

GLASS STRENGTHENING WITH EPOXY BASED COATINGS: A  
FRACTOGRAPHIC STUDY

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Coatings based on an epoxy resin, an amine hardener and a silane can be used to strengthen glass. Studies of fracture surfaces show that these coatings increase glass strength by a crack filling mechanism with failure typically initiating from the intersection of the defects and the surface of the glass. Distinct regions of adhesive and cohesive failure can be identified on the fracture surfaces and fracture stress increases as the size of the region of adhesive failure decreases. Coating adhesion is therefore an important parameter in determining the strength of coated glass. It is also shown that coating cohesion is important in determining the degree of strengthening. Finally it is demonstrated that the stress corrosion characteristics of the coated and uncoated glass are similar and that therefore the coatings do not prevent access of water to the crack tip.

INTRODUCTION

The strength of silicate glass artefacts is governed by the presence of surface flaws. It is therefore necessary to overcome these flaws in some fashion to strengthen glass. One possible approach is to use coatings. We have previously shown that coatings comprised of epoxy resin/ hardener and silane strengthen glass via crack obturation (Wang et al (1)). To obtain a greater understanding of how these coatings strengthen glass, and therefore which coating parameters are important, a fractographic study of coated glass slides tested in bending has been undertaken.

EXPERIMENTAL

The coatings were produced by mixing 100 parts of MY753, a plasticised bisphenol A epoxy resin, with 10.5 parts of HY951, an amine hardener (triethylenetetramine - TETA), for 1.5 hours at  $25 \pm 2^\circ\text{C}$ . The resultant mixture was diluted to 50% concentration by weight with acetone. The coating was applied to the glass by dipping. The coated samples were cured at room temperature for 24 hours followed by a post cure at  $100^\circ\text{C}$  for 1 hour.

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These coatings are referred to as E/H coatings.

Coatings were also applied to silane primed glass. The samples were primed by dipping the glass samples into a 1 wt% Z6020 (aminoethylaminopropyltrimethoxysilane) aqueous solution which had been mixed at room temperature for 0.5 hours. After dipping in the Z6020 solution the samples were immersed in distilled water at room temperature for 1 hour and then dried at 120°C for 5 hours. After drying the epoxy/ hardener mixture was applied to the samples by dipping and the same curing treatment as described above was carried out. These coatings are referred to as  $S_p/W_{RT}/E/H$  coatings.

The coatings were applied to commercial soda-lime-silica glass slides with polished edges. 10 kg Vicker's indents were used to produce reproducible strength limiting flaws on the glass slides; although the coatings have been shown to strengthen glass bottles (Wang et al. (2)) it is virtually impossible to elucidate the mechanism of strengthening, unless well controlled and reproducible flaws are present in the glass. Following indentation the samples were aged in air for 24 hours. This process resulted in large approximately semi-elliptical cracks with a surface length,  $2c$ , of  $950 \pm 14 \mu\text{m}$  and a depth,  $a$ , of  $285 \pm 10 \mu\text{m}$  (see figure 1); failure normally occurred from the controlled damage rather than the edge of the microscope slide (for more details see Wang et al (1)). The failure stresses of coated and uncoated control samples were measured in 4 point bending using a Mayes SM200 universal testing machine. The samples were normally tested at a loading rate of  $2.5 \text{ mm min}^{-1}$ . To assess the effect of the coatings on stress corrosion loading rates of  $0.0025$ ,  $0.025$  and  $0.25 \text{ mm min}^{-1}$  were also used.

## RESULTS & DISCUSSION

Although Vicker's indentation is a convenient way of producing controlled defects in brittle materials a fairly complex crack morphology is produced round such indents as shown in figure 1. However the cracks were reproducible and it was possible to identify whether the coating had penetrated the cracks and to identify the locus of failure. In general it was found that failure originated from one of the radial crack tips. The growing crack then propagated through the pre-existing crack, revealing the coating within the crack, as well as into the glass. However as the crack approached the centre of the indent secondary fracture initiation became increasingly likely. These secondary initiation events altered the direction of the primary crack and so that it no longer necessarily propagated within the indentation crack; complex fracture patterns were therefore observed on the half of the crack that was furthest from the fracture origin. It is the initial stages of fracture that are of most interest and therefore this study concentrates on examining of the fracture surfaces around the initiation site.

