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Strength of Epoxy/Glass Interfaces after Hygrothermal Aging

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The stability of epoxy/glass interfaces subjected to hygrothermal aging was assessed using a fracture-mechanics approach. An epoxy system consisting of diglycidyl ether of bisphenol F cured with 2-ethyl-4-methyl-imidazole was bonded to borosilicate glass adherends that were treated with various types of adhesion promoters to provide a variety of interfaces. Adhesive strength was measured under dry, as-processed conditions and as a function of exposure time to an 85°C/85% relative humidity (RH) environment. As expected, the strain-energy-release rate, G_c , dropped significantly with aging time for the bare epoxy/glass interface. The drop in G_c is assumed to be due to a loss of interfacial forces. The use of two silane-based adhesion promoters, 3-aminopropyltriethoxysilane (APS) and 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane (ECH) resulted in improved adhesive strength both before and after hygrothermal aging. The improvement in adhesive strength can be explained by the introduction of chemical bonds at the interface. The drop in G_c is assumed to be due to a loss of interfacial forces and hydrolysis of siloxane bonds. In addition to the use of organosilane-based adhesion promoters, a series of polyhydroxyaminoethers (PHAE) thermoplastic adhesive resins was also investigated as potential adhesion promoters. It was found that 2% PHAE in Dowanol[®] PM, a hydroxyl-group-containing solvent, was the best system for the PHAE-based adhesion promoters. Interestingly, both the acetic acid concentration in the solvent and maleic anhydride content in the PHAE resin were shown to affect the adhesive strength.

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INTRODUCTION

Epoxy resin-based composites and adhesives are often used for structural applications where their long-term properties are of primary importance [1–3]; however, it is well known that epoxy resins absorb moisture in humid environments and that the absorbed water can have detrimental effects on their properties [4–6]. Adhesive strength between an epoxy and a substrate surface is one of the critical properties affected by hygrothermal aging. Many researchers have investigated the mechanical properties of glass fiber- or glass bead-reinforced epoxy composites. Interfacial failure or debonding has often been observed at epoxy/glass interfaces when they are exposed to hot and humid environments. Understanding of the mechanism of hygrothermal aging can facilitate the design of reliable composite structures as well as adhesive joints.

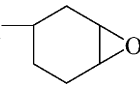
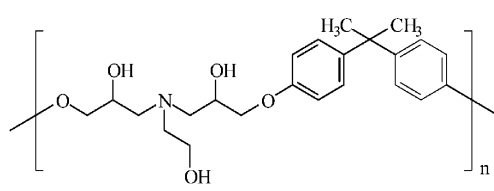

Adhesion of polymers to inorganic oxides, such as glass, has been reported to be dependent on acid-base interactions between the acidic or basic surface sites of the glass and the basic or acidic functional sites of the polymer [7]. These interactions are quite strong under dry conditions but the adhesive strength drops dramatically when such interfaces are exposed to severe conditions involving high temperature and high humidity. It is a common belief that hot/wet adhesion is improved by forming chemical bonds between the adherend and adhesive. Therefore, adhesion promoters with dual functionality are widely used to form chemical bonds between polymers and inorganic substrates. The use of such adhesion promoters can produce durable interfaces, even under severe humidity and thermal conditions.

Commercial adhesion promoters can be divided into two types, monomeric and polymeric, based upon the way these promoters are applied. Many publications have reported adhesion improvement when using various monomeric adhesion promoters, such as silanes and titanates. A major application for such silanes is as finishes on glass-fiber cloth for production of epoxy-laminate circuit boards and as additives or primers for structural epoxy adhesive bonding on glass. However, Bell *et al.* [8] have studied the durability of the polymer/metal interface region where a polymeric adhesion promoter was employed to enhance bonding. The use of polymeric adhesion promoters has some advantages. First, in practice it is difficult to

obtain a uniform monomolecular layer of monomeric adhesion promoters, thus, an imperfect cross-linked network is often formed. Unlike monomeric adhesion promoters, polymeric adhesion promoters have a propensity for forming uniform monomolecular layers. Another advantage of polymeric adhesion promoters is that they have the ability to absorb a portion of the mechanical and thermal stresses generated in the interphase region, which arise because of the mismatch between the moduli and thermal-expansion coefficients of the substrate and the polymer. A third advantage of polymeric adhesion promoters is that the ratio of hydrophobic to hydrophilic components can be controlled more easily; the composition is not fixed, but can be adjusted to suit particular needs. Moreover, incorporating hydrophobic and hydrophilic components onto a polymer chain can minimize their tendency to cluster.

PHAEs have the potential to be effective polymeric adhesion promoters [9]. Their chemical structures are shown in Table 1 [10]. These amorphous thermoplastic resins offers a unique property set, including excellent adhesion to a variety of substrates such as glass, possess superior gas-barrier properties, and are clear, mechanically strong, and tough [10]. The presence of three polar pendant hydroxyl groups in its structure makes it an attractive candidate to be used as a polymeric adhesion promoter. A probable consequence of the presence of pendant hydroxy functional groups on these macromolecules is their

TABLE 1 Chemical Structures of Adhesion Promoters and Dowanol[®] PM

Chemical name	Chemical structure
3-minopropyltriethoxysilane (APS)	$(\text{CH}_3\text{CH}_2\text{O})_3\text{SiCH}_2\text{CH}_2\text{NH}_2$
2-(3,4-Epoxy cyclohexyl) ethyltrimethoxy silane (ECH)	$(\text{CH}_3\text{O})_3\text{SiCH}_2\text{CH}_2$ 
Polyhydroxyaminoethers (PHAE)	
Dowanol [®] PM	$\text{CH}_3\text{OCH}_2\text{CHOH}$ 

ability to undergo polar interactions with the surfaces of a variety of materials. Specifically, such pendant groups offer the possibility of developing PHAE molecules for new applications such as polymeric adhesion promoters that enhance the adhesion at epoxy/glass interfaces.

