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### The Effect of a Silane Coupling Agent on the Hydrolytic Durability of Thin Epoxy Resin Films

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# The Effect of a Silane Coupling Agent on the Hydrolytic Durability of Thin Epoxy Resin Films

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A coating consisting of an aqueous emulsion of epoxy resin and a polyamidoamine hardener has been developed which effectively strengthens glass containing large flaws. By substituting a silane coupling agent for some of the resin the deleterious effects of ageing can be prevented; the strength of samples aged for two months at 52°C and 96% relative humidity was not reduced, maintaining a 197% improvement in strength with respect to uncoated samples.

X-ray photoelectron spectroscopy showed that the accelerated ageing treatment led to an increase in the concentration of hydroxyl groups in the resin resulting from the scission of amine crosslinking groups. The migration of sodium from the substrate to the surface was also demonstrated. It is concluded that the coupling agent does not render the coating immune to hydrolytic ageing or protect the substrate from hydrolytic attack. It only provides a hydrolytically-stable linkage between the two.

**Keywords:** XPS; Hydrolytic degradation; Diffusion; Epoxy; Coating; Silane; Strengthening

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## INTRODUCTION

A number of investigations have shown that an epoxy resin coating is capable of infiltrating both natural and artificially-introduced flaws in soda-lime-silica glass. When the infiltrating coating is cured the cracks are healed to some extent and, thus, the strength of the glass is improved, reducing the apparent severity of the damage [1–10].

One of the problems of using polymeric coatings for strengthening glass is that the performance of the coating is reliant on the strength of the interfacial bond between the glass and the polymer. For many years manufacturers in the composites field have been improving the bond between matrix resins and reinforcing fibres by using silane coupling agents. Such coupling agents have also been used by those developing strengthening coatings. Wang *et al.* [2] developed a system consisting of a bisphenol A-type epoxy resin cured with an amine hardener with the addition of a coupling agent to improve the bond between the polymer and the glass. It was observed that the silane improved both the initial strength and the durability of the coating.

Despite their favourable performance, preparation of these coatings has a significant disadvantage since the constituents are dissolved in acetone. Such a volume use of volatile organic solvents has significant health and environmental implications. In this paper, we examine a water-based epoxy resin coating system which is capable of providing a level of performance similar to previous solvent-based systems. Using this coating, we examine the hydrolytic ageing characteristics of epoxy resin coating systems and report some interesting observations concerning the function of silane coupling agents frequently added to polymeric coatings to improve the resistance to hydrolytic degradation.

## EXPERIMENTAL PROCEDURE

### Substrate Preparation

Soda-lime-silica glass microscope slides ( $37 \times 25 \times 1.1$  mm) were indented with a Vickers hardness testing machine (Vickers-Armstrong ltd) with a 10 kg mass. The duration of the contact was approximately

10 s—the standard duration for the Vickers hardness test. The specimens were carefully aligned such that the diagonals of the Vickers indenter were parallel to the edges of the specimen. After indentation the specimens were aged for one week in laboratory conditions to allow the post-indentation crack growth to saturate. Such a procedure produces a well characterised and reproducible system of cracks known as the median/radial (MR) and lateral cracks [11–14].

### Coating Preparation

5 g of a proprietary blend of modified diglycidyl ethers of bisphenol A and bisphenol F epoxy resin (Ciba Geigy PY 340–2) was mixed with 7.5 g of a polyamidoamine hardener (Ciba-Geigy HZ 340) using a motor-driven paddle. When the two components were thoroughly combined, 50 g of deionised water was gradually added whilst the mixing continued. Once all the water had been added, the mixture was stirred for a further 10 minutes to homogenise the emulsion. Specimens which were coated with this formulation have been designated as EH samples.

Formulations including a silane were prepared by replacing some of the resin with trimethoxy [3-(oxyran-2-ylmethoxy) propyl] silane (Dow Corning Z6040). The epoxy equivalent weights of the resin and the silane are 177 g and 236 g, respectively. Thus, 1 unit of resin may be replaced by 1 1/3 units of silane whilst maintaining the ratio of epoxy groups to active hydrogens in the hardener. 0.6 g of resin were replaced with 0.8 g of silane. The silane was mixed with the deionised water for two hours. The pH of the mixture during this time was 4.1, the pH at which aqueous solutions of the hydrolysed silane are most stable [15]. The silane/water mixture was combined with the resin and hardener immediately after the two-hour mixing period and the samples were coated within an hour of the completion of the emulsion preparation. Samples coated with this formulation have been designated as EHS samples.

The coating was applied by dipping the samples into the emulsion and withdrawing at  $1.2 \text{ mm s}^{-1}$ . Once coated, the samples were allowed to dry at room temperature for between 30–90 minutes. They were then cured at  $220^\circ\text{C}$  for 15 minutes in a fan-assisted oven.

### Accelerated Ageing

The base of a desiccator jar was filled with a saturated solution of potassium sulphate. Such a solution is capable of sustaining a relative humidity of 96% at 50°C (change in humidity with temperature =  $-0.05\%$  per °C) [16]. The samples were placed vertically on aluminium racks suspended above the salt solution and the desiccator was placed in an oven maintained at  $52 \pm 2^\circ\text{C}$  for a period of 24 hours.

### Mechanical Testing

The samples were fractured in four-point bending with the indent site being in tension and the MR cracks being perpendicular and parallel to the direction of the maximum tensile force. A universal testing machine (SM 200, Denison Mayes Ltd) with a 2 kN load cell was used at a crosshead speed of  $0.04 \text{ mm s}^{-1}$  which was equivalent to a loading rate of approximately  $40 \text{ MPa s}^{-1}$ . Prior to testing, a strip of adhesive tape was placed along the compressive side of the specimen to retain the fragments after fracture. Ten specimens were tested for each set of conditions.

### Surface Analysis

X-ray photoelectron spectroscopy (XPS) was carried out using a dual anode VG Clam 2 X-ray photoelectron spectrometer utilising  $\text{MgK}\alpha$  X-rays at a power of 100 W (10 mA and 10 kV). The spectrometer has a base pressure better than  $10^{-9}$  mbar and a normal operating pressure of  $10^{-8}$  mbar. The instrument is calibrated regularly using gold to measure its resolution. (At 20 eV pass energy, the width of the  $\text{Au}4f_{7/2}$  peak is 1.1 eV). Elemental sensitivity factors relative to carbon are calculated monthly using a variety of polymeric standards. These factors are given in Table 1.

