RESEARCH ARTICLE

WILEY **Packaging Technology and Science**
An International Journal

Food packaging simulant failure mechanisms in next generation steel packaging

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Funding information
EPSRC; European Social Fund via Welsh Government; CROWN Packaging Manufacturing UK Limited; TATA Steel Packaging Europe

Legislative pressures have led to the mature dominant chromium-coated steel (ECCS) substrate and epoxy phenolic lacquer replacement in Europe. An investigation was carried out to examine the interaction between a steel surface engineered with a novel, developmental substrate coated using Cr (III)-based electrolytes and the food stuff being canned. Samples of lacquered material were subjected to a typical retort process (121°C for 90 minutes) and examined using a variety of laboratory analytical techniques. The foodstuff being packaged has a significant impact on the substrate/lacquer adhesion with clear differences in failure mechanisms between foodstuffs. There is clear evidence of chemical species transfer through the next generation lacquer, and this can instigate corrosion at the surface where incomplete chromium coverage leads to exposed iron. In general, the novel developmental material exhibits lower adhesive properties and shows a greater sensitivity to the foodstuff, although this is largely attributed to the homogeneity of the coverage. The novel substrate proves to be a promising alternative to ECCS due to REACH legislation, but improvement is required to achieve equivalent performance.

KEYWORDS

adhesion, BPANI, chrome (VI) free substrates, packaging steel

1 | INTRODUCTION

Metal packaging is an important means by which food can be cooked, distributed, stored, and consumed in modern society with a global market of around $110 Bn in 2017, set to increase in the next 5 years.[1,2] It is robust, fully recyclable, achieves many years of shelf life (reducing food waste for producer and consumer), and has established products with whole supply chain integrity,[3] widely known for its economic effectiveness.[4] The substrate is coated to protect the foodstuff

contained from being damaged or spoiled; the coating also prevents the corrosion of the substrate material that could be induced by the interaction with the contents.[5]

Currently, steel packaging manufacture faces the dual challenges of removing chromium (VI)[6] from the substrate production process and Bisphenol-A (BPA) from the protective lacquer. A transition is therefore required from a trusted mature technology to a novel substrate/lacquer combination, and this has renewed significant research interest in their performance. Key to success is the integrity

Nomenclature: BPA, Bisphenol-A; BPANI, Bisphenol-A non-intent; EP, Epoxyphenolic; ECCS, Electrochromium-coated steel

of the metal/organic interface, particularly when subjected to the extreme environment experienced by the packaging when the foodstuff is cooked in the filled can at temperatures in excess of 120°C.[7,8]

The two coated steels primarily used for food can applications are tinplate, having a tin layer approximately 0.2 to 2 μm thick and electrochromium-coated steel (ECCS) which has a 10 to 30-nm layer of chromium/chromium oxide, produced using a Cr (VI) electroplating process.[9] Trivalent chromium-based metallic coatings for steel developed[10] as a REACH[6] compliant alternative to ECCS is under iterative development to optimise surface chemistry and characteristics. A novel developmental substrate, combined with next generation coatings (bisphenol-A non-intent) that comply with legislative moves in some European territories, presents the metal packaging industry with a system that has been shown to be less robust than the well-established ECCS/epoxyphenolic coating system.[11]

The adhesion of an organic coating to a metallic surface occurs through a variety of bonding mechanisms, including electrostatic interactions, dispersion forces, and covalent bonds,[12,13] all of which are susceptible to modification through the interaction with a simulant solution and by extension, foodstuff. Work has previously been conducted studying the effects of the sterilisation process on the quality of adhesion that is observed, a phenomenon that had not been quantified before.[11] This study focussed on the quality of adhesion varied with adjusting retort parameters, establishing relationships and highlighting strengths and failures within novel substrate/coating systems. Previous work has begun the examination process of the changing chemistry of both the coatings and the substrate, an area that is to be more fully explored here. The effect of the retort process on polymer coatings has been subject of some limited study. For example, Axelson-Larsson examined the oxygen permeability of such coatings under autoclave conditions, concluding that the conditions can affect the barrier of some materials, with water acting as a plasticiser.[14] Many studies have been carried out to investigate the effect that the chemical composition of a given foodstuff might have on the coating.[15] The migration study carried out by Errico et al where the BPA transferred into the foodstuff has been measured[16] confirms that BPA transfer does occur but the overall consumer exposure is low. This work is further evidenced by Oldring et al who worked on a model to estimate BPA-diglycidyl ether exposure, concluding that exposure for UK consumers was well below the tolerable daily intake for all derivatives.[17]

With BPA non-intent (BPANI), migration studies have been carried out on coatings of similar chemistry,[18,19] as is common with all new coating formulations, with a multitude of analytical techniques used such as gas chromatography and mass spectrometry.[20] While these methods of interaction are relatively well reported, the effect of the simulant solution/foodstuff on the adhesion of a coating to the substrate, or the substrate itself post-retort, has not been reported in depth. Some work has been conducted exploring the delamination mechanism of an epoxy coating from a steel substrate, using electrochemical impedance spectroscopy (EIS) and X-ray photoelectron spectroscopy (XPS) to determine than an acid treatment improves the resistance against cathodic delamination,[21] most notably in a NaCl solution. The purpose of this study is to investigate the effects of the sterilisation (retort) process on both the substrate and the organic coating, attempting to understand the interaction between the two at the interface,[8] or indeed where any failure may occur.

2 | MATERIALS AND METHODS

Substrates used were ECCS, supplied by Tata Steel, and a developmental chromium-coated steel substrate (294269M), also supplied by Tata Steel. The developmental substrate was electroplated using Cr (III) species in the electroplating bath, rather than the Cr (VI) species used in ECCS production. 294269M was produced on a full-scale industrial electroplating line during parameter optimisation tests and is hence a developmental only substrate, not commercially available. In each case, the bath chemistry and operation parameters of the electroplating process were manipulated to provide a controlled combination of surface species. Neither substrate has free Cr (III) or Cr (VI) present on the surface after electroplating, and chromium is then present in the form of Cr metal, oxide, or hydroxide; the details of which are shown in Table 1. 294269M shows increased levels of chromium oxide and lower values of metallic chromium when compared with ECCS, while also showing some evidence of iron at the surface.

Coatings used were an epoxy-phenolic (EP) lacquer and a polyester BPA non-intent (BPANI) lacquer, both supplied by Metlac. The former representing incumbent lacquer chemistry, the latter representing commercial state of the art. For the purposes of this research, sheets of both substrates were coated with 10 to 12 μm of either the EP or BPANI coating, providing four substrate/coating systems. For testing, sheets were cut into samples 120 mm × 45 mm.

To simulate the sterilisation process, coated substrates were placed in sealed jars filled to 80% of total capacity with simulant solution (Table 2). Simulant solutions were chosen as they represent common packing media for canned foodstuff; the associated foodstuff is

TABLE 1 Surface characteristics of each substrate as characterised by XPS, average of three replicates

%	ECCS	2017 ETL14 294269 M
CrOx	3.6	14.5
Cr	2.5	1.6
Cr (OH)x	15.5	15.6
Fe	0	0.7

TABLE 2 Simulant solution compositions and examples of representative packaged foodstuffs

Simulant Solution Composition	Typical Foodstuff
1% NaCl (standard brine)	Peas or beans
1% NaCl, 1% acetic acid (acidified brine)	Gherkins or onions
1% lactic acid (carbohydrate fermentation)	Sauerkraut or dairy products
0.25% NaCl, 0.25% citric acid (acidified brine)	Salsify

also detailed in Table 2. The filled, sealed jars were placed in a in a CertoClav MultiControl 2 autoclave and subjected to retort process for 1.5 hours at 121°C. Each test conducted used five replicates of each of the four substrate/coating systems.

