RESEARCH ARTICLE

Diffusion mechanism and properties of chemical liquids and their mixtures in 977-2 epoxy resin

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Abstract

Epoxy resin is a versatile high-performance thermosetting material with attractive properties for many engineering applications. However, epoxy resins may come into contact with various chemical liquid environments while in service which can degrade their mechanical properties and deteriorate their performance. Water diffusion into epoxy resins is well-studied; however, little research has been reported on the diffusion mechanisms of other liquids/solvents and their mixtures. Therefore, this study addresses this gap through the use of gravimetric analysis to investigate the absorption of water and various chemical liquids, and their mixtures into epoxy resin. The liquid diffusion characterizations, which include weight gain, diffusion coefficients, and edge effects have been investigated. A two-stage absorption process was observed for water, ethanol, methanol, and their mixtures. A unique three-stage diffusion process of butyl formate, decalin, and their mixtures in 977-2 epoxy resin was observed. A correction factor was used to account for the edge effects. The experimental results showed a dependency of saturation levels and diffusion coefficients on the polarity of the liquids and on the interaction level between the penetrants and the polymer. Furthermore, the absorption rate of the binary mixtures is intermediate between the rates of either penetrant.

KEYWORDS
edge effects, epoxy resin, liquids absorption, moisture diffusion, two-stage moisture uptake

1 | INTRODUCTION

Exposure of polymers to chemical liquids is a crucial mechanism for degradation in polymeric materials, therefore it is important to understand the diffusion mechanism and long-term effects of chemical liquids on polymer systems. The absorption process of the chemical liquids in the polymer depends on the interaction energy between the polymer and the absorbed liquid molecules and the concentration of the chemical liquid.[1] Moreover, the time taken for damaging liquids to diffuse in sufficient concentrations to critical regions is the rate-determining step in the aging mechanism. The absorption and diffusion processes of moisture into engineering polymers and their composites have been extensively studied and modeled[2–11] to enable accurate and reliable predictions of the long-term lifetime behavior of these materials.

Applications for epoxy resins range in terms of their use across many engineering disciplines due to their outstanding chemical corrosion resistance, mechanical properties, thermal and dimensional stability, solvent resistance, and ease of processing.[12] Epoxy resins have superiority over several other thermosets in structural applications as well as protective coatings. Moreover, the use of epoxy resins in cryogenic fields for liquid oxygen polymer composite tanks was seen in the work of Wang[13] proposing future use in the next generation of launch vehicles. Therefore, epoxy resins are often used in demanding applications where performance is important, and toughness and strength are necessary.[14]

Epoxy-based materials in many industries can come in contact with not only water, but also with other chemical liquids and solvents which might affect their properties due to swelling, plasticization, and degradation reactions. Degradation normally occurs by chemical reactions such as oxidation, hydrolysis, transesterification, and salt formation when they are in contact with chemical liquids.[15,16] These liquids or their small molecules may diffuse into the network of the epoxy resin and deteriorate the properties of this material. This absorption is largely attributed to the highly hydrophilic state of epoxy resins where moisture can easily enter due to specific functional groups of the cured epoxy resin and its highly polar nature. Research studies carried out by[17,18] confirmed that the free volume fraction is not the only factor determining the water content, but the polarity of the system is crucially important to understand how water or chemical liquids deteriorate properties.[18] This understanding may have practical importance since a wide range of chemicals such as gasoline, oil, acids, and solvents are used in many industries and can be in contact with epoxy-based composites.

The absorption behavior of liquids normally follows different physical and chemical mechanisms where the equilibrium between the liquid components and the polymer may be complex. As liquids are absorbed into a polymer, swelling may occur, which is basically a volume expansion due to the absorbed liquid molecules. In most cases, swelling affects the matrix and the severity of swelling is strongly related to the solubility, absorbed liquid molecular volume, as well as the material stiffness which plays a part.[11] In the case of mixtures of immiscible liquids, the liquid–liquid–polymer system requires the dilation of the polymer matrix to accommodate the absorbed liquids. Therefore, the two absorbed liquids will be in equilibrium throughout the polymer. The tendency of liquid molecules to partition from the liquid mixture into the polymer is measured by the equilibrium swelling.[15] If the liquid composition inside the polymer is similar to the composition of the external liquid, the two liquids will follow what is called the ideal solution behavior where the solvent sorption solvent in polymers is comparable to the Henry's law. On the other hand, if two liquid molecules are strongly attracted to each other compared with the attractions between the liquid molecule and the polymer, then the addition of one liquid to the other leads to reduction in the chance of the partition of the liquid molecules within the polymer which in turn lowers the total swelling. Moreover, if the attraction between the liquid molecules and the polymer is stronger than the attraction between the two liquid molecules, the total swelling is above the swelling of either pure component. The reason behind this behavior is the increase in the total swelling relative to the ideal behavior.[15]

