Strengthening of glass using epoxy based coatings

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Epoxy coatings may be used to strengthen glass. The performance of two such coating systems – a solvent based one and a water based one is compared. In both cases the coatings consist of epoxy resin /hardener and a silane. The silane is necessary to give hydrolytically durable epoxy based coatings. The best results are obtained when the silane is used as a primer, however systems incorporating the silane in the coating are almost as effective as well as being more practically viable. To study the strengthening mechanism large, 'model' defects were introduced into the glass surface using Vicker's indentation. It was found that the strength degradation arising from the presence of these defects could be completely overcome. Fractographic work shows that the coatings infiltrates the large 'model' defects and fills them. However the extent of crack filling is less with the water based coatings than with the solvent based coatings. A closure stress arising from the coating filling the crack may be calculated and it is shown that this level of stress may arise from thermal expansion mismatch between the glass and the coatings. Additional fractographic work shows that infiltration of flaws by the coatings is more complicated for 'natural' damage than for the large model defects. With natural damage it is found that some flaw geometries are filled more readily by the coating than others leading to different degrees of strengthening for different flaw populations.

Introduction

The strength of glass is usually dominated by surface defects. Such defects can arise at various stages of the manufacturing process and in subsequent handling. Although it would be desirable in principle to prevent flaw formation in practice it is not possible, except in the production of fibre optics which are then coated immediately on manufacture which largely prevents subsequent damage to the fibres. Accordingly these glass components can achieve strengths approaching the theoretical strength.

Given that flaw prevention is not in general practicable it is obviously desirable to try to obviate the effect of such flaws or even to remove them. Flaw removal may be achieved by etching with hydrofluoric acid, however this process is not acceptable on health and safety grounds and, in addition the strength gains arising from flaw removal are only temporary unless further protective measures are taken. Practically therefore obviating the effect of pre-existing flaws is the only viable approach. The production of a surface compressive layer by thermal or chemical tempering is effective. However thermal toughening is not suitable for products with complicated shapes such as containers and edge damage in flat glass may be problematic before the thermal tempering process can be undertaken. Meanwhile chemical tempering is a lengthy and therefore expensive process. Thus alternative routes such as coating are of significant interest for the strengthening of glass and a number of sol-gel derived coatings[1] and polymeric based coatings[2] have been reported. The work reported here examines the use of polymeric based coatings based on an epoxy resin/hardener mix used in

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conjunction with a silane and which can therefore be referred to as ormosil-polymeric coatings.

Experimental

Two sample types have been used. The first were commercial soda-lime-silicate microscope slides which were initially 76 mm long by 26 mm wide and between 1.2 and 1.5 mm thick with polished edges (solvent based coatings work) or 1.1mm thick with cut edges (water based coatings work). The slides were cut in half to produce samples for coating. Although controlled damage was introduced into the majority of these specimens the ability of the coatings studied to strengthen glass only containing 'native' flaws was also undertaken using this type of specimen. The controlled damage was introduced using a Vicker's indenter with a 10kg load. This introduced large, reproducible, approximately semi-elliptical defects with a surface length 2*c*. After indentation the samples were allowed to age for 24 hours giving $c = 461 \pm 5\ \mu\text{m}$ with an aspect ratio of 0.6 (solvent based coatings work) or 1 week giving $c = 467 \pm 19\ \mu\text{m}$ with an aspect ratio of 0.42 (water based coatings work). The discrepancy in aspect ratio arises from a) the difference in sample thickness and b) the fact that the crack can only grow horizontally and not downward during aging because the growth in the latter direction is prevented by the already formed lateral cracks.

The second sample type were float glass specimens specially prepared to contain damage typical of that formed by selvedge removal. These specimens were $200 \times 20 \times 3.9$mm in size.