For each sample, a survey spectrum was acquired at a take-off angle of  $30^\circ$  with respect to the sample surface and a pass energy of 100 eV. Core level scans were then taken of all regions of interest at a pass energy of 20 eV. The spectra were analysed using Scienta software (Uppsala, Sweden). Elemental quantification from the survey spectrum was achieved by applying a linear background to the photoelectron peaks and using the calculated sensitivity factors.

TABLE 1 Elemental composition of EH and EHS coatings before and after accelerated ageing determined from XPS survey scans

Sample	Figure	Composition, atomic % (sensitivity factor)				
		Carbon (1)	Oxygen (2.53)	Nitrogen (1.61)	Sodium (8)	Silicon (1.06)
EH	7	80.5	14.0	5.5	0	0
EH, aged	9	72.8	20.8	2.2	3.3	0.9
EHS	8	81.2	12.6	5.8	0	0.3
EHS, aged	10	77.4	17.5	3.7	0.9	0.5

Curve fitting of the C1s region was done using several Gaussian-Lorentzian component peaks corresponding to environments likely to occur in the samples using well established chemical shifts [17]. The samples were corrected for charging by setting the hydrocarbon component of the C1s region to a binding energy of 285.0 eV.

## RESULTS

### Mechanical Strength

Figure 1 shows the strength of EH and EHS samples before and after the 24-hour accelerated ageing treatment. Figure 2 displays the results of the long-term, laboratory ageing treatment of the EH and EHS

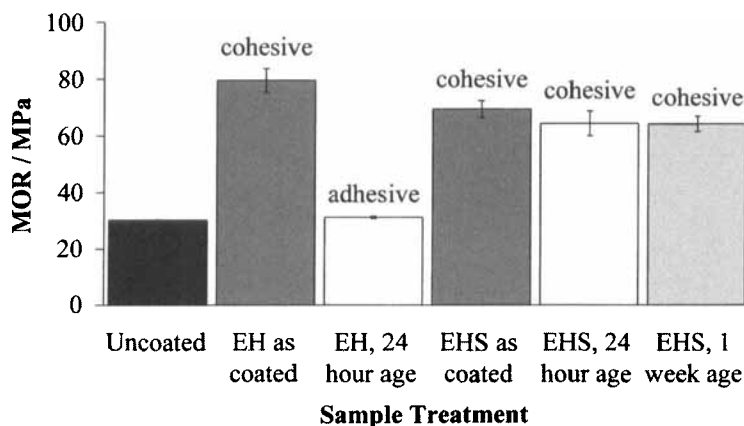


FIGURE 1 Effect of accelerated ageing (52°C and 96% RH) on the strength of EH and EHS coatings.

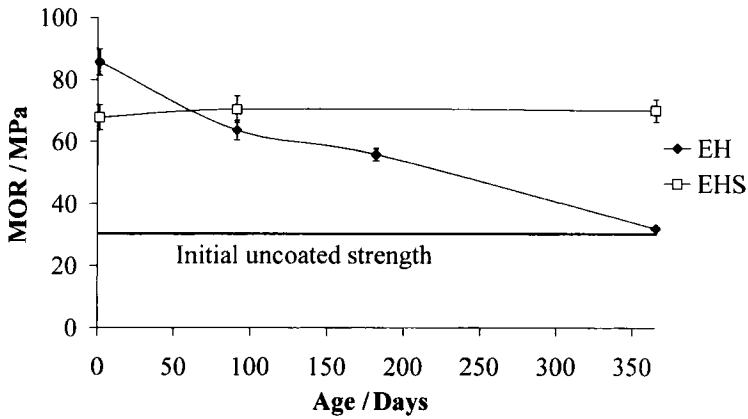


FIGURE 2 Effect of laboratory ageing on the strength of EH and EHS coatings. Lines are drawn as a guide for the eye only.

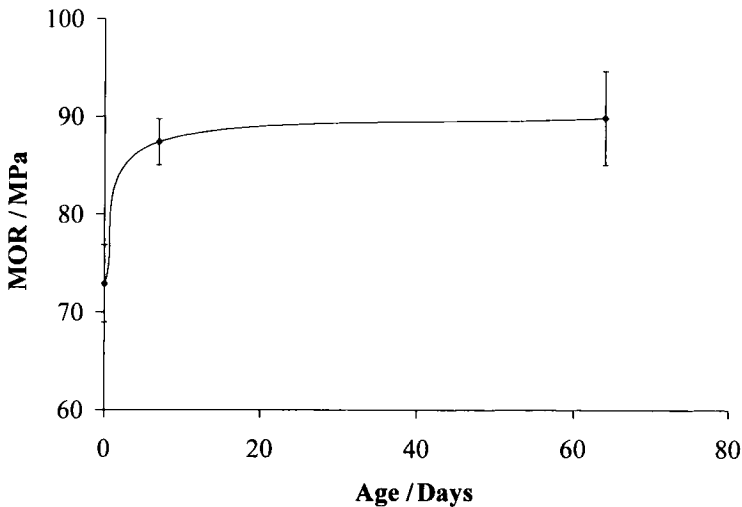


FIGURE 3 Strength of EHS coated samples subjected to accelerated ageing at 52°C and 96% RH. Line is drawn as a guide for the eye only.

samples and Figure 3 shows the results of the long-term accelerated ageing treatment of the EHS samples. The error bars represent the standard error. Figure 1 shows that, prior to ageing, the samples coated with the EH coating are actually stronger than the EHS samples. However, the accelerated ageing treatment has a catastrophic effect

on the strength of samples reinforced with a silane-free coating. After accelerated ageing the effect of the EH coating is almost entirely negated. By contrast, the EHS coating almost completely retains its strengthening characteristics. This trend is mirrored by the results of the long term ageing experiment, shown in Figure 2. Figure 3 shows that even after two months in the accelerated ageing conditions the EHS samples show no sign of performance deterioration.