In our previous work [11], monomeric adhesion promoters were shown to improve the wet adhesive strength of epoxy/glass interfaces when used either as a surface treatment or as an additive. Using adhesion promoters as a surface treatment was generally superior to the additive approach. Our current study is focused on evaluating glass/epoxy adhesion loss under hygrothermal aging. Adhesive strength is determined by using a fracture-mechanics approach and is given in terms of strain-energy-release rate (G_c). The effect of moisture-exposure time on the drop of G_c is highlighted. Also, it is of interest to investigate the kinetics of moisture uptake under this hygrothermal aging condition and relate these kinetics to interfacial strength. In addition to silane-based adhesion promoters, improvement in adhesive strength using PHAE-based adhesion promoters was also studied. In this case, percent failure as well as G_c values are reported.

EXPERIMENTAL

Materials

The model epoxy system used in this study consisted of a diglycidyl ether of bisphenol F (Bis F) resin (EPON[®] Resin 862, Shell Chemical, Houston, TX, USA) cured with 2-ethyl-4-methylimidazole (2,4-EMI) from Air Products (IMICURE[®] EMI-24, Air products, Trexlertown, PA, USA). The concentration of 2,4-EMI in the mixture is 4 parts per hundred of resin (phr). Several adhesion promoters were used: 3-aminopropyltriethoxysilane (APS) from Aldrich Chemical Company, Inc., Milwaukee, WI, USA, 2-(3,4-epoxycyclohexyl) ethyltrimethoxysilane (ECH) from Dow Corning Corporation, Midland, MI, USA and 10 different polyhydroxyaminoethers (PHAEs), from the Dow Chemical Company, Freeport, TX, USA (BLOX[®] 200 series). Solutions of PHAE were used as received. The PHAE solutions are listed in Table 2. Acetic acid (Ac.) and maleic anhydride (MAH) were used as modifiers in PHAE solutions. Dowanol[®] PM, 1-methoxy-2-propanol, from the Dow Chemical Company was used as one of the solvents for PHAE. Chemical structures of adhesion promoters and Dowanol[®] PM are shown in Table 1. A borosilicate glass (BOROFLOAT) from Erie Scientific Company (Portsmouth, NH, USA) was used in this study

TABLE 2 PHAE Solutions Used in Evaluation of Polymeric Adhesion Promoters

Adhesion promoter	Solvent
2% PHAE	5% acetic acid in water
2% PHAE	2% acetic acid in water
2% PHAE	1% acetic acid in water
2% PHAE	98% Dowanol [®] PM
2% PHAE/1% MAH	2% acetic acid in water
2% PHAE/1% MAH	5% acetic acid in water
2% PHAE/2% MAH	2% acetic acid in water
2% PHAE/2% MAH	5% acetic acid in water
2% PHAE/2% MA	2% malic acid in water
1.8% PHAE + 0.2% APS	2% malic acid in water

as a substrate for epoxy. The glass was received in the form of $12.7 \times 76.2 \times 3.2$ -mm slabs.

Double Cantilever Beam (DCB) Specimen Preparation

DCB test specimens consisted of sandwiches of APS-coated glass/epoxy/(glass coated with the experimental adhesion promoter). The two silane adhesion promoters, APS and ECH, were first diluted to a final concentration of 1% by weight in 95% methanol/5% water. Secondly, the surface of the glass substrate was cleaned with isopropanol and treated in an ultraviolet/ozone chamber for 20 min. Next, the glass substrates were dipped for 2–3 min in an appropriate adhesion promoter solution, and then air dried for 10 min. The final step involves baking the glass substrate at 110°C for 8 min. For polymeric adhesion promoters, glass substrates were dipped in the proper PHAE solutions for 2–3 min, air dried for 10 min, and then baked in an air-circulated oven at 110°C for 8 min followed by a ramp to 160°C for 5 min. The mixture of Bis F epoxy resin and 2,4-EMI was placed on the bottom plate that contains 250 μ m shims (see Figure 1). To create a weaker interface for crack initiation, an 11 mm \times 17 mm area on the bottom glass plate was sputter coated with Au/Pd. The APS-coated glass plate was placed on top, and the specimens were then cured at 60°C for 4 h and then at 150°C for 2 h. The specimen was then cooled to room temperature. Excess epoxy was removed from the edges by a grinding method. The specimen edges were polished using a 6 μ m diamond paste. Aluminum stubs were glued to the Au/Pd side of the top and bottom plate with a room temperature cured adhesive (Loctite

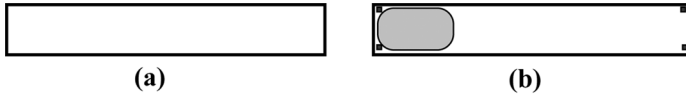


FIGURE 1 The top and bottom glass plates of DCB specimen: (a) top glass plate (APS-treated glass) and (b) bottom glass plate (experimental adhesion promoter-treated glass).

Superbonder 409, Loctite, Rocky Hill, CT, USA). The final DCB specimen is shown in Figure 2.

DCB Testing

DCB testing was performed using a computer-controlled screw-driven Instron testing machine (Canton, MA, USA) in displacement control at a speed of 0.127 mm/min. Tensile force was applied at the end of a specimen in a direction normal to the crack surface, which is often referred to as the cleavage mode. G_c values, which are in units of J/m^2 , can be calculated from Equation (1) according to Blackman et al. [12]:

$$G_c = \frac{12P^2a^2}{w^2h^3E} \tag{1}$$

where P is the applied load, a is the crack length, w is the specimen width (12.7 mm), h is beam height (3.2 mm), and E is the plane-strain modulus of glass (62 GPa).

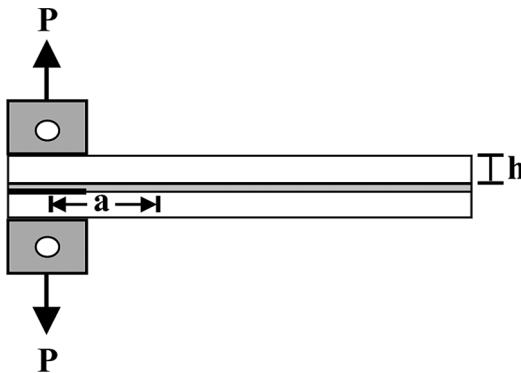


FIGURE 2 Double cantilever beam (DCB) specimen.