Coating preparation

Both solvent based and water based coating systems have been studied. The solvent based coatings were prepared by mixing 10.5 parts of triethylenetetraamine hardener (HY951, Ciba-Geigy) with 100 parts of a plasticised bisphenol A epoxy resin (MY750, Ciba-Geigy) at 25°C for 90 minutes. The resultant mixture was diluted to 50wt% with acetone. The samples were cleaned by wiping with tissue paper and then dipped into the coating mixture using a dip coating apparatus; with a dipping angle of 90° and a dipping speed of 1.5 mm s^{-1} a coating thickness of 3μm was obtained. The resin coating was cured for 24 hours at room temperature and post-cured at 100°C for 1 hour. Coatings prepared in this fashion are referred to as EH_{sol} coatings. Water based coating systems were prepared by mixing 5g of a proprietory blend of bisphenol A and F epoxy resin (PY340-2, Ciba-Geigy) with 7.5g of a polyamidoamine hardener (HZ340, Ciba-Geigy). An emulsion was created by slowly adding 50g of deionised water and mixing for 10 minutes. Again the coatings were applied the slides into the prepared mixture at an angle of 90° and a withdrawal speed of 1.2 mm s^{-1} to give a coating thickness of approximately 10μm. The coatings were dried at room temperature for 30-90 minutes and then cured at 220ºC for 15 minutes in a fan-assisted oven. Coatings prepared in this fashion are referred to as EH_W coatings.

Previous work has demonstrated that use of a silane primer prior to dip coating improves the hydrolytic durability of the resultant coating[3]. For the solvent based coating system a silane primer solution was prepared by adding an aminoethyl aminopropyl trimethoxy silane (Z6020, Dow Corning) dropwise to distilled water at room temperature. The final concentration was 1wt%. The slides were immersed in the solution for 1 hour at room temperature and then immersed in distilled water at room temperature for a further hour ($S_p/W_{RT}/EH_{sol}$ samples); this process is reported as removing a weak layer of silane gel from the surface[4]. In some cases this treatment was followed by immersion in distilled water at 60°C for 1 hour ($S_p/W_{60}/EH_{sol}$ samples). Silane primed coatings for which the water extraction treatment was not used are referred to as S_p/EH_{sol} samples. In all cases the slides were dried after the priming treatment for 30 minutes at 120°C and cooled to room temperature before coating with the solvent based coating described above. These coatings were again cured for 24 hours at room temperature followed by a post-cure for 1 hour at 100ºC. For the water based system a 1% aqueous solution of γ-glycidoxypropyltrimethoxysilane (Z6040, Dow Corning) was prepared by mixing the silane with deionised water for two hours. The slides were hand-dipped into the silane solution and dried at 100°C for 30 minutes after which they were immersed in cold water for 1 hour to give $S_p/W_{RT}/EH_W$ samples. Again in some cases this treatment was followed by immersion in water at 60°C for 1 hour ($S_p/W_{60}/EH_W$ samples). Silane primed coatings for which the water extraction treatment was not used are referred to as S_p/EH_W samples. In all cases the samples were dried and then coated with the water based coating system described above.

As the use of a silane primer to improve coating durability is a lengthy two step procedure, which would not be commercially viable, additional experiments were conducted with coatings that consisted of mixtures of silane, epoxy resin and hardener. In this case for the solvent based system after pre-reaction of the epoxy/hardener mixture 7.23wt% of Z6020 silane was added; this amount of silane has previously been shown to give the maximum strengthening effect[5]. The resultant mixture was diluted to 50wt% with acetone. To hydrolyse the silane half the stoichiometric amount of water (1.03 parts per hundred parts resin) was then added. The resulting solution was stirred for 4 hours before the slides were dip coated as detailed above. These coatings are referred to as $EH_{sol}S$ coatings and were cured in the same fashion as the other solvent based coatings. Some EH_WS coatings were also prepared by replacing 0.6g of the resin with 0.8g of Z6040 silane. In this case the silane was mixed with deionised water for two hours after which the solution was combined with the resin/hardener mixture. The coatings were applied by dipping and cured in the same fashion as the other water based coatings.

