with no voids (c) impact fracture of RA showing void (d) Side view of tensile RA showing crazes along gauge length (e) impact fracture of RAE (f) tensile fracture of RAE

that all VA samples displayed one large void while all RA samples displayed several smaller voids on both impact and tensile fracture surfaces.

Image (d) shows a side view of an RA tensile test sample with stress whitening bands along the gauge length. The bands, which look whiter than the original sample colour, are initially the result of the shear yielding deformation mechanism that occurs in ABS that can develop into crazes as the sample is continually deformed. Failure of the sample occurs at the site of the first craze to propagate sufficiently to cause catastrophic failure and following failure, some crazes can be seen to have developed into larger cracks that probably didn't quite propagate enough to cause failure. The stress whitening bands were observed only in samples of ABS (VA, RA, and RAE) and could be seen clearly during and after testing.

Images (e) and (f) are typical impact and tensile fracture surfaces of RAE showing no voids. It is not entirely known exactly what the darker part is of the sample in image (e), although it could be degraded material from the injection moulder, despite rigorous purging. This region appeared in quite a few samples, however it has had no effect on test results as would occur with degraded material within samples. Image (f) indicates that failure has occurred due to what appears to be micro-voids within the sample. These can be spotted due to circular cracks radiating from the source of weakness.

Fracture surface images of VH, RH and RHE are found in Figure 6.87. Image (a) shows the relatively smooth surface of VH, typical of both impact and tensile specimen, with the direction of fracture appearing to flow from the original source of fracture at the top right hand corner of the sample. There appear to be no defects such as voids or inclusions in the sample unlike RH, which is shown in Figure 6.87 (b). Many samples appeared to contain amounts of rubbery like degraded material, which was the cause of failure for these samples. From the image in (b) the degraded material, which probably failed first, appears to be the source of crack propagation. This radiated out until catastrophic failure of the sample occurred and the remaining sample failed instantaneously. Despite being a relatively ductile material, the fracture surface is relatively smooth, which can be said for all HIPS samples. RHE also appeared to contain rubbery like material within samples as seen in Figure 6.87 (c), which is similar to that of RH despite the fact that these samples were processed at different times.

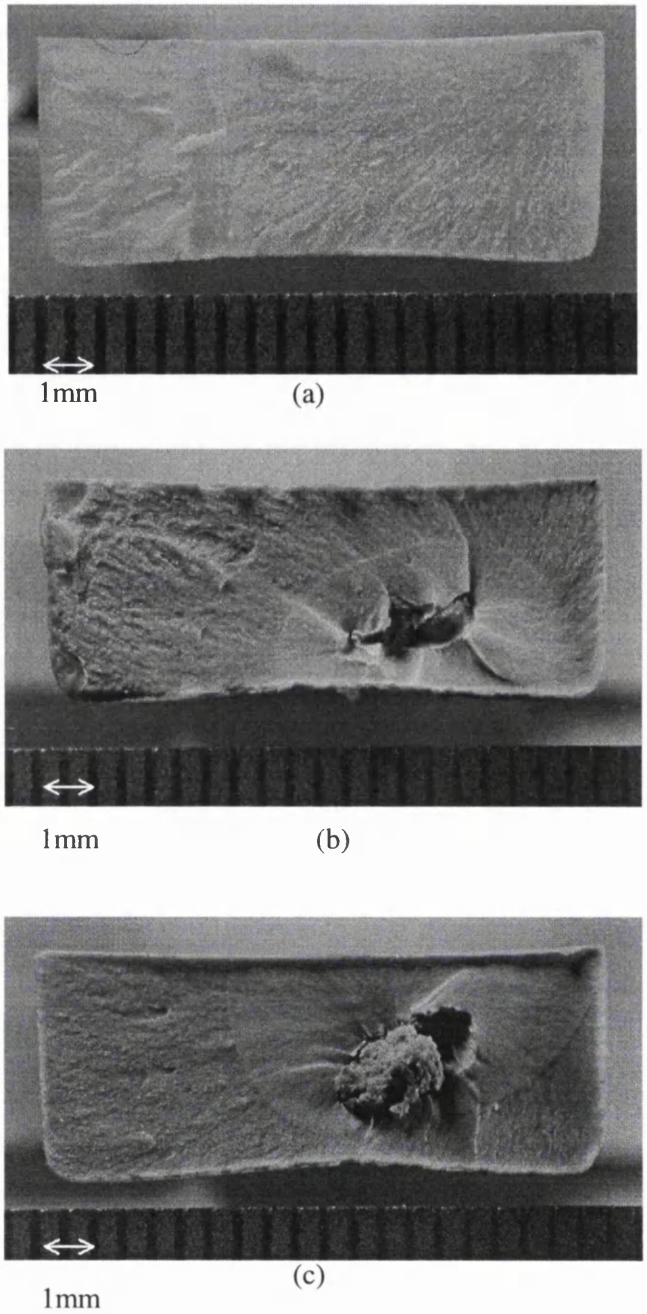


Figure 6.87 Tensile and impact fracture surface images of (a) typical impact fracture of VH (b) tensile RH showing impurity within the sample (c) RHE tensile fracture surface showing impurity inside the sample

Modified PPO was by far the most ductile material used in this study and indeed a typical fracture surface, as seen in Figure 6.88, looks more ductile than those of HIPS. While Figure 6.88 shows typical fracture of RP, there was very little variation between impact and tensile fracture surfaces of for both RP an RPE. The sample has no apparent defects and fracture appears to initiate from the surface at the bottom right hand side of the sample as the impact direction goes from right to left.

Images (a) to (c) in Figure 6.89 are typical fracture surfaces of RPC and RPCE. There are two types of fracture surface for each material as some samples failed due to large voids as seen in images (a) and (b), the results of such samples had to be discounted. Image (c) is typical of both RPC and RPCE and shows a rough looking surface that looks more ductile than samples containing air bubbles.

6.6.2.2 Blends of ABS, HIPS, PPO and PC/ABS

Images of fracture surfaces of all 50% and 25% blends are shown in Figure 6.90. Image (a) is a typical fracture of the blend 5HA. When compared with the fracture images of its two constituents it appears to be more or less in-between the two showing a rough surface in a mixture of rugged and flattish areas. Image (b) is a typical fracture surface of the blend 5HP, with failure being initiated at an inclusion in the sample. Part of the fracture surface immediate to the inclusion crack appears smooth, whereas the part further away is more rugged giving the appearance of a mixture of brittle and ductile fracture.

The blend 5PCA produced some fairly brittle looking fracture surfaces as shown in image (c). The main cause of fracture for this sample appears to be due to several small voids that were present on fracture surface of some samples. This was also a cause of fracture for some samples of 25AHPPC as shown in image (d), although these voids were slightly smaller and not so many as for 5PCA. Image (e) is a typical impact fracture surface of 25AHPPC and although fracture appears to have occurred over many different planes, the rough surface is because the samples were so brittle, parts of them practically shattered on impact.

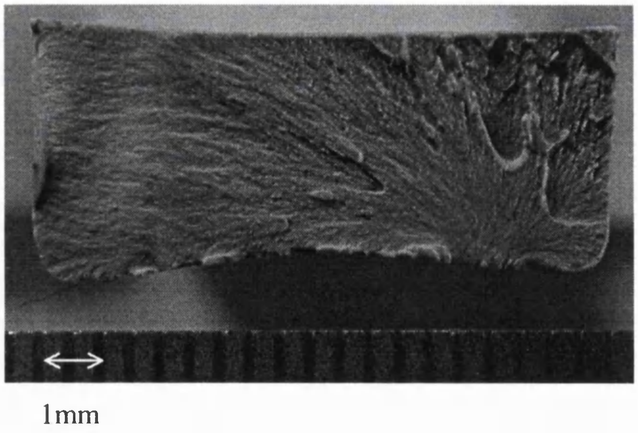


Figure 6.88 Impact fracture of RP, which is typical for both tensile and impact

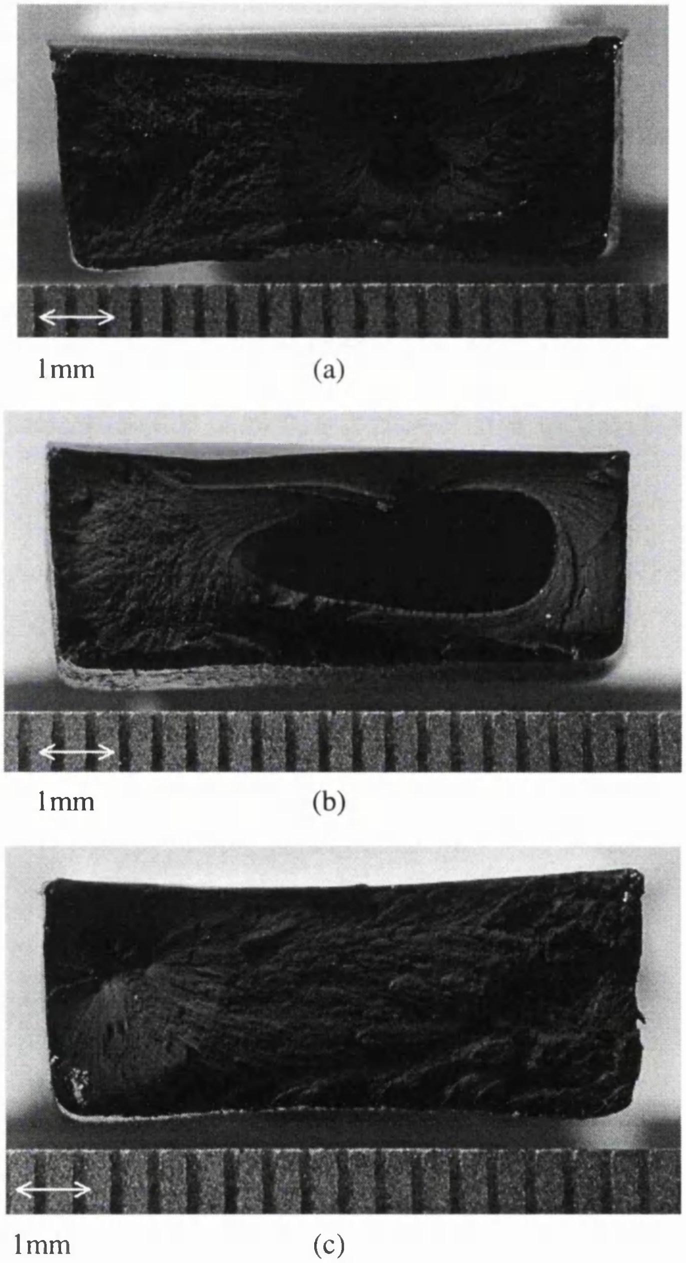
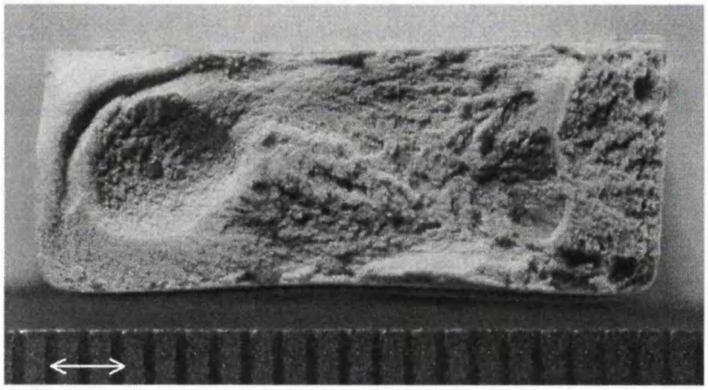
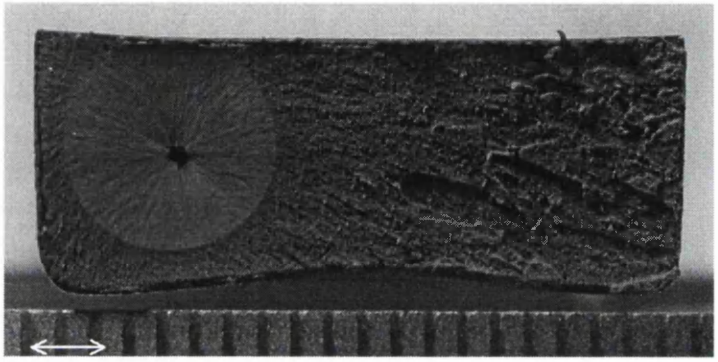


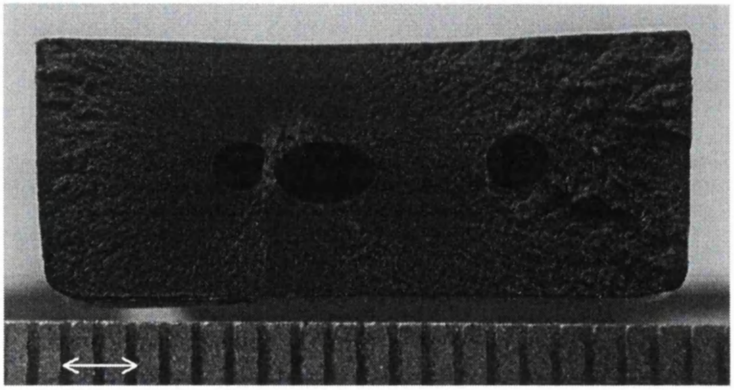
Figure 6.89 Tensile fracture surface images of (a) RPC showing voids (b) RPCE showing voids (c) fracture of RPCE fracture surface showing no voids, also typical of RPC



1mm (a)



1mm (b)



1mm (c)

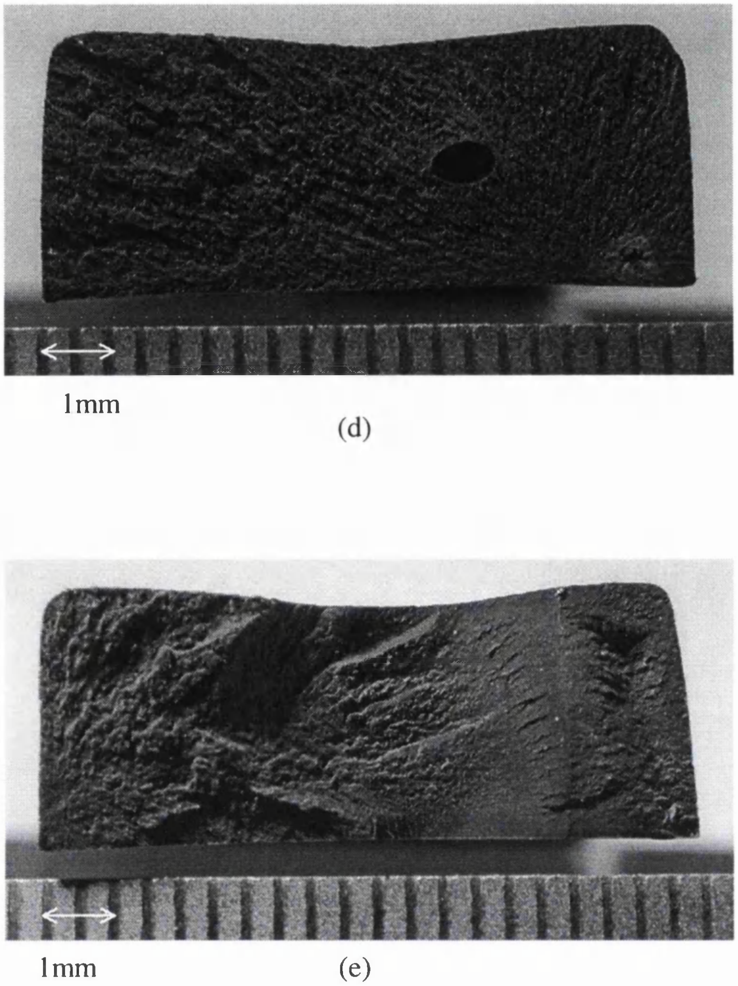


Figure 6.90 Tensile and impact fracture surface images of (a) typical tensile fracture of the blend 5HA (b) 5HP tensile fracture showing impurity within the sample (c) tensile fracture of the blend 5PCA showing voids (d) brittle tensile fracture of 25AHPPC (e) typical brittle impact fracture of 25AHPPC

CHAPTER 7:

RECYCLING PLASTICS – DISCUSSION

Of all plastic types and blends studied for this project, recycling may have the same effect on all, or may affect some in other ways. Changes to some of the properties measured for this study appear to depend mainly on changes to molecular weight. For example, a drop in impact strength and in viscosity is the effect of a decrease in molecular weight due to chain scission. On the contrary, an increase in molecular weight due to crosslinking would probably see an increase in viscosity and impact strength. The presence of impurities would mainly be seen by loss of ductility and impact strength.

The discussion of results will focus firstly on effects of reprocessing single materials. The properties of recycled ABS and HIPS are compared with those of virgin plastics, although these comparisons to virgin grades may not necessarily be the most representative to the effects of recycling, as there may be grade differences between the virgin and recycled materials. However the aim of project was to see effects of reprocessing on post-use materials. The discussion will then concentrate on the comparison of mixtures of the four plastic types with equivalent recycled constituent plastic. The comparison will be mainly to see if blending such plastics has any affects further to recycling and if not, then properties would be thought to be at levels proportionally between those of the blend constituents. Finally a comparison will be discussed between results for recycled and blended HIPS and ABS with lab scale samples of these materials tested previously.