Moisture-Uptake Measurements

Both free-standing epoxy films (cast in a silicone rubber mold) and DCB specimens (with untreated and treated glass surfaces) were prepared and then aged in a temperature controlled humidity chamber (Ecosphere Series by Despatch Industries, Minneapolis, MN, USA) at 85°C and 85% RH. The specimens were weighed at specific aging times. Water content, M_t , can be calculated by using Equation (2) [13]:

$$M_t = \frac{w_t - w_d}{w_d} \times 100 \quad (2)$$

where w_t is the weight of the sample at a certain moment in time and w_d is the weight of the dry sample. From plots of water uptake *versus* the square root of aging time, apparent water-diffusion coefficients can be calculated by using Equation (3) [14]:

$$D = \pi \left(\frac{sb}{4M_\infty} \right)^2 \quad (3)$$

where s is the slope of the diffusion curve, b is the thickness of the specimens, and M_∞ is the moisture content at saturation.

Moisture Exposure

For the effect of aging time on adhesive strength, only surface treatments with monomeric adhesion promoters (APS and ECH) were studied. The samples of untreated, APS-, and ECH-treated glass surfaces were tested after hygrothermal aging at a condition of 85°C/85% RH in a controlled humidity chamber (Ecosphere Series by Despatch Industries) for 4, 7, 11, and 14 days. The DCB specimens were precracked before the test. A started crack was created on the Au/Pd-coated end of the bottom plate by using a jeweler's saw. The length of the precrack typically ranged from 18 to 20 mm. G_c is reported as a function of aging time. Results are the average of eight loading and unloading excursions. Four specimens for each promoter were used.

For evaluation of the PHAE-based adhesion promoters, DCB specimens were also aged in a temperature-controlled humidity chamber (Ecosphere Series by Despatch Industries) at 85°C and 85% RH. DCB tests were conducted on the aged samples. If a specimen did not fail when the loading force reached 250 N, the test was stopped and the specimen was returned to the aging chamber. The specimens were tested after 4, 7, 11, 14, 21, 28, . . . , 49 days of aging. In the cases where the precrack did advance, the G_c was measured. The results are

analyzed in terms of days until G_c can be measured as well as G_c at the time the interfacial crack is propagated. Results are the averages of four specimens for each type of interface.

RESULTS AND DISCUSSION

Effect of Aging Time on G_c

It is interesting to compare the adhesive strengths of the treated samples with the untreated sample as a function of aging time. Figure 3 shows G_c values of untreated, APS-, and ECH-treated samples plotted against aging time. As seen in this figure, the G_c of unaged samples (room condition of about 25°C/50% RH) were 18.1, 45.0, and 21.4 J/m² for untreated, APS-treated, and ECH-treated surfaces, respectively. The G_c values reveal that both APS- and ECH-treated glass surfaces showed significant improvement in adhesive strength compared with the bare glass surfaces. Similar results have been reported by others [15, 16].

The G_c drop after 85°C/85% RH exposure can be explained by loss of interfacial forces. It is believed that physical interactions such as hydrogen bonding occur between the functional groups in the epoxy resin and active sites on the glass surface. Moreover, such interactions can be easily disrupted by the diffusing water molecules. Therefore, in the case of the untreated DCB specimens, which have only the physical interaction at the interfaces, the G_c dropped rapidly in short

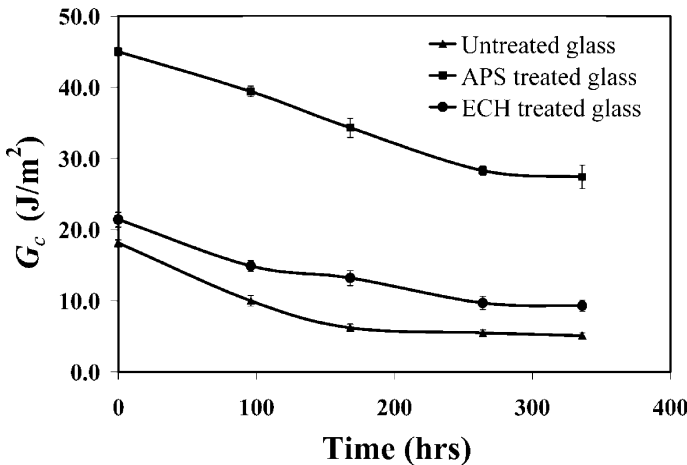


FIGURE 3 G_c drop of untreated, APS-, and ECH-treated DCB specimens under 85°C/85% RH aging condition.

exposure times but reached a plateau region at about 168 h. Wet adhesive-strength improvement can be seen in the APS- and ECH-treated specimens after hygrothermal aging. The improvement in both initial and wet adhesive strength can be explained in terms of chemical bonding introduced at the interfaces. Our work on locus of failure characterization by X-ray photoelectron spectroscopy revealed that the failure occurred in the epoxy/silane interphase region, which indicated the presence of significant interpenetration between the silane and epoxy. As a result, higher areal bond density in the silane/epoxy epoxy interphase region leads to greater adhesive strength compared with the untreated interface.