Dissolved oxygen measurements were conducted using a Mettler Toledo FiveGo dissolved oxygen portable meter, calibrated according to manufacturer guidelines. Measurements were carried out in accordance to ISO17289:2014.[22] Three measurements were taken of each solution.

Adhesion measurements were performed using a variable load scratch tester in accordance with ISO 1518:2011,[23] providing a quantitative analysis of the adhesion force without inducing a chemical change in the thin film organic coating as other methods, such as pull off tests.[24] Each of the five replicates was assessed and an average failure force taken.

Knoop hardness measurements were taken using a Zwick Indentec ZHμ microhardness tester, in accordance with ISO 6441-1, with a standard error associated with the measurements of 5.1%, across five replicates.

Surface species characteristics were measured using an Axis Supra XPS system using a monochromated Al Kα source and large area slot mode detector using a 300 × 800 μm analysis area. Binding energies were calibrated to the main hydrocarbon peak (284.8 eV). Spectra were subsequently analysed in CASA software with Shirley backgrounds.

FTIR measurements of the lacquers were carried out using a Perkin Elmer FTIR 100 with ATR attachment. Data were interpreted using Perkin Elmer Spectrum 10 STD software.

Time of flight secondary ion mass spectrometry (ToF-SIMS) analysis was conducted on a Scientific Analysis Instruments (SAI) MiniSIMS-ToF, using a gallium source to obtain positive secondary ion spectra in the form of images.

In total, each result, for each experiment conducted, represents an average of five samples providing a statistically valid measurement of each substrate/lacquer combination. Where the lacquer properties were to be examined independently of the substrate, the lacquer was coated to glass microscope slides which were unaffected by the retorting process. Further details of the experimental equipment and procedures are available in previous work.[11]

In order to examine the impact of the simulant and the retort process, the lacquers were applied to glass slides and processed in the same manner as the steel substrates. In this way, it was possible to readily obtain a free standing film as the film could readily be detached from the glass, allowing the lacquer chemistry to be investigated independently from the steel substrate.

3 | RESULTS

3.1 | Macro effects

3.1.1 | Adhesion testing

In order to appraise the impact of the simulated foodstuff on the lacquer/substrate adhesion, a methodology was adopted where each substrate/lacquer was exposed to each simulant under retort conditions and their characteristics were evaluated. On the basis of the initial findings, further investigations were initiated to identify the dominant mechanisms in each instance.

There is a clear interaction between the simulant lacquer and the adhesion failure force measured (Figure 1). The BPANI lacquer consistently shows the poorest performance when compared with the incumbent epoxy phenolic technology, and this is emphasised within certain simulant composition, reasons for which have been touched on in previous studies.[11] Those materials produced via a trivalent chromium coating perform consistently poorer compared with the incumbent chromium (VI) produced ECCS substrate. The presence of NaCl in the simulated foodstuff causes a reduction in adhesion performance for all substrates, although the presence of a secondary organic acid reduces the impact of the NaCl. Visual inspection of the surface
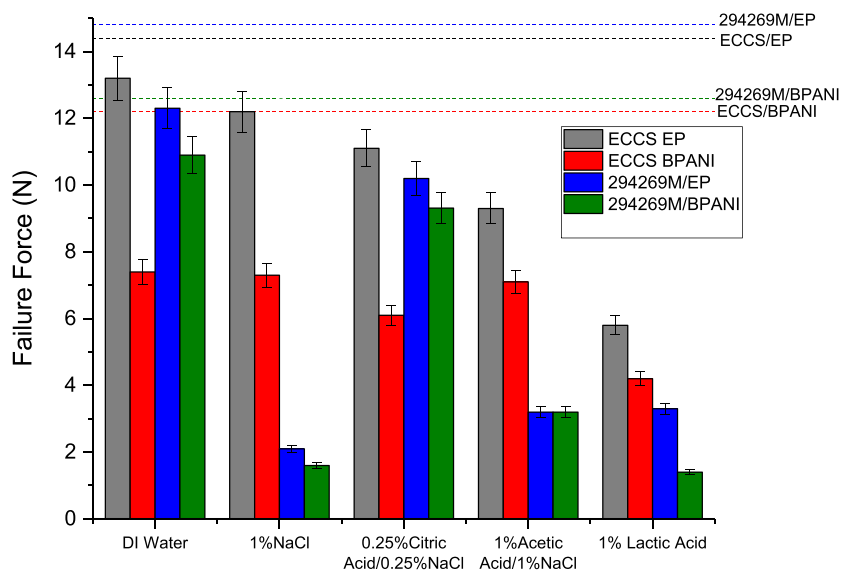

FIGURE 1 Post-retort adhesion of all substrates and all simulants with the BPANI coating. Dashed lines represent the dry adhesion measurement

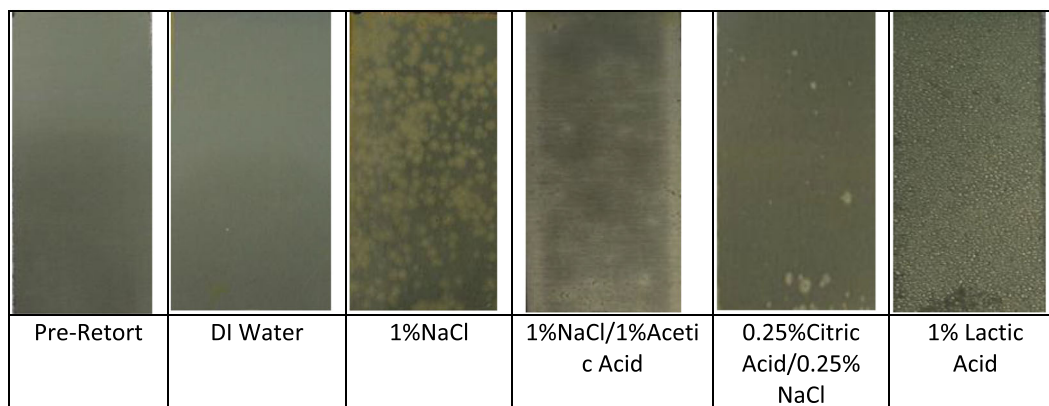| Pre-Retort | DI Water | 1%NaCl | 1%NaCl/1%Acetic Acid | 0.25%Citric Acid/0.25% NaCl | 1% Lactic Acid |

FIGURE 2 294269M substrate/BPANI lacquer combination after the retort process

identified surface corrosion, indicating transport of the Na^+ and Cl^- through the lacquer and to surface (Figure 2). Figure 2 shows representative images of the five replicates tested. With all lacquer/substrate combinations, the lactic acid has the most pronounced impact on adhesion performance, although the degree of substrate corrosion was lower than that observed with the NaCl simulants. Thus, there is evidence for a reduction in adhesion due to both surface corrosion and degradation of the lacquer/lacquer interface. Given the strong interactions between the foodstuff simulant, substrate, and the lacquer, a series of subsequent investigations were carried out to evaluate their relative impact of the corrosion/lacquer degradation and identify key mechanisms.

3.1.2 | Visual inspection

From a macroscopic perspective, trends can be observed in the visual appearance of the substrate/lacquer which indicates that the failure mechanism in each case varies (Figure 2). With deionised (DI) water, there is little change in the surface colour and with only a small number of blemishes, the same can be said for 0.25%NaCl/0.25%citric acid, where the blemishes do not appear to have the detrimental effect to adhesion that the defects on the 1%NaCl samples have, where blistering is commonplace. When 1%NaCl/1%acetic acid is used as a simulant, the visual effects are minimal; however, there is an increase in the surface roughness of the coating. 1% Lactic acid, however, shows blistering across the surface, of a diameter such that it is not practical to apply a numerical value to blistering.