The diffusion of water in epoxy resins and their composites have been extensively studied by many researchers.[2–11,19] All these studies reported Fickian diffusion behavior at the initial stage and deviations from Fick's law at latter stages which is attributed to the resin relaxation phenomena. The dynamic absorption behavior of low molecular weight organic liquids was investigated by Sahlin and Peppas[19] to determine the influence of molecular size and the affinity of the penetrants for the epoxy resin on the sorption behavior. The contents of methanol, ethanol, acetone, and MEK at saturation were about 1.8%, 2.5%, 1.5%, and 2% respectively. The diffusion behavior of methanol was found to be anomalous and could be correlated to the dynamic changes in the dimensions of the specimens. Furthermore, methanol caused changes in the chemical formation of the epoxy resin unlike the other chemical liquids. This indicated that methanol reacted with epoxy resin. Water-ethanol absorption in different polymers was carried out by Tiihonen et al.[20] and different sorption behaviors in the various polymers tested was found mainly due to the difference in hydrophilicity and sorbent-dependent phase transitions of these different polymers. Tusda[16] also studied the effect of NaOH and H_2SO_4 on cured epoxy resin at different temperatures. With NaOH solution, there was initial liquid absorption leading to weight increase followed by weight loss as degraded resin dissolved into the solution. Samples in H_2SO_4 demonstrated similar behavior of initial liquid absorption followed by degradation, but the weight change was much higher than for NaOH solution. The diffusion of water–acetic acid solutions through epoxy resins was investigated by Dutheillet et al.[21] They noticed that the penetration of the diluted acid in water was slower than concentrated acid. Fick's law was unsuitable to describe diffusion in this study partly because of the effects of swelling and also the effect of voids filling with liquid. Chemical resistance testing was carried out by immersion

studies. Samples were immersed in four very aggressive reagents: methylene chloride, 30% nitric acid, 10% acetic acid, and 10% phenol. They concluded that the swelling and diffusion processes took place first, and chemical reaction follows.[22] The diffusion process as well as the synergistic effect of temperature and water molecules was investigated by Yang et al.[23] using 3 wt % NaCl solution in DGEBA epoxy coatings. As temperature increased, the amount of saturated water content in the coating increased. At the lower temperature of 20°C swelling occurred changing the physical structure of the coating, while at 60°C deterioration and degradation of the epoxy coating chains was seen, showing once again an irreversible change to the structure.[23] Two different types of methanol bonding were observed within the structure of novolac epoxy and polyurethane coatings.[24] The experimentation showed that the methanol interacted with the network via hydrogen bonding. The bonding can be categorized into two types, type 1 showed methanol forming a single hydrogen bond, however, type 2 showed methanol forming two hydrogen bonds. The difference in the type of bonding also meant a difference in the physical properties of the epoxy coating. Type 1 produced swelling and plasticization and type 2 formed physical crosslinking restricting its mobility and declining the rate of permeability. Additionally, a comparison was made against ethanol, and methanol caused more severe degradation to the structure.[24] It is essential to understand the process of chemical attacks to polymers to evaluate diffusion behavior and any chemical degradation. Generally, the chemical attack processes of thermosets are due to chemical diffusion into the network causing swelling and subsequent chemical reaction and degradation of the network. The resistance of highly crosslinked thermosets to swelling and diffusion of chemicals will be much better compared with a more open polymer network in turn providing better chemical resistance.[22]

The aim of this study is to investigate and describe in detail the absorption behavior and diffusion process of various chemical liquids (butyl formate, decalin, heptane, ethanol, and methanol) and their mixtures in epoxy resin and compare it to water. The liquids and their binary mixtures used in this study are solvents used widely in various industrial applications. The weight gain of epoxy resin specimens in the different liquids was monitored, and the experimental absorption curves were plotted and compared. Diffusion coefficients were also determined taking in account the edge effect. The diffusion of these penetrants into epoxy resin has received a little attention. Therefore, it is of interest in this study to understand the diffusion mechanism and rate of various liquids and their dependency on the polarity of the liquids. Understanding the diffusion mechanism of various solvents and their

mixtures into epoxy resins would benefit the selection process of suitable materials for various applications in the composites industry, for example, chemical storage tanks, batteries, and protective coatings.

2 | MATERIALS

The material tested in this study is CYCOM 977-2 epoxy manufactured by Cytec Industries Incorporated. CYCOM 977-2 is a 177°C curing toughened epoxy resin with (126°C–138°C) dry and (104°C) wet service capability. The density of 977-2 epoxy resin is 1.31 g/cm³. This epoxy is formulated for autoclave or press molding. CYCOM 977-2 epoxy has an excellent impact resistance, and it has a shelf life of 12 months at (−18°C) and 42 days at (22°C).[25] Two small epoxy resin sheets of 100 × 100 × 4 mm and 100 × 100 × 1 mm were provided by the manufacture. The difference between the sample aspect ratios (geometry) is due to the insufficient amount of the 4 mm sheet for all the different liquids. Therefore, the 1 mm sheet was used for the methanol and methanol/water environments. IsoMet 1000 precision cutter was used to cut the specimens. The liquids used in this study are tabulated in Table 1.