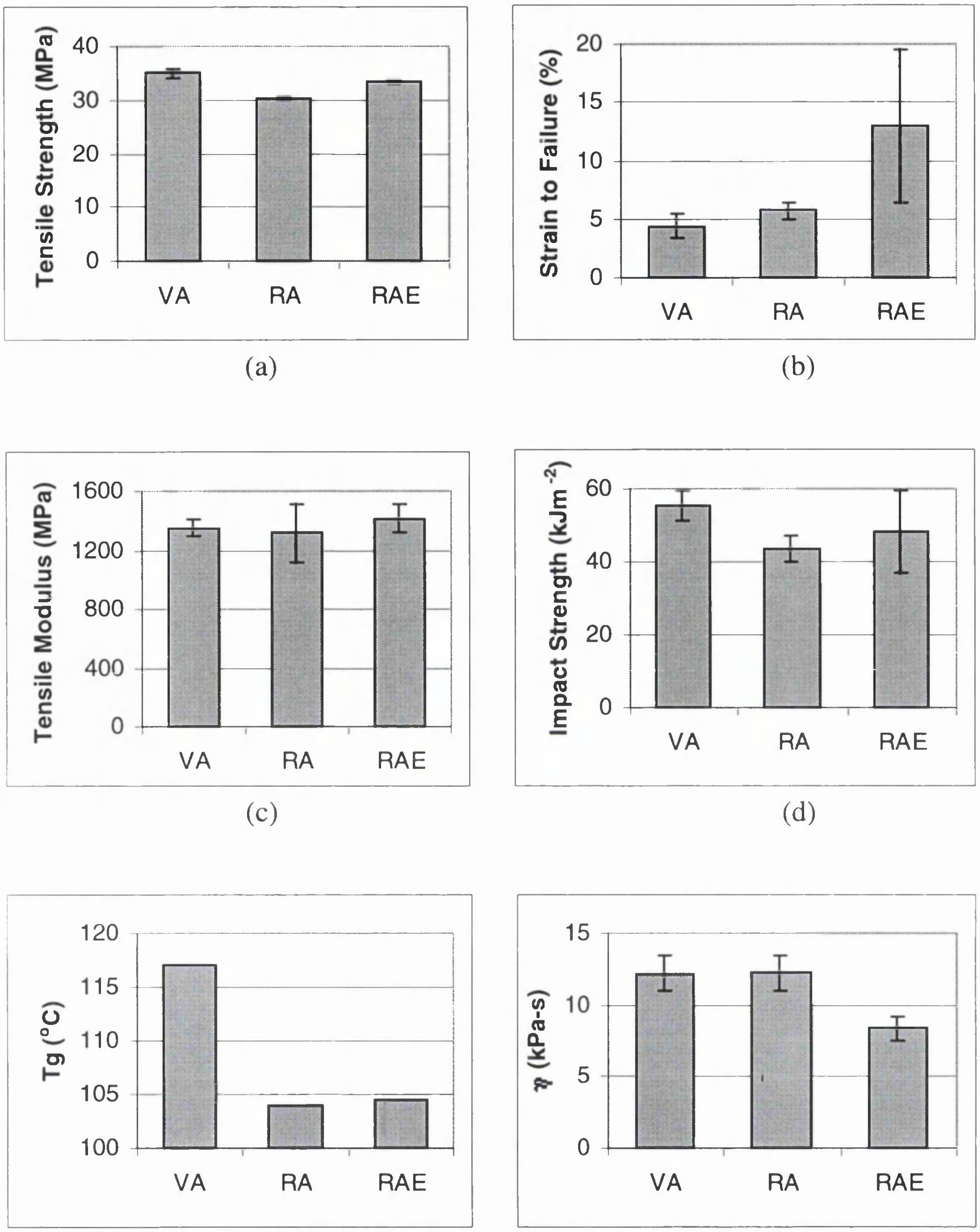
7.1 RECYCLED ABS, HIPS, mPPO, PC/ABS

7.1.1 Acrylonitrile – Butadiene – Styrene

In order to observe any changes to the properties of each plastic after the recycling process, it is useful to compare the results from several different tests. This gives the opportunity to see how a change to one property might affect another and to give an overall picture of the effects of recycling. Figure 7.1 is a series of histograms comparing results for virgin and recycled ABS from tensile testing, impact testing, DMTA, viscosity tests and molecular weight measurements. Larger versions of these histograms can be found under the various test headings in Chapter 6.

While the tensile results for VA and RA are invalid due to air bubbles at the fracture surfaces there is not too much difference between tensile strengths and moduli when compared with RAE (Figure 7.1a,c). If such results could be counted then they would probably be in agreement with previous work that concluded that the effects of recycling, over several recycling cycles, were negligible to the tensile strength and modulus of ABS [137]. The tensile strength for RAE was still well within the published data given for tensile strength (25-45 MPa) of ABS [64], although tensile modulus is actually lower than other published values (1500-2500 MPa) [64, 137].

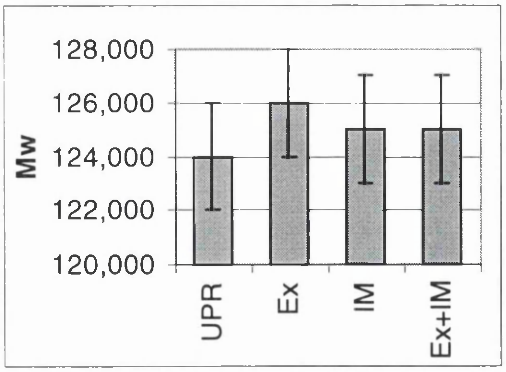
The strains to failure (Figure 7.1b) of VA and RA are considerably lower than RAE mainly due to the voids present. This would have caused premature failure of the samples and so a genuine comparison with RAE cannot be made as previous work [137] also found little variation in strain to failure of ABS over several recycling passes. The lack of air bubbles at fracture surfaces of RAE indicates that the additional extrusion process gave a better mix to the ABS recyclate enabling better quality injection mouldings. One possible explanation for the presence of such voids in VA and RA is that they could have been caused by any moisture within the plastic, despite being stored in what was believed to be dry conditions. The extra extrusion process of RAE could have eradicated any moisture in the material or it may have caused better mixing to occur within the recyclate. Another possible explanation is that the voids are produced not from water evaporation, but from some other volatile compound. The extruded material undergoes an additional thermal process, at a higher temperature (230°C for extrusion; 220°C for injection moulding). This could



(a) (b)

(c) (d)

(e) (f)



(g)

Figure 7.1 Test results for virgin and recycled ABS showing (a) tensile strength (b) strain to failure (c) tensile modulus (d) impact strength (e) glass transition temperature (f) viscosity (g) weight average molecular weight drive off the volatile gases during the extrusion process enabling injection moulding to occur with fewer large voids. This point would require further investigation.

Previous studies on the effect of recycling on ABS concluded that recycling continually reduces impact strength following each recycling pass [137, 143]. While this may have happened following the initial recycling process (Figure 7.1d), the second recycling process did not have a significantly detrimental effect. Any changes to impact strength may be influenced by M_w. Figure 7.1g shows no significant variation between stages of the recycling process, which corresponds with the negligible changes to impact strength of recycled ABS. The negligible effects of processing on molecular weight appear to agree with other work [137] that also concluded negligible change to the molecular weight of ABS over several recycling cycles. This earlier study established that changes to impact strength are instead due to the polybutadiene component of ABS that is eventually breaking down throughout the recycling process.

Following the trends of M_w and impact strength as mentioned above, the viscosity should also show no change between recycling processes. However this is not the case and while the viscosities of VA and RA are similar, that of RAE is considerably lower at the same temperature and strain rate (Figure 7.1f). This could also explain the fact that RAE was successfully injection moulded without any voids. As the molecular weights of RA (IM) and RAE (Ex+IM) are the same there appears to be no apparent explanation for this result.

Figure 7.1e shows that while there is no change to the T_g's of RA and RAE between recycling processes (104°C), the T_g of VA at 117°C is significantly higher. This could be because the VA used for this study is a different grade to the recycled ABS, which could be why VA is closer to the T_g value of 115°C for ABS as quoted by Crawford [114]. However other studies on the recyclability of ABS [137] concluded that several recycling passes did not affect the T_g of ABS and quoted T_g values around 105°C, similar to those of the recycled ABS used in this study. Again this strengthens the explanation that any large differences between results such as this are more likely to be due to differences in grades between VA and recycled ABS.

In summary, the effects of recycling on ABS are slight, with the most significant effect being a decrease in viscosity after extrusion and moulding.

7.1.2 High Impact Polystyrene

Figure 7.2 shows the series of histograms of results for virgin and recycled HIPS. Larger versions of these histograms can be found under each test heading in Chapter 6. The general pattern emerging from these results is that most properties are relatively unaffected between the two recycling processes but often differ from results for virgin HIPS. Changes are negligible between recycling processes for tensile strength, tensile modulus, impact strength and viscosity. However virgin HIPS displays higher tensile strength and stiffness than recycled HIPS, but lower impact strength and viscosity.

While all values determined for tensile strength of HIPS are well within a published range of tensile strengths (14-35MPa) [64], the stiffnesses of the HIPS materials appear to be lower than published data (1300-1800 MPa) [64], which suggests a systematic variation that could be due to the measurement technique. The impact strength for VH is comparable with RHE and the slightly higher impact strength displayed by RH can be construed as negligible when taking into consideration the ranges of scatter displayed by the results. This was not expected as other studies [129-131, 135-136] all reported a continual decrease in impact strength for every recycle experienced by HIPS and also for PS, that was attributed to the incompatibility of the pigment TiO_2 in the HIPS matrix [129].

Another unexpected result is the viscosity of VH, which is clearly lower than recycled HIPS (Figure 7.2f). This is slightly unexpected as VH has the higher molecular weight, stiffness, strength and ductility, and so it would have been logical to presume that it would have displayed a higher viscosity at 200°C. This would have agreed with previous work [129] by Covavisaruch et al who found that recycling lowered the viscosity, due to chain scissions causing a reduction in molecular weight. Therefore a higher molecular weight material would usually display higher viscosity because longer chains are generally less mobile, although the lower viscosity of VH could occur for several reasons. It is more than likely that VH is a different grade to the recycled HIPS and despite having a higher molecular weight, VH could have a more linear chain structure which would contribute to lowering the viscosity. VH could also contain additives such as plasticizers to increase the ease of processing which will reduce viscosity, although more testing would be needed to verify this.

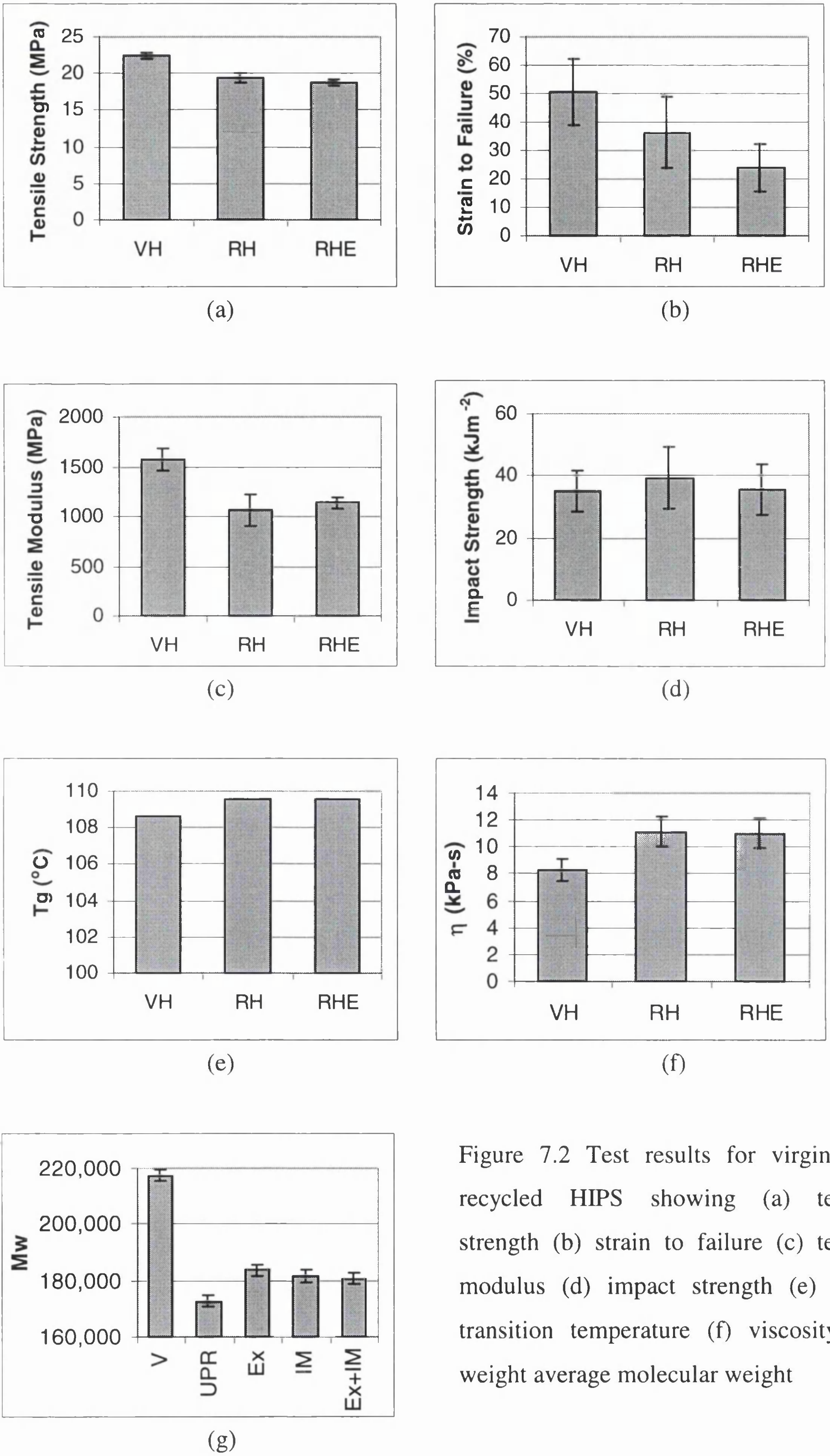


Figure 7.2 Test results for virgin and recycled HIPS showing (a) tensile strength (b) strain to failure (c) tensile modulus (d) impact strength (e) glass transition temperature (f) viscosity (g) weight average molecular weight

Another point to consider is the effect that the recycling process had on the M_w of RH and RHE when compared with unrecycled post service material. Figure 7.2(g) comparing molecular weights throughout the several stages of the recycling process shows an increase in M_w following both extrusion and injection moulding. The molecular weight distributions in Figure 6.67 display a wider curve for extruded and injection moulded samples compared with unprocessed material, indicating the effect of some crosslinking, which is likely to increase viscosity.

The strain to failure of HIPS (Figure 7.2b) progressively decreases following each recycling process, despite a large scatter range of results. Initially it was suspected that the molecular weight of HIPS could have decreased due to chain scission, due to thermal degradation during processing. The significantly higher M_w for VH could explain why the strain to failure of VH is so much higher than for RH and RHE, although this difference is probably due to a difference in grade of HIPS rather than the breakdown of polymer chains. Although the M_w of UPR-HIPS is actually HIPS at the other recycling stages, previous studies have shown that some thermal processing may instead cause crosslinking rather than breakdown of polymer chains in some polymers [138]. However despite the possibility of crosslinking occurring, there is no significant difference between molecular weights of IM (same as RH) and Ex+IM (for RHE), which indicates that thermal degradation may not be the cause of the reduction in strain to failure between recycling processes. Instead the fracture surface images in Figure 6.87 may offer an explanation.

