



## Glass Strengthening Using Ormosil Polymeric Coatings

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**Abstract.** Ormosil polymeric coatings comprised of an epoxy resin, an amine hardener and a silane have been applied to glass samples containing large, controlled defects introduced by Vicker's indentation. The coatings can completely overcome these controlled defects. The strengthening effect is due to penetration of the defects by the coatings. Therefore, the reactions between the components of these hybrid materials and the glass substrate are of crucial importance in determining both the degree of strengthening that is achieved and the hydrolytic durability of the coatings. The maximum strengthening effect of these ormosil polymeric coatings is obtained when 25% of the active hydrogen is supplied by the silane (7.2 wt% silane). More than 7.2 wt% silane reduces coating cohesion and thus gives a reduced strengthening effect. Studies on silane primed systems show that both good coating adhesion and cohesion are required for significant strengthening. Coatings with good adhesion also have greater hydrolytic durability.

**Keywords:** coatings, strengthening, glass, hybrids

### Introduction

The ubiquitous presence of surface flaws limits the strength of glass articles. No method exists for completely overcoming these flaws. However, coatings can, to some extent, counteract flaws in glass surfaces and thereby increase the strength of glass artifacts [1–3]. We have developed a series of hybrid ormosil polymeric coatings which may be used to strengthen glass [4, 5]. The coatings are synthesized from epoxy resin, amine hardener and silane mixtures (E/H/S coatings). We have previously shown that these coatings strengthen glass by penetrating pre-existing defects [6]; this paper discusses the effects that coating parameters have on the degree of strengthening achieved.

### Experimental

The hybrid ormosil polymeric coatings are comprised of mixtures of MY753, a plasticized bisphenol A epoxy resin, HY951 amine hardener (triethylenetetramine—TETA) and aminoethylaminopropyltrimethoxysilane (Z6020). In addition to investigating the ormosil

polymeric (E/H/S) coatings some work has been conducted on MY753/HY951 coatings applied to glass primed with Z6020 silane ( $S_p$ /E/H coatings).

The coatings were applied to commercial soda-lime glass slides with polished edges. Ten kg Vicker's indents were used to produce reproducible strength limiting flaws on the glass slides. Following indentation the samples were aged in air for 24 hours. This process resulted in large semi-elliptical cracks with a surface length,  $2c$ , of  $950 \pm 14 \mu\text{m}$  and a depth,  $a$ , of  $285 \pm 10 \mu\text{m}$ ; failure normally occurred from the controlled damage rather than the edge of the microscope slide (for more details see [6]).

Both the hardener and silane can react chemically with the epoxy group (see below). Therefore, the relative amounts of hardener and the silane will affect the detailed structure of this network and thus the resulting properties of the coating. Five coating compositions were examined; the ratio of total active hydrogen from both the hardener and the silane to epoxy was maintained at stoichiometric for all of the coatings (see Table 1 for details). All of the coatings were prepared by mixing appropriate amounts of epoxy and hardener

Table 1. E/H/S coating compositions.

Composition	Percentage of active hydrogen from Z6020	Wt% of Z6020 (excluding solvent)	Wt% of HY951 (excluding solvent)
a	0	0.00	9.50
b	10	2.98	8.35
c	25	7.23	6.71
d	50	13.60	4.23
e	100	24.60	0.00

for 1.5 hours at  $25 \pm 2^\circ\text{C}$  followed by addition of the silane. The resultant mixture was diluted with acetone. To hydrolyze the silane half the stoichiometric amount of water was then added. The resulting solution was stirred for 4 hours. 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. Bulk samples ( $40 \times 29 \times 2$  mm) were also cast from the above mixtures for dynamic mechanical thermal analysis (DMTA). DMTA measurements were conducted at a strain rate of 1% and a frequency of 1 Hz with a heating of rate of  $5^\circ\text{C min}^{-1}$  on a Polymer Laboratory Mark 2 DMTA. Glass transition temperatures were determined from the variation of glassy modulus with temperature using the intercept method [9].