Water and alcohols have similar properties because water molecules contain hydroxyl groups that can form hydrogen bonds with other water molecules and with alcohol molecules, and vice versa. Due to alcohols producing a formation of hydrogen bonds with water, they tend to be relatively soluble in water. Methanol and ethanol are both miscible with water. Therefore, their polarity is strong, and this make them better solvents for ionic compounds and other polar substances compared with hydrocarbons. Methanol has a lower molecular weight and weaker intermolecular forces compared with ethanol. On the other hand, water molecules have smaller diameter compared with the molecules of both ethanol and methanol and this allows them to have much easier diffusion through polymers.[26]

Butyl formate (BF) consists of a single hydrogen atom attached to the carboxyl group (HCOOH) and it has the lowest molecular weight compared with the other carboxylic acids. BF reacts with alcohols to form esters as an acid, and it can also oxidize easily which gives it the nature of an aldehyde. Pure BF is a colorless, toxic, corrosive, and fuming liquid and has good solubility in water and alcohol. Butyl formate is normally used as a chemical intermediate, solvent, and disinfectant.[27]

Decalin (decahydronaphthalene) is a bicyclic organic compound and is generally used as an industrial solvent for many resins or fuel additives. It is a colorless liquid with an aromatic odor.[28] Heptane is a hydrocarbon which is commonly used as a laboratory solvent thanks

TABLE 1 The liquids and their mixtures used in this study

Liquid/solution	Chemical formula	Concentration (vol%)	Specimens' dimensions (mm)
Water	H_2O	100	$22 \times 20 \times 4$
Ethanol	CH_3CH_2OH	100	$27 \times 20 \times 4$
Water/ethanol		50/50	$24 \times 20 \times 4$
Butyl formate	$HCOO(CH_2)_3CH_3$	100	$25 \times 20 \times 4$
Butyl formate/ethanol		50/50	$25 \times 20 \times 4$
Methanol	CH_3OH	100	$26 \times 12 \times 1$
Water/methanol		50/50	$20 \times 12 \times 1$
Water/methanol		25/75	$20 \times 12 \times 1$
Decalin	$C_{10}H_{18}$	100	$23 \times 20 \times 4$
Decalin/butyl formate		50/50	$26 \times 20 \times 4$
Heptane	C_7H_{16}	100	$23 \times 20 \times 4$

to its low reactivity with other molecules. Many substances that do not dissolve in water, normally dissolve in heptane. Heptane is a volatile, colorless, and odorless liquid when pure.[29]

3 | TEST METHOD

All samples were dried in an oven at 70°C until reaching constant weight. The specimens were weighed and then fully immersed in the liquids and their mixtures at room temperature. This process continued until equilibrium was reached. Two epoxy samples were immersed in each of the liquids to obtain averaged diffusion properties. Specimens were taken out at predetermined time durations started with four measurements on the first day of absorption followed by one measurement a day for 2 weeks and then one measurement every week for the rest of the experiment. Surface moisture was removed by using clean tissues. The samples were weighed after wiping them off by putting them in a small tube to make the error resulting from liquid evaporation negligible. The time out of the medium was around 30 s. An analytical balance having a precision of 0.1 mg was used to measure the weights of the samples. Liquid uptake was calculated as weight gains related to the weights of the dry samples. The weight gain was calculated using Equation (1):

$$\text{Weight gain } (M_t)\% = \frac{W_t - W_0}{W_0} \times 100 \quad (1)$$

where, W_0 is the original dry weight and W_t is weight after immersion at time t.

Diffusion properties were characterized using maximum liquid content and diffusion coefficients. Some samples did not reach saturation and would have continued to absorb

liquids if the experimental time were lengthened. Since the Fickian diffusion model is used, it is necessary to extract the Fickian component of the measured data. Therefore, a parametric estimation technique similar to the one used in Refs. [2–10] was used to determine the quasi-equilibrium moisture uptake. In order to fit the measured curves to a Fickian diffusion curve, a tangent was drawn onto the moisture weight gain curve at the long-term diffusion stage. The gradient of this tangent (G_{LT}) is then determined and used to get the best fit to the Fickian diffusion curve and thus the quasiequilibrium moisture content ($M_{\infty,f}$) by using Equation (2). This method was applied for all absorption curves.

$$M_{\infty,f} = M_t - G_{LT}\sqrt{t} \quad (2)$$

The diffusion coefficient is used to determine how fast a liquid can travel through a polymer which is also used to predict the liquid absorption rate with time.[30] Using the derived saturation values ($M_{\infty,f}$ %), the apparent diffusion coefficients with no edge effects considered were determined using Equation (3).

$$D_{app} = \frac{\pi G^2 h^2}{16 M_f^2} \quad (3)$$

where h is the thickness of the sample and G is the gradient determined using Equation (4). It is important to note that the apparent diffusivity is associated only with the initial part of diffusion curve which is Fickian diffusion.

$$G = \left(\frac{(M_{t_2} - M_{t_1})}{\sqrt{t_2} - \sqrt{t_1}} \right) \quad (4)$$

The apparent diffusion coefficient is a one-dimensional approximation and does not consider diffusion through the edges of the specimen. Therefore, a correction derived by Shen and Springer[31] was used to account for the edge effects on diffusion. The true diffusion coefficient (D) was calculated using Equation (5) where (l) is the length, (b) is the width and (h) is the thickness of the samples.

$$D_{\text{true}} = \left(1 + \frac{h}{l} + \frac{h}{b}\right)^2 \times D_{\text{app}} \quad (5)$$

4 | RESULTS AND DISCUSSION

Thermoset polymers normally swell to some degree when immersed in liquids and the swelling is normally demonstrated as weight gain.[1] The weight gain of all samples was monitored and plotted against the square root of time. Figures 1–5 illustrate the absorption profiles of the 977-2 epoxy resin in the pure liquids and their mixtures.