Figures 4 and 5 are representative of the two contrasting types of morphologies observed on the resin layer inside the flaws. The terms "cohesive" and "adhesive" are used to describe these morphologies. However, the use of such terms can lead to confusion since in some instances where a casual inspection has suggested adhesive failure, closer examination of the exposed substrate surface has revealed traces of the resin indicating that the failure has in fact been cohesive, albeit extremely close to the interface. Since no chemical analysis of the failed interfaces has been undertaken in the present work the terms adhesive and cohesive are used only as labels to illustrate the change in the appearance of the resulting fracture surfaces. The failure mode is described as being adhesive when the resin remaining on the opposing fracture surfaces exhibits complementary topography and cohesive when the topography is identical. Thus, when a coating is said to have failed adhesively we are not explicitly specifying that no trace of the coating remains adhered to the substrate, or that no trace of the substrate may be found attached to the debonded coating.

Prior to ageing all samples failed cohesively, *i.e.*, the crack propagated through the layer of resin which had infiltrated the flaw, which is exemplified by Figure 4. After the accelerated ageing treatment the EH samples exhibited adhesive failure (Figure 5) whereas the EHS samples continued to fail cohesively. All the EH samples which had been subjected to a laboratory ageing treatment lasting three months or longer failed adhesively. EHS samples behaved in an identical manner to the accelerated ageing EHS samples—cohesive failure was maintained.

### Surface Analysis

A comparison of Figure 6 (data from an uncoated piece of glass) with Figures 7 and 8 shows that the coatings had formed coherent layers on



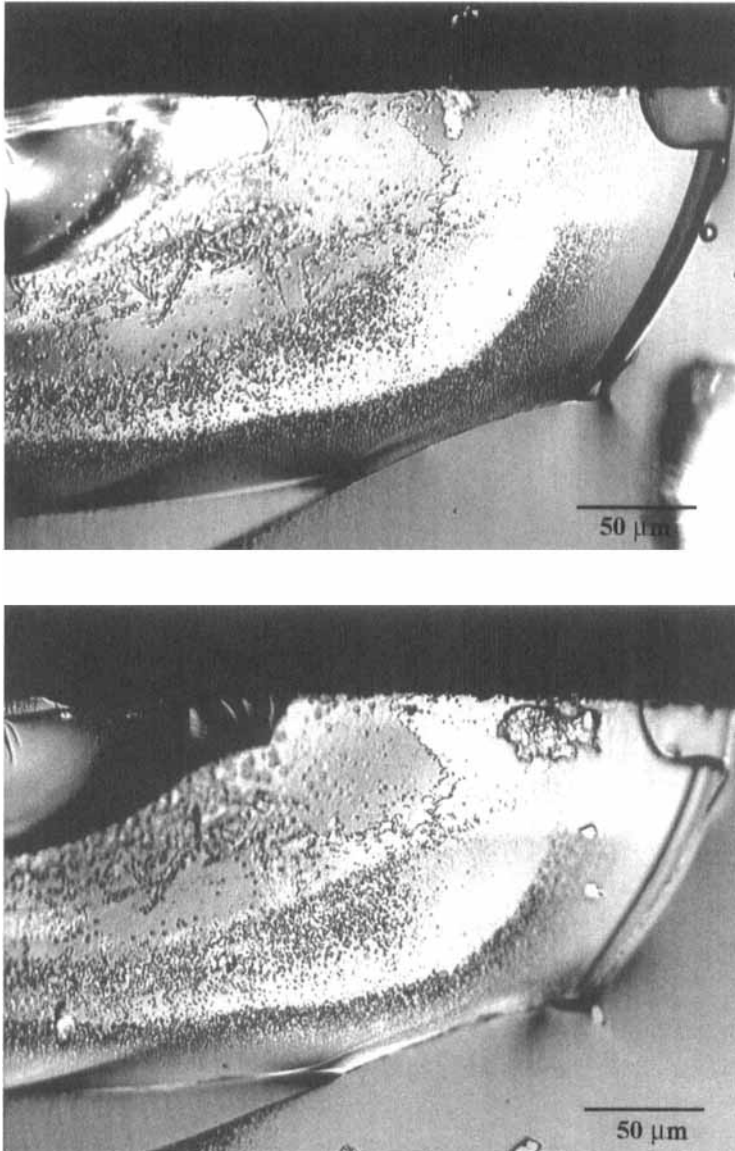


FIGURE 4 The two opposing fracture surfaces of an EH specimen prior to ageing exhibiting cohesive failure. One picture has been reversed to ease comparison.