Some silane primed samples were also prepared. In this case the glass samples were dipped into a 1 wt% Z6020 aqueous solution which had been mixed at room temperature for 0.5 hours. After dipping and before coating the samples were either (i) dried ( $S_p/E/H$  coatings); or (ii) immersed in distilled water at room temperature for 1 hour and then dried ( $S_p/W_{RT}/E/H$  coatings); or (iii) given treatment (ii) followed by immersion in distilled water at  $60^\circ\text{C}$  for 1 hour and drying ( $S_p/W_{60}/E/H$  coatings). In all cases drying was carried out at  $120^\circ\text{C}$  for 0.5 hours.

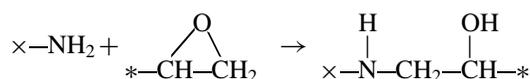
The failure stresses of coated and uncoated control samples were measured in 4 point bending using a Mayes SM200 universal testing machine. To assess the hydrolytic durability of the coatings coated samples were tested after an accelerated ageing treatment of 96% r.h. at  $50^\circ\text{C}$  for 7 days.

## Results and Discussion

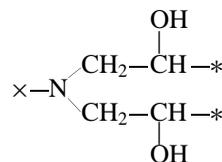
Figure 1 shows the variation of strength of the E/H/S coated samples with the concentration of the silane.

Independent of the amount of silane, all coatings lead to significant increases in strength of coated samples compared to uncoated samples. Maximum strength was observed at 7.23 wt% silane (composition c) which is equivalent to 25% of the active hydrogen being supplied by the silane. As the amount of silane is further increased the strength sharply decreases. This reflects changes in the network structure at higher silane concentrations that also lead to reductions of both the glassy modulus and the glass transition temperature of the coatings, as obtained from DMTA (see Fig. 2).

Both an epoxy network and a siloxane network are formed during the curing process. The amine hardener has active hydrogen atoms which react with epoxy groups to form secondary amines:



These in turn react with an epoxy group to form a tertiary amine [7]:



The rate of this latter reaction is slower than that of the primary amines. As well as the two primary amines there are, of course, two secondary amine hydrogens initially present on TETA and these again react more slowly than the primary amines. The silane Z6020 has initially one primary and one secondary amine group which also react with the epoxy groups. In addition, the silane forms a siloxane network through hydrolysis

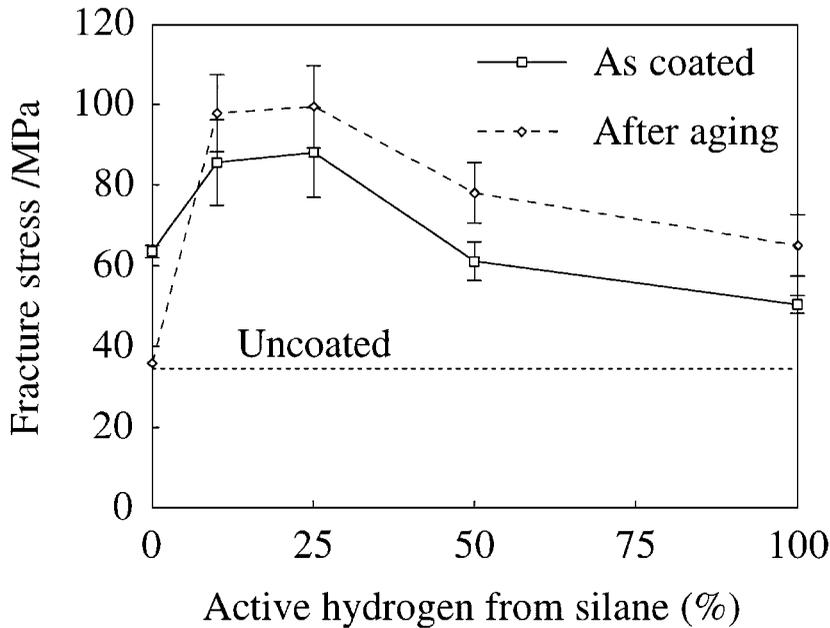


Figure 1. Fracture stress of E/H/S coated samples as a function of active hydrogen supplied by silane before and after ageing at 50°C/96% r.h. for 7 days.

