

THE USE OF A WATER-BASED EPOXY RESIN COATING FOR STRENGTHENING GLASS

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ABSTRACT

A water-based emulsion consisting of an epoxy resin and a polyamidoamine hardener has been developed which is capable of strengthening soda-lime-silica glass containing artificially introduced flaws via a bridging mechanism. It is less effective on naturally occurring damage although significant increases in strength are observed. The epoxy resin coating has poor hydrolytic resistance resulting in rapid loss of strengthening unless a silane coupling agent is incorporated into the formulation whereupon ageing in humid environments for up to 64 days no longer affects the strength. X-ray photoelectron spectroscopy showed that accelerated ageing of the coating was accompanied by the diffusion of sodium from the substrate through polymer layer to the surface. It was also demonstrated that polymer undergoes some degradation. The presence of the coupling agent did not significantly influence these effects. The coupling agent therefore, provides hydrolytically stable linkages between the glass and the resin but does not alter the durability of the resin network nor does it prevent sodium extraction from the underlying glass substrate.

KEYWORDS

Strengthening, glass, silane, epoxy resin, ageing, hydrolytic durability.

INTRODUCTION

Soda-lime-silica glass may be strengthened by the application of an epoxy resin coating. The coating infiltrates and bridges the flaws on the surface of an item and upon curing these flaws are healed to some extent, thus reducing the apparent severity of the damage [1]. Coatings consisting of only epoxy resin and hardener suffer from hydrolytic degradation of the interfacial bond between the resin and the substrate resulting in the loss of the strengthening effect. By incorporating a silane coupling agent however, the hydrolytic stability of the glass-polymer bond is improved. Hand *et al.* [2] have developed a system of bisphenol A epoxy resin and an amine hardener containing an aminosilane which exhibits exceptional resistance to hydrolytic degradation as well as an improvement in the initial strength of coated specimens. However, the system uses acetone as the solvent which is a significant disadvantage with respect to health and environmental regulations.

We have developed a similarly effective system consisting of an emulsion of epoxy resin in an aqueous solution of a polyamidoamine hardener. Using this formulation we have compared the hydrolytic ageing

characteristics of formulations of the coating with and without a silane addition which enables us to report some interesting observations concerning the influence of the silane on the ageing process.

EXPERIMENTAL PROCEDURE

Soda-lime-silica glass microscope slides (37 x 25 x 1.1 mm) were indented with a Vickers hardness testing machine with a 10 kg mass such that the diagonals of the impression were perpendicular to the longest edges of the specimen. Following indentation, the specimens were allowed to age for one week in laboratory conditions. This procedure results in a well characterised, reproducible system of cracks known as the median/radial and lateral cracks which measure approximately 1 mm in diameter [3,4].

Two coating formulations were used. The first formulation, coded EH, was prepared by mixing 5 g of a bisphenol A/F blend of epoxy resin (Ciba-Geigy PY 340-2) with 7.5 g of a polyamidoamine hardener (Ciba-Geigy HZ 340). 50 g of deionised water was then slowly added to create an emulsion and mixed for 10 minutes. The second formulation contained γ -glycidoxypropyltrimethoxy silane and was coded EHS. 0.8g of the silane was added to 50 g of deionised water and mixed for two hours. 4.4 g of the resin was mixed with 7.5 g of the hardener and then the water/silane solution was gradually incorporated and mixed for 10 minutes. The coating was applied to the samples by dipping and withdrawing at 1.2 mm s⁻¹. After drying at room temperature for 30-90 minutes, the samples were cured at 220°C in a fan-assisted oven.

After curing the samples were given an accelerated ageing treatment of 24 hours at 52°C in an atmosphere of 96 % relative humidity. This was achieved by suspending the samples above a saturated potassium sulphate solution inside a desiccator jar and placing the desiccator jar in an oven. Control samples were aged for 24 hours in laboratory conditions (roughly 22°C and 50 % r.h.). The strength of the samples was measured in four-point bending with the indent in tension on a Mayes SM 200 universal testing machine. A strip of adhesive tape was used to contain the fractured fragments. A stressing rate of approximately 35 MPa s⁻¹ was used.

X-ray photoelectron spectroscopy (XPS) was performed with a VG Clam 2 X-ray photoelectron spectrometer using MgK α x-rays. Survey scans were taken at a pass energy of 100 eV and experimentally calculated sensitivity factors were used to determine the composition. Core level scans of the C1s region of the samples were performed at a pass energy of 20 eV and Gaussian-Lorentzian component peaks were fitted using Scientia software (Uppsala, Sweden) to estimate the distribution of carbon bonding environments.