In order to understand the underlying chemical and physical mechanisms which occur in each case, analytical tools were used to examine the impact of the retort on the substrate and the lacquer.

3.2 | Substrate mechanisms

3.2.1 | ToF-SIMS analysis

ToF-SIMS surface maps have been employed with the blue areas representing iron and the green areas representing the chromium

present on the surface (Figure 3) (areas with no chromium or iron are depicted in black). In an unretorted state, the surface of each substrate is dominated by chromium, with small areas of iron on 294269M which most likely reflects the nonoptimized nature of the manufacturing process settings used to produce the material. Post-retort, the surface of substrate 294269M changes substantially. Following retort in DI water and 0.25%citric acid/0.25%NaCl, 294269M is very similar to the pre-retort image. However, for 1%NaCl, the amount of chromium is greatly reduced, and the amount of iron is increased. The same can be observed for the 1%NaCl/1%acetic acid simulant and the 1%lactic acid simulant. This suggests a breakdown of the metallic coating, leading to exposure of the steel blackplate. The ECCS material shows some increase in surface iron content, but the overall presence of iron is significantly lower.

3.2.2 | XPS analysis

The changes identified in the findings of the ToF-SIMS are corroborated and by examining the XPS surface analysis for 294269M (Table 3), which also identifies changes in key surface species. Under DI water conditions, the chromium metal exhibits some hydration, while the 1% NaCl produces a significant increase in the iron oxide and metallic iron observed on the surface.

The other notable feature of Table 3 is the increase of Cr_2O_3 for the citric and lactic acid for 294269M and the elimination of iron oxide from the surface with citric acid. In order to examine this mechanism, ECCS and 294269M substrates were subjected to retort in increasing concentrations of citric acid in a 1% NaCl solution. In contrast to increasing NaCl concentrations, there is an increase in the measured adhesion when the citric acid concentration is raised (Figure 6). The increase is significant and raises the adhesion between the pre-retort dry adhesion. The role of citric acid as a surface passive has been reported in stainless steel processing[25,26] where it provides a more environmentally friendly and safer passivation treatment compared with conventional nitric acid passivation. The passivation treatment results in preferential dissolution of iron oxide[25,27] and oxidation of
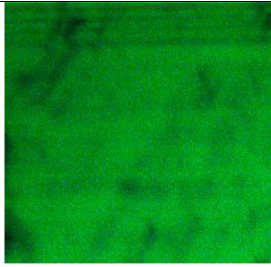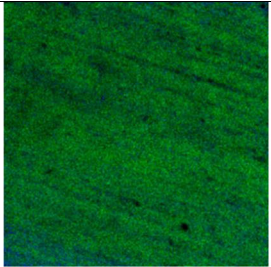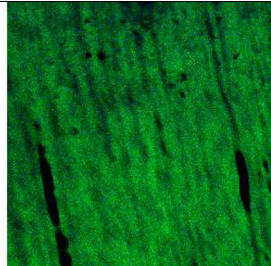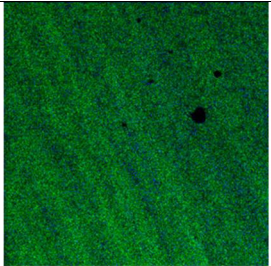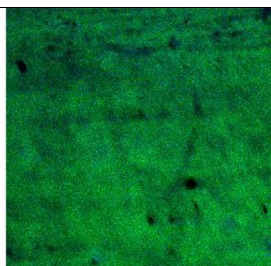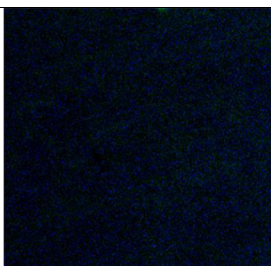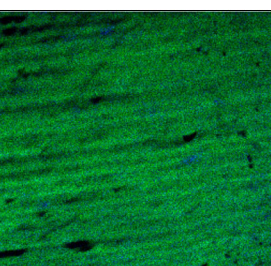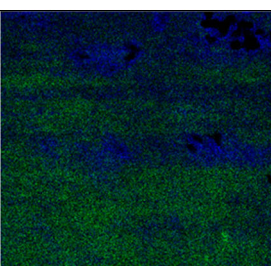
	ECCS Substrate	294269M Substrate
(A) Surface pre-retort.	Ratio Cr:Fe 2000:1	Ratio Cr:Fe Ratio 12:1
(B) Surface following DI Water retort.	Ratio Cr:Fe 229:1	Ratio Cr:Fe 8:1
(C) Surface following 1% NaCl retort	Ratio Cr:Fe 14:1	Ratio Cr:Fe 2:1
(D) Surface following 1%NaCl/1%Acetic Acid retort.	Ratio Cr:Fe 11:1	Ratio Cr:Fe 2:1

FIGURE 3 Elemental surface maps of the surfaces pre-retort (A) and post-retort with each simulant (B-F). Each area represents 1.125 mm × 1.125 mm

the surface chromium to Cr_2O_3. Surface Cr_2O_3 films are advantageous because of their inherent corrosion resistance, low ion/electron diffusivities, and low electrical conductivity[28] and thus increase the chromium oxide layer thickness on the surface and protect the chromium and the iron subsurface. Although stainless steel has a variety of elemental constituents in the bulk, the major constituent parts of iron and chromium in the near surface region[27] are similar to ECCS and

294269M. It is therefore postulated that a similar mechanism is taking place in these packaging substrates.

3.2.3 | Effect of NaCl concentration on adhesion

The role of NaCl was investigated by varying the concentration of NaCl in the simulant and exposing the substrates to the retorting
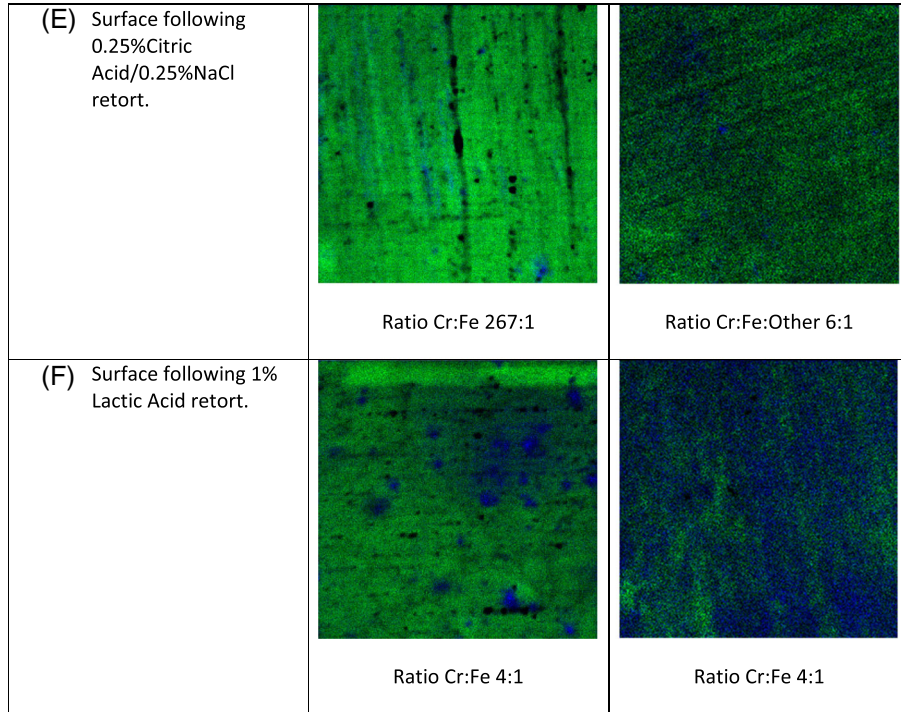
(E) Surface following 0.25%Citric Acid/0.25%NaCl retort.