Figures 2 to 4 shows the fracture surface of an E/H coated sample. The coating penetrated to both the radial and median crack fronts. Penetration to the radial crack front can be seen in figure 3 (point c). This means that these coatings completely fill the crack

unlike the sol-gel coatings studied by Fabes and Uhlmann (3) which did not penetrate right to the crack tip. In addition it should be noted that the sol-gel coatings of Fabes and Uhlmann (3) required heat treatments at temperatures between 500 and 1000°C; whereas the coatings studied here were cured at a maximum temperature of 100°C.

Figure 2 shows that there is smooth, roughly triangular region close to the top surface of the glass and which originates from the fracture origin at the crack tip (region a). Closer inspection revealed that this region is associated with adhesive failure of the bond between the coating and the glass. Adhesive failure of the coating/ glass interface was also observed near the median crack tip. As controlled defects, with essentially the same surface crack length, were used throughout this study, it is possible to assess the size of the triangular area of adhesive failure (region a) by simply measuring the vertical extent of this region at a fixed point. Examination of E/H coated samples cured under different conditions (which resulted in different mean fracture stresses) showed that, for the same defect size, the fracture stress decreased as the area (depth) of adhesive failure increased (see figure 5). This implies that the stress intensity factor at the radial crack tip, and thus the failure stress, for a coated system is influenced by the adhesion of the coating to the glass and that therefore coating adhesion is important in determining the failure stress of coated glass.

Below the near surface region of adhesive failure there is a relatively rough region the lower boundary of which is the lateral crack (figure 2; region b). Within the relatively rough region parabolic markings were observed (see figure 4). These markings are characteristic of failure within polymers (Doll (4)) and therefore indicate that this is a region of cohesive failure. The markings are formed by the interaction of the primary crack front with secondary fracture sites and the open end of the markings indicates the direction in which the primary crack was travelling (Andrews (5)). The density of the markings increases towards the centre of the indent indicating that the primary crack accelerated as it approached the centre of the initial defect.

Use of a silane primer improves the adhesion of the coating to the glass and, as shown in figure 6, use of a silane primer therefore reduces the size of the region of adhesive failure (region a) in the  $S_p/W_{RT}/E/H$  coatings. Although the fracture surface in the median crack region of  $S_p/W_{RT}/E/H$  coated samples appears to be reasonably smooth (figure 6; region b), closer inspection reveals that failure in this region is also cohesive (figure 7). Thus the presence of the silane primer so improves the adhesive strength that failure is predominantly cohesive. This implies that coating cohesion may also have an effect in determining the failure stress of coated glass. This was confirmed by applying a coating that just consisted of silane primer. In this case, although there was a good adhesive bond between the coating and the glass, the stiffness of the coating was low and the coating will have had a low cohesive energy. It was found that the fracture stress of the samples coated with silane was effectively unchanged from the uncoated samples (37 MPa compared to  $34 \pm 4$  MPa). Therefore effective coatings must both bond well to

the glass and be suitably stiff to prevent cohesive failure.

As well as modifying the effective crack size it is possible that these coatings prevent stress corrosion by limiting the access of water to the crack tip. The dynamic fatigue strength of glass ( $\sigma_f$ ) may be related to the loading rate ( $\beta$ ) by

$$\sigma_f = k\beta^{1/(n+1)} \quad (1)$$

where  $k$  is a constant and  $n$  is the stress corrosion index for the glass (Charles (5)). If stress corrosion is reduced,  $n$  is increased and therefore the slope of a log stress versus log loading rate graph should be reduced towards 0. It can be seen from figure 8 that the slope of such a graph is little changed compared to uncoated samples, whether or not a silane primer is present. In fact the stress corrosion index for  $S_p/W_{RT}/E/H$  coated glass seems to be reduced compared to that for the uncoated case (9.1 compared to 19.2), although this may be due to scatter in the data. However it may be safely concluded that epoxy based coatings do not reduce stress corrosion of the glass and therefore such coatings do not strengthen the glass by acting as a diffusion barrier to water.

#### CONCLUSIONS

The effect of epoxy based coatings on the fracture behaviour of glasses containing large controlled defects has been studied. The coatings completely fill the cracks but they do not modify the stress corrosion characteristics of the underlying glass and therefore the strengthening behaviour is not due to the coatings acting as a diffusion barrier.

Features associated with both adhesive failure of the coating glass bond and cohesive failure of the coatings can be identified on the fracture surfaces. The measured strengths are roughly, inversely proportional to the extent of adhesive failure so for good coating performance a good interfacial bond is required. Good coating cohesion is also required for significant strengthening effects.