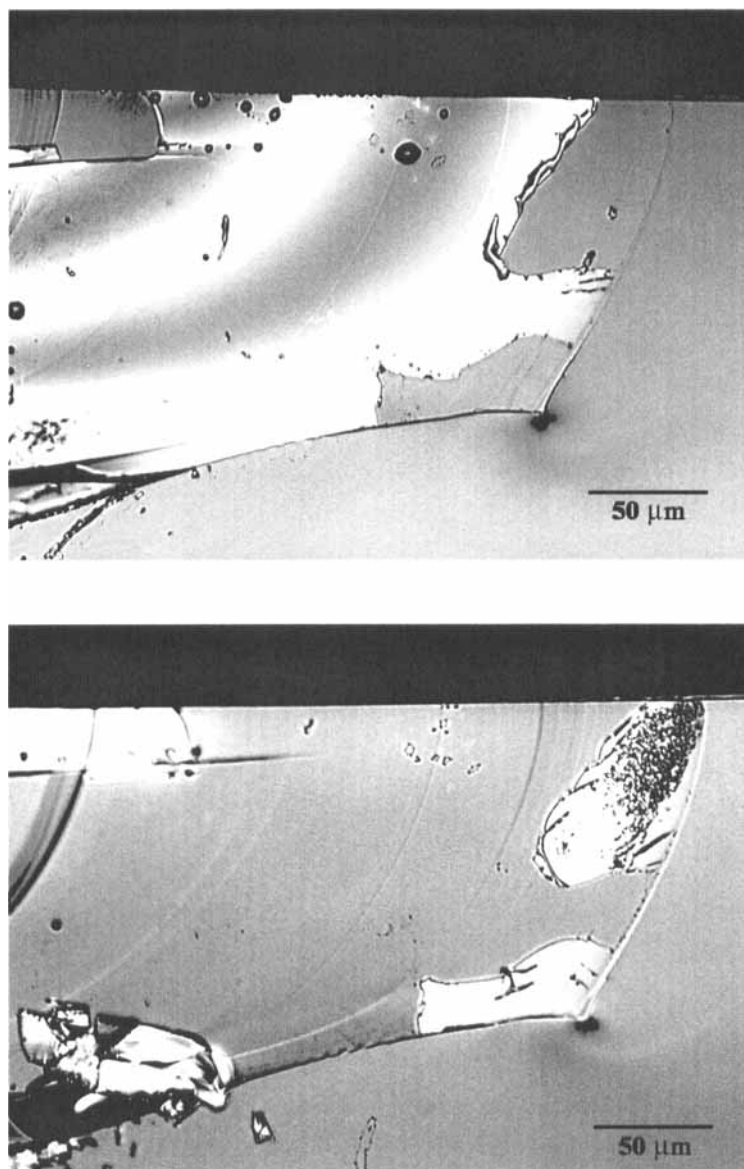


FIGURE 5 The two opposing fracture surfaces of an aged EH specimen exhibiting adhesive failure. One picture has been reversed to ease comparison.

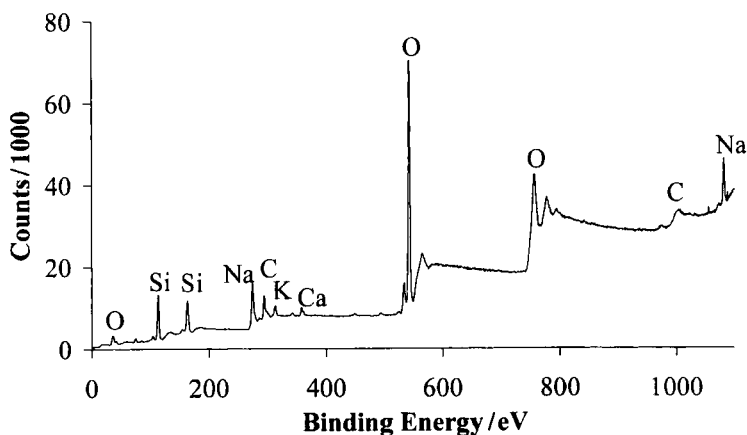


FIGURE 6 XPS survey scan of an uncoated glass surface.

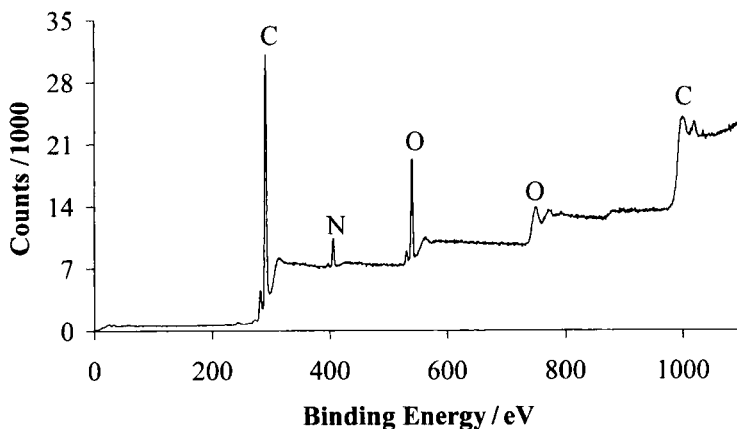


FIGURE 7 XPS survey scan of unaged EH coating.

the surface of the glass since in Figures 7 and 8 there is no evidence of sodium, calcium or potassium. Had there been pinholes in the coatings then signals from sodium, calcium and potassium from the plain glass substrate would have been detected. A small silicon signal is detected from the EHS coating which originates from the silicon in the silane. Although this signal appears to be unusually small, it should be considered that as there is only one silicon atom per silane molecule

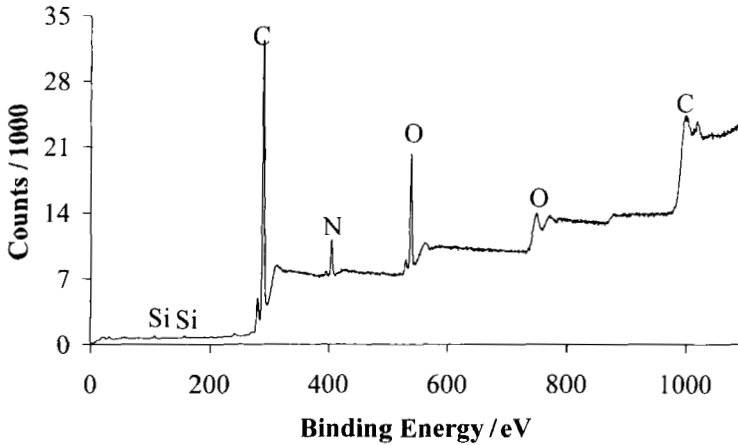


FIGURE 8 XPS survey scan of unaged EHS coating.

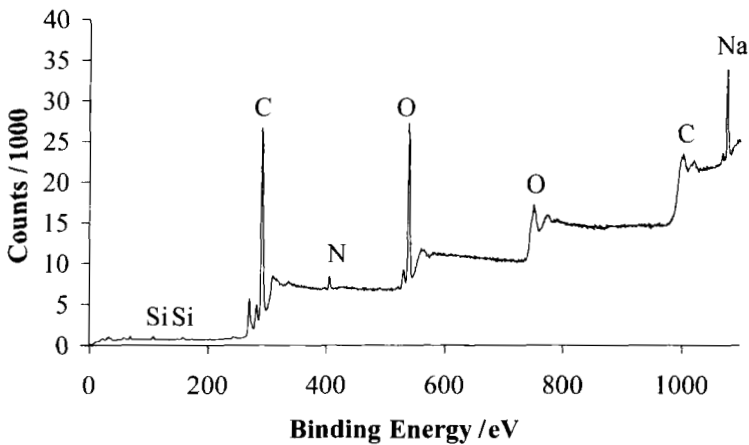


FIGURE 9 XPS survey scan of EH coating after 24 hours accelerated (24 hours at 52°C and 96% RH) ageing.

the concentration of silicon in the cured mixture is only expected to be 1 weight %.