Ratio Cr:Fe 267:1   Ratio Cr:Fe:Other 6:1

(F) Surface following 1% Lactic Acid retort.

Ratio Cr:Fe 4:1   Ratio Cr:Fe 4:1

FIGURE 3 Continued.

TABLE 3 XPS analysis of the change in surface of the 294269M substrate pre-retort and post-retort, average of three replicates

	C_2O_3	$Cr(OH)_3$	Cr-M	Fe-M	Fe_2O_3
DI water	+0.9	+2.3	−0.8	0	0
1%NaCl	−3.8	−3.4	−1.4	+1.3	+5.3
1%NaCl/1% acetic acid	−1.9	−2.7	−0.8	0	+2.1
1%NaCl/0.25% citric acid	+5.3	−1.7	−0.9	−0.6	0
1% lactic acid	+5.6	−3.3	−0.2	+1.9	+2

process. Even small quantities of NaCl have a significant detrimental effect on the lacquer/substrate adhesion, and this is particularly the case with the next generation materials (294269M/BPANI) (Figure 4). With both substrates, the epoxy phenolic provided superior adhesion during the retort process. The role of the NaCl on corrosion is clearly illustrated in Figure 3 and Table 3 where the exposed iron levels are greater than the other simulants. For 294269M, the small points of corrosion are evident in the surface defects of thin or no chromium coverage results in oxidation of the substrate. These corrosion points then form the initiation focus of any delamination with blisters being formed at the interface, resulting in interlayer failure. In the areas away from the corrosion initiation, the lacquer adhesion appears better, although no numerical values can be obtained due to the random nature of the blisters and the measurement length required (120 mm) for a consistent adhesion measurement.
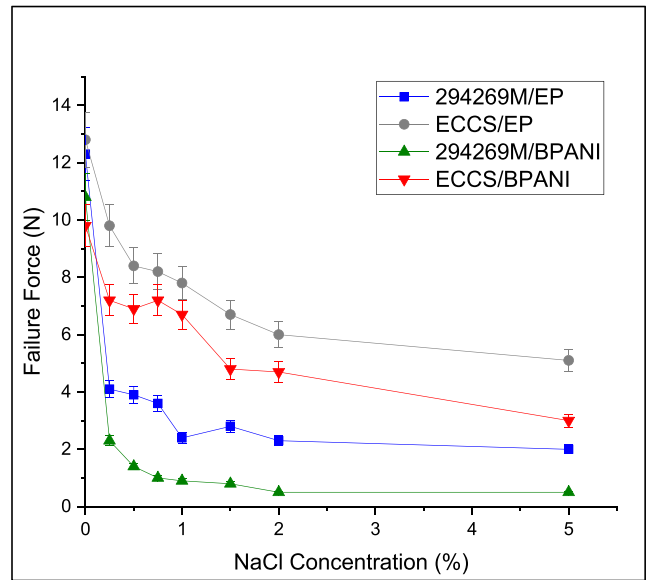

FIGURE 4 The impact of NaCl concentration on lacquer adhesion

3.2.4 | Effect of oxygen on adhesion

Corrosion of chromium-coated steel substrates is enhanced by the presence of oxygen, which acts as an oxygen source in the simulant.[29] Thus, by elimination of the oxygen from the simulant fluid, it was possible to examine the role of oxygen in the corrosion of the substrate.
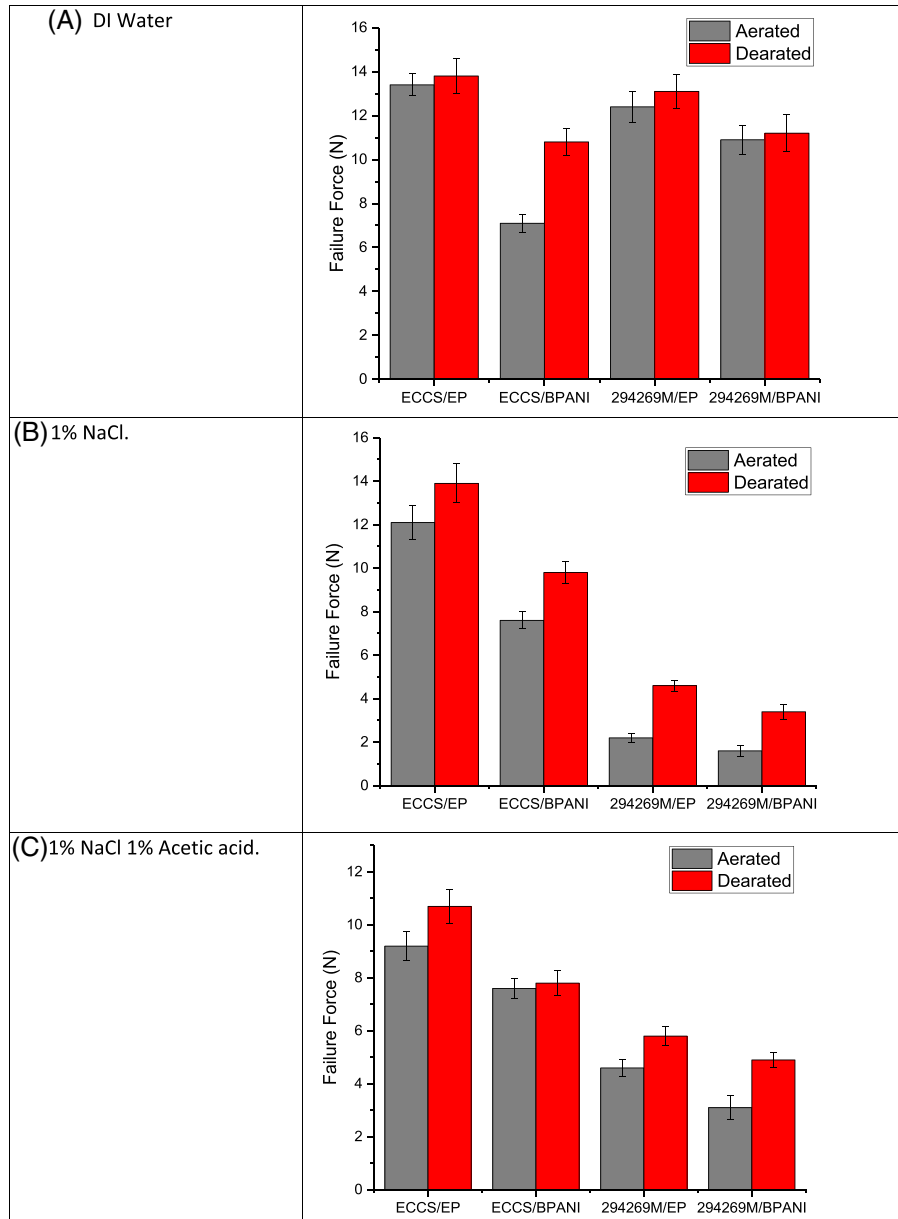
FIGURE 5   A-E, Measured adhesion in the presence of simulants where oxygen has been removed