These images show the presence of rubber like inclusions within RH and RHE despite being processed at different times. All samples of RHE contained these inclusions whereas the ones found in RH were slightly smaller and were not always present, indicating that some samples could have failed prematurely. The presence of such materials could have come from the injection moulder, despite rigorous purging prior to processing. However, all three HIPS batches were processed at different times and such inclusions are not at all found in VH or any other material. Another possibility is that such impurities may have been picked up from the industrial granulater that was used for size reduction for the recycled materials. However as all recycled materials were also granulated in that way, no other material picked up such impurities. The only other thought is that the other material was somehow mixed with the recycled HIPS, maybe as rubber feet attachments, however further tests would need to be made to identify whether such inclusions were HIPS or another material

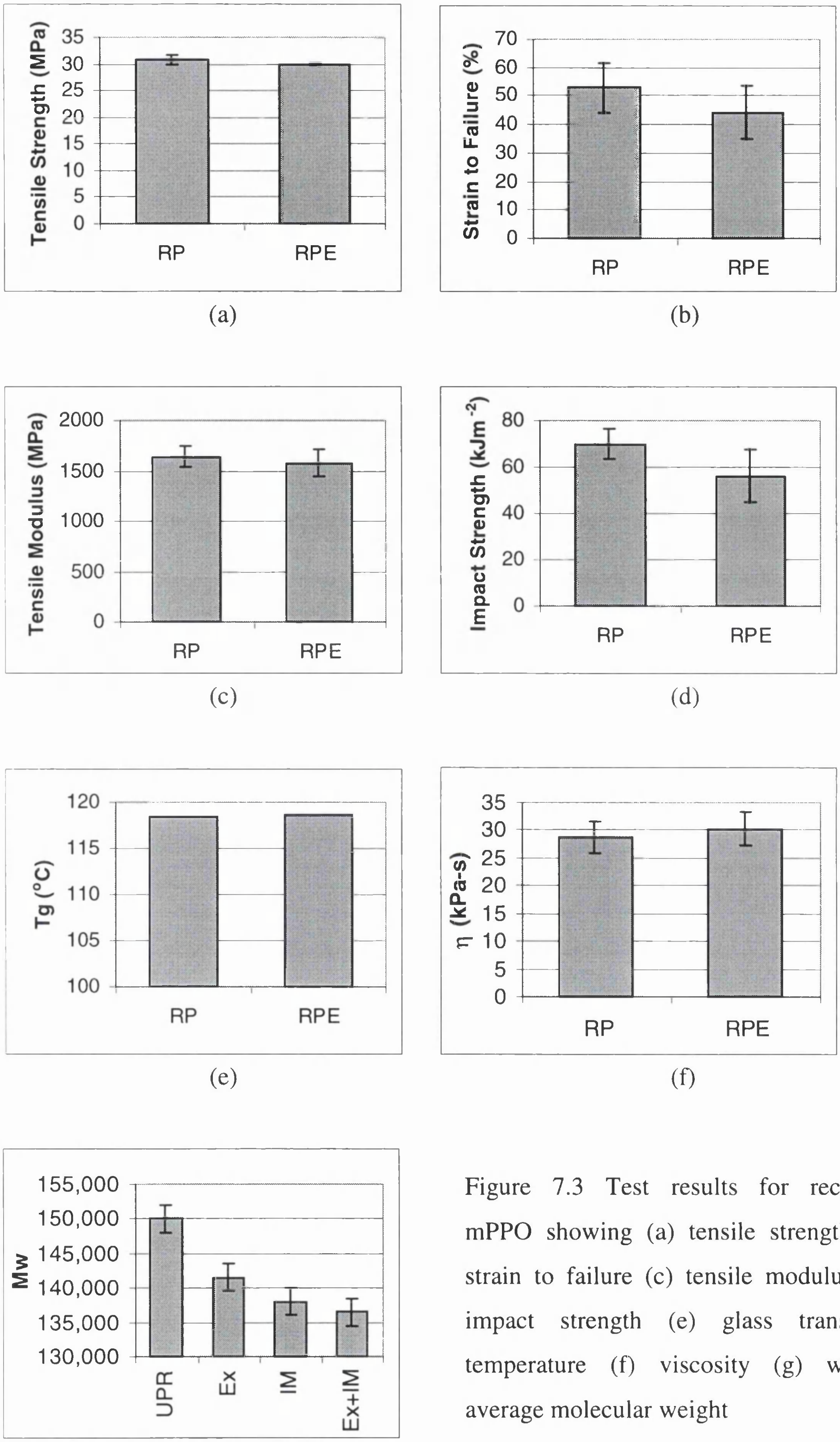
There are no significant changes to the T_g's of all HIPS materials studied, however these values are all a little higher than the T_g value published for PS (100°C) [114]. This could be due to differences in the measurement technique, either in the definition of T_g (onset or tan delta peak) or maybe the positioning of the measurement thermocouple.

7.1.3 Modified Polyphenylene Oxide

Figure 7.3 shows all test results for mPPO. Changes in properties due to differences between recycling processes are negligible for tensile strength, tensile modulus, glass transition temperature and viscosity. However tensile strength and tensile modulus for mPPO are lower than for published values of PPO at 45 MPa [114] and 2100 MPa [64] respectively. These differences could be due to differences in grade of material or the amount of PS or HIPS copolymer, or they could actually be due to the onset of degradation from the material's product lifetime and thermal degradation as a result of the recycling process. Some thermal degradation does seem to be evident from the molecular weight results, however this is between recycling processes and probably does not account for the differences between published and recycled values. Differences in the test method could explain the lower modulus, as this is seen with the other materials, however the tensile strength measurements are in agreement for the other materials. Differences in grade of mPPO probably account for the majority of differences.

Although the glass transition temperatures show no real change for both recycled mPPO, at 118°C, they are significantly lower than the T_g value generally quoted for PPO (between 200°C and 212°C [101, 102,103]). This confirms that this material is a blend of PPO probably with PS or HIPS. The cold impact fracture surface image in Figure 6.80 suggests that the PPO is blended with HIPS. PS and PPO blend into a single phase and so the presence of particles throughout the matrix, suggest an immiscible phase that could be due to PB rubber. However it is also possible these particles are other immiscible additives. The higher processing temperatures of PPO could explain the reduction in M_w following each recycling process step, as being due to the thermal degradation of the PS or HIPS component.

There is a distinct reduction in both the strain to failure and impact strength of RPE compared to RP (Figure 7.3b, d), despite some scatter overlap in results. The



(a) (b)

(c) (d)

(e) (f)

(g)

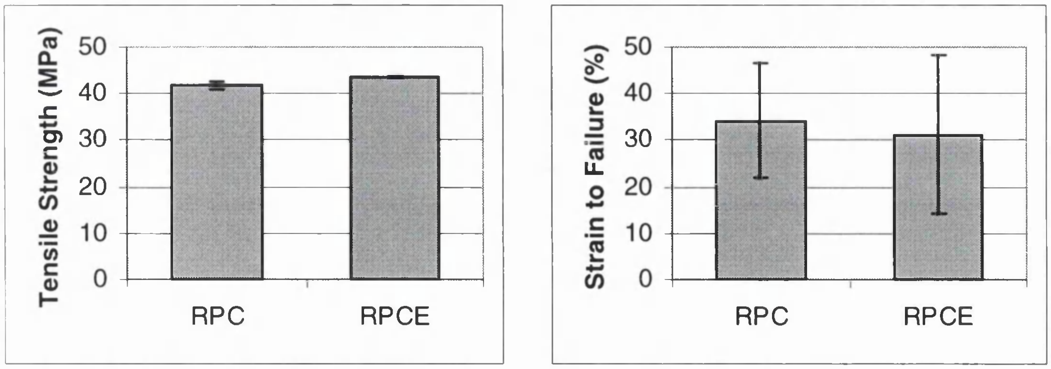
Figure 7.3 Test results for recycled mPPO showing (a) tensile strength (b) strain to failure (c) tensile modulus (d) impact strength (e) glass transition temperature (f) viscosity (g) weight average molecular weight strain to failure of RP is also lower than a published value for PPO (70%) [114]. The fracture surface of mPPO (Figure 6.88) does not reveal anything that would significantly contribute to the deterioration of ductility and toughness. Studies into the recyclability of PPO/Nylon 66 alloys [138] also showed a deterioration in impact properties, which was attributed to thermal/oxidative degradation of polybutadiene based rubber impact modifiers. Suggestions to overcome such loss in properties include using different impact modifiers or processing blends or alloys containing polybutadiene based rubber impact modifiers at lower temperatures [138].

Another possible cause of changes to impact and elongational properties of recycled mPPO could be due to the break down of the polymer chains. Figure 7.3g shows the M_w of mPPO decreasing continually throughout processing. Although the M_w of extruded mPPO is a lot lower than unprocessed mPPO, the injection moulding part of the process appears to have a more detrimental effect on M_w and IM-PPO is even lower than Ex-PPO. Although the extruded material does show a decrease to M_w, it is to a lesser extent than the mPPO that was injection moulded only.

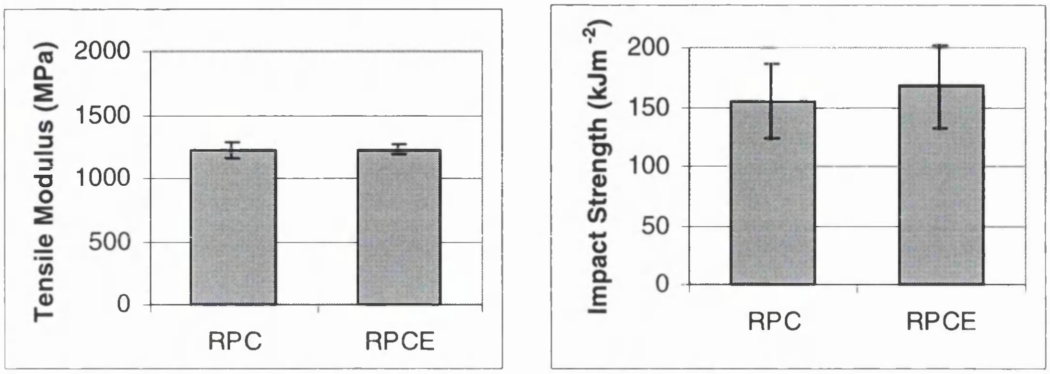
7.1.4 Polycarbonate/ABS

Recycling PC/ABS shows negligible changes to tensile properties, impact strength and T_g (Figure 7.4). While values for tensile strength are lower than published values for PC (65MPa) [114] this is probably due to the PC plastic types used for this study being alloyed with ABS and so are not pure PC. The tensile strengths of recycled PC/ABS are still at the higher end of the range given for the tensile strength of ABS (25-45 MPa)[64]. Even so, the tensile modulus values are still lower than published data for both ABS (1500-2500 MPa) and PC (2760 MPa) [64]. The tensile and impact results for recycled PC/ABS were the average of approximately five tests as opposed to ten. This was due to the presence of air bubbles in some samples and throughout recycling, the recycled PC/ABS had to be dried constantly before any thermal process, as even just short periods of exposure to air seemed to increase the moisture content. The voids seen on fracture surface images in Figure 6.89 are probably due to the presence of moisture within PC/ABS despite continual efforts to keep the material dry.

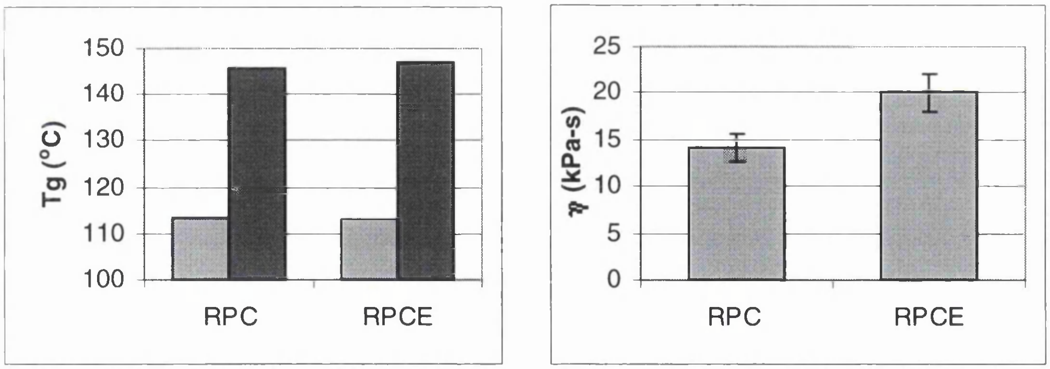
Although there were no significant changes to T_g's of recycled PC/ABS between recycling processes, there are two T_g values displayed at around 114°C and 146°C. This is a clear indication that PC and ABS are an incompatible blend and are



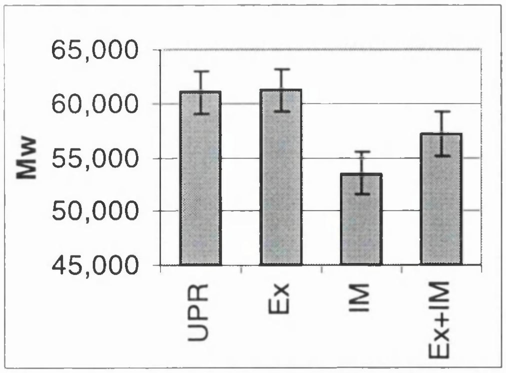
(a) (b)



(c) (d)



(e) (f)



(g)

Figure 7.4 Test results for recycled PC/ABS showing (a) tensile strength (b) strain to failure (c) tensile modulus (d) impact strength (e) glass transition temperature (f) viscosity (g) weight average molecular weight instead a two-phase polymer alloy with T_g values pretty much corresponding to those of ABS (115°C) and PC (149°C) [114].

Injection moulding decreases the M_w of recycled PC/ABS whereas the extrusion process has no more effect on M_w when compared with the unprocessed PC/ABS. Material that was extruded prior to injection moulding also appears to withstand such a reduction to M_w. The same behaviour is also seen in viscosity (Figure 7.4f), where the viscosity of RPCE is higher than RPC, coupled with the higher M_w for RPCE. This suggests that extrusion process could be causing some chain branching or crosslinking [138] or enabled better inter-phase adhesion between the two-phase alloy. However total miscibility did not occur as RPCE still exhibited two different glass transition temperatures.

7.1.5 Summary

It seems that the changes due to recycling of single materials are quite small. None show any real changes in strength or stiffness after the extra recycling step, although there are slight reductions in ductility for HIPS and mPPO. For HIPS, this seems to be due to impurity particles. For mPPO, it is probably due to degradation of the PB rubber at the higher processing temperatures for this material. In contrast, the impact strength of ABS and M_w of PC/ABS seem to increase with extra processing, probably due to better mixing and inter-phase adhesion that helps to remove moisture that may be extracted from exposure to air.

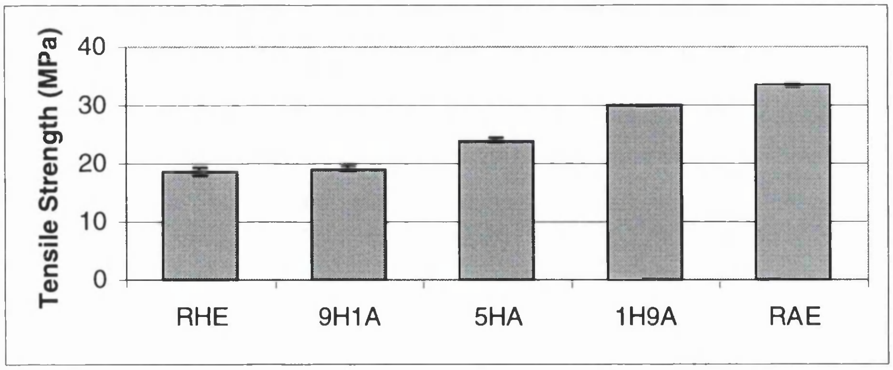
7.2 BLENDING AND RECYCLING ABS, HIPS, PPO AND PC/ABS

7.2.1 Blends of HIPS and ABS

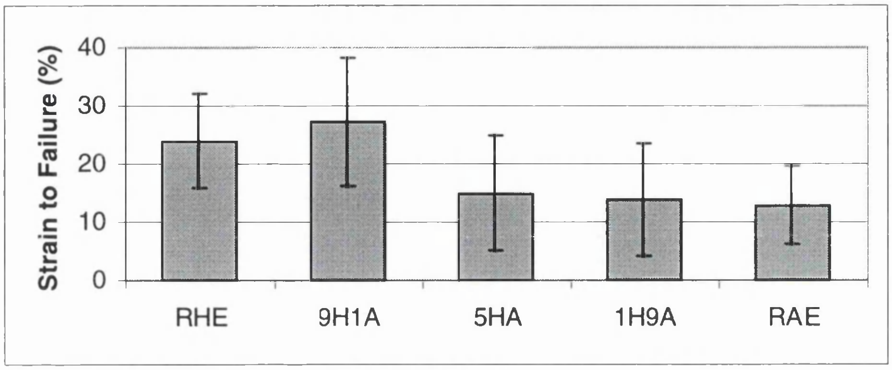
Results from testing blends of HIPS and ABS are consolidated into Figure 7.5. When observing blends of two or more plastics, it can be more or less expected that the blend properties will be at a level somewhere between those of the constituents, according to the linear law of mixtures [108]. Properties of HIPS/ABS blends that showed changes more or less in accordance with this rule include tensile strength, tensile modulus, glass transition temperature and weight average molecular weight. All blends displayed just one T_g value indicating that the two polymer types were blended sufficiently into a single-phase material.

All blends of ABS and HIPS reduce impact strength to some extent, which is an indication that HIPS and ABS blends may not necessarily be compatible despite bending into a single phase material [105]. The macro fracture surface image of 5HA (Figure 6.90a) illustrates this and shows a structure that appears a lot rougher and more granular than those taken of ABS (Figure 6.86) and HIPS (Figure 6.87), suggesting that the two constituents are not too well bonded. Close-up, images taken from studies on the SEM of the bulk structure of ABS and HIPS (Figures 6.78 & 6.79) show different features on the cold brittle fracture surfaces, with ABS featuring a smoother surface than HIPS with larger and more frequent particle debonding. Both show the impact modifying particles, while HIPS also shows poorly mixed filler or pigment particles. The SEM image taken of 5HA (Figure 6.82) shows a general appearance in-between that of ABS and HIPS and is less granular than HIPS but less smooth than ABS. It has been suggested by Keskulsa et al [165] that mechanical properties of incompatible HIPS/ABS blends, could be improved by adding a compatibiliser such as MMA (Methyl Methacrylate)-graft rubber.