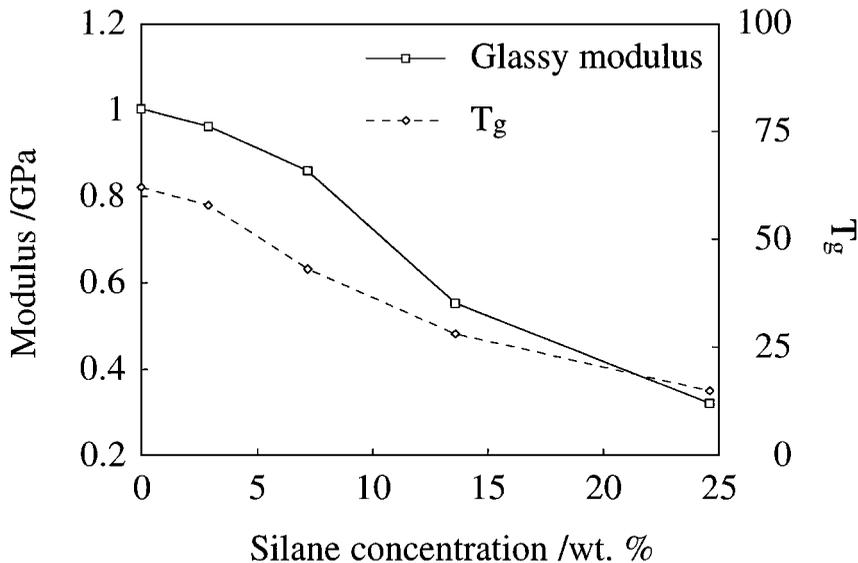


Figure 2. Glassy modulus and  $T_g$  as a function of silane concentration in E/H/S coatings.

of the methoxy groups on the silane followed by condensation of the silanol groups to form siloxane bonds. Thus, a covalently bonded interpenetrating network is formed because the silane participates in the formation of both the epoxy and siloxane networks [8]. The relative rates of formation of the epoxy and siloxane networks are significantly different with formation of

the epoxy network being essentially complete after the standard curing treatment, although further changes can occur after a prolonged cure [6], whereas the siloxane network forms more slowly.

In fact the siloxane network continues to form with ageing and this can be seen in Fig. 1 where the effect of the accelerated ageing treatment on the strength of