In order to achieve this, each solution was deaerated by purging with N$_2$ gas for 30 minutes prior to retorting resulting in a reduction in dissolved oxygen from 3.47 to 0.04 mg/L (+/− 0.01 mg/L). Every simulant solution shows an improvement in the lacquer/substrate adhesion (Figure 5), while visual inspections of the sample showed a reduction in the number and intensity of the blistering. The presence of oxygen therefore plays an appreciable role in the failure mechanism and thus reinforces the ToF-SIMS and XPS analysis in Figure 3 and Table 3. This result has an impact for can fillers as dissolved oxygen in the foodstuff will tend to increase the corrosion and hence substrate/lacquer adhesion. Similarly, any free air head space in the can will have an impact on the substrate/lacquer adhesion. From a material testing viewpoint, any DI water will need to be left for a period of time prior to use in a retort environment in order to equilibrate the dissolved O$_2$ in the DI water. Given the liquid volume to substrate surface area employed in the testing, any corrosion will not be limited by the quantity of dissolved oxygen in the liquid. In a sealed can where the liquid volume to surface area is far lower, the availability of dissolved oxygen may become a limiting factor in corrosion.[30,31] In this instance, the failure force measured is likely to be overestimated in this research. In the environment of a can, the surface area of coating and substrate is much higher than that of the testing regime, where a small number of samples are tested in a glass container, limiting the substrate that is available for oxidation.
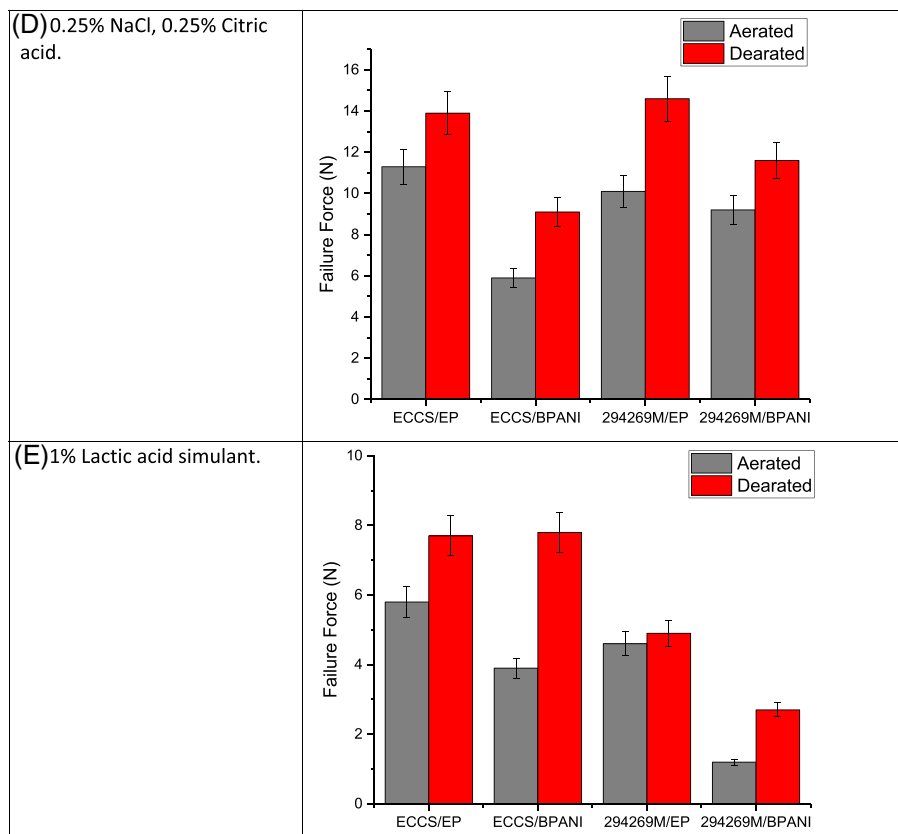
(D) 0.25% NaCl, 0.25% Citric acid.

(E) 1% Lactic acid simulant.

FIGURE 5 Continued.

3.2.5 | SEM analysis

Where failure occurs on the novel material, further insight on the mechanisms can be established through cross section SEM examination of the interface (Figure 6). In each instance, key dimensions and layer labels are applied, and all observations are representative of three replicates of each cross section.

SEM analysis shown in Figure 6A-F shows the effect that the retort process has on the interface between the novel substrate and the BPANI coating. The pre-retort, DI water, and 0.25%NaCl/0.25%citric acid samples show little in the way of failures of the interface (Figure 6A,B,E, respectively). In the case of the 1% NaCl simulant, a clear void between the coating and substrate is observed of around 3 μm of and was present along the entire interface area. This is attributed to the presence of the chloride ions causing corrosion at points in the surface where iron is present at the interface.[31] The thermal expansion of the gaseous corrosion product then leads to organic/metal separation. At a lower pH, according to the revised pourbaix diagrams at elevated temperatures[32] for Cr^{3+}, Cr_2O_3 is no longer the stable state of Cr^{3+}. Instead, chromium is more likely to be in the aqueous Cr^{3+} state or in the $CrOH^{2+}$ state. This suggests that the mechanisms of corrosion are different when an acid is added to the system; at low pH, the chromium oxide layer is likely to be affected, whereas at neutral pH, the oxide layer is stable, and hence the corrosion mechanism is likely to be related to the

exposed iron in this developmental substrate. In the case of 1%NaCl/1% acetic acid, a corrosion effect is observed with no micro delamination shown in SEM; the same can be said of the samples exposed to 1% lactic acid.

3.2.6 | Citric acid effect

The effect of citric acid, demonstrated in Figure 7, is more pronounced on 294269M than the ECCS, and this attributed to the higher chromium level which is applied which allows greater conversion to chromium oxide and thus an increased number of lacquer bonding sites.[33] This mechanism also results in higher substrate/lacquer adhesion on 294269M compared with ECCS which is in contrast to that observed in the remainder of this investigation. This suggests that a chromium surface deposited from a chromium (III) can therefore perform to the standard of ECCS, provided the surface uniformity and species are optimized. Although high chromium oxide values may lead to an improvement in the adhesion properties, it may lead to surface cracking when the brittle metal oxide is subjected to deformation during the can-making process.