The diffusion behavior of the liquids, Figures 1–5, follows Fickian diffusion in the first stage where the moisture uptake is linear versus the square root of time. This linear stage was then followed by a slow increase toward the final equilibrium value over the period of immersion. A two-stage diffusion behavior is observed for water, ethanol, methanol, and their mixtures as well as heptane, while an interesting three-stage diffusion mechanism was observed for butyl formate, decalin and their mixtures. The three stages were observed within the same time phase, indicating that this behavior might be due to the specific diffusion mechanism of these liquids and their mixtures instead of the 977-2 epoxy resin characteristics. This anomalous diffusion or non-Fickian diffusion is seen as a departure from Fickian behavior. Fick's law likely applies over the entire diffusion process unless degradation occurs. The deviation of the square root of time dependence is a result of the differential equation solution not having a square root of time dependency if the actual boundary conditions are applied. In other words, the actual diffusion behavior of many polymers derives from the concentration-dependent forms of Fick's law with constant boundary conditions, particularly when an extensive swelling of the polymer results from the penetrant diffusion. Normally, anomalous influences may be attributed to the effect of the structural changes of polymer due to diffusional mobility or may be related to the internal stresses applied by one part of the medium on another as diffusion is in progress.[32,33] Swelling leads to potential for capillary flow in which liquid ingresses through the pores in the bulk resin. Sorption of liquids can cause swelling in the resin that can bring about residual stresses which leads to microcrack formation and thus higher diffusion rates. The occupied volume of the resin will contain the bound water molecules which cause swelling, whereas the unbound water molecules exist in the free volume without causing swelling. Swelling normally occurs when the difference between polymer and solvent solubility parameters is very small (1 MPa$^{1/2}$), with crazes occurring when the difference is larger.[34] The two-stage absorption behavior can also be attributed to the polymer relaxation phenomenon.[2,3,5,11] This behavior was noticed by Tusda[16] for different glassy polymers. Sahlin and Peppas[19] also attributed the two-stage water uptake to resin relaxation phenomena.

The moisture uptake in mixtures of some of the liquids have been determined and compared with the measured values of the pure liquids, Figures 1–5. The measured weight gain of the binary mixtures is a mass weighted average (g of mixture/g of resin) of the two individual components. Equilibrium liquid values were determined using the experimental graphs and tabulated in Table 2. The mass uptake of epoxy in methanol, W50%/M50%, W255/M75%, and W25%/E75% was scaled by the thickness since these samples are thinner (1 mm) than the other samples (4 mm) and the diffusion will be faster. The saturation values are seen to be significantly affected by the liquid polarity.

The maximum moisture content of all liquids in Table 2 is seen to be much lower than that of water where $M_\infty\%$ are around 1.15%, 1.55%, 1.2%, 0.9%, 1.1%, and 3.3% for ethanol, butyl formate, decalin, heptane, methanol, and water, respectively. This is due to the high polarity of water compared with the other liquids and thus stronger interaction between water molecules and polar groups of the epoxy network. The absorption process of all binary mixtures followed similar two-stage trend to the pure liquids. Even though the solvent uptake of epoxy in pure ethanol is lower than the uptake in water and other liquids, the measured solvent uptake in ethanol/water mixtures (W50%/E50%) and (W25%/E75%) is higher than that in pure ethanol and other liquids, Figure 1. On the other hand, the absorption of water–ethanol mixtures showed similar absorption behavior to water, while their absorption rates are slightly slower than water uptake but faster than ethanol absorption. Similar behavior was observed with methanol and (water/methanol) mixtures. As the concentration of ethanol and methanol decreases in their mixtures with water, the amount of hydrogen bonding in the mixture increases because the proportion of hydrogen atoms in water is higher than in ethanol and methanol. This explains the higher moisture content of the mixtures compared with pure ethanol and methanol. The maximum content of