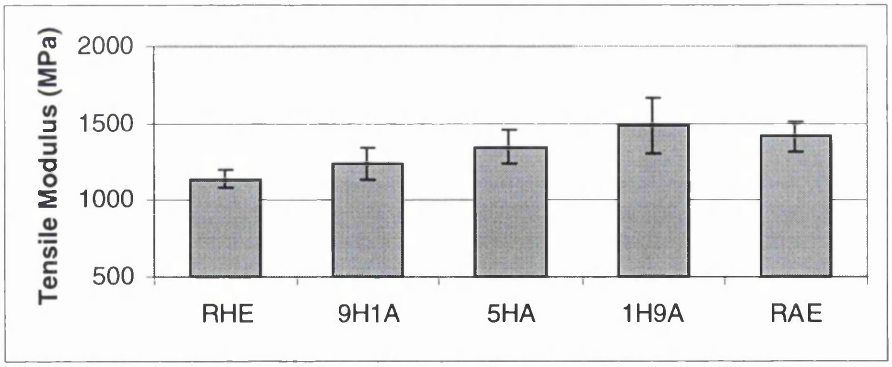
Ductility and viscosity of HIPS/ABS blends remain largely unchanged from properties of the major phase at ratios of 90/10 while an increase of the minor component to 50% is generally detrimental. Previous work by Tall et al [139] found that blending even smaller proportions (such as 4%) of HIPS into ABS actually increased the strain to failure of ABS, although this dropped back as the amount of HIPS increased. This more or less agrees with results from this present study where 10% HIPS in ABS, shows no change to the strain to failure. This previous work [139]


Tensile Strength (MPa)
0
10
20
30
40
RHE
9H1A
5HA
1H9A
RAE

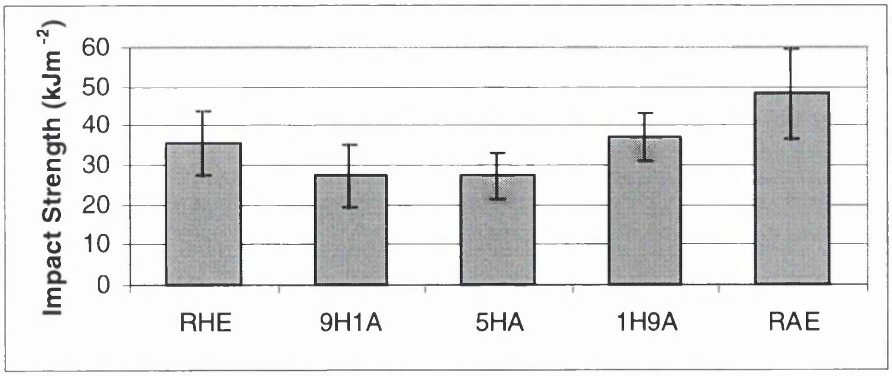
(a)


Strain to Failure (%)
0
10
20
30
40
RHE
9H1A
5HA
1H9A
RAE

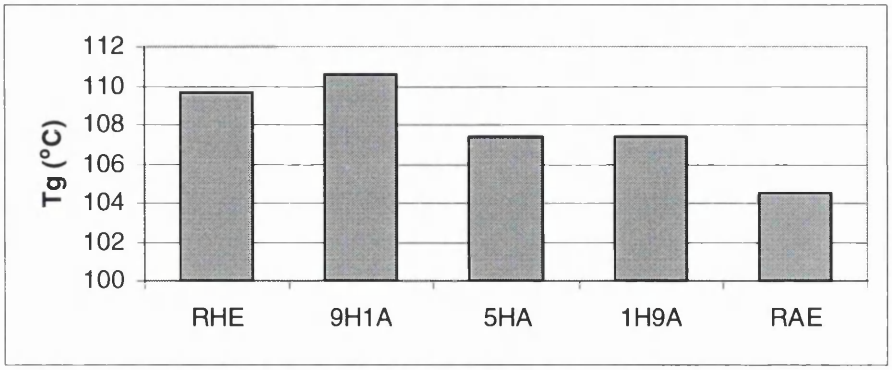
(b)


Tensile Modulus (MPa)
500
1000
1500
2000
RHE
9H1A
5HA
1H9A
RAE

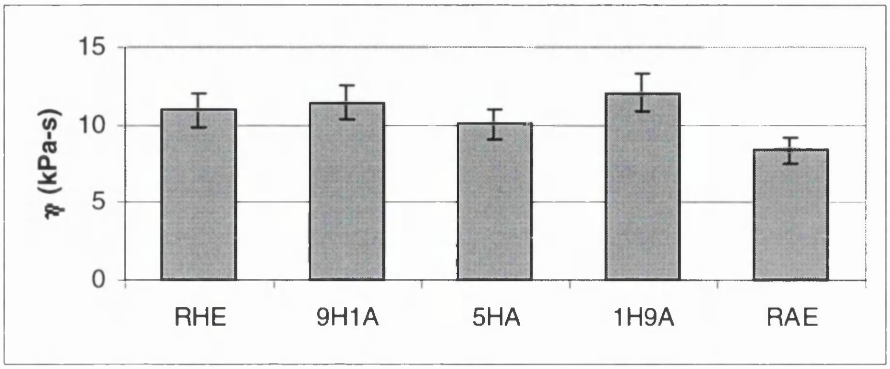
(c)


Impact Strength (kJm-2)
0
10
20
30
40
50
60
RHE
9H1A
5HA
1H9A
RAE

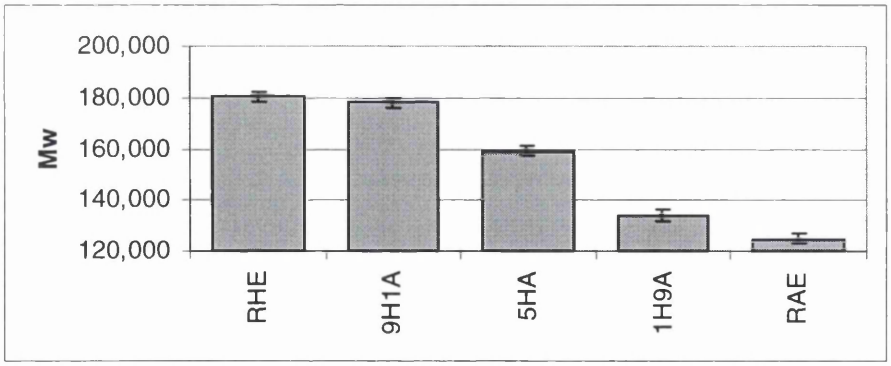
(d)



(e)



(f)



(g)

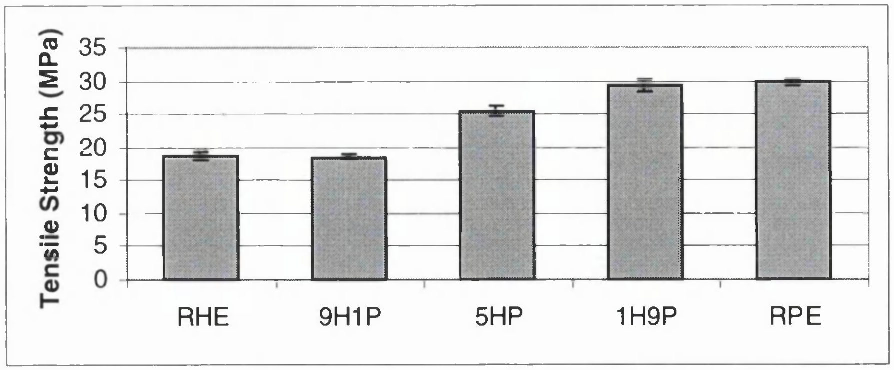
Figure 7.5 Comparison of test results of blends of recycled HIPS and ABS, showing (a) tensile strength (b) strain to failure (c) tensile modulus (d) impact strength (e) glass transition temperature (f) viscosity (g) weight average molecular weight also indicates negligible change to the tensile modulus of ABS due to the presence of HIPS.

The lower viscosity of the blend 5HA indicates that changes to viscosity of ABS and HIPS due to the presence of the other will be negligible up to a critical proportion. It is also interesting to note that while the viscosity of ABS is slightly higher than HIPS, recycled HIPS displays the higher molecular weight as seen in Figure 7.5g. Because viscosity is proportional to the weight average molecular weight, the higher the molecular weight, the higher the viscosity, which means that it is probably down to the structural differences between HIPS and the co-polymer ABS to explain why the viscosity of ABS is that little bit higher. Indeed there do not appear to be any abnormalities to the molecular weight results in Figure 7.5g and each blend seems to have a M_w according to the proportion of its constituents.

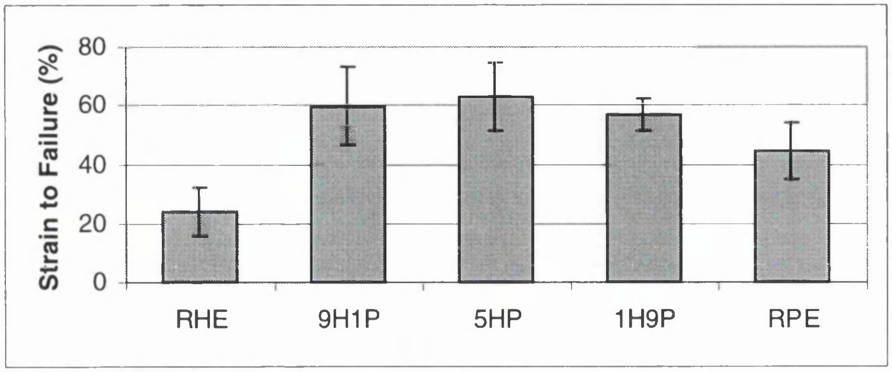
7.2.2 Blends of HIPS and mPPO

Figure 7.6 shows results from testing HIPS/mPPO blends. Tensile strengths, tensile moduli, glass transition temperatures and weight average molecular weights of these blends change more or less according to blend proportions and follow the trend of a linear law of mixtures. Viscosity results are not quite in accordance with the rule of mixtures because the viscosities of the 10% blends are no different to the main constituent, and the viscosity of 5HP is significantly closer to that of RPE (Figure 7.6f). This indicates that the viscosity of any HIPS/mPPO blends could be similar to RHE until a critical amount of mPPO is reached. This could then suddenly increase to a level more comparable with RPE, however the critical amount of mPPO content could only be verified by further testing of blends at 20, 30 and 40% proportions.

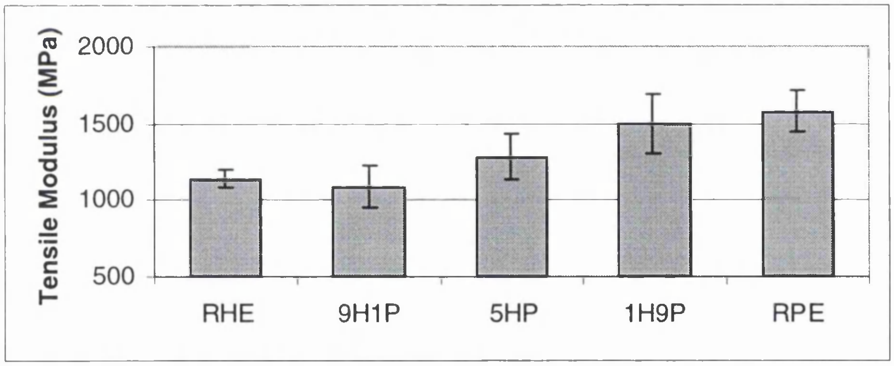
Impact strength and ductility of HIPS/mPPO blends are improved dramatically at all proportions tested to levels greater than those reached by the recycled un-blended materials. However, while the blend 1H9P has an impact strength greater than RPE, this does not fully restore the amount of impact strength lost during the extrusion process. Increasing the HIPS content to 50% continues to increase impact strength and that of 5HP is more or less equal to that of RP. Such favourable results can only illustrate the excellent compatibility of HIPS and PPO, which is thought to be due to a strong interaction between the aromatic rings of the two polymers [107]. As just 10% of one material in the other is sufficient to see an improvement to these properties, it would therefore be interesting to determine the minimum amount of


Tensile Strength (MPa)
35
30
25
20
15
10
5
0
RHE
9H1P
5HP
1H9P
RPE

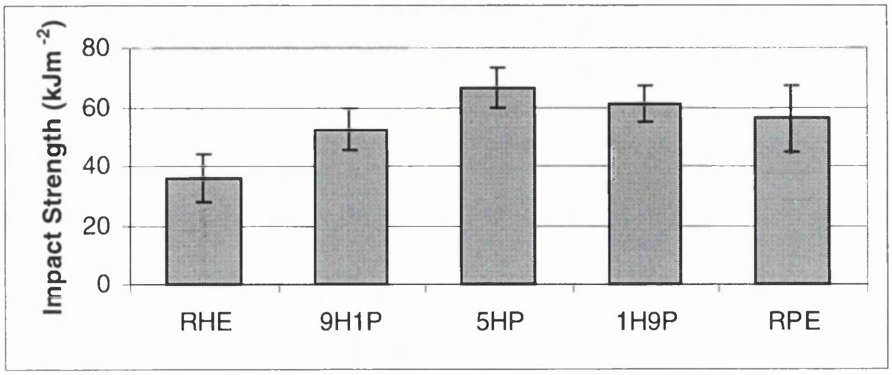
(a)


Strain to Failure (%)
80
60
40
20
0
RHE
9H1P
5HP
1H9P
RPE

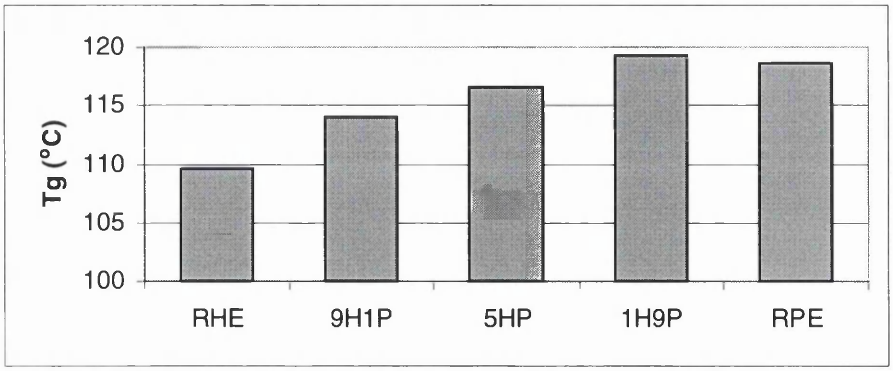
(b)


Tensile Modulus (MPa)
2000
1500
1000
500
RHE
9H1P
5HP
1H9P
RPE

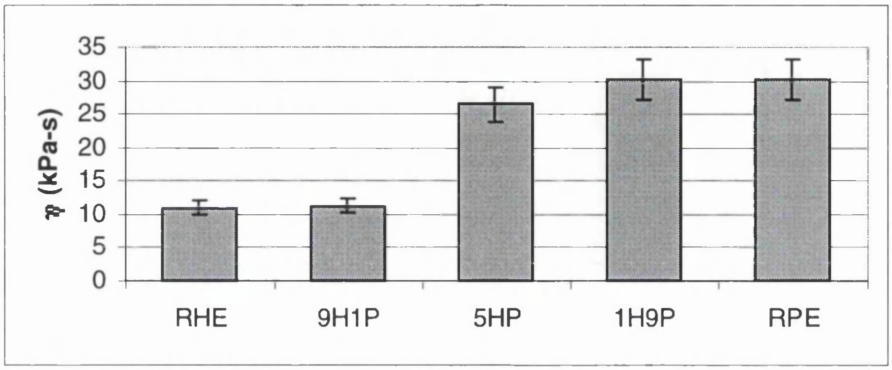
(c)


Impact Strength (kJm^{-2})
80
60
40
20
0
RHE
9H1P
5HP
1H9P
RPE

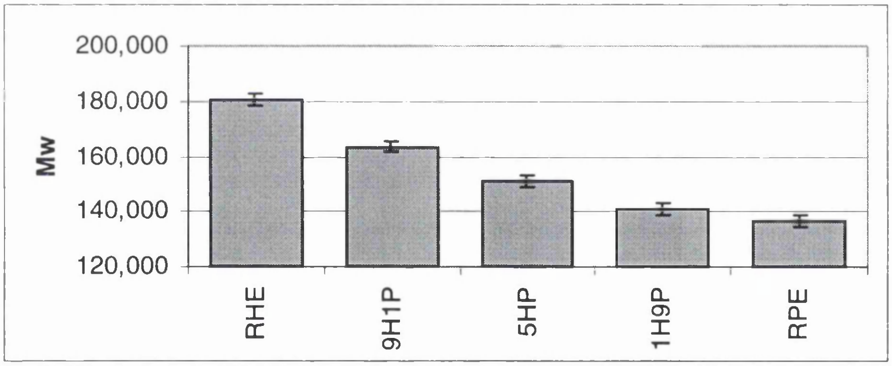
(d)



(e)



(f)



(g)

Figure 7.6 Comparison of test results of blends of recycled HIPS and mPPO, showing (a) tensile strength (b) strain to failure (c) tensile modulus
(d) impact strength (e) glass transition temperature (f) viscosity
(g) weight average molecular weight

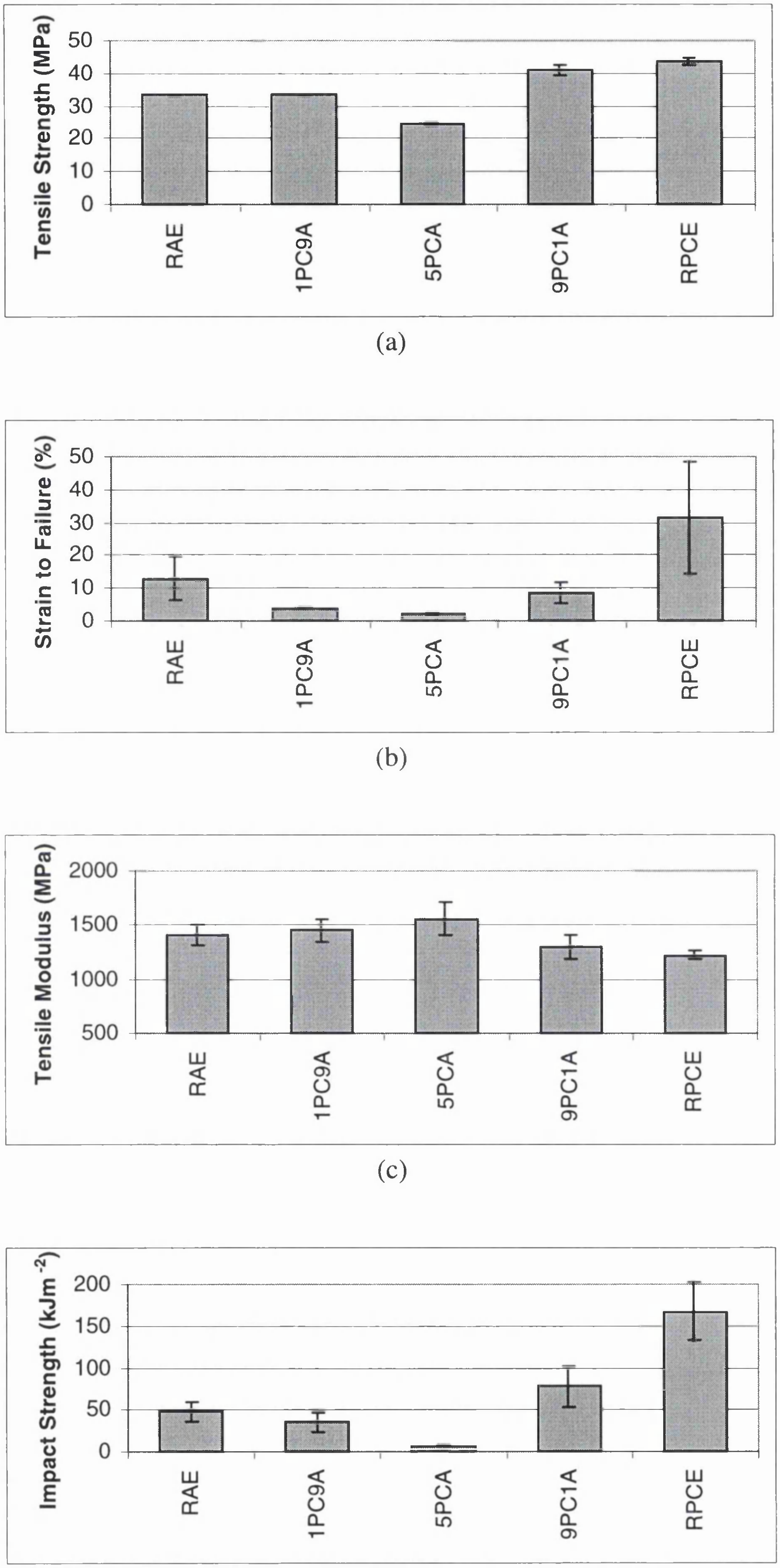
mPPO in HIPS (and vice versa) that is needed, below 10%, before such significant increases to ductility and impact strength occur.