Silane-based adhesion promoters are known to form Si–O–Si bonds to the glass substrate and to exist as multilayer films on the glass [17, 18]. It is reasonable to assume that organofunctional groups at the other end of silane molecules would form covalent bonds to epoxy resin [19]. An APS molecule has an amino functional group forming the bond with epoxy resin whereas an ECH molecule has a epoxy functional group instead. The amino groups of APS can react with the epoxide ring of the Bis F part in the epoxy resin. However, the epoxide ring of ECH can react with the 2,4-EMI curing agent in the resin. Note that 2,4-EMI has two amino groups that can react with the epoxide group of ECH: the tertiary amino group of 2,4-EMI is more reactive to the epoxide group of ECH compared with the secondary amino group in the same molecule because the electron pair of the secondary amino group is a part of the aromatic ring and, therefore, does not accept a proton readily [20]. The other electron pair of the tertiary amino group is much more available to an attacking proton, and, as a result, the tertiary amino group is likely with the react to epoxide group of ECH. The chemical reaction scheme for both APS and ECH adhesion promoters with epoxy resin is shown in Figure 4. The G_c values of APS-treated specimens were higher than those of ECH-treated specimens, because the number of epoxy-amine bonds formed on APS-treated surfaces is greater than the number of bonds formed on the ECH-treated surface (only 4 phr. of 2,4-EMI in the Bis F/EMI mixture), and primary amine (from APS) reacts readily with epoxy functional groups compared with secondary and tertiary amine (from 2,4-EMI) [1]. Note that our results agree with those reported by Walker [21], who studied the effect of different silanes on the bond strength of two epoxy adhesives (amine and polyamide-cured epoxy) to glass. Walker found that ECH was totally ineffective as an adhesion promoter on glass for his epoxy system, whereas APS was effective and its use resulted in a marked improvement in the bond strength of both adhesives.

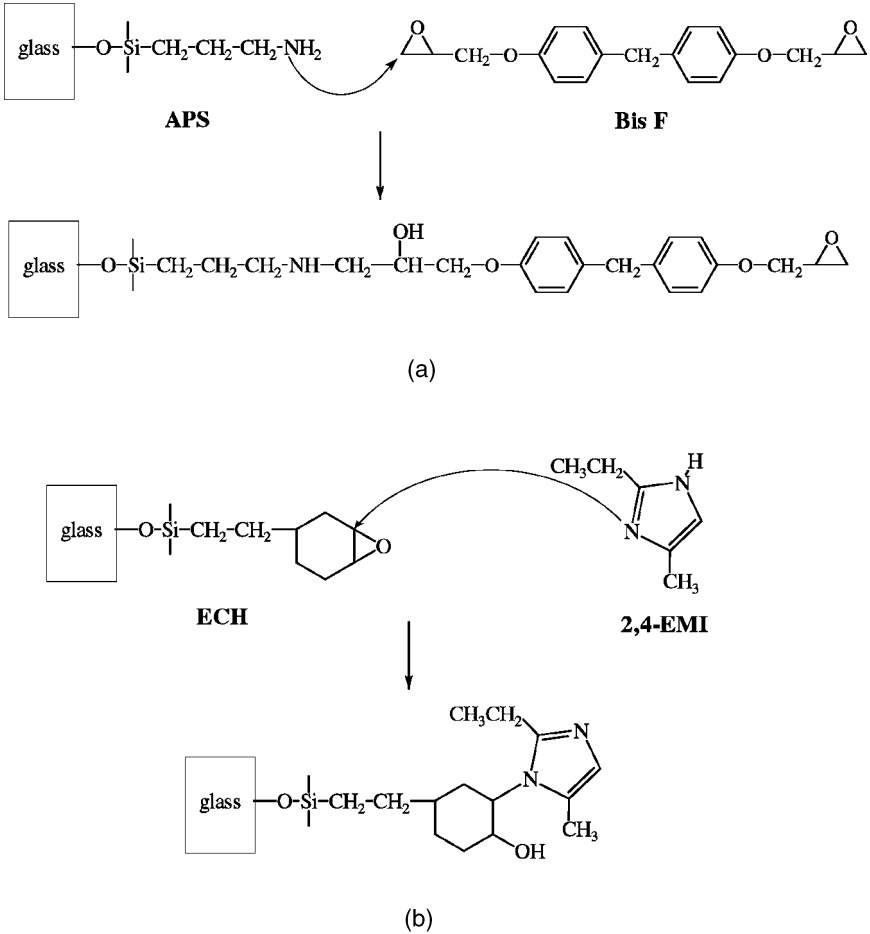
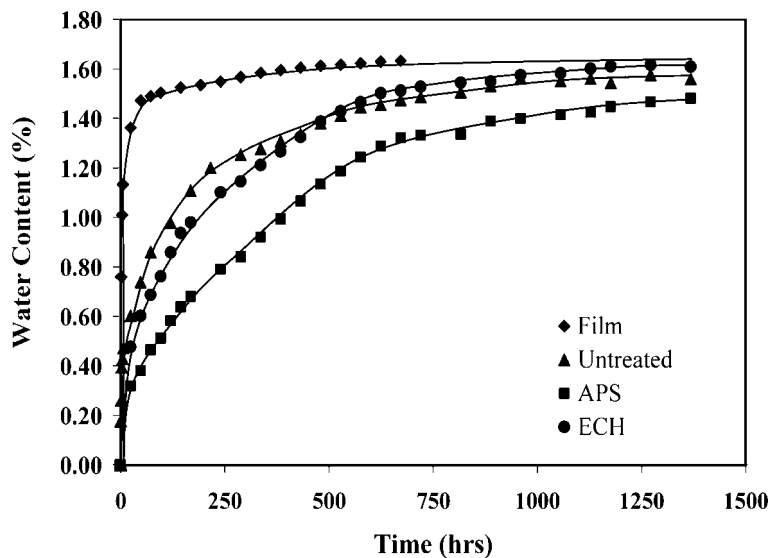


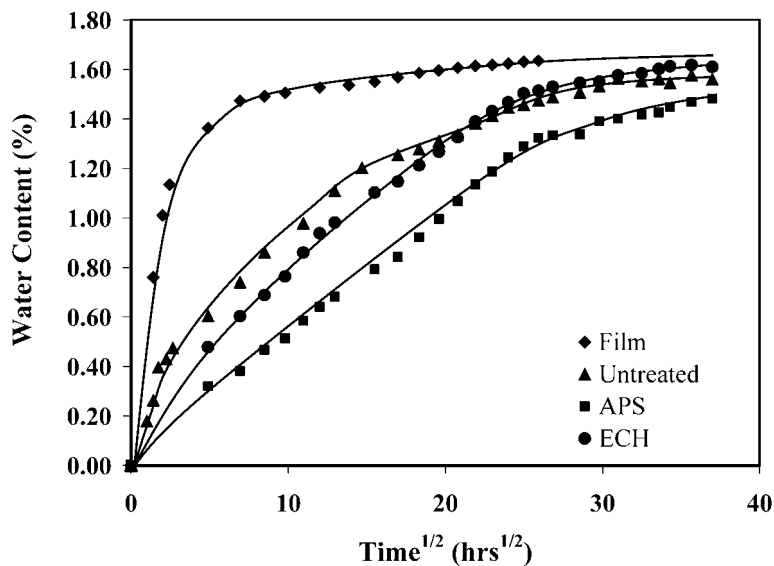
FIGURE 4 Chemical reaction scheme of (a) APS with Bis F and (b) ECH with 2,4-EMI.