Following the period of accelerated ageing some important changes are observed on the traces. Figure 9 shows a significant amount of sodium on the EH sample. There is only a small signal originating from silicon. The ratio of sodium to silicon is, therefore, completely different from the ratio for the glass surface and, hence, the

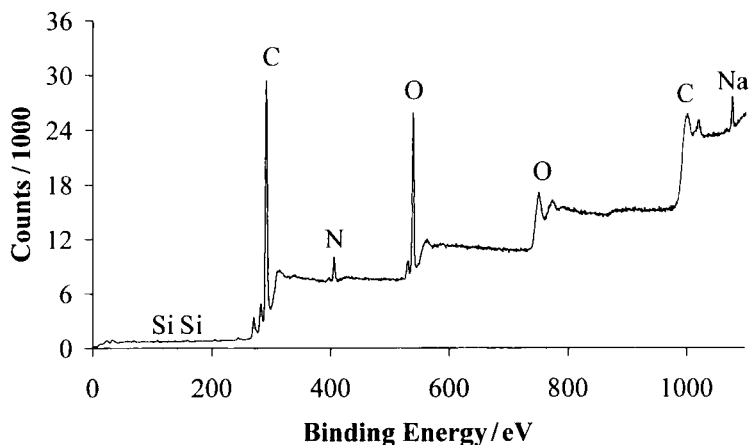


FIGURE 10 XPS survey scan of EHS coating after 24 hours accelerated (24 hours at 52°C and 96% RH) ageing.

appearance of sodium cannot be attributed to holes in the coating. The trace for the EHS sample (Figure 10) shows an identical trend. A large sodium signal is observed and the silicon signal is almost completely absent. This implies that sodium is originating from the same source as the EH samples. Although Table 1 shows that there is proportionally more sodium in the EH sample than in the EHS sample, it should be considered that XPS is very sensitive to sodium and this, along with the fact that sodium is a minor constituent with a relatively small signal, means that the value quoted for the atomic percentage of sodium is subject to a greater degree of error than the 10% often quoted for atomic composition determined by XPS.

Figures 11a–11d depict the peaks corresponding to the C1s region at 20 eV pass energy of the EH and EHS coatings. The data for the unaged EH coatings are identical to the EHS coatings within the bounds of experimental variation. By fitting Gaussian-Lorentzian component peaks to the core level scans it was determined that most of the bonds in the unaged EH and EHS coatings are C-C or C-H bonds, *i.e.*, the bonds which make up the backbones of the resin and hardener molecules. There are also quantities of C-O and C-N bonds present; the product of epoxide ring opening reactions and amine crosslinks at chemical shifts of 1.6 eV and 0.9 eV relative to hydrocarbon, respectively. There are also a number of N-C=O groups with

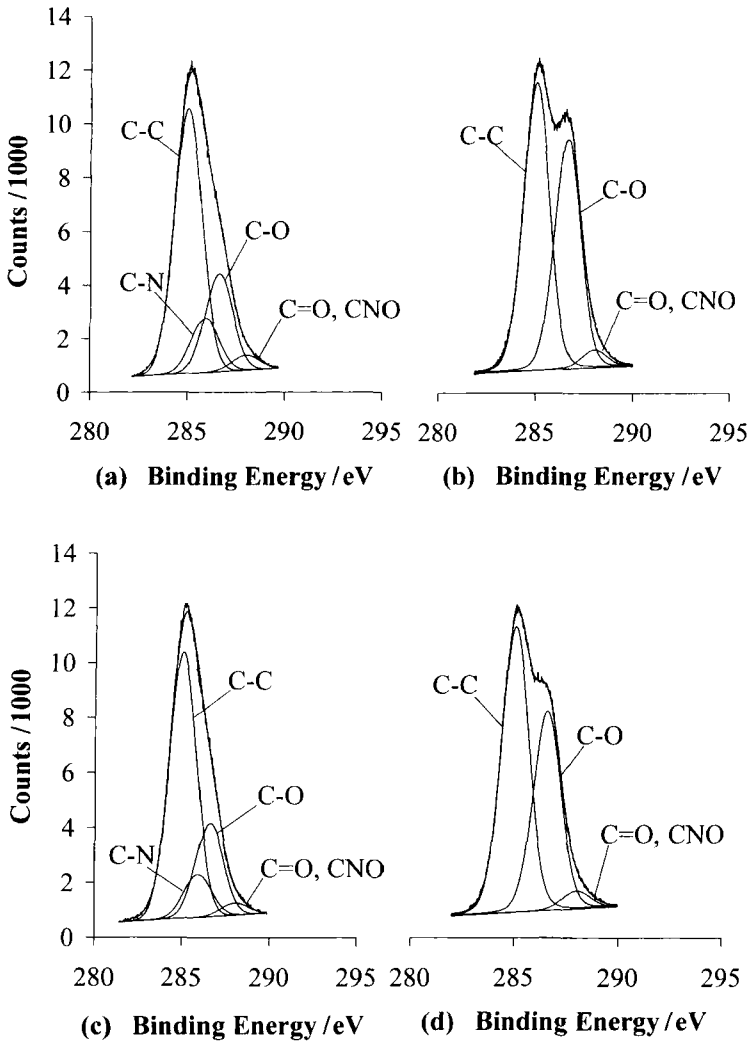


FIGURE 11 C1s core level scans of a) the EH coating prior to accelerated ageing, b) the EH coating after accelerated ageing, c) the EHS coating prior to accelerated ageing and d) the EHS coating after accelerated ageing. The accelerated ageing treatment was 24 hours at 52°C and 96% RH.

a shift of 3.0 eV originating from the amide groups on the hardener molecule. It is difficult to achieve a more detailed estimate of the composition of polymeric materials containing oxygen and nitrogen

groups due to the spread of possible chemical shifts that exist for differing environments [18].