FIGURE 1 Water, ethanol, and
weighted average (water/ethanol) mixture
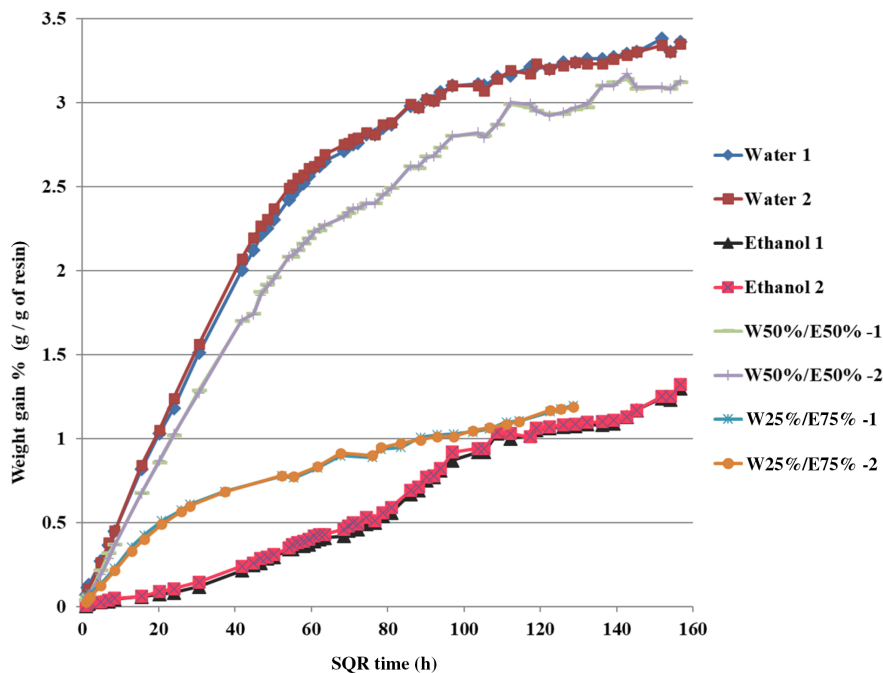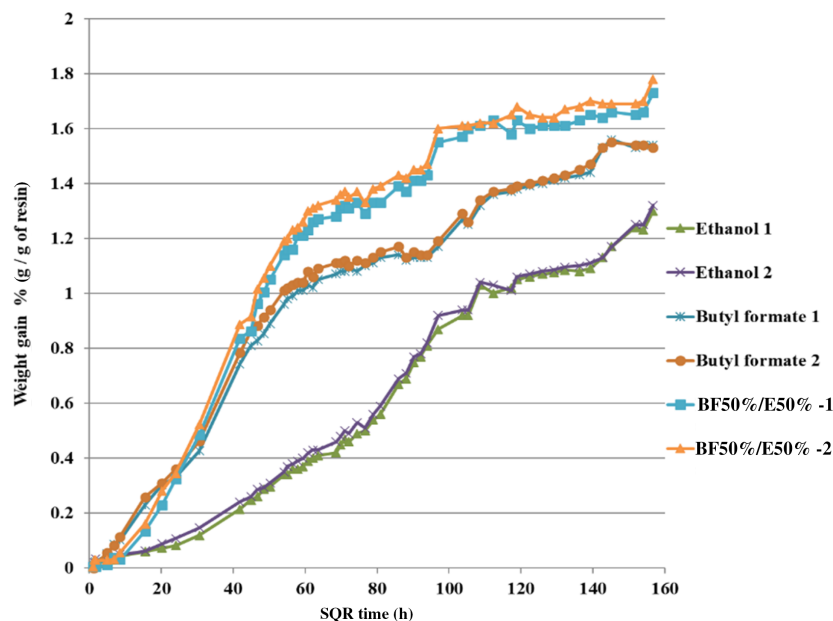uptake in 977-2 epoxy resin

FIGURE 2 Ethanol, butyl formate (BF), and
weighted average (ethanol 50%/BF50%) mixture
uptake in of 977-2 epoxy resin

(50%W/50%E) and (25%W/75%E) mixtures and ethanol are around 3.2%, 1.2%, and 1.15%, respectively. The mass uptake and diffusion rate of epoxy in methanol is higher than those in ethanol due to the higher polarity of methanol compared with ethanol. Figure 4 illustrates that water molecules enhanced the solubility of the methanol molecules and thus the rate absorption and equilibrium values of the mixtures are higher than the methanol itself. The maximum content of (50%W/50%M) and (25%W/75%M) mixtures are around 1.4% compared with 1.1% of the methanol uptake.

Butyl formate, decalin, and their mixture showed a unique three stage absorption started with linear increase followed by leveling off and then increased slowly toward the equilibrium. Similar behavior was observed by epoxy resins in acids.[35] The moisture content of these liquids is higher compared with ethanol and methanol but lower than water. This can be attributed to the higher polarity of these liquids compared with ethanol and methanol and lower than water polarity. as it can be seen in Figure 2, exhibited slower absorption than butyl formate but faster than ethanol, but the moisture content is much
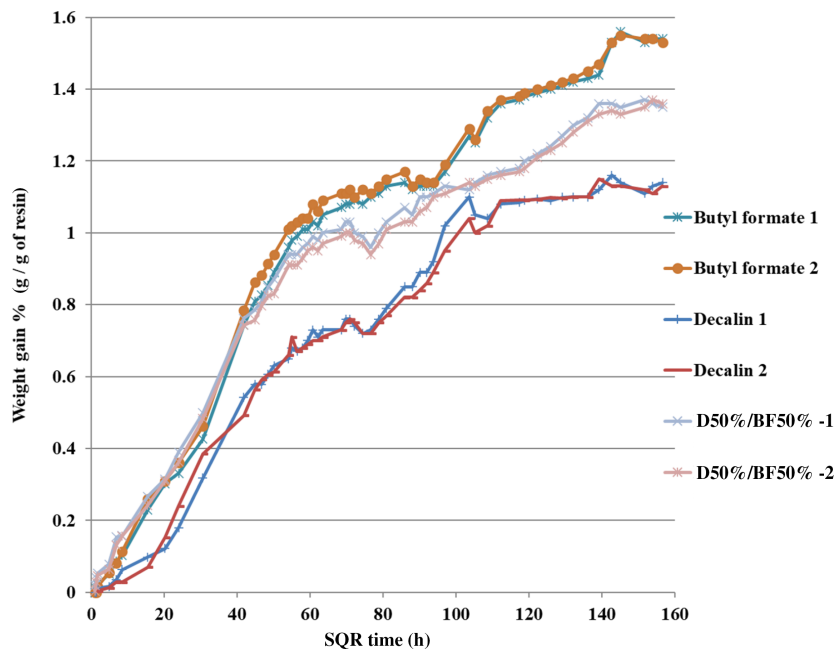
FIGURE 3 Decalin, butyl formate (BF), and weighted average (decalin/BF) mixture uptake in specimens of 977-2 epoxy resin
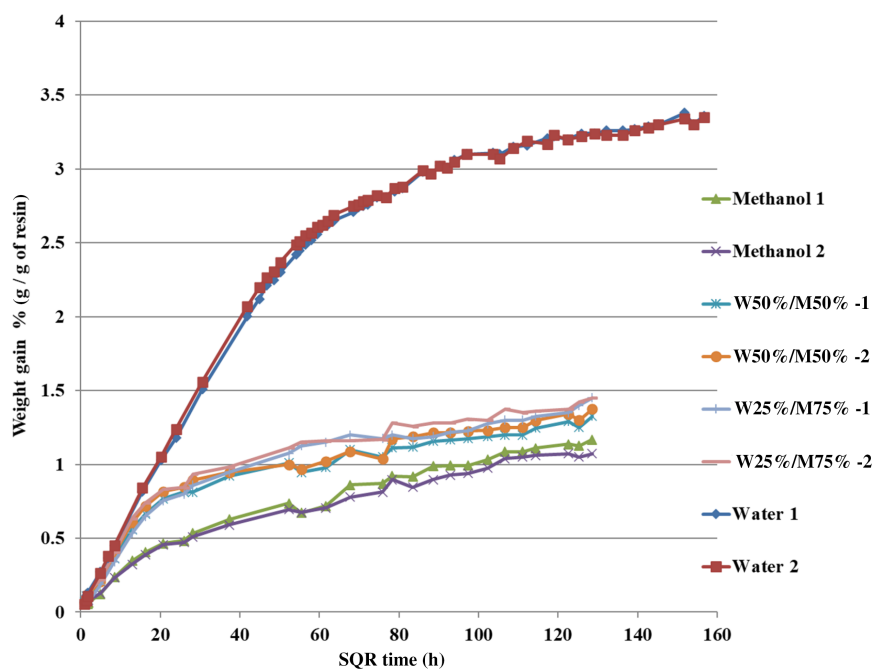