Moisture Uptake

Percent water content as a function of exposure time of epoxy film, DCB specimens of untreated, APS-, and ECH-treated glass surface is shown in Figure 5a. At short times, water content in all samples increases rapidly and then slows down. The epoxy films were considered to be saturated with moisture at 1368 h of moisture exposure because the weight-gain data exhibit a well-defined plateau at a water content of 1.63 wt%. Free films absorbed water faster because of their



(a)



(b)

FIGURE 5 Water content (%) as a function of (a) aging time, (b) the square root of aging time of epoxy films (untreated, APS-, and ECH- treated DCB specimens) under 85°C/85% RH aging condition.

large surface area (two free surfaces). Interestingly, the application of adhesion promoters to glass surfaces retarded the water-absorption kinetics in the DCB specimens.

Percent water content as a function of the square root of aging time is shown in Figure 5b. At the early stages of moisture exposure, the absorption curves are linear with the square root of time. This linearity suggests that absorption is predominately diffusion controlled in this region [14]. By applying the one-dimensional case of Fick's second law, the diffusion coefficients can be calculated from the initial slope of the diffusion curve [14]. Epoxy films have a diffusion coefficient of $1.79 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, which is comparable with the diffusion coefficient reported in the literature, $1.40 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ [22]. For DCB specimens, the diffusion coefficients of untreated, ECH-, and APS-samples are 64.41, 16.52, and 8.32 ($10^{-8} \text{ cm}^2 \text{ s}^{-1}$), respectively. That means that using an organosilane as a surface treatment for the DCB specimen led to a significant drop of diffusion coefficient.

It is generally accepted that the penetrant diffuses rapidly into the polymer, which is accompanied by reversible elastic swelling of the matrix. The stress developed is then slowly relieved by a molecular-relaxation process such that the chemical potential of the sorbed water is decreased, leading to further sorption [23]. Zanni-Deffarges and Shanahan [22] have investigated the diffusion of water at inorganic substrate/polymer interfaces. In Figure 6, water is entering the system by seepage close to the interface or in the interphase region by a phenomenon called "capillary diffusion." Moreover, it is relevant to note that the surface treatment is an important factor in controlling interfacial diffusion. Clearly, the stronger interface would have a lower rate of moisture absorption. From this reason, APS-treated specimens had the lowest water content because they had the strongest interfaces, allowing a lesser amount of water to seep through at the

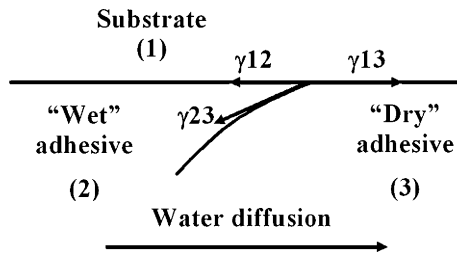


FIGURE 6 Model of diffusion front near the substrate/polymer transition. Terms γ_{12} , γ_{23} , and γ_{13} represent interfacial "tension" between the substrate, "wet" and "dry" adhesive.

interface or in the interface region by capillary diffusion. This result is well supported by the work of Wu *et al.* [24]. In their work, neutron reflectivity was applied to measure the concentration of water at the buried interface between a polymer and a silicon wafer that was kept under high-humidity conditions. Wu discovered that excess water existed within 3 nm of the interface, where the water concentration reached 17 vol% for the samples without an adhesion promoter and 12 vol% for the ones with an organosilane adhesion promoter.

It is interesting to relate the G_c drop with moisture-uptake behavior of the DCB specimens. Figure 7 shows the relation between the G_c drop and water content of untreated, APS-treated, and ECH-treated DCB specimens after 85°C/85% RH aging. The results show a correlation between moisture uptake and the drop in G_c . Obviously, the water in the DCB specimens weakens the interfaces, leading to a G_c drop. The amount of G_c drop correlates well with the initial amount and rate of moisture absorbed. Initially, the water uptake increased rapidly, leading to dramatic drops in G_c , which can be explained in terms of the loss of physical interactions. In the case of untreated samples, there is no chemical bonding at the interface between epoxy and glass; therefore, the G_c was very low initially and dropped to a plateau at about 5.1 J/m² after 336 h of aging. APS- and ECH-treated glass exhibited G_c drops as well but higher plateaus in G_c were maintained: 27.4 and 9.3 J/m², respectively. Table 3 reveals that the adhesive

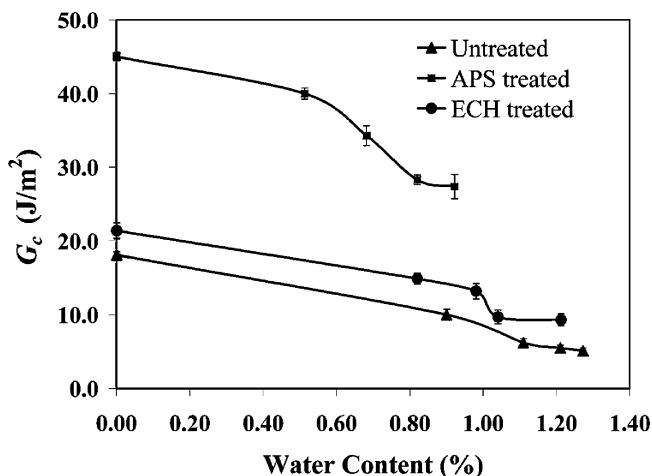


FIGURE 7 Relation between G_c and water content of untreated, APS-, and ECH-treated DCB specimens under 85°C/85% RH aging condition.