Strips of soda-lime-silica float glass were used to test the effectiveness of the coating on naturally occurring edge flaws. The glass had been cut into strips measuring approximately 200 x 20 x 3.9 mm and the cutting process had been carefully controlled to ensure that one of the long sides of the strip contained damage typical of that which might be formed by the selvedge removal process. These samples were hand-dipped into a batch of the EHS coating formulation and cured in the manner described above. Ten indented samples were also coated in the same batch of coating to enable the performance of the coating on the natural flaws and artificially introduced flaws to be more rigorously compared. The float glass samples were fractured in four point bending with the spans at separations of 100 mm and 160 mm and at a loading rate of approximately 35 MPa s⁻¹. Adhesive tape was used to contain the resulting fragments.

RESULTS AND DISCUSSION

Figure 1 shows that the EH and EHS coatings dramatically improve the strength of indented samples. The EH coating improves the strength by 160 % and the EHS coating by 130 %. There is a certain amount of variability between different batches of nominally the same formulation. Improvements in strength of more than 210 % have been noted with EH formulations prepared on several different occasions. It is an encouraging strengthening effect but investigations have previously shown that silane-containing systems should be stronger than systems consisting of epoxy resin and hardener alone [5,6]. The present results do not concur with these investigations but this may be explained by considering the locus of failure within the

resin layer. Previous investigations have demonstrated that the failure of epoxy/substrate bonds occurs at the interface. Examination of opposing fragments from the present investigation shows a complimentary morphology indicative of the failure path being within the resin layer itself. Therefore the silane coupling agent, which strengthens the interfacial bond, would not be expected to increase the strength beyond the level of the EH samples.

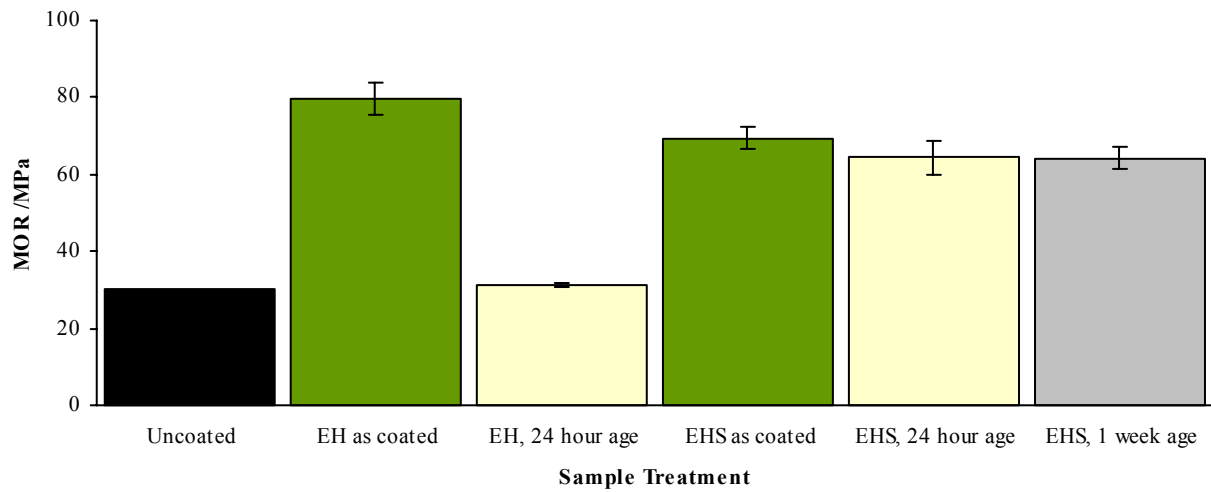


Figure 1 : Effect of accelerated ageing on the strength of EH and EHS coatings

Although impressive improvements were made to the strength of indented samples, float glass samples containing natural damage were not so effectively improved. Figure 2 illustrates that whereas the strength of artificially flawed specimens was improved by around 170 % from 30 MPa to 81 MPa, the strength of the float glass strips with the scoring damage were improved by only 41 % from 50 to 71 MPa. Kingston and Hand [7] have demonstrated that epoxy resin coatings are more effective on certain types of flaw. The effectiveness of the coating could simply be a function of the flaw size. The coating has an ability to penetrate flaws only down to a certain width due to the physical size of the resin and hardener molecules therefore, a large flaw may be reinforced over a greater fraction of its length than a small flaw hence large flaws would be expected to be strengthened to a greater extent. Flaw size may not be the only factor affecting the effectiveness of the coating. A different flaw geometry could be responsible for impeding the ingress of the emulsion, or the loading mechanism could change the way that the stresses are applied through the coating leading to premature failure.