The C1s regions of the aged EH and EHS coatings are shown in Figures 11b and 11d. The two spectra are very similar, suggesting that the aging treatment has affected both coatings in the same way. The spectra have been fitted with 3 peaks corresponding to hydrocarbon at 285.0 eV with hydroxyl/ether (C–O) at a shift of 1.6 eV relative to the hydrocarbon peak, and carbonyl/amide at a shift of 3.0 eV. There is a clear increase in the contribution of hydroxyl/ether functionality to the overall shape of the C1s region as a result of the aging treatment, but no significant change in the size of the carbonyl/amide peak. No amine peak was included in this fit because of the overlap with the much larger hydrocarbon and hydroxyl/ether peaks. The hydrocarbon and hydroxyl/ether peaks are so well resolved that the intensity of an extra peak to account for the contribution of amine functionalities at 0.9 eV tends to zero as the iterative curve fit progresses. Although it is not possible to distinguish between C–OH and C–O–C groups by XPS, since the aggressive species is water it is sensible to assume that the increase in the C–O contribution indicates an increase in the concentration of C–OH groups.

## DISCUSSION

Silane coupling agents are often referred to as adhesion promoters, since it has been frequently observed that they improve the interfacial bond strength between organic coatings and ceramic, metallic or vitreous substrates. In a comprehensive investigation, Walker found that the torque shear strength of the bond between an epoxide paint and an aluminium substrate was improved by 50–65% when a range of silane coupling agents was used. It was also noted that the area of adhesive failure was reduced from 100% for silane-free systems to 0% for systems containing a silane [19–22]. Hand and co-workers investigated the strengthening effect of a solvent-based epoxy resin coating system on Vickers indent flaws in soda-lime-silica glass. It was found that the addition of a silane leads to a 35% improvement over coatings consisting only of epoxy resin and a hardener [6, 7]. Concordant with the results of Walker, the silane was also found to reduce the degree of adhesive failure [23].

Of the systems investigated in the literature, the weakest region of an epoxy-substrate system (epoxy/aluminium or epoxy/soda-lime-silica glass) has always been the interface. Being weaker than the cohesive strength of the resin network, the interface would be the path of the ultimate failure of the system. With the addition of the silane the interface is strengthened such that cracks no longer propagate through the interface but through the resin network itself, hence, the mode of failure is observed to change from being adhesive to cohesive [19–23]. The results of the present investigation are not concordant with this observed trend. Figure 4 shows that even for systems containing no silane the adhesive mode of failure was not observed—the interface is stronger than the resin network. It should be expected, then, that the silane addition does not improve the strength of Vickers indents coated with the emulsion since, although the interface may well be stronger for the addition of the silane, its strength was not pertinent to the failure.

Although prior to ageing the performance of the EH and EHS systems is comparable, their resistance to hydrolytic ageing strongly contrasts. Figure 1 shows that after 24 hours treatment at 52°C and 96% RH the strength imparted by the EH coating is entirely lost, whereas there has been a negligible effect on the EHS coating. An examination of the failed specimens revealed that the mode of the failure of the EH samples had changed from being cohesive to adhesive, illustrated by Figures 4 and 5. The EHS coatings continued to fail cohesively after accelerated ageing. The samples which had been aged under laboratory conditions reveal that the change from cohesive to adhesive failure for the EH samples is complete before the reinforcing qualities of the coating are entirely lost. This indicates that the interface is gradually deteriorating as a whole, not instantaneously deteriorating along an advancing “front” of chemical attack. The progress of this reaction is apparently not controlled by the diffusion of water through the epoxy film since an equilibrium moisture content is attained very rapidly compared with the time required for the strength of the coated specimens to decrease; therefore, it must be the rate of the interfacial bond scission reaction itself which is slow. We are able to distinguish between the effect of the diffusion rate and the hydrolysis rate by using small samples. In the present geometry the diffusion path is less than 200  $\mu\text{m}$  and by using the data collected by Ellis and Rashid [24] it can be estimated that moisture equilibrium



may be attained in approximately 6 1/2 hours. Watts *et al.* [25] observed a mixture of cohesive and adhesive failure for epoxy/aluminium joints stored in water, which contradicts the present results. The discrepancy may have arisen because the epoxy/soda-lime-silica glass system contains potentially aggressive agents such as sodium which are absent in the epoxy/aluminium system. However, since it is not clear why the *global* absence of sodium would result in the *partial* retention of cohesive failure, we believe that the reason for the discrepancy is that their samples were much larger. The length of time required for water to diffuse throughout the joint may have been a significant factor in retarding the progress of the degradation reaction at the centre of their specimens. Chang *et al.* [26] state that a lap joint 25 mm wide may take several years to reach moisture equilibrium.

The performance of EHS samples subjected to a laboratory ageing treatment of one year were not significantly affected and they continued to exhibit cohesive failure. Hand *et al.* [6, 7] have reported that silane-containing coatings actually improve with ageing by around 40% in six months. It is believed that the hydrolysed silanes in the bulk of the resin continue to condense with adjacent molecules, leading to an increase in network crosslink density *via* the formation of a polysiloxane network. Figure 1 shows that the strength decreases slightly with accelerated ageing; however, since the strengthening mechanism proposed by Hand *et al.* is slow, over a period of one week its effect would be slight and so the observed decrease in strength could be caused by experimental scatter. Figure 3 demonstrates that under accelerated ageing conditions for longer periods an increase in strength may be observed. The increase in strength is small and could be accounted for by experimental scatter. However, an observation of a specimen aged for six months in accelerated conditions suggested that some improvement in strength was probably taking place. The ageing behaviour of the coating at long ageing times appears to be complex and more exhaustive experiments over longer periods are necessary to confirm this behaviour. The disparity of performance of EH and EHS samples is evidence that the silane does not merely strengthen the bond between the resin and the glass but fundamentally changes the mechanism of bonding.

The adhesion of amine-cured epoxy resins to glass is thought to occur through a hydrogen bonding mechanism and is, therefore,

susceptible to hydrolytic degradation. Clark-Monks and Ellis have investigated the adhesion of n-butylamine and ethylene oxide (which has the structure of an individual epoxy group) onto silica [27]. The amine was found to be adsorbed primarily on the isolated hydroxyl groups *via* hydrogen bonding. A subsequent reaction between ethylene oxide and the adsorbed amine resulted in the possible formation of a quaternary ammonium salt. Such polar bonds might also be expected to be susceptible to hydrolytic attack. Andrews *et al.* [28] have proposed that the condensation between hydroxyl groups on the glass surface and on the resin molecules provides the covalent linkages between the resin and the substrate. These linkages are susceptible to hydrolysis but in the dry state would have a strength similar to the covalent bonds formed by the condensation of surface hydroxyl groups with coupling agent silanols.