Some EH_WS coatings were also applied to the float glass samples in which case they were hand-dipped into a trough and then dried and cured as described above.

Mechanical testing

The slide samples were tested in four bend bending with a loading rate of 2.5 mm min^{-1} on a Mayes SM200 universal testing machine. A flexible support stage was used to avoid parasitic bending moments. Adhesive tape placed on the compressive surface of the samples ensured retention of the fragments after fracture.

Results and discussion

Figure 1 shows the mean bending strengths for the solvent based coating system and the water based coating system. It can be seen that there are noticeable differences between the two systems with there being a much less significant variation in the degree of

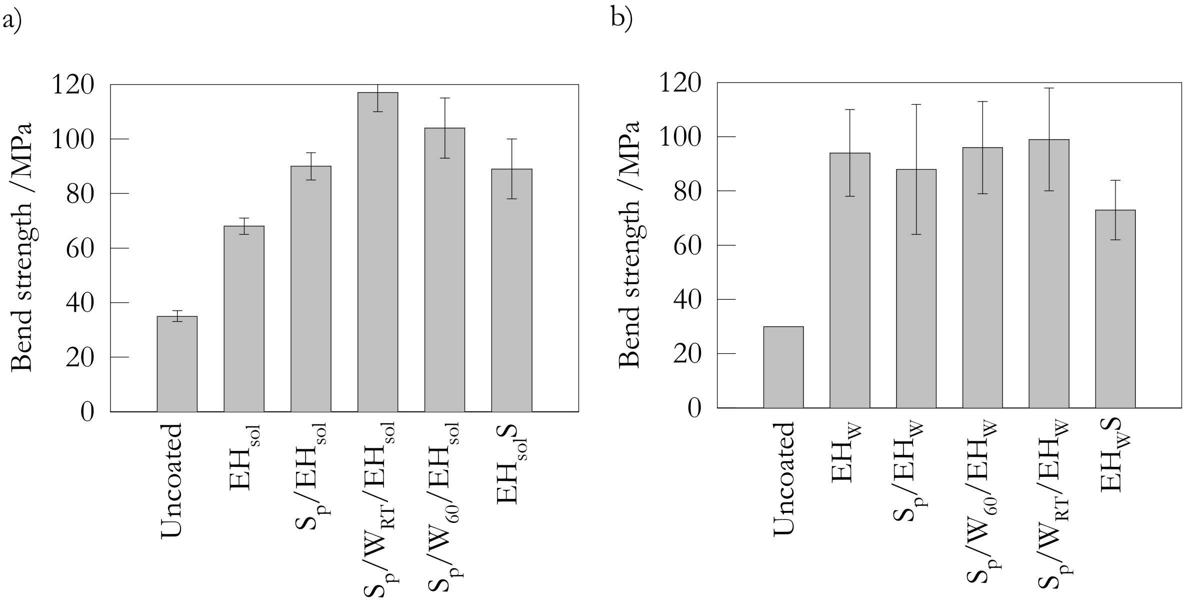

Figure 1: Bend strengths for silane primed and silane containing coatings a) solvent based coating systems and b) water based coating systems.

strengthening obtained with different silane priming treatments in the water based coating system than in the solvent based coating system. The results for the solvent based system however are compatible with the suggestion that the room temperature water extraction treatment does remove a layer of weakly bonded silane. In both cases it is clear that the coatings in which the silane is incorporated with epoxy and the hardener rather than applied separately as a primer give rise to lower strength increases than the silane primed systems. However as noted above the combined systems are of greater practical interest as the application process is simpler.