TABLE 3 Percent Adhesive Strength Loss after 14 Days under Hygrothermal Condition

Sample	G_c (J/m ²)		Percent adhesive strength loss
	Dry	14 days after aging	
Untreated	18.1	5.1	71.8
APS treated	45.0	27.4	39.1
ECH treated	21.4	9.3	56.5

strength of untreated DCB specimens falls rapidly, losing 71.8% of the original adhesive strength after 14 days of hygrothermal aging, whereas the APS- and ECH-treated specimens lost 39.1 and 56.5%, respectively. The improvement can be explained in terms of the chemical bonding introduced by the adhesion promoters.

Evaluation of Polymeric Adhesion Promoters

In a previous study [11], a protocol for evaluating the drop in adhesive strength was developed because the DCB testing of dry specimens proved difficult. This protocol defined “failure” as when a crack propagated in a DCB specimen with a 19-mm starter crack loaded to 250 N. Four specimens for each interface were used. We used the same protocol for the polymeric adhesion promoters. Percent failure and G_c values of DCB specimens treated with PHAE adhesion promoter compared with those of untreated and APS-treated samples are shown in Figure 8. Untreated samples completely failed within 4 days of aging and exhibited a G_c of 6.8 J/m². APS-treated specimens showed significant improvement in both dry and wet adhesive strength. It took 49 days to get 100% failure of the APS-treated specimens and the G_c was 18.1 J/m². Because the G_c of 42-day aging was 18.9 J/m², which was almost identical with that of 49-day aging, a plateau in G_c appears to be reached. In Table 4, exposure time for 100% failure and average G_c values at 100% failure of untreated, and for all the various PHAE-treated, glass surfaces are reported. The PHAE adhesion promoters in all solvent systems showed improvement in wet adhesive strength compared with the untreated samples. This can be seen in Table 4. Aging time for 100% failure shows that it took longer than 4 days under hygrothermal aging for all of PHAE-treated specimens evaluated. BLOX[®], which is a family of commercial resins based upon PHAE, has been claimed by the Dow Chemical Company to be an amorphous material that exhibits excellent adhesion to a variety of

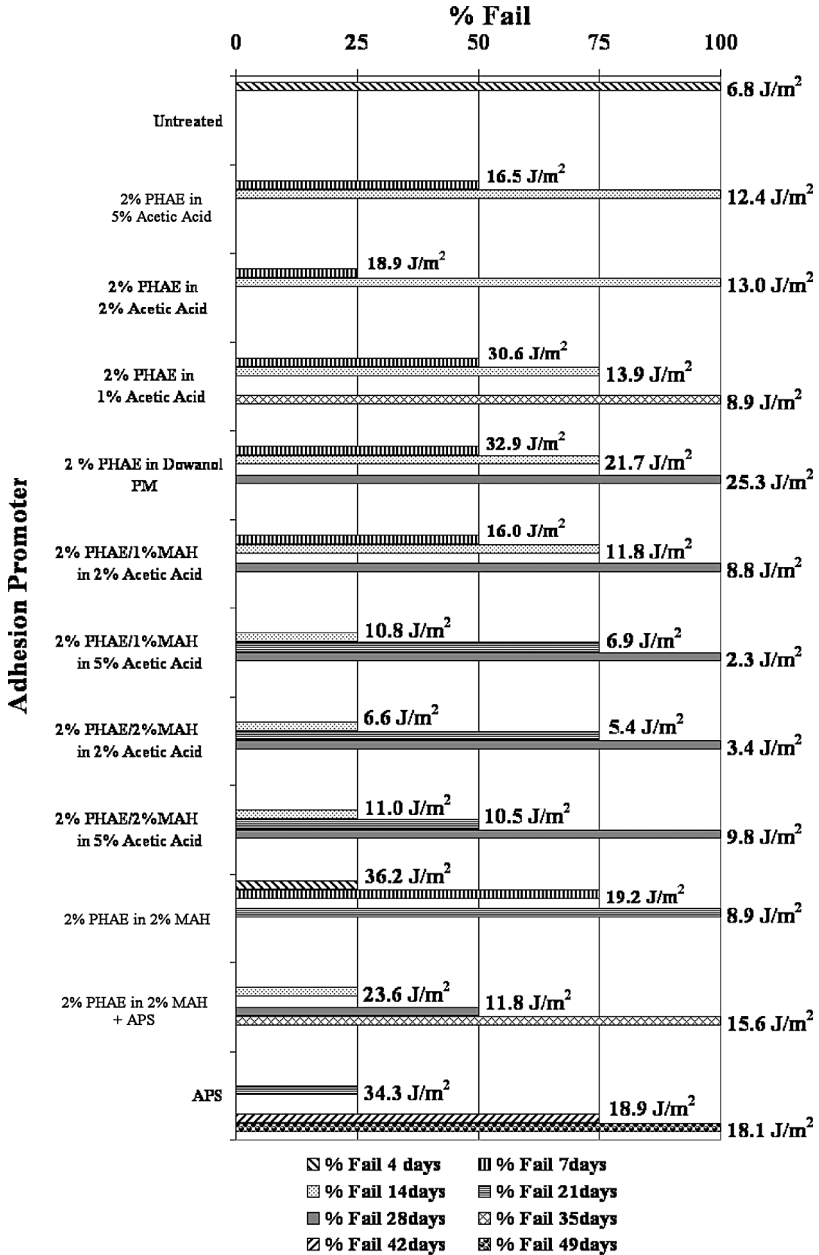
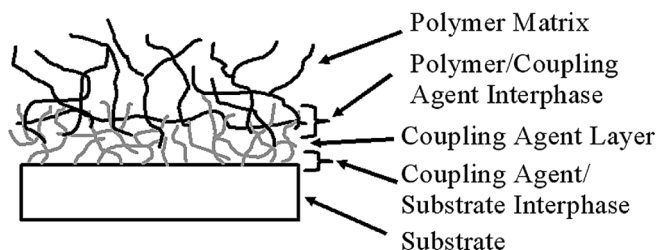


FIGURE 8 Percent failure and G_c values of DCB specimens surface treated with PHAE polymeric adhesion promoter.