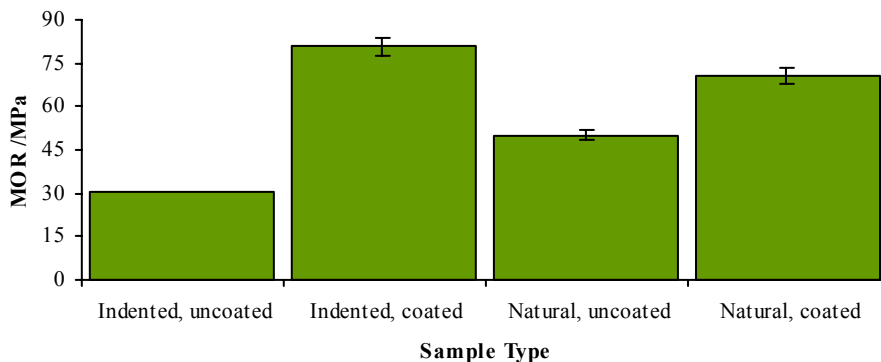


Figure 2 : Comparison of the effect of an EHS coating on artificial and naturally arising flaws

With any strengthening treatment it is hoped that when it is applied to a population of samples, the low-strength tail is eliminated. Since the coating is more effective in strengthening large flaws than small flaws it might be expected that by coating the specimens the distribution of strengths is reduced but unfortunately this is not the case. At this stage of development ensuring perfect and uniform penetration of the coating into all the flaws has not been achieved. Consequently the Weibull modulus of a set of coated specimens is reduced compared to the Weibull modulus of the uncoated specimens. The Weibull modulus of the indented

specimens typically falls from around 25 (the exceedingly high value for a brittle material being testament to the reproducibility of the median/radial crack system produced by indentation) to 7.3 ± 0.5 . For natural flaws there is no change and the Weibull modulus remains at 4.3 ± 0.1 .

Whereas prior to ageing the performance and behaviour of the EH and EHS coatings is similar, after accelerated ageing the behaviour of the coatings diverge. Figure 1 shows that the accelerated ageing treatment entirely negates the effect of the EH coating yet the EHS coating retains most of its strengthening characteristics. A further experiment showed that after a period of 64 days at 52°C and 96 % r.h. a different batch of EHS specimens retained a 200 % improvement in strength. Examination revealed that the EH coating had failed interfacially whereas the EHS coating retained the cohesive failure pattern observed in the unaged samples. The silane at the interface changes the bonding mechanism between the glass substrate and the polymer. Epoxy resin/amine hardener systems bond to glass via hydrogen bonding between amine groups on the hardener and hydroxyl groups on the substrate. These bonds are susceptible to hydrolytic degradation [8]. The bonding of polymers via silanes is more complex and involves the condensation of surface Si-OH groups with Si-OH groups on the silane molecules [9]. The resulting Si-O-Si linkages are non-polar and therefore hydrolytically more stable.