Coating penetration into model flaws

Fractographic work on samples containing controlled defects coated with solvent based coatings clearly showed that the coatings completely filled the median/radial cracks of the model defects and that coating penetration was a necessary condition for strengthening. Two types of failure were observed on the fracture surface – adhesive wherein failure occurred at the coating/crack surface interface and cohesive wherein failure occurred within the coating (see figure 2a). The region of adhesive failure was adjacent to the top surface of the glass and was roughly triangular in shape (see figure 2a) with a surface length equal to the (fixed) surface crack length. The extent of adhesive failure was dependent on coating composition and as shown in figure 2b the fracture stress increased as the extent of adhesive failure decreased.

In contrast it was found that water based coatings did not fully fill the cracks at the coating concentration used. Instead it was observed with the EH_W coatings that, if the coating concentration was altered by changing the amount of deionised water added to the epoxy/hardener mixture, the extent of flaw filling increased up to a emulsion concentration of 25% (see figure 3). As one would expect the mean bend strength also increased with increasing emulsion concentration up to a concentration of 20% (the concentration used in the rest of the work on water based coatings described here). However as shown in figure 3

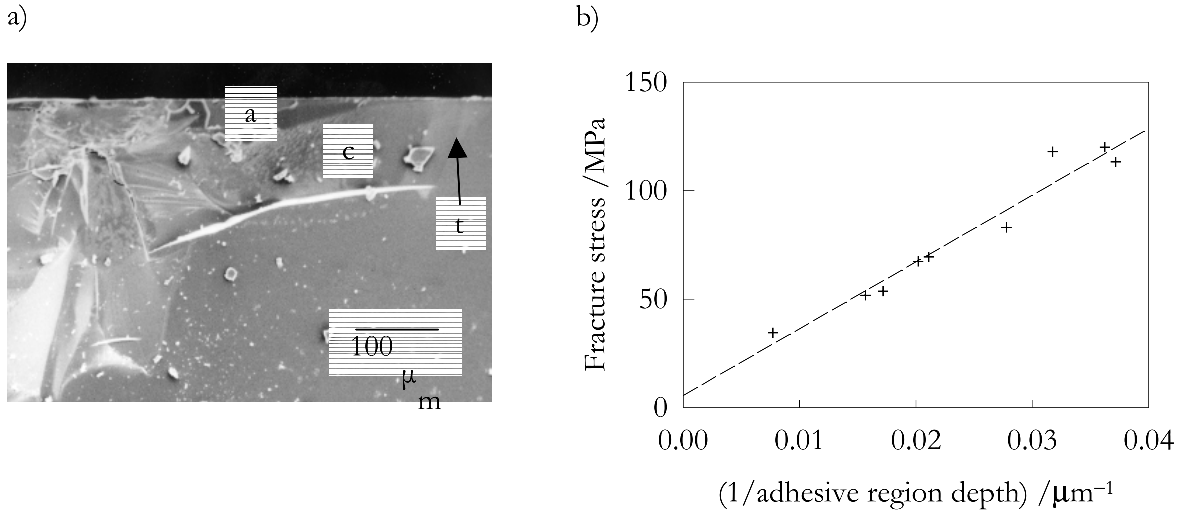

Figure 2: a) Typical fracture surface for an EH_{sol} coated crack – *a* is the region of adhesive failure, *c* is the region of cohesive failure and *t* marks the crack tip; b) fracture stress versus 1/(adhesive region depth) for solvent based coatings

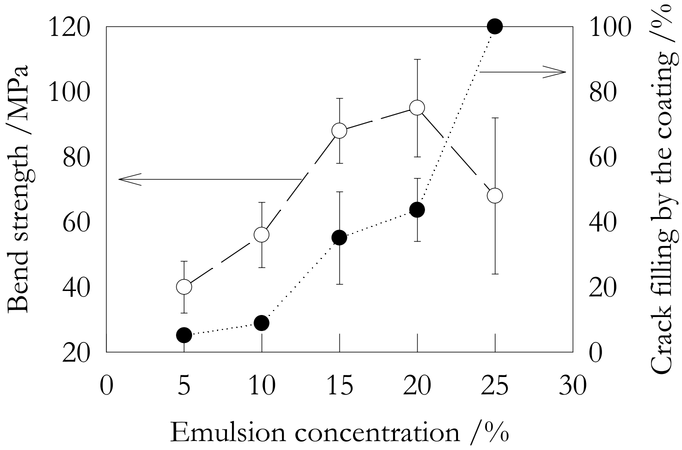

Figure 3: The effect of emulsion concentration for EH_W coatings on bend strength and percentage filling of the crack by the coating (lines drawn to guide the eye only).