TABLE 4 Aging Time Required for 100% Failure and Average G_c Values at 100% Failure of Untreated and PHAE Treated Specimens

Sample	Aging time treated for 100% failure	Average G_c values at 100% failure
Untreated	4	6.8
2% PHAE/5% Ac.	14	12.4
2% PHAE/2% Ac.	14	13.0
2% PHAE/1% Ac.	35	8.9
2% PHAE/98% Dowanol	28	25.3
2% PHAE/1% MAH/2% Ac.	28	8.8
2% PHAE/1% MAH/5% Ac.	28	2.3
2% PHAE/2% MAH/2% Ac.	28	3.4
2% PHAE/2% MAH/5% Ac.	28	9.8
2% PHAE/2% MA	21	8.9
1.8% PHAE + 0.2% APS/2% MA	35	15.6
APS	49	18.1

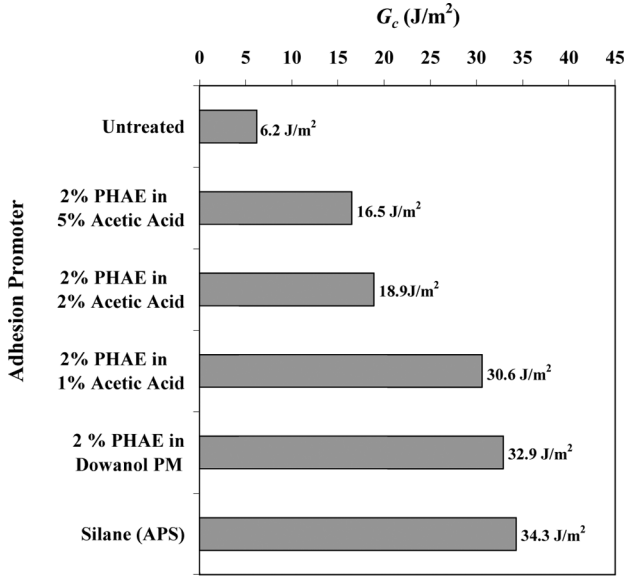
substrates [25]. The excellent adhesion-promoting characteristics of PHAE are, at least in part, a result of the ability of the pendant hydroxyl functional groups to undergo interfacial, polar interactions with material such as glass, metal, and other polar polymers, such as epoxy [10]. The adhesion enhancement of polymer/glass interfaces using a polymeric adhesion promoter is shown in Figure 9 (redrawn from Ref. 8). For polymeric adhesion promoters, the hydrophobic polymer backbone is tailor-made to have specific pendant functional groups. Some of these groups interact with the substrate surface, whereas others interact with the polymer [26]. Polymeric adhesion promoters behave very differently from low-molecular-weight monomeric adhesion promoters. The inherent strength of a polymeric coupling agent and the entanglements of the adhesion promoter with itself

**FIGURE 9** Adhesion enhancement of polymer/glass interfaces using a polymeric adhesion promoter (redrawn from Ref. 8).

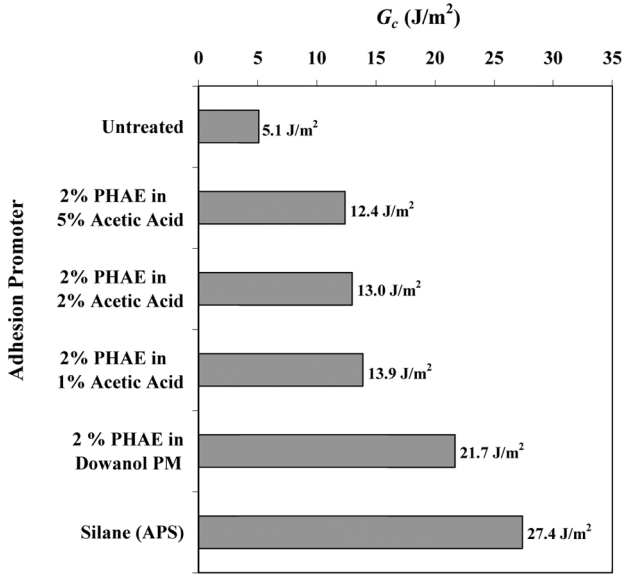
as well as with the polymer layer lead to strength enhancement of polymer/glass interfaces [27]. Although a monomeric adhesion promoter, *i.e.*, silane, can be polymerized during drying, thus giving the possibility of entanglements, the degree of entanglement in silanes is dependent upon drying conditions after applying silane solution on glass surfaces [28]. However, entanglement in polymeric adhesion promoters is less sensitive to drying conditions.

As seen in Figure 8, 2% PHAE in Dowanol[®] PM, a hydroxyl-group-containing solvent, was the best system of PHAE series. Such interfaces can resist cracking for 28 days while exposed to 85°C/85% RH conditions and showed the highest G_c value of 25.3 J/m². It is confirmed that Dowanol[®] PM is the best solvent for PHAE for the use as an adhesion promoter as seen from the highest G_c values shown in both Figure 10a and b. The variation of acetic acid concentration was studied and the results of G_c values after 7 days and 14 days under hygrothermal conditions are shown in Figure 10a and b, respectively. Fowkes *et al.* found that maximizing acid–base interaction at interfaces by modifying acidity or basicity of glass surfaces increases interfacial adhesion [7]. For this reason acetic acid was used as a modifier in the PHAE solution, which might increase the acidity of the glass surface and lead to stronger interaction with a basic Bis F/2,4-EMI epoxy. Note that 1% acetic acid in PHAE aqueous solutions led to the highest wet adhesive strength. It is possible that excess acetic acid molecules can react with hydroxy groups on glass surface by an esterification reaction, so there were fewer active sites on the glass surface that can react with the PHAE adhesion promoter. A higher number of functional groups to react gives higher adhesive strength [8].