#### REFERENCES

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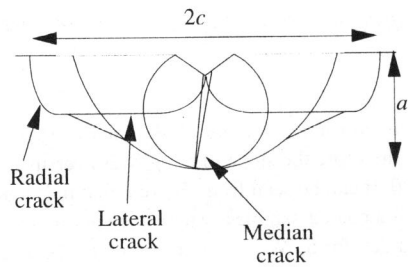


Figure 1 Schematic cross section of a Vickers indentation

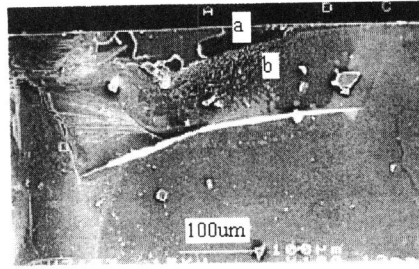


Figure 2 Fracture surface of an E/H coated sample

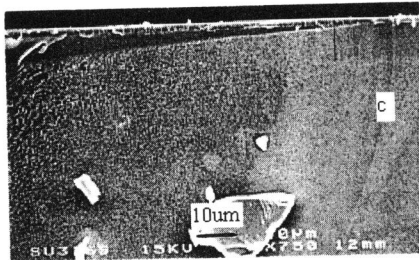


Figure 3 Penetration of coating to the radial crack tip

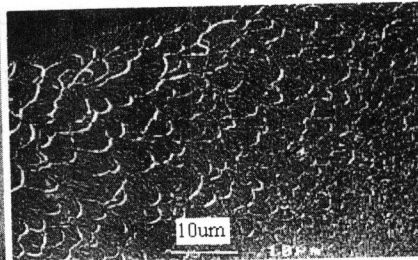


Figure 4 Region of cohesive failure (E/H coated sample)

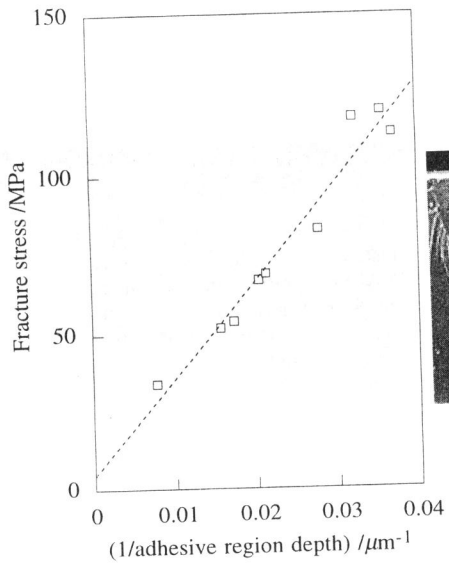


Figure 5 Fracture stress versus 1/ (adhesive region depth)

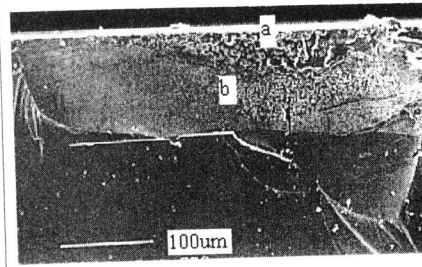


Figure 6 Fracture surface of an  $S_p/W_{RT}/E/H$  coated sample

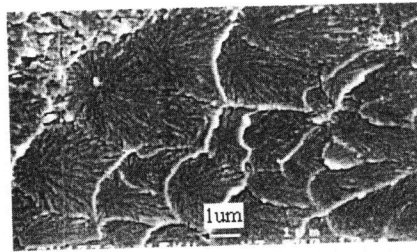


Figure 7 Cohesive failure region for an  $S_p/W_{RT}/E/H$  coated sample.

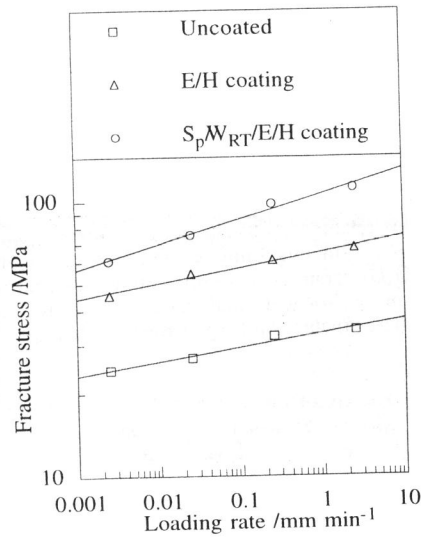


Figure 8 Failure stress as a function of loading rate