FIGURE 4 Methanol uptake and weighted average of (water/methanol) mixtures uptake in 977-2 epoxy resin

higher than both BF and ethanol. The maximum moisture contents are 1.15%, 1.4%, and 1.8% for ethanol, BF, and the mixture correspondingly. Figures 2 and 3 also showed that the (50%BF/50%E) has higher moisture content than their pure liquids and (50%D/50%BF) displays higher moisture content than decalin but lower the BF. This is because BF enhanced the solubility of both ethanol and decalin. Heptane is a nonpolar solvent and is used to evaluate the effect of bound molecules on long-term liquid absorption because heptane does not create bound molecules with the resin. Hence, the heptane

specimens showed the lowest content of around 1% after 11 months of conditioning. The low content of the absorbed heptane may be attributed to its nonpolar nature which makes it harder for heptane to diffuse and bond to the hydroxyl groups in the epoxy network. Heptane only diffuses in the free volume and voids creating clusters within epoxy resin which can normally be removed at low temperature.[11] Conversely, those liquids which are more polar can bond to hydroxyl groups in the epoxy network and highly enrich themselves in the polymer phase.[36]
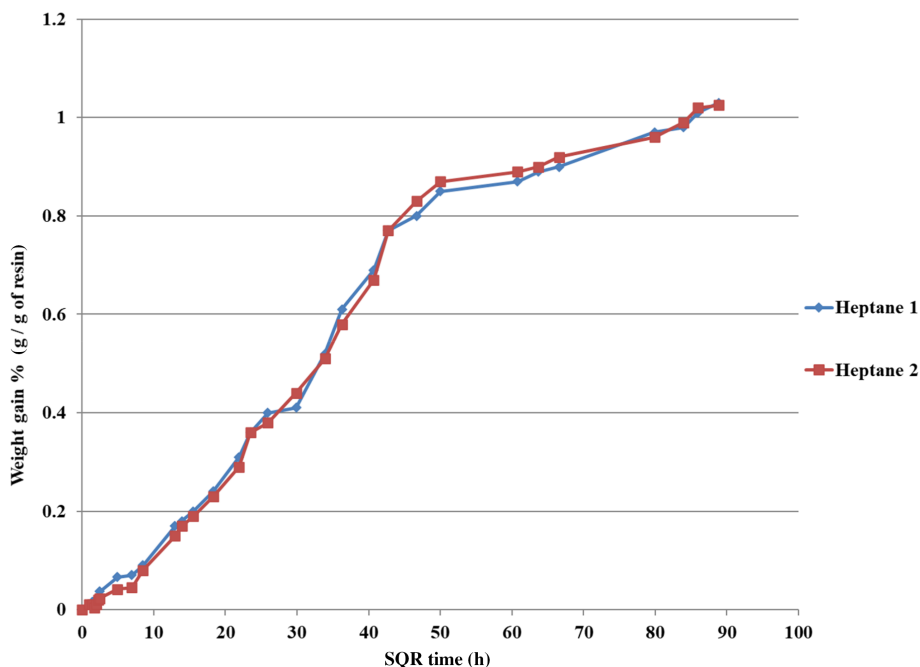
FIGURE 5 Heptane uptake in 977-2 epoxy resin

TABLE 2 Saturation values

Liquid/mixture	Saturation values (experimental) [$M_\infty\%$]
Heptane	1
Methanol	1.1
Ethanol	1.15
Decalin	1.2
W25%/E75%	1.2
D50%/BF50%	1.4
W50%/M50%	1.4
W25%/M75%	1.4
BF	1.55
BF50%/E50%	2
W50%/E50%	3.2
Water	3.3