the mean bend strength then decreased from 95±15MPa with a 20% concentration emulsion to 68±24MPa with a 25% concentration emulsion despite the continued increase in penetration. It is not entirely clear why this drop in mean bend strength with a further increase in concentration occurred. However as the 25% emulsion was more viscous than the other formulations it is suspected that this emulsion was less well mixed and therefore less homogeneous than the others.

As well as incomplete penetration of the large model flaws by the water based coatings it was found that there was no indication of any adhesive failure with any of the water based coating systems studied unlike with the solvent based system. The fact that fracture at all

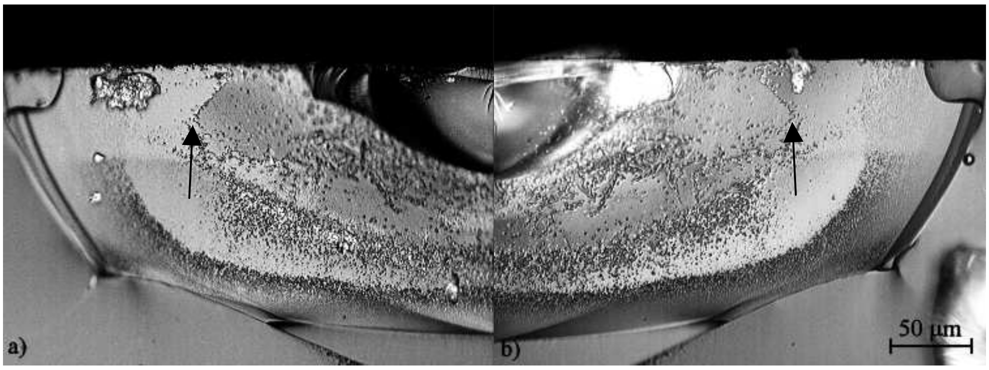

Figure 4: Matching fracture surfaces from a EH_W coated specimen showing cohesive failure. The arrowed line indicates the maximum extent of flaw filling by the coating.

Table 1: Calculated closure stresses for both solvent and water based coating systems.

Solvent based coating system	Calculated closure stress /MPa	Water based coating system	Calculated closure stress /MPa
EH_{sol}	−33±4	EH_W	−105±9
S_p/EH_{sol}	−55±7	S_p/EH_W	−94±8
$S_p/W_{RT}/EH_{sol}$	−82±10	$S_p/W_{RT}/EH_W$	−106±9
$S_p/W_{60}/EH_{sol}$	−69±9	S_pW_{60}/EH_W	−111±10
$EH_{sol}S$	−54±7	EH_WS	−69±6

stages propagated cohesively suggests that the resin-glass bond is stronger than the resin network. Therefore using a silane primer with an EH_W coating will not further increase the strength of the coated specimens since, although the interface strength may well be improved when the primer is present, the strength of this interface is not pertinent to the failure as it already exceeds the cohesive strength of the coating.