Even the fracture surface images of 5HP (Figure 6.90b) show this blend to be better mixed than the 50% HIPS/ABS blend (Figure 6.90a). The SEM fracture image of the cold fracture surface of 5HP (Figure 6.83) appears to be more similar to mPPO than HIPS (Figures 6.80 and 6.79 respectively), and again indicates a good mix of the two polymers. The blending of these two polymers into a single phase impact-modified plastic type was also indicated by DMTA results showing just a single T_g value for all HIPS/mPPO blends.

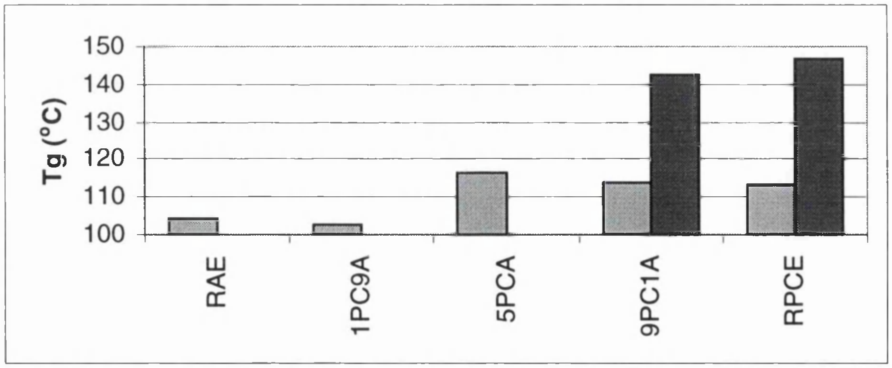
7.2.3 ABS and PC/ABS Blends

Test results for blends of ABS and PC/ABS are consolidated into Figure 7.7. Not one set of results for these blends were entirely close to following the linear law of mixtures. While the tensile strengths and moduli of both PC/ABS and ABS remain largely unaffected when blended with 10% of the other plastic type, an increase in blend proportions to 50% actually reduces the tensile strength but increases in stiffness (Figure 7.7a,c). Both strain to failure and impact strength are reduced fairly significantly for all ABS/(PC/ABS) blends with the most detrimental effects being displayed by the blend 5PCA indicating that this blend was exceedingly brittle. These results agree with those from previous work that also recorded detrimental effects to impact strength of ABS and PC/ABS blends on reprocessing [119, 140-141]. This has been attributed to oxidative degradation of the butadiene rubber phase, which degrades the impact strength of the material during its service life and during reprocessing [119, 140-141]. Also the presence of the flame retardant has been said to degrade the PC phase [119]. As the majority of ABS plastics used in computer equipment is flame retarded, it is highly likely that the ABS used in this project will also contain flame retardants. Therefore there is a distinct possibility that the flame retarded ABS blended with PC/ABS could cause further degradation to the PC phase, thus decreasing impact properties to a much larger extent than usual. It has been suggested that the impact strength of blends of ABS and PC/ABS can be improved by the addition of a core shell impact modifier such as methyl-methacrylate-butadiene-styrene (MBS) [140-141].

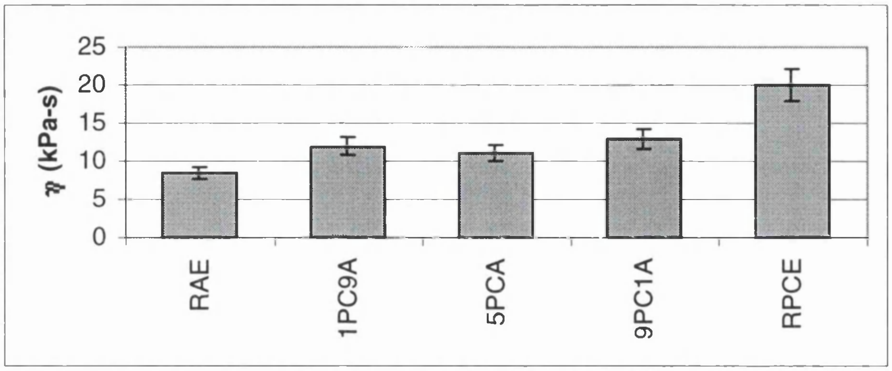
The fracture surface image of 5PCA (Figure 6.90d) appears a lot more brittle than those of both ABS and PC/ABS (Figures 6.86 and 6.89). It is interesting to note


Tensile Strength (MPa)
0
10
20
30
40
50
RAE
1PC9A
5PCA
9PC1A
RPCE
(a)
Strain to Failure (%)
0
10
20
30
40
50
RAE
1PC9A
5PCA
9PC1A
RPCE
(b)
Tensile Modulus (MPa)
500
1000
1500
2000
RAE
1PC9A
5PCA
9PC1A
RPCE
(c)
Impact Strength (kJm -2)
0
50
100
150
200
RAE
1PC9A
5PCA
9PC1A
RPCE

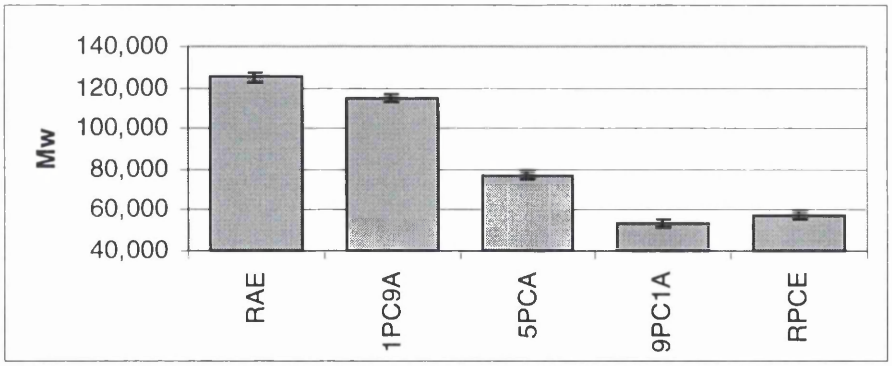
(d)



(e)



(f)



(g)

Figure 7.7 Comparison of test results of blends of recycled ABS and PC/ABS, showing (a) tensile strength (b) strain to failure (c) tensile modulus (d) impact strength (e) glass transition temperature (f) viscosity (g) weight average molecular weight that studies into the alloying of ABS with PC [107] showed a selection of fracture surface micrographs taken of different PC compositions from 100% to 0%. Images of 80% and 75% PC appeared to be very similar to fracture surface images of PC/ABS in Figure 6.89, indicating possible compositions of the PC/ABS used for this project. The fracture surface image of the blend 5PCA (Figure 6.90d) appears similar to images of 40% and 20% PC. This could indicate the extent of the reduction of the PC content and possible compositional information when continually alloyed with recycled ABS. Throughout the recycling process, PC/ABS was processed at a higher temperature than ABS and when blending PC/ABS with ABS the processing temperature was also raised or lowered according to blend proportions (See Table 5.3). Therefore if the blend 5PCA contained mostly ABS with just 20% PC, then it is possible that the processing temperatures for this blend could have been too high for the ABS content. This means that the deterioration of tensile and impact properties may not be due to lack of cohesion between the two plastic types, but could instead be due to thermal degradation of the ABS component. Also an indication of the blend composition could indicate the blend structure and whether it is a solution of ABS in a PC matrix or PC in a ABS matrix. A blend composition of 20-40% PC is more than likely to be an ABS-rich continuous matrix with PC domains as opposed to a PC matrix containing ABS domains [116], although the ductility and impact strength indicated extremely poor interfacial adhesion between phases.

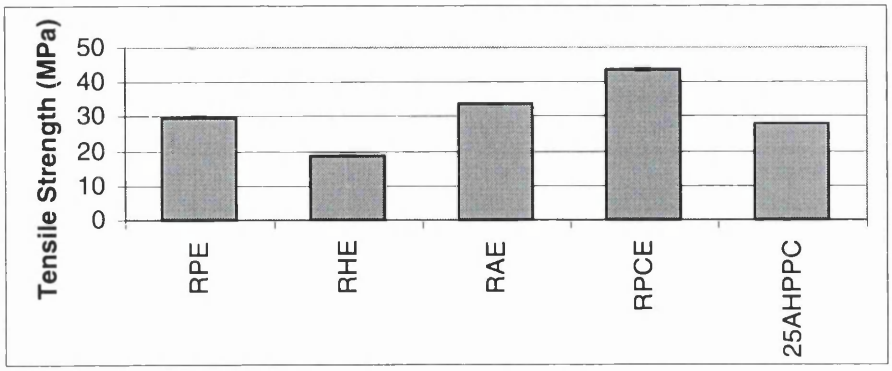
The bulk microstructure of 5PCA (Figure 6.84) reveals a structure that resembles neither ABS (Figure 6.78) nor PC/ABS (Figure 6.81) although it does possess a few similarities. The bulk fracture surface of 5PCA is much flatter than that of RAE, although it is not entirely smooth. However it does not appear to contain the array of micro-cracks that is seen all over the surface of RAE, indicating that there is no mechanism within the structure of 5PCA for crack termination at particles such as polybutadiene rubber. The image of the bulk structure of RPCE prominently displays particles and pull out sites of these particles. However the structure of 5PCE has very little features and although there is the presence of some particles, they are significantly smaller and are fewer. The presence of just a few impact particles within the 5PCA matrix is probably why this blend gives the worst impact performance. This also indicates the structural change of 5PCA from a two phase to a single-phase system as highlighted by the DMTA results.

The T_g's of the 10% blends show negligible changes compared with their main constituents, and 1PC9A remains a single phase material and 9PC1A remains a multiphase alloy. Again the blend 5PCA displays significant changes and actually displays a single T_g value that is higher than ABS but lower than that of PC. This is an indication of a single phase material, although the tanδ curve in Figure 6.48 is broad, which could mean that there are two T_g's, but that they are too close to be distinguished. The bulk fracture surface image in Figure 6.84 shows very few features suggesting a better mixed material, although by what is shown by the above results, this is not necessarily a beneficial effect. A likely explanation for these results is that with the 50% mix, the PC and ABS chains are still intermingled, and the amount of PC causes an increase in chain rigidity. This leads to a single but higher T_g or two T_g's closer together, as well as a higher tensile modulus. This will also tend to cause less ductile yielding and so give a more brittle material, with lower impact strength.

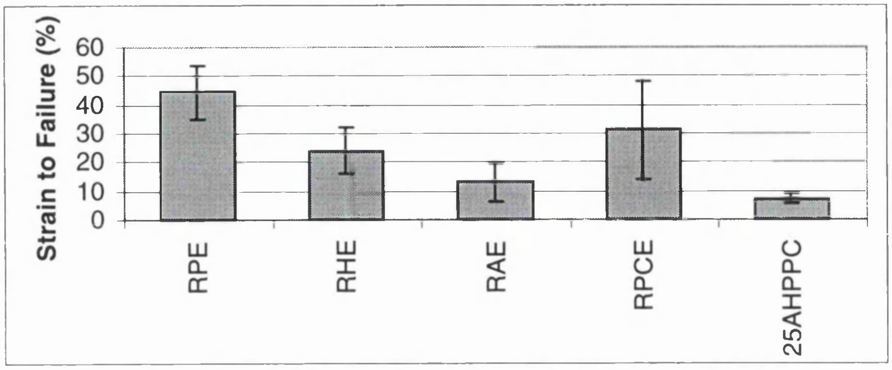
Previous work has concluded that a change in molecular weight results in a change in viscosity [166] and a change in viscosity results in a change in polymer microstructure [141]. The linear law of mixtures applies only to the M_w of the blend 1PC9A. Blending proportions of ABS in PC/ABS is more detrimental to M_w and causes chain scissions. The viscosities of all three ABS/(PC/ABS) blends all give a similar value that is actually comparable with RA, again indicating that the viscosity of RAE is unusually low. The blend 9PC1A, while displaying a similar viscosity to RA and other blends, is significantly lower than its main constituent RPCE. Despite the addition of 10% of ABS, the blend 9PC1A was still processed at temperatures closer to those of PC/ABS than ABS. This could have caused degradation of the ABS part of the blend, which in turn may be responsible for the slight decrease in M_w and also the reduction in viscosity.

7.2.4 25% Blend of ABS, HIPS, mPPO and PC/ABS

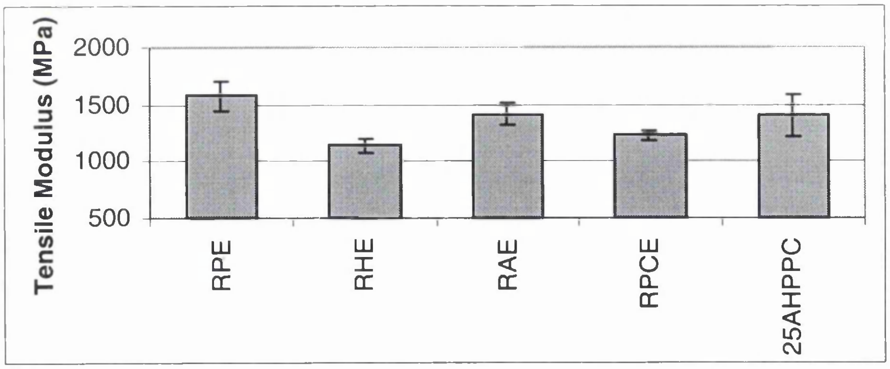
Test results of an equal blend of the four plastics studied for this project are compared with the four constituent plastics in Figure 7.8. For properties including tensile strength, tensile modulus, glass transition temperature, viscosity and weight average molecular weight (Figure 7.8a,c, e, f, g), the 25% blend displays a result that is more or less the average of the four constituents, which is probably what could be


Tensile Strength (MPa)
50
40
30
20
10
0
RPE
RHE
RAE
RPCE
25AHPPC

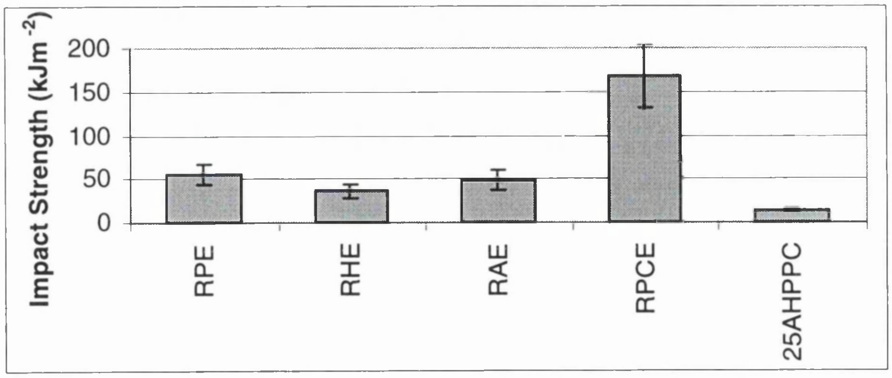
(a)