TABLE 3 Saturation values derived using the parametric estimation technique

Liquid/mixture	Saturation values (parametric estimation) [$M_{\infty f}\%$]
Heptane	0.6
Methanol	0.5
Ethanol	0.9
Decalin	0.8
W25%/E75%	0.5
D50%/BF50%	1.1
W50%/M50%	0.8
W25%/M75%	0.8
BF	0.9
BF50%/E50%	1.2
W50%/E50%	2.2
Water	2.8

The true diffusion coefficients were calculated using Equation (4) with $M_{\infty f}\%$ values (Table 3) and the edge effects consideration and plotted in Figure 6. Figure 6 shows that water had the fastest diffusivity (16.6×10^{-14} m^2/s) and ethanol and decalin had the slowest diffusivity ($<5 \times 10^{-14}$ m^2/s) compared with the other liquids and their mixtures. For ethanol and decalin, this might be due to the obstruction effect of these liquids being stronger than for other liquids since their diffusivities are about four times slower than that of water and three times slower than BF, heptane, and methanol. Compared with water diffusivity, there is much stronger interaction with water than with other liquids where some groups are inaccessible to these liquids while still accessible to water. Furthermore, this absorption behavior can be attributed to the larger size of all liquids molecules as compared with water molecules, hence the larger the penetrant, the lower its mobility in the resin.[37] The higher diffusivity of methanol (12.5×10^{-14} m^2/s) compared with the other pure liquids apart from water can be due to the reason that when the methanol transports into the resin network, its hydroxyl groups interact with the free hydroxy group of the resin

creating hydrogen bonding. Thus, this will promote the disruption of intermolecular hydrogen bonding in the matrix itself allowing the network of the rein to expand. This will lead in turn to a higher methanol uptake and a faster diffusion rate. This is in agreement with the behavior reported by Sahlin and Peppas[19] on the other hand, the diffusion rates of water/ethanol ($\sim 15 \times 10^{-14}$ m^2/s) and water/methanol mixtures ($\sim 14 \times 10^{-14}$ m^2/s) was higher compared with the diffusivity of ethanol and methanol and closer to the diffusion rate of water. The smaller size of water molecules and their stronger polarity allow them to have much easier diffusion through the less polar epoxy resin causing this behavior. In other words, that the higher concentration of water in the ethanol and methanol mixtures the higher the diffusivity is.

Faster diffusion of butyl formate (11.6×10^{-14} m^2/s) compared with ethanol and decalin ($<5 \times 10^{-14}$ m^2/s) might be due to the reason that butyl formate has carboxyl group (COO-H$^+$) where its′ cation H$^+$ can be easily removed and create bonds with epoxy groups much easier than these liquids but harder than methanol and water. The faster diffusion of non-polar heptane molecules (11.7×10^{-14} m^2/s) compared with the other polar liquids (ethanol, BF, and decalin) can be due to the rapid diffusion of its small molecules in the free volume and voids of the epoxy resin which in turn forms clusters within the polymer. Furthermore, it is worth to be mentioned that water absorption and diffusion are largely related to the free volume in the epoxy system in addition to the polymer–water affinity. Therefore, depending on the molecular packing of the epoxy system, this would result in the amount of free volume, which is affected by both the crosslink density and the physical aging. If water molecules attach to the network, hydrogen bonds are created and these bonds end up disrupting the interchain hydrogen bonds, resulting in swelling.[38] The diffusion rate of butyl formate–ethanol mixture is seen to be similar to the diffusivity of BF and much higher than ethanol which can be down to the water formation produced by the mixing of ethanol and BF, since mixing carboxyl and hydroxyl groups produces ester and water. In this case, water enhances the solubility of the mixture leading to faster absorption. Furthermore, (50%BF/50%D) mixture exhibited higher diffusivity (12.3×10^{-14} m^2/s) compared with the individual penetrates (11.6×10^{-14} m^2/s) for BF and (4.5×10^{-14} m^2/s) for decalin where it is believed that BF enhanced the solubility of decalin since it has higher polarity than decalin and epoxy resin. Furthermore, comparing the true diffusion and D_{app} values of specimens used in methanol and its mixtures with 1 mm thickness shows that D_{true} values are close to the D_{app} values which shows the significant effect of the edges have on the diffusion rate in the epoxy resin samples.
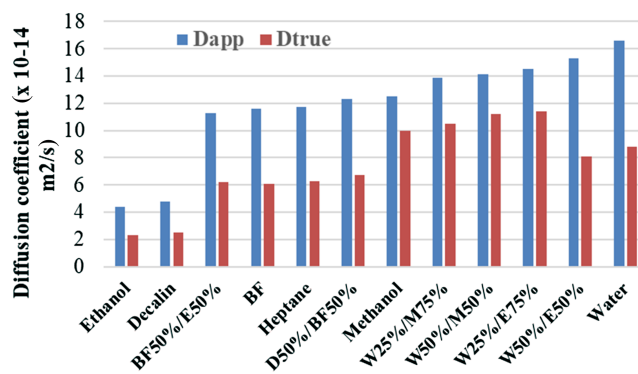