Roach *et al.*[6] have suggested that when a material fills and therefore bridges a crack then this material exerts a closure stress σ_{cl} on the crack. The stress intensity factor at the tip of a completely filled indentation crack (such as those seen with the water based system) is therefore given by[7]

$$K_{\mathrm{Ic}} = 0.49\sigma\sqrt{\pi c} + \frac{0.9614}{c^{3/2}} + 0.49\sigma_{cl}\sqrt{\pi c} \qquad [1]$$

where K_{Ic} is the fracture toughness of the glass. The calculated closure stresses are given in table 1 (the negative sign indicates that the closure stress is compressive). With the water based system the crack is filled between a distance c_1 from the center of the indent to the indentation tip and thus the stress intensity factor at the crack tip is given by

$$K_{\mathrm{Ic}} = 0.54\sigma\sqrt{\pi c} + \frac{1.0791}{c^{3/2}} + 1.08\sigma_{cl}\left(\frac{c}{\pi}\right)^{1/2}\left[\frac{\pi}{2} - \sin^{-1}\frac{c_1}{c}\right]. \qquad [2]$$

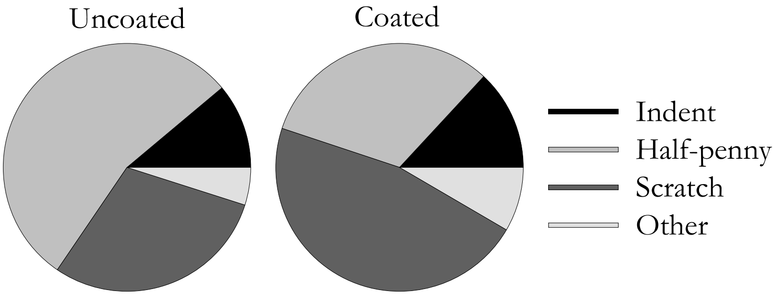

Figure 5: Types of surface flaw causing failure with uncoated and EH_{sol} coated samples (data from Kingston and Hand[5])

The slight differences in the numerical terms in equations 1 and 2 arises from the differences in the model flaw dimensions used in the solvent and water based coatings work (see above). Again the calculated closure stresses are given in table 1. It can be seen that in general the closure stresses are greater for the water based coatings than for the solvent based coatings. Hand *et al.*[7] have shown that closure stresses of this size may arise from thermal expansion mismatch between the coating and the glass, however an exact calculation is not possible because the thermal expansion coefficient of the resins used is not well characterised and because the interlayers that may occur, particularly in the silane containing systems, are also poorly characterised. Such an approach does, however, suggest that the water based coating systems should give higher closure stresses because of higher thermal expansion mismatch stresses since the water based coatings are cured at a significantly higher temperature. Thus although the water based coatings do not fill the crack as completely as the solvent based coatings, because the water based coatings are cured at higher temperatures, the thermal expansion mismatch stresses and thereby the closure stresses are greater giving a similar overall coating performance.

Filling of natural flaws by the coating

It is clear therefore that filling of the flaw by the coating is an important aspect of the strengthening process for samples containing large 'model' flaws. Kingston and Hand[8] studied the coating of glass surfaces that had only 'natural' damage with EH_{sol} coatings. These 'natural' surface flaws were categorized as indent flaws, half-penny flaws (when a median crack had formed), scratches and others. It was found the percentage of failures from the differing flaw types was different for coated as compared to uncoated samples (figure 5). Within each category of flaw it was also found that the size of the flaws from which failure was occurring was reduced which suggested that larger flaws are more effectively filled by the coating and are thereby more effectively obviated.

In the current work the strengthening of edge flaws occurring on the 'cut' edges of float glass has been studied. Edge flaws can be categorized into shark's tooth flaws (also known as teeth[9]), scoring damage and breakout damage and the studies were carried out on samples specially prepared to contain one flaw type. As the edge flaw work was carried out on specially prepared samples each containing only one defect type the type of flaw causing failure did not change on coating however, as shown in figure 6, the level of strength improvement did vary from one flaw type to another. It will be appreciated that figure 6 also indicates that the severity of each edge flaw type is different and thus any percentage