We have used the accelerated ageing treatment as a method of obtaining data regarding hydrolytic durability in a conveniently short time. However, Lefebvre *et al.* [29] have shown that the adhesive behaviour undergoes a transition when a certain threshold of humidity is surpassed. Gravimetric measurements showed that above 70% RH the uptake of water by epoxy resins is enhanced and the adhesion between an epoxy resin coating and a borosilicate glass substrate was observed to decrease at this point. Since the relative humidity during the laboratory ageing was less than 70% (typically 50%) and the relative humidity during the accelerated ageing test was 96%, due consideration ought to be given to the possible implications of this change of behaviour. Lefebvre *et al.* related the loss of adhesion in conditions of high humidity to a disruption of hydrogen bonds between matrix C-OH groups and surface Si-OH groups. The observation of a loss of adhesion at a certain threshold of humidity might be expected to hold for soda-lime-silica glass substrates, because the adhesive mechanism still involves the interaction of Si-OH groups with functional groups of the coating. Given that the threshold of humidity marks a change in the behaviour of the polymer, not the substrate, a different substrate should not affect the transition of behaviour. Since in the present case the morphology of the fracture surfaces for laboratory and accelerated ageing samples is the same, we believe that the same bonds are being attacked in each case, but that the mechanism of the attack may be different. It is possible that above

a certain threshold humidity there is a sufficient quantity of absorbed water to allow multiple water molecules to attack individual hydrogen bonds resulting in more efficient scission.

The present results show that the addition of the silane has resulted in greatly improved hydrolytic durability. Neither the laboratory or the accelerated ageing samples have been weakened by their ageing treatments. This result is entirely in agreement with the accepted knowledge that coupling agents provide hydrolytically-stable linkages between organic matrices and inorganic substrates. Hydrolysed silane coupling agents covalently bond with inorganic substrates *via* the condensation of the Si-OH groups on the silane with M-OH groups on the substrate. Soda-lime-silica glass has a somewhat hygroscopic surface and, consequently, contains many Si-OH groups to condense with the coupling agent silanols. The retained functional group of the silane, in the present case an epoxy group, is then capable of reacting to form a covalent bond with the resin coating. In this way, by using a coupling agent the polar bonds adhering the resin directly to the glass have been replaced with non-polar and, therefore, hydrolytically-stable covalent bonds. Although broadly correct, this is an oversimplification of the mechanism of bonding *via* silanes. Erickson and Plueddemann [30] have detailed several possible mechanisms. A common feature of the more widely accepted mechanisms is that the silane layer allows for stress relaxation across the interface to occur. This may be from the deformation of a silane multilayer at the interface or by the continuous breaking and reforming of the bonds between the silane and the substrate. It is believed that individual silane-substrate bonds are not hydrolytically inert but the reversibility of the bonding/scission reaction between the substrate and the coupling agent network means that the two phases are bonded in a hydrolytically-stable manner.

Several investigations have revealed that when the coupling agent is applied as a primer prior to the application of the coating resin the coupling agent has a multilayered structure [31–35]. It is necessary to remove all but the chemically-adsorbed layers (leaving a layer roughly 2–4 nm thick [34]) to obtain a strong bond between the glass and the polymer [6]. When the coupling agent is applied by directly mixing it with the resin, as in the present case, the formation of an interphasal silane layer has not been proven; however, the efficacy of silane

additions as small as 0.1% by weight [21] would suggest that some preferential segregation is taking place. Some segregation would seem to be a necessity, since to retain interfacial integrity during hydrolytic attack the silane must be present in a sufficient concentration to replace the resin-substrate hydrogen bonds with resin-silane-substrate linkages. Since the silane addition has negated the effect of hydrolytic attack, it is tempting to conclude that it has rendered the coating-substrate system immune to the effects of humidity. However, this conclusion would be incorrect.

Figure 11 depicts the core level scans of the EH and EHS coatings. The similarity of the appearance of the unaged curves is not unexpected, since the only difference between the samples is the presence of the silane whose only remaining carbon atoms are in a glycidoxy configuration identical to that of the epoxy resin molecules. Both the EH and the EHS coatings appear to age in the same way, exhibiting an increase in the proportion of C–O bonds probably from an increase in the number of C–OH groups. C–OH groups are produced by hydrolysis reactions, thus, either scission of the backbones of the resin or hardener molecules or the scission of the secondary and tertiary amine crosslinking groups must be taking place. Xiao *et al.* [36, 37] have studied the effects of hygrothermal ageing on epoxy resin coatings and films immersed in water using XPS and Fourier transform infrared spectroscopy (FTIR), respectively. An increase in the concentration of C–O bonds is observed, concordant with our results. However, the FTIR study in [37] revealed an increase in the concentration of carbonyl groups. This contradicts the data afforded by the present core level scans (Figure 11) and is not entirely consistent with their own XPS data in [36]. An increase in the proportion of carbonyl groups would produce a shoulder on the high binding energy side of the peak. Xiao *et al.* reasoned that the increase in carbonyl groups was not a direct consequence of the hydrolytic attack but that the carbonyl groups were formed by further reactions of the species initially liberated by the hydrolysis. FTIR revealed an increase in the absorption band corresponding to N–H and an increase in the concentration of C–O was revealed by XPS. This suggested that water was adding across the C–N bond of the tertiary (or secondary) amine resulting in the production of a hydroxyl group on the carbon and the reduction of the tertiary/secondary amine to a secondary/primary

amine. XPS results alone are not capable of revealing such complicated relationships between amines and, therefore, our results cannot be used to confirm the mechanism of hydrolysis. However, since the information which it has been possible to gather by XPS is in good agreement with the work of Xiao *et al.* [36], we concur that the hydrolysis reaction is probably manifesting itself as the scission of the amine crosslinks.