FIGURE 6 Diffusion coefficients of all liquids and their mixtures in 977-2 HTS epoxy resin
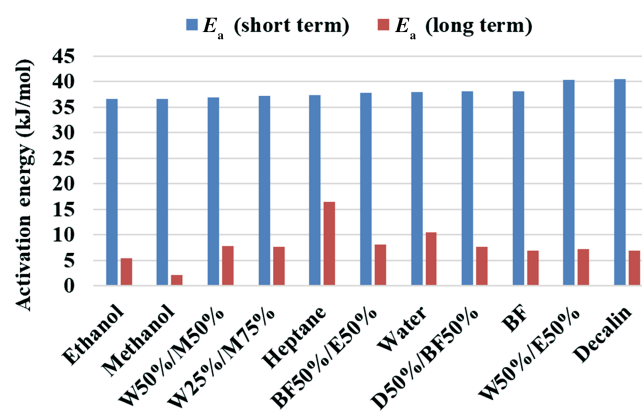

FIGURE 7 The activation energy values for the short- and long-term diffusion stages

Furthermore, the diffusion coefficient in both first and second stages is dependent on the activation energy according to Arrhenius equation.[2,11] For simplification, it was assumed that D_0 and E_a are independent of temperature and the polarity and size of diffusing species, and the diffusion of liquids has no influence on the physical and chemical properties of the polymer since no degradation was observed.[39] Therefore, based on these assumptions, the pre-exponential factor value (D_0) of the liquids investigated in this study was assumed to be equivalent to the pre-exponential factor value of water absorption in the same resin (977-2 epoxy resin). Since all liquids exhibited similar absorption behavior in 977-2 epoxy resin, it is approximately right to use D_0 of water for the other liquids despite the differences in polarity and the size of the diffusing species. The pre-exponential factor value (D_0) of water absorption in 977-2 epoxy resin used is 2.3×10^{-7} derived from.[2,11] The activation energies were calculated using the Arrhenius equation and plotted in Figure 7. The activation energies of the resin are seen to be similar which suggests that liquid diffusion

TABLE 4 Pseudo-diffusion (D_L) values

Liquid	$D_L \times 10^{-14}$ (m²/s)
Ethanol	0.0000025
Methanol	0.000009
W25%/E75%	0.0000033
W25%/M75%	0.000001
D50%/BF50%	0.000001
W50%/M50%	0.0000009
BF50%/E50%	0.0000008
BF	0.0000013
W50%/E50%	0.0000012
Water	0.00000031
Heptane	0.000000028
Decalin	0.0000013

through the matrix was the only mechanism of penetration. The values of activation energy are around 40 kJ/mol which are similar to those found for secondary chain relaxation of 977-2 epoxy resin immersed in water.[2,11] The similarity between the values of all the liquids confirms that there is no influence of sample size on activation energy.

From the second stage absorption, the rate at which the weight gain increases can be calculated by deriving a "pseudo-diffusion" (D_L) rate. D_L was determined by taking the gradient of the weight uptake versus square root (time) graph for the second stage and then dividing by the Fickian saturation. This rate assumes that specimen geometry has no effect, and therefore no account was made of edge effects. Table 4 shows that the diffusion rates in the second stage are much slower than those in the first stage which can be attributed to the polymer relaxation. The activation energy in the second stage was also calculated using Arrhenius equation with a pre-exponential factor value (D_0) of 2.2×10^{-5} based on the same assumption made for D_0 in the first stage.[2,11] The E_a values for the second stage are quite similar apart suggests no significant dependency on the polarity of the liquid, Figure 7. Generally, the activation energies of the resin should be the same if diffusion through the matrix was the only mechanism of liquid penetration.[40] The activation energies for the second stage for the liquids and their mixtures are around 5–10 kJ/mol which are lower than that recognized for secondary chain relaxation which is about 40 kJ/mol. It may well be that the presence of the liquids led to plasticization of the polymer which in turn reduced the activation energy for secondary bond relaxation. The activation energy of epoxy hydrolysis has been reported to be much higher at about

120 kJ/mol,[41] which does not match the value of about 10 kJ/mol obtained for the long-term uptake. Therefore, it might be possible to say that degradation is unlikely to be the main cause of the long-term behavior, but however this needs further consideration and investigation.

5 | CONCLUSION

The absorption of various industrial chemical liquids/solvents in 977-2 epoxy resin was investigated in terms of weight gain and diffusion rate. The weight uptake curves showed that absorption kinetics is a two-stage absorption process for water, ethanol, methanol, and their mixtures in addition to heptane. More interestingly, butyl format, decalin, and their mixtures exhibited three-stage absorption. In all cases, the diffusion cannot be completely explained by Fickian diffusion. Generally, for all liquids the weight increased in the first stage by the rapid diffusion of the liquid into the epoxy resin structure, and then increased and plateaued slowly toward the equilibrium moisture value. This can be attributed reasonably to swelling and polymer chain relaxation phenomenon. The diffusion properties of all pure liquids are found to be dependent on their polarity, molecule size and their interaction with the polymer chains. For the diffusion of binary mixtures into 977-2 epoxy resin, there is a dependency on the interaction between the two liquids and between mixtures and epoxy resin. The diffusion rates of the binary mixtures were seen to be an intermediate between the rates of either liquids. This is right for most of the binary mixtures used in this study apart from (decalin + butyl formate) mixture. Moreover, for binary liquid mixtures the presence of more soluble liquid can enhance the solubility of the other liquid. The activation energy for all liquids and their mixtures is faster in the first stage than the second stage due to the secondary chain relaxation of 977-2 epoxy.

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