Strain to Failure (%)
60
50
40
30
20
10
0
RPE
RHE
RAE
RPCE
25AHPPC

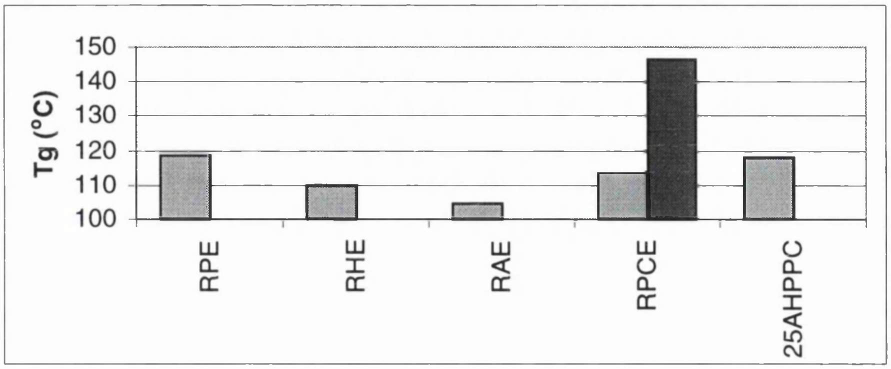
(b)


Tensile Modulus (MPa)
2000
1500
1000
500
RPE
RHE
RAE
RPCE
25AHPPC

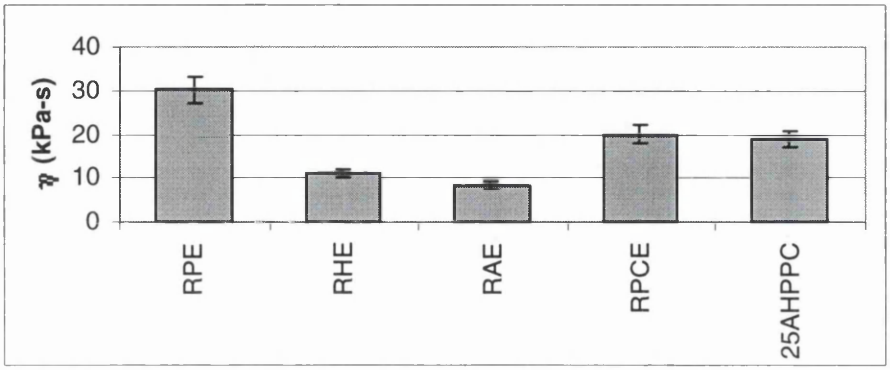
(c)


Impact Strength (kJm^{-2})
200
150
100
50
0
RPE
RHE
RAE
RPCE
25AHPPC

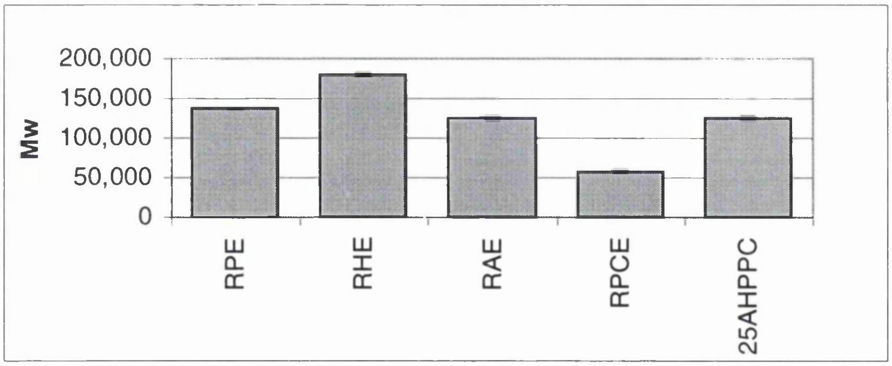
(d)



(e)



(f)



(g)

Figure 7.8 Comparison of test results of recycled ABS, HIPS, PPO and PC/ABS, with a 25% blend of all four plastics, showing (a) tensile strength (b) strain to failure (c) tensile modulus (d) impact strength (e) glass transition temperature (f) viscosity (g) weight average molecular weight expected as these results did not see a great deal of variation between recycling processes.

If all results of the blend 25AHPPC had shown an average of the constituent plastics for all results, this would have been an indication of blend compatibility. As a result it could have been possible to assume that blending these four plastics at any proportion would not have been too detrimental to properties, and so this could have reduced the need for such accurate plastics identification systems in a recycling process. However this is not the case, as strain to failure and impact strength were reduced to extremely low levels, much lower than the lowest constituent plastic (ABS for strain to failure and HIPS for impact strength). On the whole both tensile and impact fracture surfaces appear fairly brittle (Figure 6.90). A bulk fracture surface studied with a SEM (Figure 6.85) does not resemble that of any of the constituents, and certainly seems to show many separate regions, with poor compatibility between them. This is despite the fact that a single T_g value was recorded. Some particles that are probably impact modifiers can be seen, but the coarse microstructure seems to have been the main cause of poor ductility and impact strength. To improve these values, better compatibility between the materials would be needed, which could probably be obtained via the use of compatibilising additives.

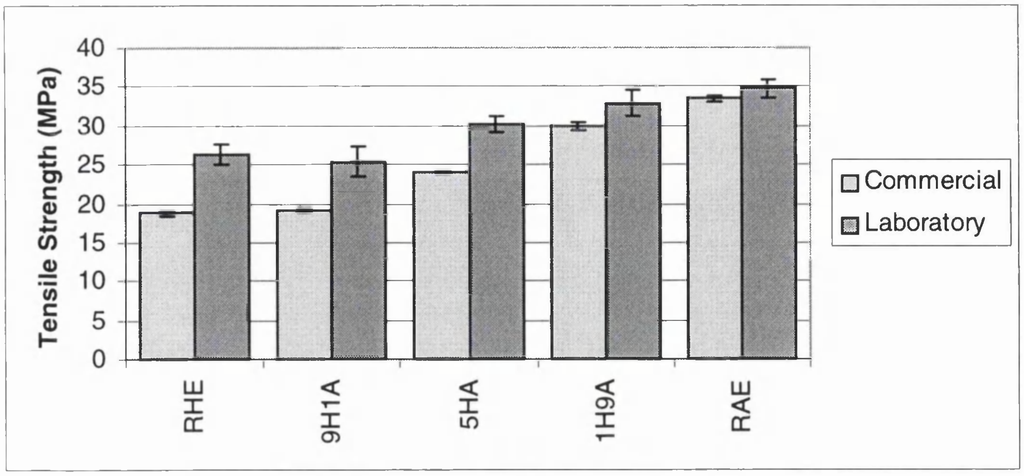
7.3 COMPARISON BETWEEN A COMMERCIAL SCALE RECYCLING PROCESS WITH A LABORATORY SCALE RECYCLING PROCESS.

The histograms comparing test results from samples reprocessed under laboratory conditions with those reprocessed on commercial scale are assembled in Figure 7.9. Results are only compared for tensile testing, impact testing and DMTA, as this was the extent of the testing undertaken by the previous project [17]. The purpose of this part of the project is to evaluate whether or not reprocessing under laboratory conditions could provide sufficiently realistic results, or whether results are more accurate when generated on a commercial scale.

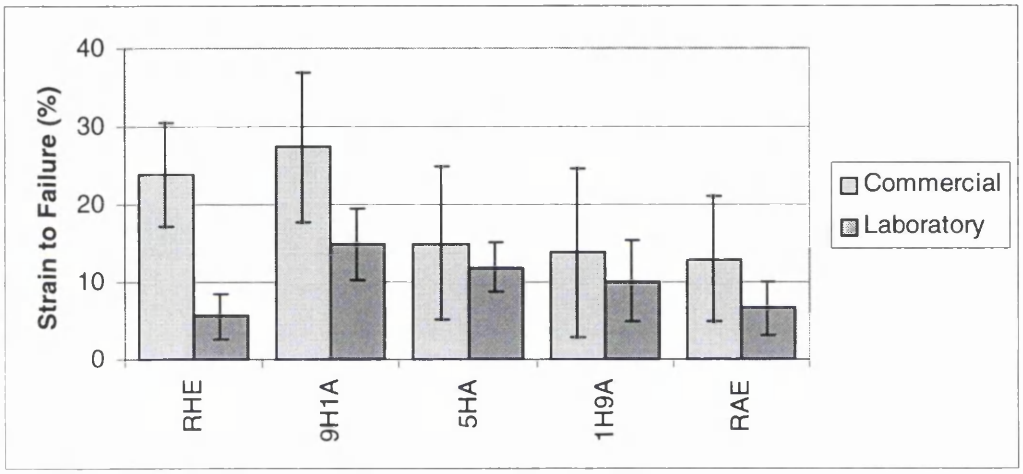
In general the trend for both commercial and laboratory results are the same in that the effects of blending ABS and HIPS on properties are no more than already seen by recycling however the two scales of recycling display different levels of results for each property. The laboratory scale samples display higher tensile strengths and stiffness, while the commercially recycled samples exhibit higher levels of ductility, impact strength and T_g. Therefore the main aim of this section is to determine possible reasons for such differences between each set of results.

Comparison of tensile moduli in Figure 7.9c certainly show the laboratory produced samples to display the higher stiffness by a substantial amount. All tensile moduli from the results of all materials tested in this project are thought to be lower than published text book figures, while the small laboratory samples, appear to exhibit a more realistic modulus. Commercial samples that were tested using the crosshead movement of the Hounsfield tensometer with no laser extensometer were found to show higher stiffness, although not to the same extent as the laboratory samples. This indicates that different test techniques produce slightly different results, although this is not the only factor contributing to differences between each set of results.

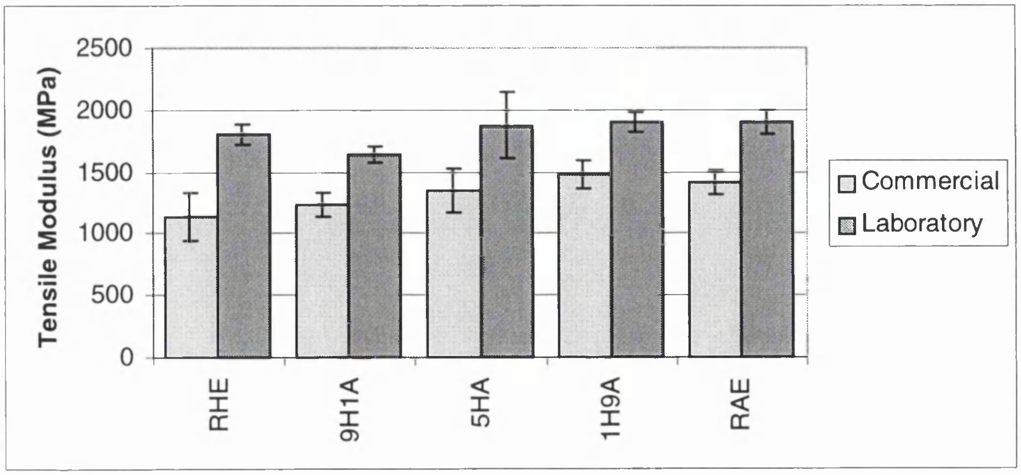
Other factors include differences in sample geometry. It was thought that the overall differences between strains to failure could be due to different sample geometry, as the commercially recycled samples were considerably larger than the laboratory produced samples in all dimensions. For example the cross-sectional area of the tensile gauge was 4x4mm for laboratory samples and 4x10mm for the commercial samples. Although the sample size should be irrelevant to results, this factor could be true if the lab scale samples had higher residual orientation of polymer


Tensile Strength (MPa)
0
5
10
15
20
25
30
35
40
RHE
9H1A
5HA
1H9A
RAE
Commercial
Laboratory

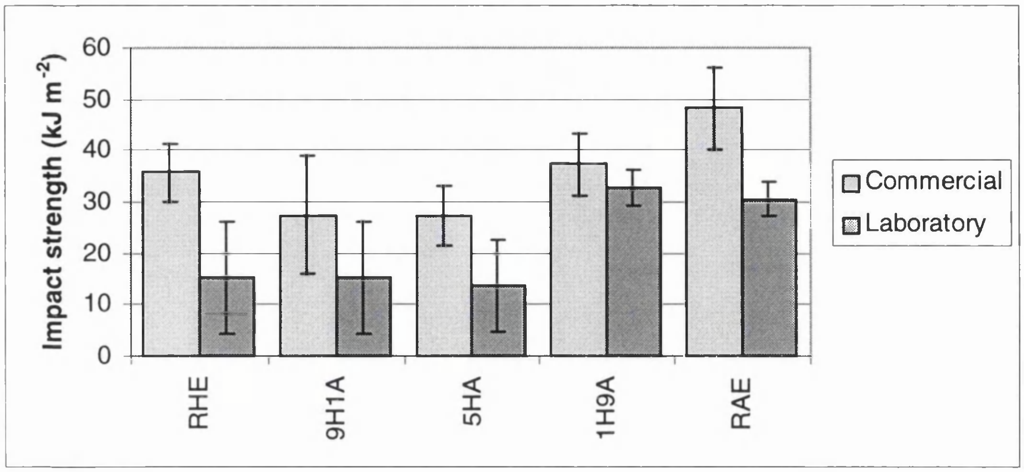
(a)


Strain to Failure (%)
0
10
20
30
40
RHE
9H1A
5HA
1H9A
RAE
Commercial
Laboratory

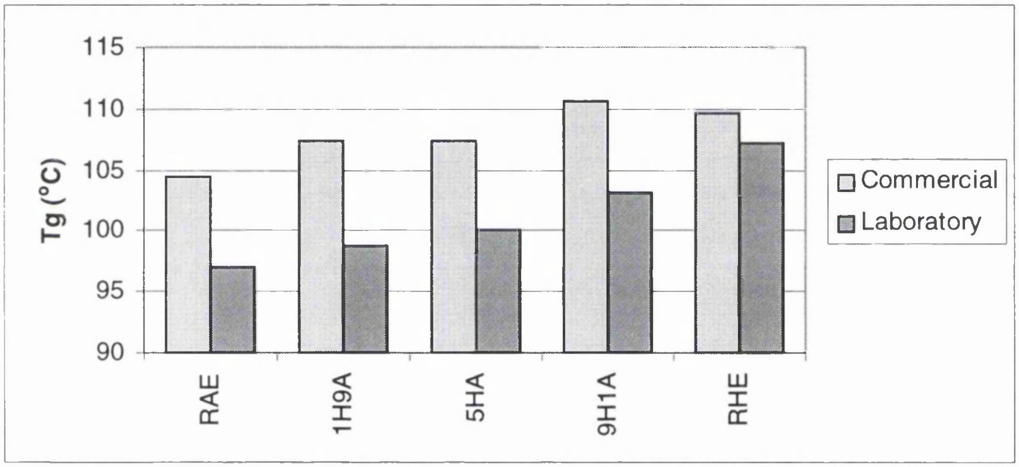
(b)


Tensile Modulus (MPa)
0
500
1000
1500
2000
2500
RHE
9H1A
5HA
1H9A
RAE
Commercial
Laboratory

(c)



(d)



(e)

Figure 7.9 Comparison of test results of blends of recycled ABS and HIPS using comparing samples made for this project using a commercial scale recycling process with results from previous work [14] that used a laboratory scale recycling process, showing (a) tensile strength (b) strain to failure (c) tensile modulus (d) impact strength (e) glass transition temperature chains along the gauge length following injection moulding. This is probably due to a faster injection rate and differences in mould temperature and cooling rate. If this were the case, the smaller more oriented samples would be expected to have higher strength and stiffness and lower ductility. It would have been possible to determine the extent of orientation by various methods, including thermal expansion measurements and birefringence measurements on thin sections. The easiest methos would have been one of annealing the samples and measuring the amount of shrinkage as residual orientation recovers. However due to unavailability of such samples, sample orientation could not be studied.

Another possible explanation as to differences between the results of commercial and laboratory recycling would be to consider reprocessing differences. Essentially, both recycling processes are the same and involve granulation, thermal mixing, re-granulation and injection moulding. However apart from the scale, the main difference lies in the thermal mixing part of the process. The commercial samples were extruded, while the laboratory samples were mixed in a torque rheometer. Previous work [138] found that extrusion could cause crosslinking of some plastics and results show that this may have happened to ABS and HIPS (Figures 6.62 and 6.63 respectively). The extrusion process involves feeding the granulated plastic along a rotating screw, passing it through a die and into a cooling bath, and as the polymer chains of the material are sheared, the temperature will be sufficient that they will be just as likely to link up with other chain ends. Thermal mixing using a torque rheometer however, involved encasing the granulated material into a cavity with two rotating mixers. The material is not able to travel anywhere and stays in the cavity until the process is manually stopped. The possibility for chain scission and crosslinking is just as likely as extrusion if not more and previous conclusions [17] had speculated that this method of thermal mixing could be a lot harsher on the material than an extrusion process. If more crosslinking did occur in plastics processed in the torque rheometer than when extruded, it is highly likely that such plastics would be a stronger, stiffer material at the expense of ductility and impact properties, which could explain the general differences in results between the commercial scale and laboratory scale recycling processes. However this is difficult to positively conclude as studies on a laboratory scale did not include molecular weight, which would have been an extremely useful piece of information.

The commercial glass transition temperatures results are several degrees higher than those of the laboratory results. This was not expected as the T_g of a material should be the same, especially considering the similarities of processing histories. The simple explanation for this can only be attributed to the placing of the thermocouple during testing, which can give quite varied results for the same material when placed in different parts of the testing oven. Several DMTA experiments for this project were repeated when quite different results were obtained with the thermocouple placed near the floor of the oven to when it was placed higher up beside the sample. Therefore the laboratory recycled samples could possibly have been tested with the thermocouple in a different place, although differences in results indicate that this was not necessarily at the bottom of the furnace.

Overall both the commercial and laboratory recycling processes had the same effects on recycling and blending HIPS with ABS in that blending has no more effect on properties than already seen by recycling. The main differences between the sets of results are due to a combination of factors including scale differences in thermal mixing and injection moulding, which probably caused more orientation in laboratory processed samples, as well as differences between testing techniques.