It is interesting to note that the EHS samples whose networks have been chemically altered by the ageing treatment have not suffered from a degradation of strength. The cohesive strength of the resin matrix has apparently not been affected by the scission of the crosslinking bonds. It is unclear why this might be the case. It is conceivable that as the crosslink density is reduced, so too is the brittle character of the resin. The toughness consequently improves, mitigating the effect of the reduced ultimate strength. Cantwell and Kausch [38] show that there is an inverse relationship between toughness and glass transition temperature and Xiao and Shanahan [37] demonstrated that hydrolytic ageing does lead to a substantial depression of the glass transition temperature (a depression of 60°C from an initial value of 160°C). Since the EH coatings have shown the same pattern of network ageing as EHS coatings it may be assumed that resin coating on the aged EH samples is as strong as the unaged resin and it is only the interfacial bonds which have mechanically suffered from the effects of the humidity. A corollary to this is that the mechanism of network modification is different from the mechanism of interfacial bond scission.

A comparison of the survey scans of the EH coating before and after ageing (Figures 7 and 9) shows that a large amount of sodium has migrated to the outer surface. The only possible source of this sodium is the underlying glass substrate since it is well known that sodium ions can exchange with hydroxonium ions. Before the glass was coated there would have been a certain amount of liberated sodium at its surface which would be free to diffuse through the coating. However, this quantity is insufficient to account for the amount of sodium at the surface of the aged sample; therefore, it may be stated that the epoxy resin coating is not protecting the underlying glass structure from further extraction and, hence, the glass is still under chemical attack. This notion is in agreement with the work of Wang *et al.* [2] and Ritter

and Lin [1], who showed that the stress corrosion constant for epoxy-resin-coated glass is the same as for uncoated glass, thereby confirming that the coatings do not prevent stress corrosion by water vapour.

The EHS coating also contains sodium at the surface, as shown by Table 1 and Figure 10. This is an important result since it proves that the EHS coating also fails to protect the underlying substrate from the effects of water so that the glass structure is still being compromised in that region. Pawson and Jones [39] have investigated the effect of sodium ions in silane deposits. They also observed the extraction and diffusion of sodium ions away from the substrate surface (in their case AR-glass). The ions promoted water absorption which, in turn, expedited the degradation of the silane-rich interphase.

Table 1 shows that silicon is present at the surface of the aged EH coating, whereas it is absent on the unaged sample. A piece of clean aluminium foil subjected to the ageing treatment was analysed as a control and verified that the silicon signal was not the result of polydimethylsiloxane contamination. The only possible source of the silicon is the underlying substrate. Silica becomes increasingly soluble as the basicity of the environment increases. Above pH 10 the solubility increases rapidly [40]. Since there is no silicon at the surface of the unaged samples it may be concluded that the environment at the interface is very different with respect to pH before and after ageing. The cause of the change of pH may be explained by considering the nature of the interfacial bonds which are hydrolysed by the absorbed water. When the hydrogen bonds between the substrate silanol groups and the hardener amine groups are disrupted, the basic amine groups are freed. These freed amine groups accordingly increase the pH to beyond the threshold at which silica solubility increases. Before the accelerated ageing treatment many of the amine groups at the interface are still involved with interfacial bonding, thus, samples which have retained interfacial integrity do not exhibit silica dissolution and, therefore, have no liberated silicon at the surface. This tentative suggestion is supported by the behaviour of the EHS samples. The integrity of the interfacial bond is maintained, preventing the increase in the pH at the interface and the silicon concentration at the surface of the aged and unaged EHS samples is almost equal, implying that the accelerated dissolution of the Si-O network has not taken place. Liberated sodium does affect pH and could be responsible for the

extraction of silicon in EH samples but sodium is also present in the EHS samples which do not show silicon extraction. Therefore, the effect of sodium on silicon extraction is not clear. It is plausible that there is a concentration gradient of sodium and that its concentration at the interface is low compared with where it has accumulated on the surface of the polymer; *i.e.*, that the concentration at the interface is too low to raise the pH enough to effect silica dissolution.

In summary, it has been shown that upon hydrolytic ageing silane-coupled epoxy resin reinforcing films undergo changes in the resin network. The underlying substrate is not protected from the humid atmosphere and is chemically altered as a result. The liberated sodium ions are reputedly instrumental in the breakdown of the silane network which replaces the hydrolytically-unstable hydrogen bonding between the resin and the substrate. However, it is not yet clear which of these three potential weaknesses is responsible for the ultimate failure of EHS systems.

## CONCLUSIONS

- An epoxy resin/polyamidoamine system applied as an aqueous emulsion has been demonstrated to be effective in repairing model flaws produced by Vickers indentations in soda-lime-silica glass.
- When the coated specimens were fractured, the coating was observed to fail in a cohesive manner but, after a 24-hour accelerated ageing treatment at 52°C and 96% RH, the interfacial bond between the resin and the substrate was compromised to such an extent that all the strengthening effect of the coating was lost and the coating failed in an adhesive manner.
- Laboratory ageing treatments showed that the transition from cohesive to adhesive failure was complete before the strengthening effect of the coating was entirely lost. A mixture of adhesive and cohesive failure was not observed.
- The time required for the degradation of the interfacial bond greatly exceeds the time required for moisture equilibrium to be reached; therefore, the degradation reaction rate is not diffusion controlled.
- An epoxy-functional coupling agent was incorporated into the emulsion and it was found that the hydrolytic resistance of the

resulting coating was greatly improved. The strengthening effect of the coating was unchanged by a laboratory ageing treatment of one year or by an accelerated ageing treatment of two months.

- Surface analysis showed that some changes in the epoxy resin network took place during the accelerated ageing treatment, and that these changes were the same for samples with and without coupling agents. It is believed that the scission of C–N bonds led to the observed increase in the concentration of C–OH groups within the resin network.
- The presence of sodium at the surface of aged samples indicated that the glass substrate was being attacked by the absorbed water and that the coating, with or without silane, was incapable of protecting it.
- In summary, the coupling agent does not render the epoxy resin network any less susceptible to hydrolytic ageing and it does not protect the glass substrate from hydrolytic attack. It only provides a hydrolytically-stable linkage between the organic resin matrix and the inorganic substrate.

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