Having established the key impacts and mechanisms by which interlayer adhesion is reduced by substrate mechanisms, predominantly corrosion, those mechanisms associated with the lacquer were investigated.
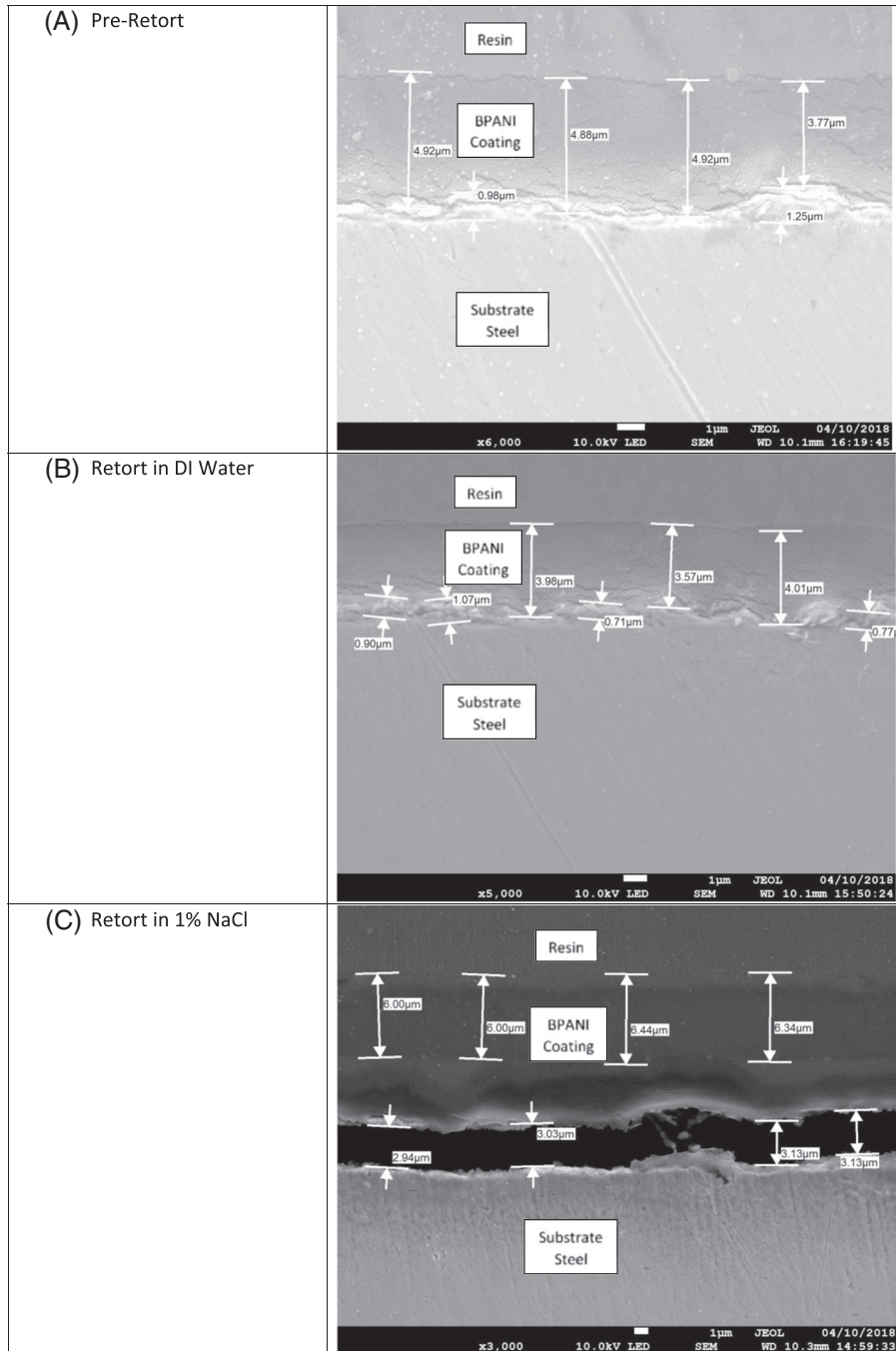
FIGURE 6   A-F, SEM cross-sectional images of the adhesion interface following the retort process for the 294269M/BPANI system

3.3 | Lacquer mechanisms

3.3.1 | Knoop hardness measurements

The retort process has an appreciable effect on the Knoop hardnesss of the BPANI but has less effect on the Knoop hardness of the epoxy phenolic coating (Figure 8). When Knoop hardness measured immediately after retort is compared with the hardness values taken after a 14-day relaxation period, the recovery of the lacquer can be examined. When allowed to recover under 20°C conditions, the lacquer regains the majority of its original hardness for all simulants. The exception for this is where the BPANI lacquer is retorted in 1% lactic acid solution, where there is a 10% reduction after the recovery period, despite the large change in Knoop hardness directly after retort. Thus, there is a degree of reversibility in the impact of the retort conditions on the lacquer bulk hardness (and mechanical properties), except for the 1% lactic acid retort.
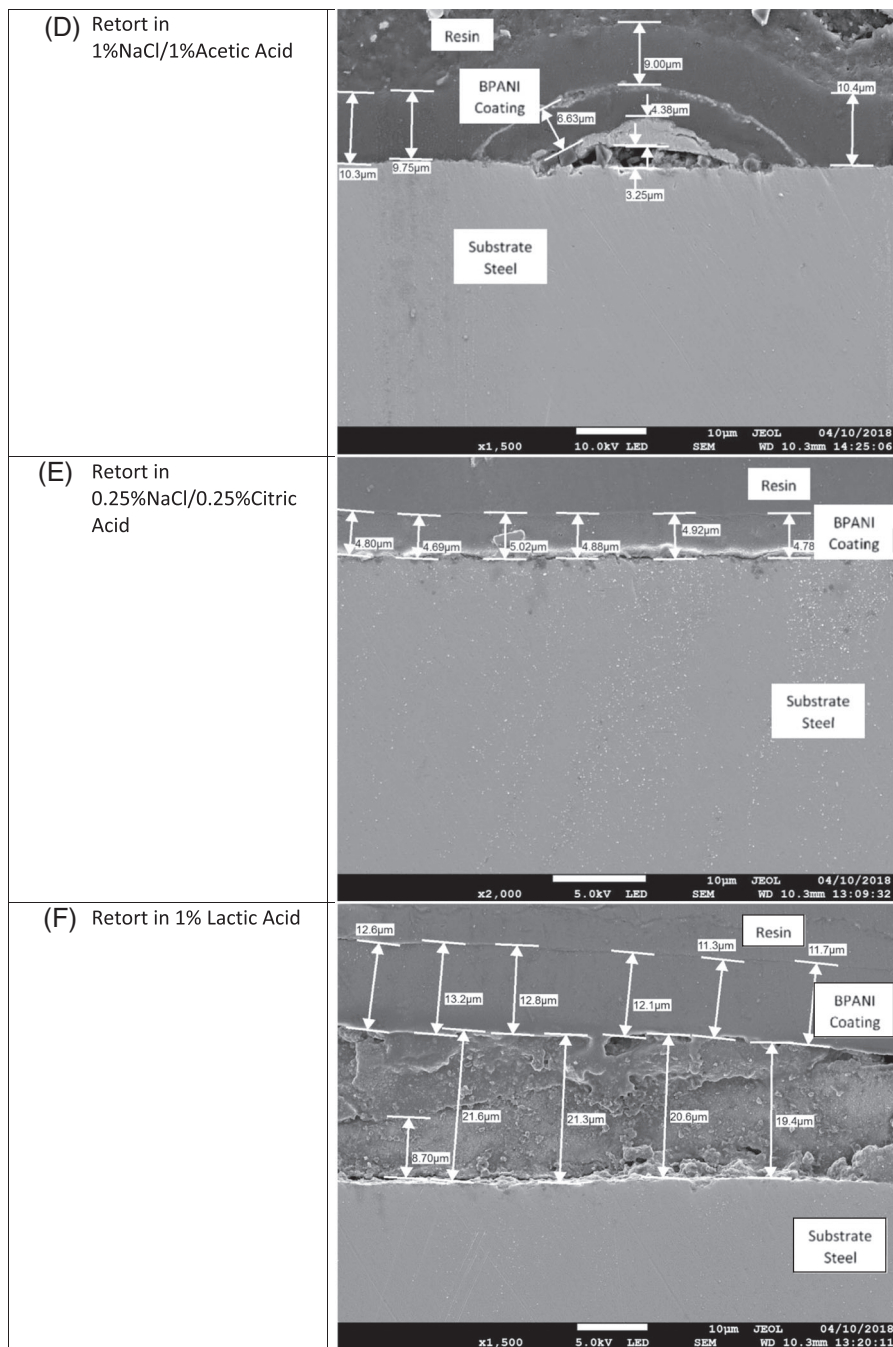
FIGURE 6 Continued.

3.3.2 | SEM analysis

A distinct increase in lacquer thickness is observed via SEM (Figure 6), especially prevalent for the BPANI coating retorted in 1% lactic acid solution, showing an increase in thickness of approximately 3 times that of the original pre-retort value. Thermogravimetric analysis (TGA) has previously[11] suggested a large uptake of water into the coating, something that could be further evidenced here, where the thickness changes depending on the simulant that is used.