CHAPTER 8:

CONCLUSIONS AND FURTHER WORK

8.1 CONCLUSIONS

8.1.1 Identification

- A study was undertaken in an attempt to identify the presence of flame retardant additives using the FTIR spectra of different plastics used in computer equipment as well as comparisons with IR spectra from different flame retardants. Comparisons could only be made with ABS due to insufficient numbers of spectra of the other plastics. These comparisons are inconclusive because the IR spectrum of a flame retardant will change when incorporated into a plastic, and would probably be no different for the other plastics. Therefore the only significant conclusion drawn is that while infrared spectroscopy provides accurate identification, in the current state of technology it cannot be used to determine the content of flame retardants in a plastic and must therefore be combined with other methods in order to ensure accurate detection.
- Several plastics identification systems were analysed using one hundred samples from various computer housings used in previous work [17]. Comparisons of results from FTIR spectroscopy from previous work [17] with several rapid plastics identification systems, found that all systems appeared to be unable to identify the samples thought to be acrylic. Further analysis using FTIR spectroscopy found that these samples were double sided with one side HIPS and the other acrylic, which explains the conflict between results from different

techniques. This raises additional points to consider, as to the implications that mixing HIPS and acrylic would have on recycling.

- Another conflict between results of different techniques of elemental analysis of plastics from previous work [17] brought about further analysis of PPO and PC/ABS using x-ray microanalysis. It was found that the P peaks had similar energy levels to those of the gold conductive coating, which could be seen as slight shoulders on the Mα and Mβ gold peaks. Samples of PPO and PC/ABS that were analysed further were therefore all found to contain P, which is commonly used in flame retardant in these plastic types.
- Other systems studied and compared with FTIR spectroscopy and elemental analysis include NIR and MIR spectroscopy and sliding spark, a form of pyrolytic spectroscopy. From this study it has been found that all systems have the need of some improvement in order to increase identification accuracy. A main issue with all systems is the need for a better reference library database to suit the types of plastics more common to the electrical and electronic sector. Most systems also need some fine-tuning to be able to better distinguish between styrenic plastics, such as ABS, HIPS and PPO. This could be accomplished by programming a system to look for the presence of absence of specific peaks.
- The mIRo, which is based on NIR, was found to be the most potentially accurate identification system at present, however it was not able to identify any black or dark plastics. Both MIR systems had no problems regarding plastic colour, however not one of the infrared systems was able to successfully distinguish flame retardant additives, which illustrates the conclusion that IR spectroscopy at the present time is unable to detect the presence of additives in a plastic.
- The SSS2 is not as accurate in plastics identification as what could potentially be reached by the infrared systems. However it was found to be the most effective at flame retardant detection. Therefore the most effective way of identifying plastics from waste computer equipment and detecting flame retardants would be through a combination of techniques such as an IR system, preferably one that can identify dark coloured plastics, with the SSS2 for flame retardant detection.
- FTIR spectroscopy as well as many other plastics identification systems, generally identify a plastic by trying to match the whole spectra with those usually stored on a database. A possible way of improving the speed and accuracy of identification

would be to use a simple process of elimination and match just a few prominent peaks rather than the whole spectrum, or a combination of both. By applying the flow chart in Figure 4.14 into a software programme, this could change the way a plastic is identified and contribute significantly to the improvement of rapid plastics identification technology.

8.1.2 Mechanical Recycling

- From this study it appears that the changes in properties due to recycling of individual materials are quite small. None shows any real changes in strength or stiffness following extrusion, although there are slight reductions in ductility for HIPS and mPPO. For HIPS, this seems to be due to impurity particles that were present on fracture surfaces (Figure 6.87). As mPPO is likely to be a commercial blend with HIPS, the decrease in ductility is probably due to degradation of the PB rubber at the higher processing temperatures for this material. In contrast, the impact strength of ABS and M_w of PC/ABS seem to increase with extra processing. This is probably due to better mixing and inter-phase adhesion that helps to remove any moisture that may have been extracted from exposure to air.
- On the whole, it appears that blending HIPS and ABS has negligible effect on almost all properties and any changes are according to blend proportions. The only exception is seen in impact strength, which decreases significantly for all blends. This is probably due to poor adhesion between the two polymer types at any proportion but could also be due to the deterioration of the butadiene rubber that is present in both plastic types. It has been suggested that impact properties may be improved by adding MMA graft rubber [165].
- Blending HIPS and mPPO has no effect on most properties following recycling apart from changes according to the linear law of mixtures. Blending is actually beneficial to ductility and impact strength, both of which are significantly improved, more than restoring any ductility lost due to recycling. These properties continue to increase with the most favourable results being seen at the blend of equal quantities. This shows excellent compatibility between the two plastic types, which means that they may be recycled and blended at any proportion.

- Blending and recycling ABS with PC/ABS also has negligible effects on most properties according to the law of mixtures, apart from ductility and impact strength, both of which decrease following blending. The worst results are for the 50% blend, which not only sees the lowest strain to failure and impact strength, but shows a decrease in tensile strength too. This is thought to be due to oxidative degradation of the butadiene rubber phase or the presence of flame retardants in the ABS part of the blend that can also degrade the PC phase. Other work has suggested that impact properties can be improved with a core shell impact modifier such as MBS. It appears that recycling and blending small proportions of ABS in PC/ABS and vice versa is tolerable however, increasing the content of either plastic type in the other is detrimental to properties and creates a very brittle material.
- Recycling and blending ABS, HIPS, mPPO and PC/ABS together gives an average value for each property when comparing with those from each constituent plastic. However the strain to failure and impact strength are drastically reduced indicating poor compatibility of all four materials. This indicates that an accurate rapid plastics identification process is still very necessary as part of an economical recycling process. However as properties of all plastics used in this study appear unaffected by the presence of a small proportion of another plastic, an identification system probably does not need to be exactly 100% accurate.
- Overall both the commercial and laboratory recycling processes showed the same trends for recycling and blending HIPS with ABS in that blending has no more effect on properties than already seen by recycling. The main differences between the sets of results are due to a combination of factors including differences in scale of thermal mixing and injection moulding, which probably caused more orientation in laboratory processed samples, and differences between testing techniques. However as trends were the same the laboratory scale experiments would be valid for predicting the behaviour of commercially recycled plastics.

8.2 FURTHER WORK

- Some of the samples identified in this study by FTIR spectroscopy were found to be double-sided plastics of HIPS and acrylic. As the recycling implications of this find regarding the contamination of HIPS with acrylic are unknown, it would be useful to conduct further investigative studies. Some considerations could include the extent of how much more material is double sided, whether this occurs with other plastics apart from HIPS, the thickness of each plastic layer, how they are bonded and also how what will become a blend of HIPS and acrylic will be affected by a recycling process.
- It is currently concluded that IR spectroscopy cannot be used in flame retardant detection within a plastic at the current proportion of flame retardancy. However it could be interesting to see if varying levels of flame retardant would have any effect on an IR spectrum and if so just what proportion of flame retardant would need to be present before it could be detected. This could also be applied to other identification systems in order to find out the minimum amount of flame retardant that would need to be present for detection by the SSS2 for example.
- When looking at the different systems that are available for rapid plastics identification, part of the testing of the P/ID22 from Bruker Optics Ltd involved setting up a new library database using some of the samples being tested for reference spectra. The results of the P/ID22 using the new library were excellent and so it would probably be useful to be able to do this with the other identification systems that were looked at. This could be a study to see if each system would produce more accurate results by tailoring the library of spectra to a specific application.
- The blends of plastics that were chosen for this project are just a few of the combinations that could have been studied, however time limitations restricted the types of blends chosen to what seemed to be the most compatible. It could therefore be possible to explore other blend combinations possible of the four plastics used in this project. Some of these could include HIPS/(PC/ABS), mPPO/(PC/ABS), ABS/mPPO and ABS/HIPS/mPPO for example as well as a more proportionally representative mix of the four plastics as opposed to the 25% blend. Studies could also include combinations with some of the lesser used

plastics on computer housings such as acrylic and PMMA, PP, ABS/PVC, PC and PVC.

- Impact properties deteriorated as a result of recycling and blending some of the plastics, especially in HIPS and ABS. It has been suggested that this may be overcome by using a suitable impact modifier, however little is known how that will affect a plastic during the next recycling process. As many plastics will contain a substantial amount of additives, it would be useful to find out the extent to which such additives incorporated before and during recycling affect properties of a plastic.
- Some of the problems faced when recycling computer equipment housings include dismantling difficulties. Many computer casings have attached rubber feet and often have labels fixed by adhesive that are time consuming to remove but are considered as impurities in the recyclate. However as little is known about the effects of contamination from such labels, adhesives and rubber feet, it is a possible aspect to investigate as well as different solutions for removal during different stages of a recycling process.
- The WEEE directive, which has recently become part of European legislation has stipulated an increasing quantity of recycled or refurbished material in electrical and electronic equipment. It could therefore be quite practical to investigate the feasibility of blending proportions of recycled plastics with virgin material with the view to become new/recycled housings for computer equipment.

BIBLIOGRAPHY

---

[1] Eisenreich N., Rohe T.., 'Infrared Spectroscopy in Analysis of Plastics Recycling.', Encyclopedia of Analytical Chemistry., pp 7623-7644, John Wiley & Sons 2000

[2] APME Positioning Paper., 'Plastics Recovery.', November 1996

[3] Trautz V., 'Die Entwicklung Der Westeuropaischen Kunststoffindustrie.', Kunststoffe Vol.88 (10) pp.1648-1652, 1998

[4] Mayne N., 'Energy from Waste Projects; Integration of Plastics Recovery Routes for Success.', Waste to Energy International Management Industry conference., Brussels Dec. 2000

[5] APME Report., 'Plastics: An Analysis Of Plastics Consumption And Recovery in Western Europe 1998.', Spring 2000

[6] APME Report., 'Plastics: An Analysis Of Plastics Consumption And Recovery in Western Europe 1999.', Spring 2001

[7] APME Summary Report., 'Assessing The Potential For Post-Use Plastics Waste Recycling–Predicting Recovery In 2001 And 2006.' 1998

[8] APME Report., 'Plastics: A Material Of Choice For the 21st Century. Insight Into Plastics Consumption And Recovery In Western Europe 1997.', February 1999

[9] Rowatt R.J., 'The Plastics Waste Problem.', Chemtech, January 1993 pp.56-60

[10] APME Report., 'Plastics: Resource Optimisation.' 1995

[11] APME Summary Report., 'Assessing The Eco-Efficiency Of Plastics Packaging Waste Recovery.', 2000

[12] TNO Report., 'Best Practices For The Mechanical Recycling Of Post-User Plastics.', TNO Institute of Industrial Technology, 2000

[13] Brandrup E.J., 'Recycling And Recovery Of Plastics.', Hanser 1996

[14] APME Report., 'Plastics: An Analysis Of Plastics Consumption And Recovery in Western Europe 2000.', Spring 2002

[15] APME Press release, 'Growth in Plastics Waste Recovery Outpaces Consumption.', ENDS., 10 April 2000

[16] APME Report., 'Plastics: A Material Of Innovation For The Electrical And Electronic Industry. Insight Into Consumption And Recovery In Western Europe 2000.', Summer 2001

[17] Brennan L.B., 'Recycling ABS And HIPS From Waste Electrical and Electronic Components.', MPhil Thesis., University of Wales, Swansea., 2000

[18] Cosentino F., Clasper I., 'Waste From Electrical And Electronic Equipment: A Review Of Proposed Legislation.', Measurement and Control., Vol.32 (10) December 1999

[19] Anon. 'Design Issues In Waste Avoidance.', Carnegie Mellon University Department of Engineering and Public Policy, 1991

[20] Matthews H.S., McMichael F.C., Hendrickson C.T., Hart D.J., 'Disposition And End-Of-Life Options For Personal Computers.', Green design initiative technical report, Carnegie Mellon University, 1997

[21] APME Report., 'Plastics: Mechanical Recycling.' 1995

[22] APME Report., 'Plastics: A Material Of Choice For The Electrical And Electronic Industry; Plastics Consumption And Recovery In Western Europe 1995.', 1998

[23] APME Report., 'Plastics: A Material Of Choice For The Automotive Industry; Plastics Consumption And Recovery In Western Europe 1995.', 1998

[24] APME Report., 'Plastics: A Material Of Choice In Building And Construction; Plastics Consumption And Recovery In Western Europe 1995.', 1998

[25] APME Report., 'Plastics: A Material Of Choice For Packaging; Insight Into Consumption And Recovery In Western Europe.', 1999

[26] Kingsbury T., 'Source Reduction Expressed In Recycling Terms.', Conference Report RRR99, 1999

[27] APME Summary Report., 'Plastics, Less Is More.', 1996

[28] APME Report., 'Plastics: Prevention And Re-Use.' 1995

[29] Anon., 'For Our Children's Children…..A Future.', Information brochure by REPRISE, a division of the PVC group plc., 1999

[30] Schalles H., 'Recycling Technologies.', Kunststoffe Plast Europe., Vol. 87 (11) November 1997

[31] Sasse F., Emig G., 'Chemical Recycling Of Polymer Materials.', Chemical Engineering Technology., Vol. 21 (10), pp.777-789, 1998

[32] APME Report., 'Plastics: Feedstock Recycling.' 1995

[33] Sodero S.F., Berruti F., Behie L.A., 'Ultrapyrolytic Cracking Of Polyethylene – A High Yield Recycling Method.', Chemical Engineering Science., Vol.51 (11) pp.2805-2810, 1996

[34] APME Report., 'Plastics: Energy-From-Waste.' 1995

[35] Anon., 'European Parliament And Council Directive 94/62/EC Of 20 December 1994 On Packaging And Packaging Waste.', Official Journal Of The European Communities Vol. L 365, pp 0010-0023, 31 December 1994

[36] Tomlins P., Scoggins C., 'Saving More Plastics From The Scrap Heap.', Materials World., Vol.7 (3) March 1999

[37] Recyclers World, January 1999

[38] Anon., 'No Increase to Packaging Targets.', Materials Recycling Weekly., 25 October 2002

[39] Anon., 'Packaging Revision Could Lead to Stagnation.', Materials Recycling Weekly., 1 November 2002

[40] Anon., 'The MRW Report – Legislation. Regulation Timetable.', Materials Recycling Week., 17 January 2003

[41] Anon., 'Recycling PVC; Less waste, More value.', European Vinyls Council 1991

[42] Commission of the European Communities., 'Directive 2000/53/EC Of The European Parliament And Of The Council Of 18 September 2000 On End Of Life Vehicles.', Official Journal Of The European Communities Vol. L 269, p.34, 21 October 2000

[43] Recyclers World., January 1999

[44] Belmann K., Khare A., 'European response to issues in recycling car plastics.', Technovation, Vol. 19, pp. 721-734, 1999

[45] APME Report., 'Plastics: A Material Of Choice For The Automotive Industry. Insight Into Consumption And Recovery In Western Europe.', Summer 1999

[46] Pett R.A., Golovoy A., Labana SS., 'Automotive Recycling.', Plastics, Rubber and Paper Recycling., Vol 69, pp 47-61, 1995

[47] Allred R.E., Buselle L.D., 'Tertiary Recycling Of Automotive Plastics And Composites.', Journal Of Thermoplastic Composite Materials., Vol. 13 (2), pp. 92-101 March 2000

[48] Commission of the European Communities., 'Explanatory memorandum – Proposal For A Directive Of The European Parliament And Of The Council On Waste Electrical And Electronic Equipment And On The Restriction Of Use Of Certain Hazardous Substances In Electrical And Electronic Equipment', European Union., Brussels., June 2000

[49] Commission of the European Communities., 'Proposal For A Directive Of The European Parliament And Of The Council On Waste Electrical And Electronic Equipment.', European Union., Brussels., June 2000

[50] Commission of the European Communities., 'Directive Of The European Parliament And Of The Council On The Restriction of the Use of Certain Hazardous Substances in Electrical And Electronic Equipment.', European Union., Brussels., November 2002

[51] Anon., 'Bromine: Frequently Asked Questions.', Report by BSEF., October 2001

[52] Anon., 'An Introduction to Brominated Flame Retardants.', Report by BSEF (Bromine Science and Environmental Forum)., October 2000

[53] Commission of the European Communities., 'Working Paper For a Directive Of The European Parliament And Of The Council On The Impact on the Environment of Electrical And Electronic Equipment (EEE).', European Union., Brussels., February 2001

[54] News Article., 'Deadline Set For WEEE Law.', Materials Recycling Week., 21 February 2003

[55] Bennett J., 'Electronics; Refurb or Recycle.', Materials Recycling Week., 7 February 2003

[56] Bennett J., 'Electronics; Multi-White Goods Waste Facility Set to Open.', Materials Recycling Week., 7 February 2003

[57] Bennett J., 'Electronics; E-waste to be Transformed.', Materials Recycling Week., 14 March 2003

[58] Thyer R., 'Transform Joint Venture to Meet WEEE Needs.', Materials Recycling Week., 28 February 2003

[59] Humes A., Grimes S., Boyce J., 'Environmental Product Attributes In End-Of-Life Management In The UK. Part I: And End-Of-Life Ecodeclaration For Waste IT And Office Equipment.', International Journal of Environment and Pollution., Vol.18 (2), p.109., 2002

[60] Rose C.M., ' Development Of Products Embedded Disassembly Process Based On End-If-Life Strategies.', EcoDesign 99: First International Symposium In Environmentally Conscious Design And Inverse Manufacturing Forum Japan., Japan Environment Management Association for Industry., Tokyo Japan., 1999

[61] Humes A., Grimes S., Boyce J., 'Environmental Product Attributes In End-Of-Life Management In The UK. Part II: Problems Encountered with Informational Systems For The Management of End-Of-Life IT And Office Equipment.', International Journal of Environment and Pollution., Vol.18 (2), p.126., 2002