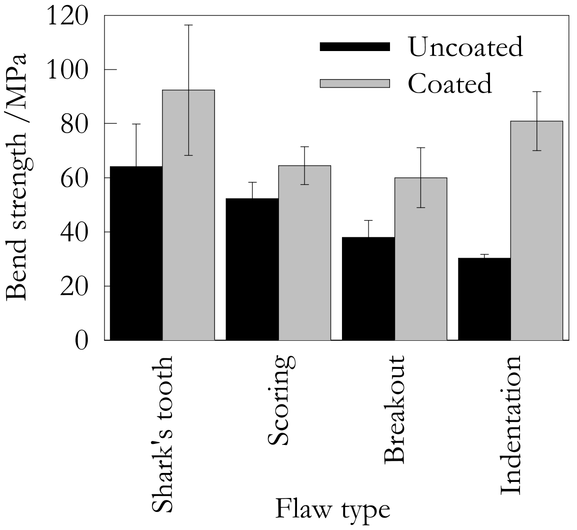

Figure 6: Strength of specimens containing edge damage coated with EH_WS coatings. The data for indented samples is included for comparison

improvement in strength is liable to be different. However the absolute levels of strength achieved are also different and it is notable that samples containing model (indentation) flaws, shown for comparison in figure 6, were initially weaker than the edge flaw samples (*i.e.* they contain the most severe flaws) but they achieved high absolute strengths on coating. This again suggests that larger flaws are in fact more readily filled by the coating leading to a greater strengthening effect.

The exact flaw geometry is also important in determining whether filling of the flaw by the coating can occur. Fractographic investigations failed to reveal any coating penetration into the fracture initiating flaws for either scoring or breakout damage (see figure 7a and b). In comparison with shark's tooth flaws infiltration of the fracture initiating flaw by the coating can be identified (see figure 7c). Clearly because the mean fracture strength has increased with the application of the coating (see figure 6) the coating has had an effect on at least some of the scoring damage and breakout damage flaws. Calculation of the Weibull moduli for the various flaw types indicates that there is little or no change in the width of the flaw distribution on coating (see table 2) which suggests that all the flaws are effected to a similar extent. Interestingly the Weibull modulus for the indented samples drops significantly on

Table 2: Weibull moduli for uncoated and EH_WS coated edge damage samples. Indentation data are included for comparison.

	Weibull moduli	
Damage type	**Uncoated samples**	**EH_WS coated samples**
Shark's tooth	4.2	4.1
Scoring	9.5	9.4
Breakout	6.6	5.7
Indentation	25.3	7.3