3.3.3 | "Relaxation" of adhesion

While the change in lacquer bulk is largely reversible, this measurement is taken on the upper surface of the lacquer and does not consider the lacquer/substrate interface. The change in adhesion post-retort was investigated through measurement at regular intervals over a 168-hour period (Figure 9). In all instances, the substrate/lacquer adhesion increases with relaxation time, although it does not return to its original adhesion level in any case. This
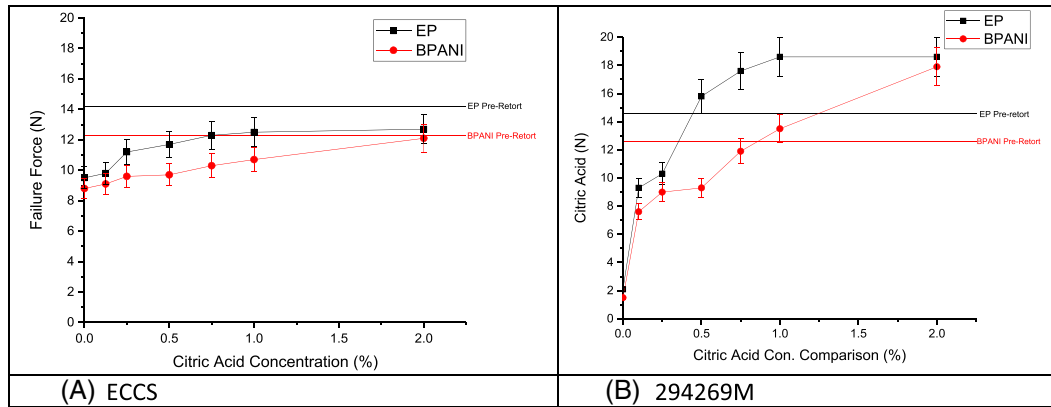
FIGURE 7 The impact of citric acid concentration in the simulant on the measured adhesion
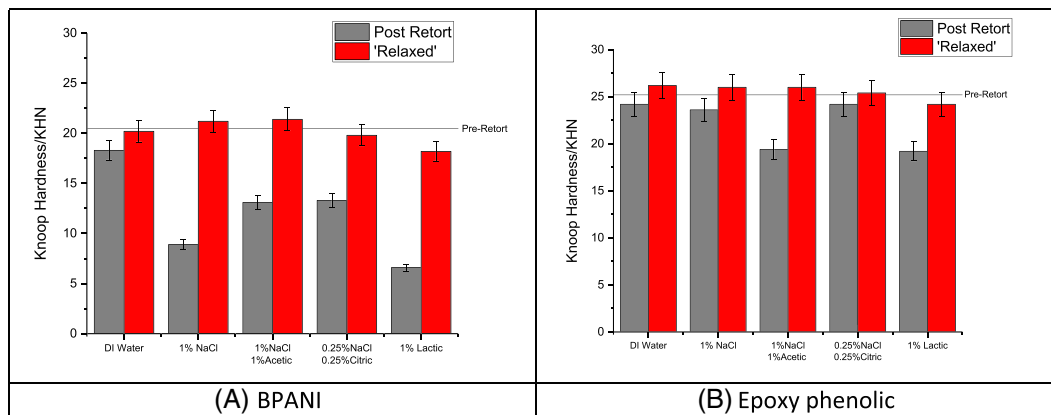

FIGURE 8 Knoop hardness of substrates immediately after retort and after "relaxation" for 14 days

may be associated with the corrosion of the substrate surface. The increase in failure force is initially rapid and, in most instances, reached 90% of its final value within 50 hours. In the case of 1% NaCl samples, as an example, the recovery is likely to be the cohesive force of the coating as the likelihood of the delamination reversing is small. As reported previously, to provide a statistically valid and reproducible quantitative measurement, scratch testing has been used which by nature of the testing will take into account both adhesive and cohesive forces.

3.3.4 | FTIR analysis

The chemistry that is observed by FTIR shows (Figure 10) that there is no marked change in the chemistry of the coating as shown by this technique. Where the Knoop hardness values change (Figure 8), this is a measure of the mechanical properties, which has been linked to the amount of simulant solution that is absorbed into the coating.

Figure 10A shows there is no significant change in the chemistry of the BPANI coating post-retort. There is one noticeable difference for

the epoxyphenolic coating, this being post-retort using 1% lactic acid as a simulant, where a carbonyl is evident with the peak shown at 1730 cm^{-1}.

4 | DISCUSSION

A number of failure mechanisms of novel materials, designed to be compliant with future legislation, have been identified. Their performance is generally lower than the incumbent technology and the failure mechanism changes with the simulant (or the food being packaged). The interaction which occurs at the interface between the simulant and surface chemistry determines the failure mechanisms, and this is summarised in Table 4.

The overall performance of the novel trivalent substitute substrate is not comparable to the incumbent ECCS material. SEM analysis (Figure 6) shows a visual representation of how the coating/substrate interface is failing and relates to the adhesion measurements taken and shown in Figure 1, further evidencing the ranking of adhesion values for the 294269M/BPANI system. This is attributed to developmental nature of the method by which the Cr is deposited from the Cr
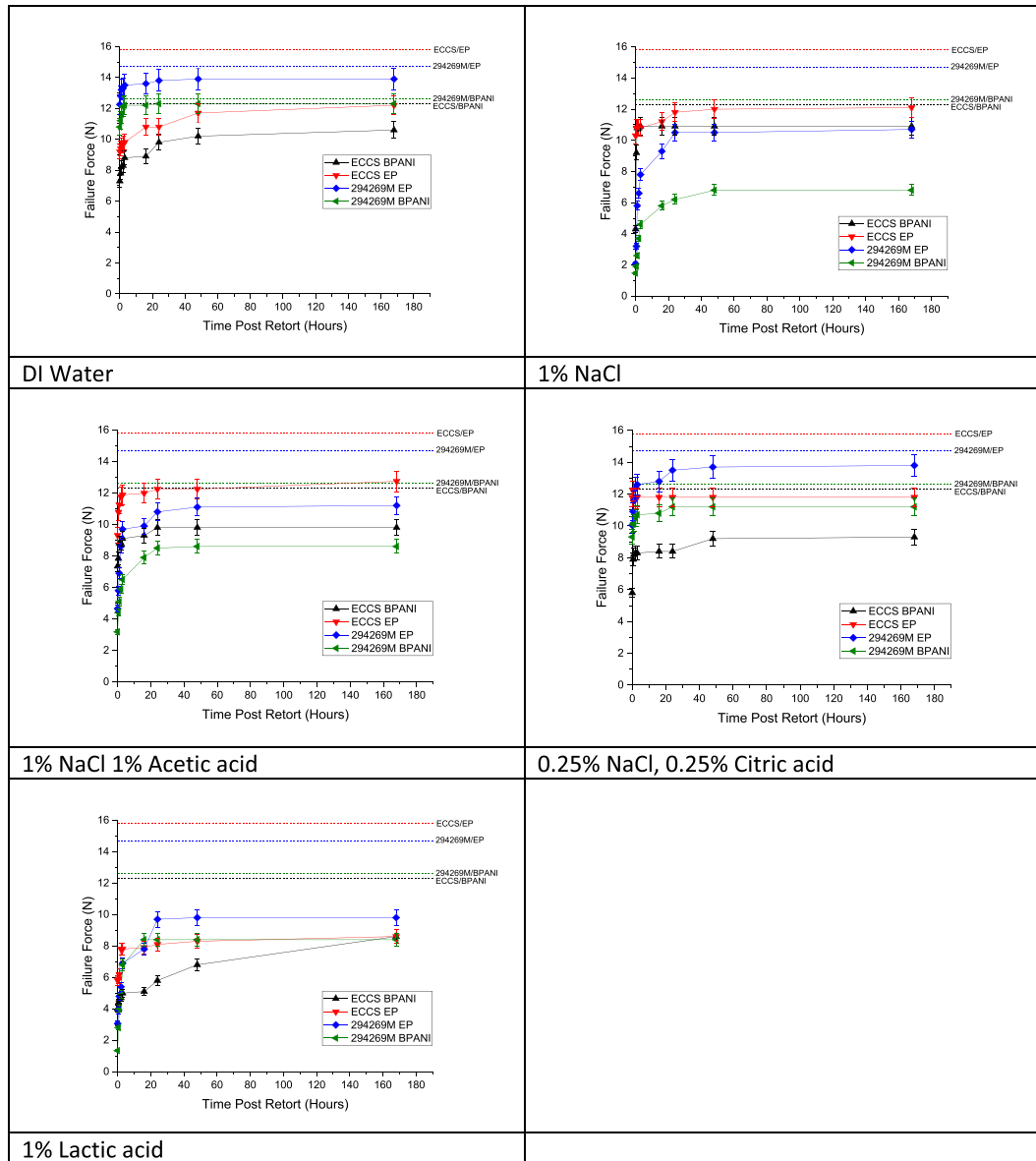
FIGURE 9 Post-retort adhesion during relaxation at room temperature