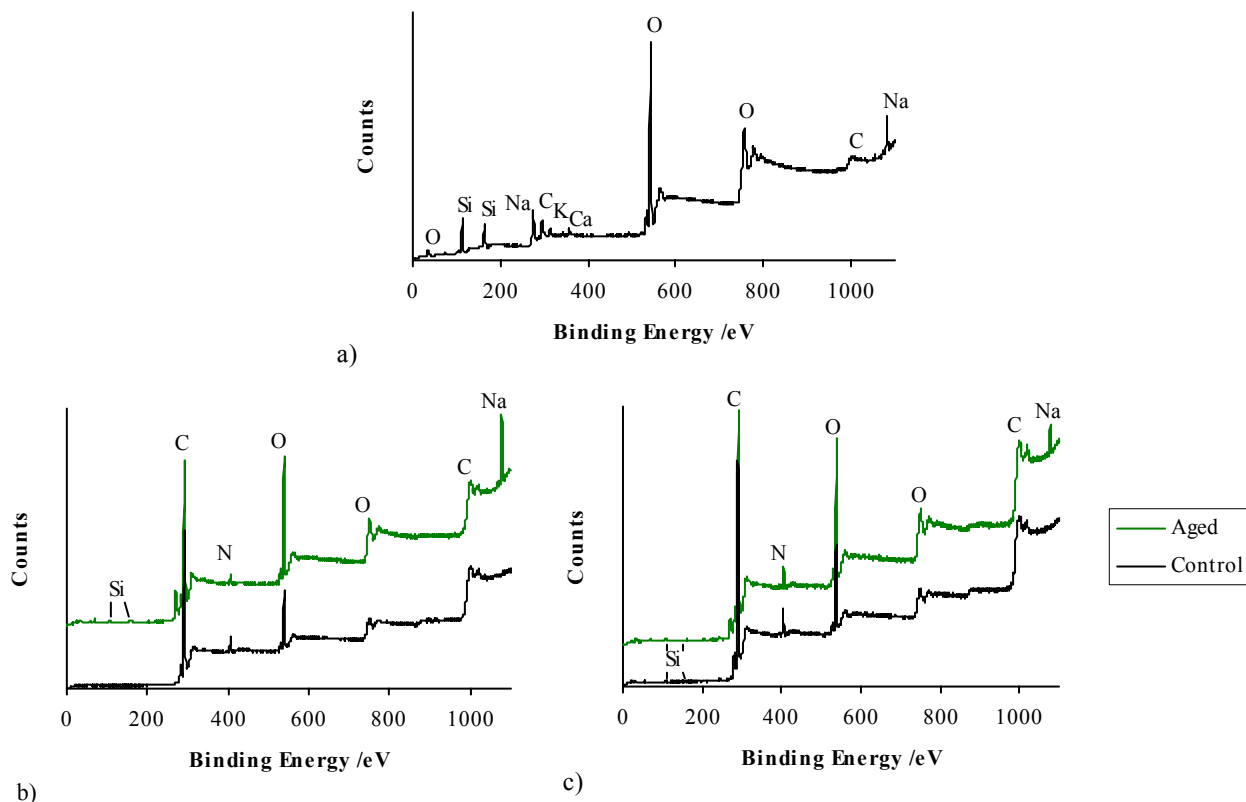


Figure 3 : Survey scans of a) uncoated glass, b) EH coating and c) EHS coating

XPS revealed that even though the silane addition had inhibited the effect of humidity on the strength of the coated specimens, reactions were still taking place within the bulk of the resin. Figure 3 shows the survey scans from EH and EHS coatings after 24 hours of laboratory ageing and accelerated ageing. Comparing the data for the unaged coatings to the data for uncoated glass it is clear that a coherent layer has been deposited on the glass since there is no signal corresponding to calcium, potassium or sodium.

The ageing treatment has affected both the EH and EHS coatings. Most apparent is that sodium is now detectable at the surface. Table 1 displays the chemical composition of the EH and EHS surfaces. It shows that there is more sodium than silicon detectable at the surface of the aged specimens. This indicates that the sodium signal is not due to pinholes in the coating since if this were the case then the silicon signal would be stronger than the sodium signal. The sodium must have been extracted from the underlying substrate since it

is well known that hydroxonium ions can exchange with sodium ions. It therefore may be stated that neither the EH or the EHS coating can completely protect the underlying substrate from water vapour.

Naturally both the unaged and the aged EHS samples contain a small amount of silicon, however it is interesting to note the appearance of silicon on the EH sample following ageing. This is an indication that there has been some dissolution and diffusion of silicon through the epoxy layer. Since there is essentially no change in the silicon concentration of the EHS coatings this dissolution process must be specific to the EH coating system. It is tentatively speculated that as the interface of the EH coating is hydrolysed, the liberated amine groups increase the local pH to a level where silica dissolution may take place. Since the EHS interface remains intact during the ageing process the pH remains unchanged and silica dissolution does not take place.

TABLE 1
COMPOSITION OF EH AND EHS COATINGS DETERMINED BY XPS

Specimen	Composition, atomic %				
	C	O	N	Na	Si
EH	80.5	14.0	5.5	0	0
EH, aged	72.8	20.8	2.2	3.3	0.9
EHS	81.2	12.6	5.8	0	0.3
EHS, aged	77.4	17.5	3.7	0.9	0.5

Narrowscans of the C1s regions of the samples can be used to show how the ageing treatment alters the nature of the carbon bonding in the coatings. Figure 4 shows the C1s narrowscans of the EH and EHS coatings before and after ageing. The unaged EH and EHS spectra are very similar, which is to be expected since the silane only contains carbon in epoxide groups exactly the same as those on the epoxy resin molecules.