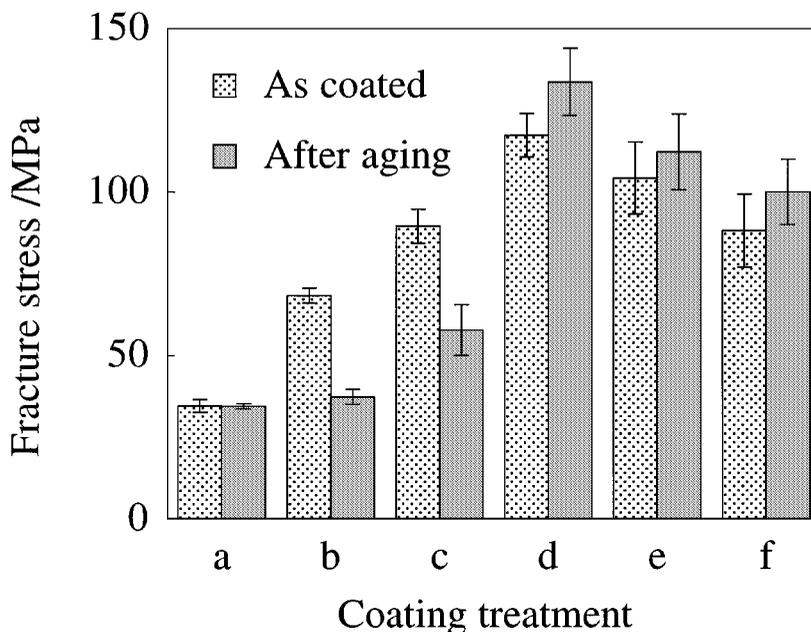


Figure 3. Fracture stress of various silane primed coatings systems before and after ageing at 50°C/96% r.h. for 7 days. (a) Uncoated, (b) E/H coating, (c)  $S_p$ /E/H coating, (d)  $W_{RT}$ /E/H coating, (e)  $W_{60}$ /E/H coating, and (f) E/H/S coating with 7.23 wt% silane.

E/H/S coated samples is also shown. The measured strengths increased following the accelerated ageing treatment except when the silane content was zero. The siloxane network is modified by the ageing treatment because only half of the stoichiometric ratio of water was used and therefore the hydrolysis of the methoxy groups may not be completed. Hence, during ageing under humid conditions hydrolysis of the remaining methoxy groups can take place. This hydrolysis may then be followed by condensation of the resulting silanol groups. The condensation reaction can, in theory, occur either between adjacent silane molecules in the coating or between the silane and the glass surface. The latter reaction is apparently limited because some debonding of the coating is seen during the ageing treatment. The former reaction increases the number of linkages within the siloxane network thereby leading to a tighter siloxane network structure. Studies of the locus of failure of these samples show larger regions of cohesive failure compared to the locus of failure seen on unaged samples [10], and thus it is thought that the tighter siloxane network produces a coating with improved cohesion.

The importance of both coating cohesion and coating adhesion in determining the overall strengthening is

further demonstrated by the behavior of silane primed systems. Figure 3 shows the degree of strengthening achieved with silane primed systems. The maximum degree of strengthening was obtained with the  $S_p$ / $W_{RT}$ /E/H coatings. Currently accepted models for a silane on glass state that there is a physisorbed silane layer overlaying a chemisorbed silane layer which in turn overlays a silane monolayer bonded to the glass surface [11, 12]. According to these models the room temperature water treatment ( $S_p$ / $W_{RT}$ /E/H) removes the physisorbed layer of silane primer whereas the treatment at 60°C ( $S_p$ / $W_{60}$ /E/H) also removes the chemisorbed layer. The chemisorbed layer is necessary to achieve good adhesion of the coating to the substrate and therefore to avoid adhesive failure during loading. However, the physisorbed layer has low cohesion, and if this layer has not been removed ( $S_p$ /E/H coatings) the coatings tend to fail cohesively at lower applied stresses.

We have previously demonstrated that good coating adhesion is required to achieve a strength increase with simple E/H coatings [5]. The current studies indicate that coating cohesion is also important. Silane is required to improve the adhesion of the coating to the glass and can be included either as part of a hybrid

coating or as a primer; both E/H/S and S<sub>p</sub>/E/H give significantly greater increases in strength than simple E/H coatings (see Figs. 1 and 3). Although the primer route gives greater increases in strength, the hybrid approach will have greater commercial application as it involves less processing. Both the E/H/S and S<sub>p</sub>/E/H coatings studied strengthen glass. However, if *excess* silane is present then the coating cohesion is relatively low and this reduces the strengthening effects that may be achieved with these coatings.

## Conclusions

Studies on silane primed coatings (S<sub>p</sub>/E/H) show that greater coating adhesion gives greater increases in strength. The maximum strengthening effect with the ormosil polymeric hybrid (E/H/S) coatings is obtained when 25% of the active hydrogen is supplied by the silane. Although more active hydrogen from the silane might lead to improved adhesion of the coating to the substrate it also creates a looser network which has a lower cohesive strength that more than offsets any improvements in adhesion. Therefore, the degree of strengthening obtainable from the hybrid ormosil polymeric coatings is dependent on both the cohesive strength of the coating and the adhesion of the coating to the glass.

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