(III) electrolyte. This is evident from Figure 3A,B where the novel substrate shows a lower chromium:iron ratio on the surface prior to any testing. Any improvement which increases the coverage of chromium on the surface and reduces the exposed iron would result in improvements in performance.

Testing under dearated conditions (Figure 5) further shows the impact of the oxygen in the system, with all substrate/coating systems giving better adhesion results in deaerated conditions. However, the effect on each system differs depending upon which simulant solution is used. Oxygen has a consistently large effect on the 1% NaCl simulant samples, with other simulants showing varied degrees of effect.

Knoop hardness testing (Figure 8) shows how the mechanical properties of the coating return to their pre-retort state, given time to dry after the retort process. Combined with the FTIR data

(Figure 10), this shows that the coating itself, either chemically or mechanically, is not being permanently changed through processing. Conversely, the relaxation testing, where adhesion measurements have been taken after removal from the retort, shows that there is, in most instances, a permanent loss of adhesion quality, signified by the difference in pre-retort adhesion values and the fully relaxed values, indicated in Figure 9.

The implications of the work are significant. The performance of the canning integrity is highly dependent on the simulant being packaged. Significant reductions in performance are obtained when NaCl is present in the food stuff, even at concentrations of 0.25%; however, when small concentrations of citric acid are introduced, the reduction in adhesion quality is mitigated.

The work has shown the novel substrate performs less well that the incumbent technology. This is primarily associated with the
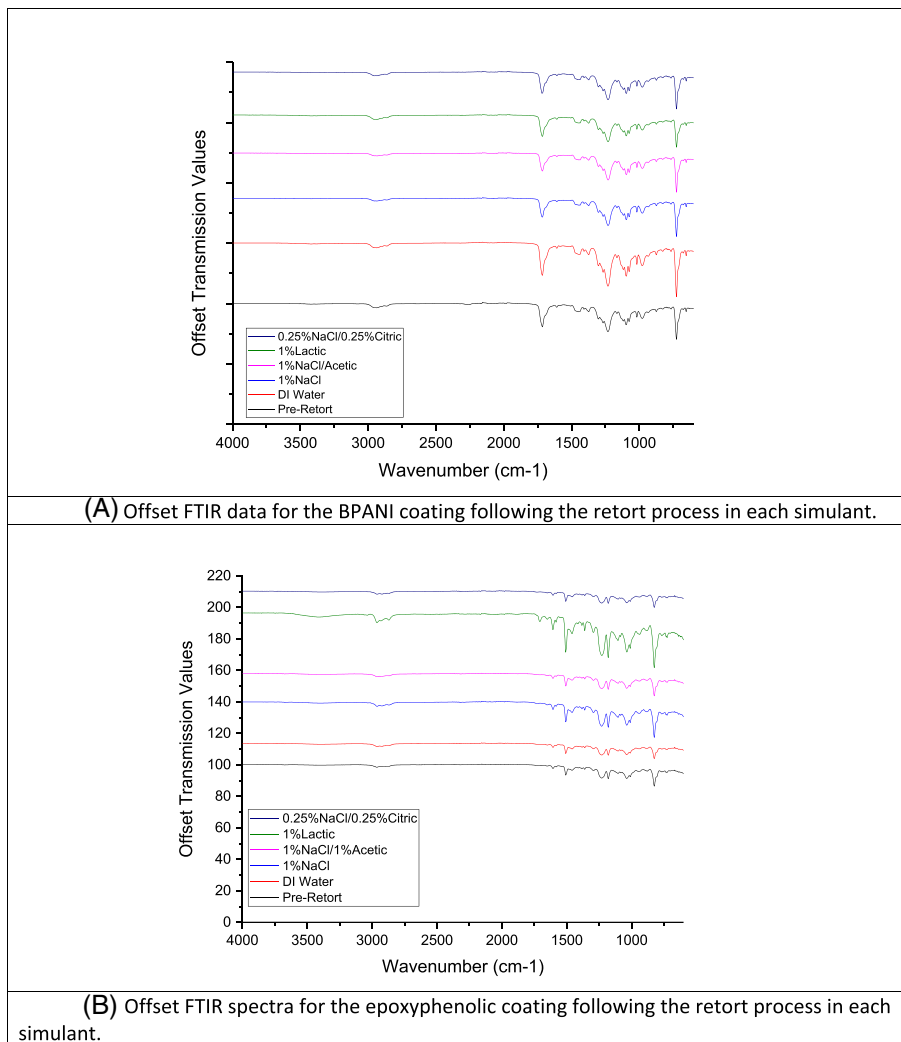
(A) Offset FTIR data for the BPANI coating following the retort process in each simulant.

(B) Offset FTIR spectra for the epoxyphenolic coating following the retort process in each simulant.

FIGURE 10 Post-retort FTIR spectra of BPANI and EP coating

TABLE 4 Visual appearance and failure mechanisms for each simulant on the novel 294269M substrate

Simulant	Visual Appearance	Severity	Dominant Mechanism	Secondary Mechanism	Reversible/Permanent
DI water	Blemishes	Mild	N/A	N/A	Reversible
1% NaCl	Blisters and delamination	Severe	Point corrosion	Gas evolution leading to delamination	Permanent
1% NaCl 1% acetic acid	Increased surface roughness	Moderate	Point corrosion	Delamination	Permanent
0.25% NaCl, 0.25% citric acid	Blemishes	Mild	N/A	N/A	Reversible
Lactic acid	Blisters, increased surface roughness and delamination	Severe	Corrosion	Delamination	Permanent

evenness of the chromium coating over the substrate on micro scale with small point areas exposure of the iron, leading to corrosion and hence a failure of the adhesion. In addition to this, SEM work has given further evidence that the coating swells, implying that the simulant solution is in the coatings, allowing the chemical species in the simulant to interact at the interface readily.

5 | CONCLUSIONS

The investigation has demonstrated that there exists a significant interaction between the chemical nature of the canned foodstuff, the packaging materials, and the lacquer/substrate lacquer adhesion. While past substrate/lacquer combinations have been robust, those

materials whose manufacture and formulation have been driven by legislative requirements are far more sensitive to the foodstuff being canned. The Cr (III)-plated product is a promising alternative for ECCS due to REACH legislation. For the early developmental iteration tested here, there is, however, still some improvement required to exhibit equivalent behaviour to ECCS in all tests. Results presented here are based on a selected commercial lacquer; hence, other lacquers may give differing results but are out of the scope of this work.

ACKNOWLEDGEMENTS

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