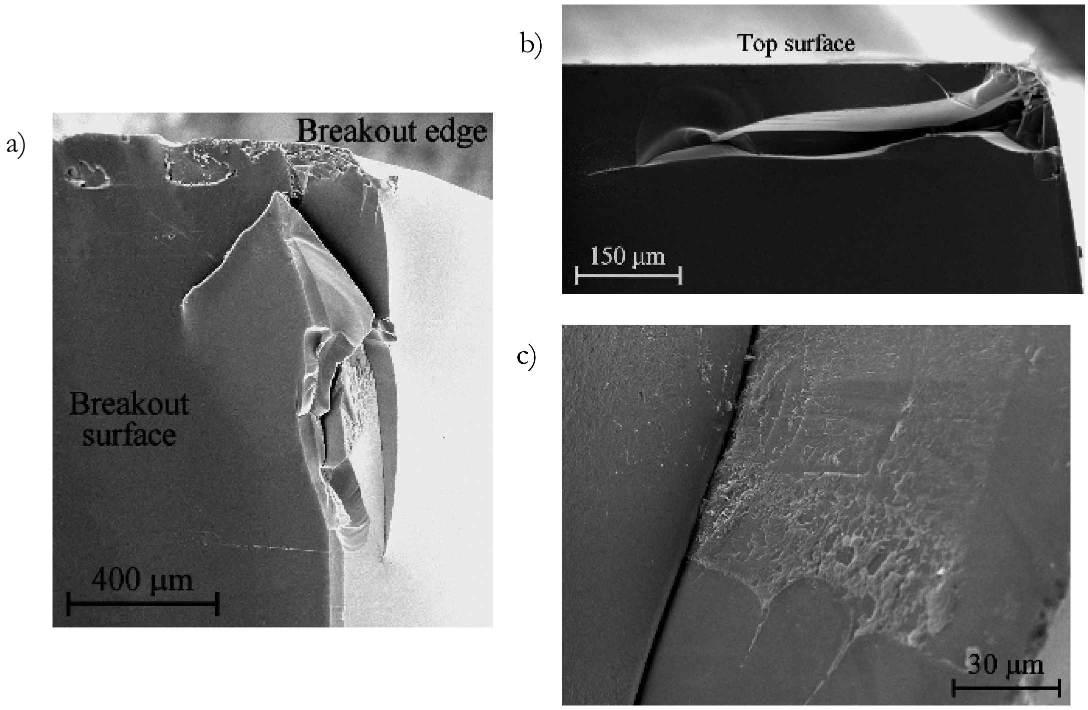

Figure 7: Fracture initiating flaws in EH$_W$S coated samples with a) scoring damage; b) breakout damage and c) shark's tooth flaws. Coating infiltration can only be observed in c).

coating indicating that although the level of damage produced by indentation is very consistent the interaction of the coating with these nominally identical flaws is less consistent.

Overall there is clear evidence that both solvent based and water based epoxy/hardener coatings incorporating a silane can strengthen glass by flaw infiltration. However the extent of the infiltration is dependent on flaw type and thus the types of flaws to be found in any particular piece of glass will to some extent determine the efficacy of the coating.

Conclusions

Epoxy based coatings strengthen glass by a flaw filling mechanism. As the coatings are cured at temperature it is suggested that thermal mismatch stresses arising on cooling are sufficient to give a closure stress that acts to strengthen the glass. The level of closure stress generated is higher for the water based system studied than for the solvent based system studied. Thus although the water based coatings are less effective at filling the cracks they give rise to an overall similar level of strengthening as the solvent based systems.

With both coating systems priming the surface with a silane before applying the epoxy/hardener coating leads to more effective strengthening than incorporating the silane in the coating mixture before application. However the latter route will obviously be cheaper and more practical from a commercial perspective.

Samples containing real edge damage have been successfully strengthened using the water based EH_WS coating system. The level of strengthening is less than that seen with the 'model' damage and this reflects the fact that it is easier for the coating to infiltrate and thereby obviate some flaws geometries than others.

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[1] BD Fabes and GD Berry, J. Non-Cryst. Solids **121**, p. 357-364 (1990); M Chen, PF James and FR Jones, J. Non-Cryst. Solids **155**, p. 99-109 (1993).

[2] FH Wang, XM Chen, B Ellis, RJ Hand and AB Seddon, Mater. Sci. Technol. **13**, p. 163-171 (1997); V Verganelakis, PD Nicolaou and G Kordas, Glass Technol. **41**, p. 22-29 (2000).

[3] RJ Hand, FH Wang, B Ellis and AB Seddon, Phys. Chem. Glasses **39**, p. 305-310 (1998).

[4] T-H Cheng, FR Jones and D Wang, Composites Sci. Technol. **48**, p. 89 (1993).

[5] RJ Hand, FH Wang, B Ellis and AB Seddon, J. Sol-Gel Sci. Technol. **13**, p. 695-699 (1998).

[6] DH Roach, S Lathabai and BR Lawn, J. Amer. Ceram. Soc. **71**, p. 97-105 (1988).

[7] RJ Hand, B Ellis, BR Whittle and FH Wang, J. Non-Cryst. Solids.(submitted for publication)

[8] JGR Kingston and RJ Hand, J. Phys. Chem. Glasses **41**, p. 1-5 (2000).

[9] LA Shitova, NV Lalykin and TA Kuznetsova, Glass and Ceramics **48**, p. 327-329 (1991).