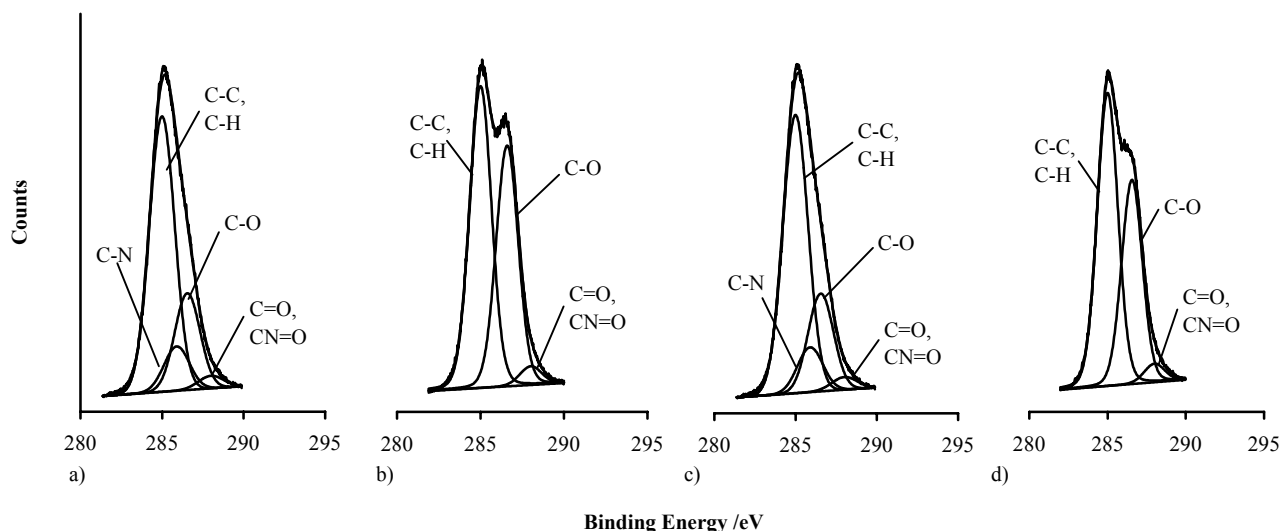


Figure 4 : C1s core level scans of a) EH sample, laboratory aged b) EH sample, accelerated aged c) EHS sample, laboratory aged d) EHS sample, accelerated aged

After the accelerated ageing treatment the C1s signals of both the EH and EHS samples exhibit a change which may be attributed to an increase in the proportion of C-O bonds surely corresponding to an increase in the population of C-OH groups. Note also that Figure 3 and Table 1 indicate an increase in the concentration of oxygen from chemisorbed water. The C-OH groups are the probably the result of

hydrolysis reactions of secondary and tertiary amine crosslinking sites, a theory also proposed by Xiao *et al.* [10]. An intriguing point to note is that even though the EHS coating has apparently degraded in the same way as the EH coating, the strength is maintained. This suggests that the resin on the EH samples retains most of its strength and it is only the interfacial bonds which lose integrity due to ageing.

CONCLUSIONS

It has been shown that on large Vickers indent flaws improvements in strength of around 200 % are achievable by using epoxy resin coatings. Promising increases in the strength of naturally occurring flaws have also been demonstrated and it is believed that by improving the application method further improvements will be made. The disadvantage of poor hydrolytic durability leading to a reduction of strength was overcome with the addition of a silane coupling agent. With such an addition periods of accelerated ageing of up to two months did not result in a loss of strength. The silane addition does not curtail all the effects of ageing in humid conditions however. The evidence presented showed that water still interacts with the glass substrate resulting in the extraction of sodium ions. XPS also showed that the cured resin network is affected by the humidity. Secondary and tertiary amine crosslinking sites suffer from hydrolytic scission resulting in an increase in the population of C-OH groups but curiously not a decrease in the strength of the coated specimens.

After ageing of EH coatings the failure path changes from the bulk of the resin to the interface between the resin and the glass. The failure of EHS coatings is always cohesive. Since in all other respects the ageing characteristics are the same it is concluded that the hydrolytic degradation only has a detrimental effect on the strength of the polar interfacial bonds of the EH coatings which are replaced with non-polar bonds by the addition of the silane. The function of the silane therefore, is not to render the epoxy resin network immune to hydrolysis or to protect the underlying substrate but to provide hydrolytically stable linkages between the inorganic substrate and the resin matrix.

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