[62] Pritchard G., 'Plastics Additives An A – Z Reference.', Chapman and Hall., 1998

[63] Birley A.W., Haworth B., Batchelor J., 'Physics of Plastics. Processing, Properties and Materials Engineering.' Hanser Publishers 1991

[64] Brydson J.A., 'Plastics Materials.' Sixth Edition. Butterworth-Heineman Ltd., 1995

[65] Callister W.D., 'Materials Science and Engineering and Introduction.' Third Edition., John Wiley and Sons Inc., 1994

[66] Heijboer A., Utevskii L., Bar Yaakov Y., 'Beneficial Effects of Brominated Flame Retardants in Polymeric Systems.', Report for the Dead Sea Bromine Company., 2001

[67] Hardy M.L., 'Regulatory Status And Environmental Properties Of Brominated Flame Retardants Undergoing Risk Assessment In The EU: DBDPO, OBDPO, Pebdpo And HBCD.', Polymer Degradation And Stability, Vol. 64, pp.545-556, 1999

[68] Zaivov G.E., Lomakin S.M., 'Ecological Aspects Of Polymer Flame Retardation.', International Journal Of Polymeric Materials., Vol. 41, pp.153-169, 1998

[69] Anon., 'What does the Emerging European Legislation on WEEE and RoHS Mean for Brominated Flame Retardants.', Report by BSEF., June 2002

[70] Allchin C.R., Law R.J., Morris S., 'Polybrominated Diphenylethers In Sediments And Biota Downstream Of Potential Sources In The UK.', Environmental Pollution, Vol. 105 pp.197-207, 1999

[71] Hooper K., McDonald T.A., 'The PBDE's: An Emerging Environmental Challenge And Another Reason For Breast Milk Monitoring Programs.', Environmental Health Perspectives, Vol. 108 (5) pp.387-392, May 2000

[72] Kaufer H., Von Quast O., 'Recycling Halogen-Containing Plastics.', Kunststoffe Plast Europe., Vol. 87 (2), February 1997

[73] Sjodin A., Hagmar L., Klasson-Wheler E., Kronholm-Diab K., Jakobsson E., Bergman A., 'Flame Retardant Exposure: Polybrominated Diphenyl Ethers In Blood From Swedish Workers.', Environmental Health Perspectives, Vol. 107 (8) pp.643-648, August 1999

[74] Hamm S., Strikkeling M., Ranken P.F., Rothenbacher K.P., 'Determination of Polybrominated Diphenyl Ethers and PBDD/Fs During the Recycling of High Impact Polystyrene Containing Decabromodiphenyl Ether and Antimony Oxide.', Chemosphere., Vol.44, p.1353., 2001

[75] Kennedy, Donkin, 'Prefeasibility Study On Feedstock Recycling.', APME Executive Summary Report., May 1999

[76] Munchen V. K. and Wiesbaden B.W., 'Rapid Identification Of Plastics.', Kunststoffe Plast Europe, Vol.84, March 1994

[77] Shent H., Pugh R.J., Forssberg E., 'A Review Of Plastics Waste Recycling And The Flotation Of Plastics.', Resources, Conservation and Recycling, Vol.25, pp.85-109, 1999

[78] Ablas Marques G., Soares Teno'rio J.A., 'Use Of Froth Flotation To Separate PVC/PET Mixtures.', Waste Management., Vol.20, pp. 265-269, 2000

[79] Krummenacher B., Peuch P., Fisher M., Biddle M., 'Automatic Identification And Sorting Of Plastics From Different Waste Streams.', APME Status Report, November 1998

[80] Inculet I.I., Castle G.S.P. and Brown J.D., 'Electrostatic Separation Of Plastics For Recycling.', Particulate Science and Technology Vol.16, pp.91-100, 1998

[81] Peter Walker Systems (Plastics Identification Technology), http://www.walkersystems.de

[82] APME Technical Report, 'IDENTIPLAST International Conference And Exhibition On The Automatic Identification, Sorting And Separation Of Plastics.', April 1999

[83] Knauf U., Maurer A., Luck T., 'Effective Recycling Of Valuble Plastics By Selective Extraction.', Conference report RRR99, 1999

[84] Bledzki A.K., Kardasz D., 'rapid identification of plastics in recycling processes.', Polimery, Vol.43 (2), pp.79-86, 1998

[85] Campbell D., White J.R., 'Polymer Characterisation; Physical Techniques.', Chapman and Hall, 1989

[86] Kroenig J.L. 'Spectroscopy of Polymers.' Washington D.C. American Chemical Society., 1991

[87] Spells S.J., 'Characterisation Of Solid Polymers, New Techniques And Developments.', Chapman and Hall, 1994

[88] Eisenreich N., Rohe T., 'Identifying Plastics.', Kunststoffe, Vol.86(2), pp.222-224, 1996

[89] Scott D.M., 'A Two Colour Near-Infrared Sensor For Sorting Recycled Plastic Waste.', Measurement Science and Technology Vol.6, pp.156-159, 1995

[90] Freitag H., Huth-Fehre T., Camman K., 'Rapid Identification Of Plastics From Electronic Devices With NIR-Spectroscopy.', Analytical Letters, Vol.33 (7), pp.1425-1431, 2000

[91] Graham J., Hendra P.J., 'Rapid Identification Of Plastics Components Recovered From Scrap Automobiles.', Plastics Rubber and Composites Processing and Applications, Vol.24, pp.55-67, 1995

[92] Zachmann G., Turner P., 'Rapid Characterisation Of Black Polymeric Material By Mid Infrared Reflectance Spectroscopy.', Bruker Analytische Messtchnik GmbH

[93] Murase A., Sato N., 'rapid identification of plastics by pyrolysis infrared spectroscopy with a new pyrolysis probe.', Applied Spectroscopy, Vol.53 (6) pp.745-747 1999

[94] Anon., 'Slidespec-S2 – Sliding Spark Spectrometer For Identifying Plastics.', AGR GmbH company information brochure.

[95] Eisenreich N., Hardle T., Kull H and Rohe T., 'Fast Identification of Polymers and Additives of Mass Consumer Products.', Fraunhofer-Institut fur Chemische Technologie, company information, 1996

[96] Neckel W., 'Radio Frequency Identification (RFID): Applications To Re-Use And Recycle Computers And Other Products.', Department of Electrical Engineering, Princeton Summer Institute, 1998

[97] Ahmed R. 'Marking Of Products With Fluorescent Tracers In Binary Combinations For Automatic Identification And Sorting.', Assembly Automation, Vol.20 (1), pp.58-64, 2000

[98] Woodward A.E., ‘Understanding Polymer Morphology.’, Hanser Publishers., 1995

[99] Boustead I., ‘Eco profiles of the European plastics industry, Report 4; Polystyrene.’, APME report., April 1997

[100] Critchley, Knight, Wright., ‘Heat Resistant Polymers. Technologically useful materials.’, Plenum Press, New York, 1983

[101] Utracki L.A., Weiss R.A., ‘Multiphase Polymers: Blends and Ionomers.’, American Chemical Society., 1989

[102] Yang J., An L., Xu T., ‘The Glass Temperatures of PS/PPO blends.’, Polymer., Vol. 42, p.7887, 2001

[103] Anon., ‘DSC Transitions of Common Thermoplastics.’, Perkin Elmer Report., Perkin Elmer, Norwalk CT USA., 2000

[104] Boustead I., ‘Eco profiles of the European plastics industry, Report 13; Polycarbonate.’, APME report., September 1997

[105] Folkes M.J., Hope P.S., ‘Polymer blends and Alloys.’, Blackie Academic & Professional., 1993

[106] Chiang W., Hwung D., ‘Properties of Polycarbonate/Acrylonitril-Butadiene-Styrene Blends.’, Polymer Engineering and Science, Vol 27 (9) p.632, 1987

[107] Shonaike G.O., Simon G.P., ‘Polymer Blends and Alloys.’, Marcel Dekker Inc., 1999

[108] Kleiner L.W., Karasz F.E., Macknight W.J., ‘Compatible Glassy Polyblends Based upon Poly(2,6-Dimethyl-1, 4-Phenylene Oxide): Tensile Modulus Studies.’, Polymer Engineering and Science., Vol.19 (7) p.519, 1979

[109] Utracki L.A. ‘Polymer Alloys and Blends.’, New York: Hanser, 1989

[110] Paul D.R., Newman S., ‘Polymer Blends, Vol.2.’, New York Academic Press, 1978

[111] Markham R.L., ‘Introduction to Compatibilization of Polymer Blends.’, Advanced Polymer Technology., Vol.10(3), p.231, 1991

[112] Paul D.R., Barlow J.W., Journal of Macromolecular Science Review Macromolecular Chemistry., Vol.C18, p.109, 1980

[113] Yee A.F., Engineering Science., Vol.17, p.213, 1977

[114] Crawford R.J., ‘Plastics Engineering.’ Third Edition. Butterworth-Heineman Ltd., 1998

[115] Kim W.N., Burns C.M., 'Thermal Behaviour, Morphology and Some Melt Properties of Blends of Polycarbonate with Poly(styrene-Co-Acylonitrile) and Poly(Acrylonitrile-Butadiene-Styrene).', Polymer Engineering and Science., Vol.28 (7) p.1115, 1988

[116] Lee M.P., Hiltner A., Baer E., 'Phase Morphology of Injection-Moulded Polycarbonate/Acrylonitrile-Butadiene-Styrene Blends.', Polymer Vol.33 (4) p.685, 1992

[117] Chiang W., Hwung D., 'Properties of Polycarbonate/Acrylonitrile-Butadiene-Styrene Blends.', Polymer Engineering and Science Vol.27 (9) p.632, 1987

[118] Babbar I., Mathur G.N., 'Rheological Properties of Polycarbonate with Poly(Acrylonitrile-Butadiene-Styrene).', Polymer Vol.35 (12), p.2631, 1994

[119] Klason C., Bertilsson H., Xiaodong L., 'Quality Assurance of Recycled Engineering Plastics Using Blend Technology.', Macromol. Symp., Vol. 135, p.193, 1998

[120] Bucknall C.B., 'Toughened Plastics.', Applied Science Publishers Ltd, London.,1977

[121] Donald A.M., Kramer E., 'Plastic Deformation Mechanisms in Polyacrylonitrile-Butadiene-Styrene (ABS).', Journal of Materials Science, Vol.17 p.1765, 1982

[122] Wu S., 'Impact Fracture Mechanisms in Polymer Blends: Rubber Toughened Nylon.', Journal of Polymer Science (Physics) Vol. 21, p.699, 1983

[123] Bucknall C.B., Smith R.R., 'Stress Whitening in High Impact Polystyrene.', Polymer., Vol.6, p.437 1965

[124] Bucknall C.B., Clayton D., Keast W.E., 'Rubber Toughening of Plastics Part 2 Creep Mechanisms in HIPS/PPO Blends', Journal Of Materials Science., Vol.7, p.1443 1972

[125] Bucknall C.B., Clayton D., 'Rubber Toughening of Plastics Part 1 Creep Mechanisms in HIPS.', Journal Of Materials Science., Vol.7, p.202, 1972

[126] Boustead I., 'Eco profiles of the European plastics industry, Report 11; Co-polymers of acrylonitrile-butadiene-styrene (ABS) and styrene-acrylonitrile (SAN).', APME report., October 1997

[127] Newman S., Strella S., 'Stress-Strain Behavious of Rubber-Reinforced Glassy Polymers.', Journal of Applied Polymer Science., Vol.9, p.2297, 1965

[128] Schnabel W., ‘Polymer Degradation. Principles and Practical Applications.’, Hanser International., 1981

[129] Covavisaruch S., Tangratanasophon S., Pisitpong S., ‘Effects of the Number of Recycling Passes in High Impact Polystyrene.’, Conference Report RRR99., Vol.III p.443, 1999

[130] Jamil F.A., Shubber S.D.A., ‘Some Effects of Recycling High Impact Polystyrene.’, Plastics and Rubber Processing and Applications., Vol.9 (3), p.187, 1988

[131] Salman S.R., Al-Jarrah M.F., ‘The Effect of Thermal Aging on the Thermal Stability of Recycled High Impact Polystyrene.’, Polym.-Plast. Technol. Eng., Vol.28 (9), p.1003, 1989

[132] Salman S.R., ‘Photochemical Degradation of Recycled High-Impact Polystyrene.’, Polym-Plast. Technol. Eng., Vol. 32 (1&2), p.115, 1993

[133] Salman S.R., Al-Jarrah M.F., Hammo S.A., ‘Thermal Aging on the Dielectric Properties of Recycled High Impact Polystyrene.’, International Polymer Processing., Vol.4 (1), p.32, 1989

[134] Salman S.R., Al-Jarrah M.F., Hammo S.A., ‘Effect of Thermal Aging on the Optical Properties of Recycled High Impact Polystyrene.’, Polymer Degradation and Stability., Vol.23 (1), p.75, 1989

[135] Tang H.Y., Chaffey C.E., ‘Mechanical and Flow Properties of Recycled Filled Polystyrene.’, Plastics and Rubber Processing and Applications., Vol.12 (1), p.53, 1989

[136] Djidjelli H., Benachour D., ‘Effects of Recycling on Mechanical and Thermal Properties of Polystyrene.’, Macromol. Symp., Vol.127 p.181, 1998

[137] Kim J.K., Kang C.K., ‘Basic Studies of ABS Resin.’, Polym.-Plast. Technol. Eng., Vol.34 (6), p.875, 1995

[138] Laverty J.J., Ellis T., ‘Effect of Processing on the Recyclability of Nylon 66/Poly(2,6 Dimethyl-1,4 Phenylene Oxide) (PPO) Alloys.’, Polymer Engineering and Science., Vol.36 (3), February 1996

[139] Tall S., Karlsson S., Albertsson A., ‘Improvements in the Properties of Mechanically Recycled Thermoplastics.’, Polymers and Polymer Composites., Vol.6 (5), p.261, 1998

[140] Liu X.D., Bertilsson H., ‘Recycling of ABS and ABS/PC Blends.’, Journal of Applied Polymer Science., Vol. 74 p.510, 1999

[141] Liu X.D., Boldizar A., Rigdahl M., Bertilsson H., 'Recycling of Blends of Acrylonitrile – Butadiene – Styrene (ABS) and Polyamide.', Journal of Applied Polymer Science., Vol. 86 p.2535, December, 2002

[142] Bledzki A.K., Barth C., 'Contaminants in Polycarbonate.', Kunststoffe Plast Europe., Vol. 87 (9), p.1124, September 1997

[143] Brennan L.B., Isaac D.H., Arnold J.C., 'Recycling of Acrylonitrile-Butadiene-Styrene and High Impact Polystyrene From Waste Computer Equipment.', Journal of Applied Polymer Science., Vol.86, p.572., 2002

[144] Ashby M.F., Jones R.H., 'Engineering Materials 1 An Introduction to their Properties and Applications.', Pergammon Press., 1991

[145] Higgins R.A., 'Properties of Engineering Materials.', Edward Arnold., 1977

[146] Brown W.E. (Editor), 'Testing of Polymers.', Volume 4., Interscience Publishers., 1969

[147] Cowie J.M.G., 'Polymers: Chemistry and Physics of Modern Materials 2nd Edition.', Blackie Academic and Professional, 1991

[148] Hall C., 'Polymer Materials An Introduction for Technologists and Scientists 2nd Edition.', Macmillan Education Ltd, 1989

[149] Cowie J.M.G., European Polymer Journal., Vol. 11, p.297, 1975

[150] Anon., 'DMTA MkIII User Mannual for Software Release V5.41.', Rheometric Scientific

[151] Whorlow R.W., 'Rheological Techniques.' Second Edition., Ellis Horwood., 1992

[152] Barnes H.A., Hutton J.F., Walters K., 'An introduction to Rheology.' Elsevier., 1989

[153] Ravji S.J., 'Rheological Evolution of Fractal-Like Gel Structures.' PhD Thesis., University of Wales, Swansea., 2000

[154] Arnold J.C., 'Materials Resources (Part B).', Part I Lecture course., Materials Engineering., University of Wales, Swansea., 1993

[155] Bovey F.A., Winslow F.H., 'Macromolecules an Introduction to Polymer Science.', Academic Press, 1979

[156] Sawyer L.C., Grubb D.T., 'Polymer Microscopy.', Second Edition., Chapman and Hall., 1996

[157] Kemp W., 'Organic Spectroscopy Third Edition.', Macmillan Education Ltd, 1991

[158] Szymanski H.A., 'Infrared Band Handbook.', Plenum Press New York 1966

[159] Steele D., The Interpretation of Vibrational Spectra.', Chapman and Hall Ltd, 1971

[160] Daimay L. V., Colthup N.B., Fately W.G., Grasselli J.G., The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules.', Academic Press 1991

[161] Haslam J., Willis H.A., Squirrel D.C.M., 'Identification and Analysis of Plastics. 2nd Edition', Butterworth & Co Ltd, 1972

[162] Sutliff T.M., Scott R.W., Anderson D.G., Duffer J.K., 'An Infrared spectroscopy Atlas for the Coatings Industry.', Chicago Society for Coatings Technology, 1980

[163] Seidel T., 'mIRoSpark – Universal Solution For Identifying Plastics.', Individual Optical Systems, Company information brochure.

[164] Anon., 'Plastics-Multipurpose Test Specimens ISO 3167:2002.', European Committee for Standardization, 2003

[165] Keskula, Paul D.R., 'Methyl-Methacrylate Grafted Rubbers as Impact Modifier for Styrenic Polymers.', Polymer Science and Engineering., Preprint., Vol. 57, P.674, 1987

[166] Torikai A., Murata T., Fueki K., Polymer Degradation and Stability., Vol. 7, p.55, 1984