The effect of a carboxyl-containing additive, MAH (maleic anhydride), was also studied. Figure 11 shows aging time for 100% failure of 0, 1, and 2% MAH-modified PHAE-treated specimens. For both 2% PHAE/2% acetic acid and 2% PHAE/5% acetic acid, the specimens failed completely after 14 days under the 85°C/85% RH aging condition. By adding 1% or 2% of MAH to the PHAE solution, the specimens can resist cracking up to 28 days under the hygrothermal condition. A comparison of the results of PHAE solutions with and without MAH shows that the specimen treated by MAH-modified PHAE improved adhesive strength at glass/epoxy interfaces better than PHAE itself. It is believed that MAH is the part that has active functional groups that react with functional groups in the epoxy resin. Therefore, the higher MAH content provides more active sites, leading to larger areal bond density at the interphase. As seen in Figure 8, the system of 2% PHAE/2% maleic acid showed some improvement in



(a)



(b)

FIGURE 10 G_c values at after (a) 7 days and (b) 14 days under hydrothermal condition of PHAE-treated specimens.

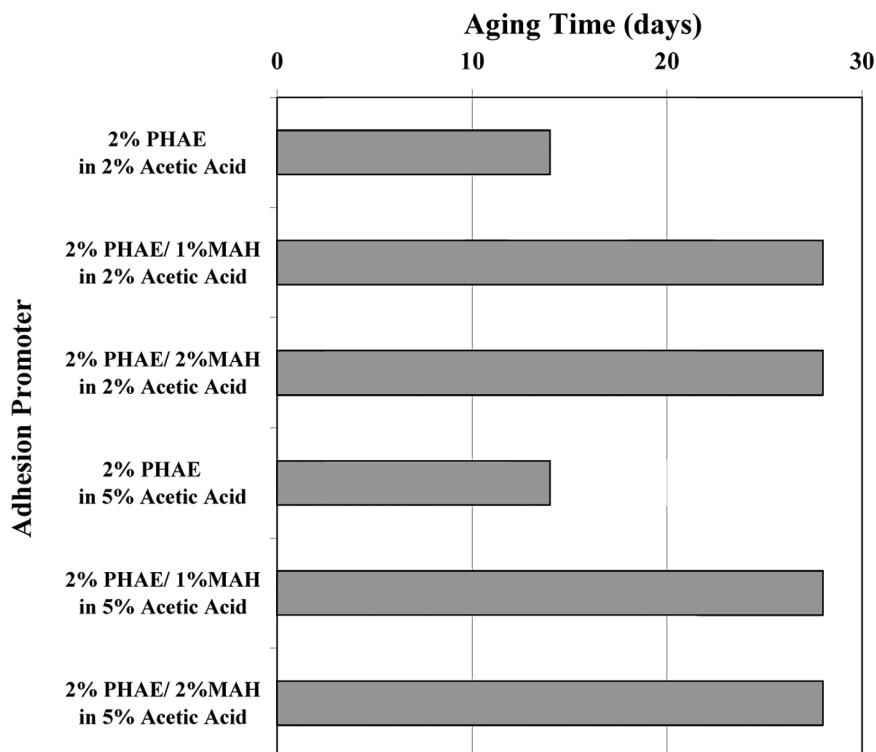


FIGURE 11 Aging time treated for 100% failure of 0, 1, and 2% MAH-modified PHAE-treated specimens.

stability of epoxy/glass interfaces under hygrothermal conditions shown from its higher G_c and better crack resistance under hygrothermal aging compared with untreated samples. Samples treated with a mixture of 2% PHAE/2% maleic acid and APS have higher adhesive strength compared with those treated with 2% PHAE/2% maleic acid alone because of the strong interaction of APS with the glass surface near the interphase region.

CONCLUSIONS

As expected, the adhesive strength between epoxy and glass is improved when organosilane adhesion promoters are applied to glass surfaces prior to adhesive joint formation. Both the APS- and ECH-treated glass surfaces showed improvement in adhesive strength before and after aging. These increases in adhesive strength are

presumably due to the introduction of chemical bonds in the interphase. APS treatments were found to be superior to ECH treatments. These results can be explained by the number of bonds expected to occur in each interphase zone. The number of chemical bonds should be greater in the APS system.

The rate of G_c drop of specimens treated by two silane adhesion promoters, APS and ECH, under hygrothermal aging of 85°C/85% RH, was also investigated. As expected, the G_c drop after moisture exposure is believed to be due to the disruption of physical interfacial forces. Interestingly, the rate of adhesive strength loss was related to the rate of moisture uptake. The results showed that adhesion promoters on glass surfaces retard water absorption in the interphase region, and hence, reduce the rate of adhesion loss.

In addition to the use of silane adhesion promoters, PHAE thermoplastic adhesive resins were also investigated as potential adhesion promoters. It was found that 2% PHAE in Dowanol[®] PM was the best system in the PHAE series. Acetic acid concentration has an influence on adhesive strength. The effect of MAH content on the adhesive strength for the PHAE adhesive resin series is also reported. The MAH-modified PHAE showed higher adhesive-strength enhancement compared with PHAE itself. In summary, polymeric adhesion promoters based on the PHAE adhesive resin can improve the stability of epoxy/glass interfaces under hygrothermal conditions and result in performance that approaches the more conventional silane-based adhesion promoters.

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REFERENCES

- [1] Lee, H. and Neville, K., *Handbook of Epoxy Resins* (McGraw Hill, New York, 1967), Chap. 1, pp. 1-1-1-8.
- [2] Nicodemo, L., Bellucci, F., Marcone, A., and Monetta, T., *J. Membr. Sci.* **52**, 393-403 (1990).
- [3] Schultz, W. J., in *International Encyclopedia of Composites*, S. M. Lee, (Ed.) (VCH Publishers, New York, 1990), Vol. 2, pp. 77, 78.
- [4] Moy, P. and Karasz, F. E., *Water in Polymers*, ACS Symposium Series 127, (American Chemical Society, Washington, DC, 1980), pp. 505-513.
- [5] Ellis, T. S. and Karasz, F. E., *Polymer* **25**, 664-669 (1984).

- [6] McKague, E. L., Reynolds, J. D., and Halkias, J. E., *J. Appl. Polym. Sci.* **22**, 1643–1654 (1978).
- [7] Fowkes, F. M., Dwight, D. W., Cole, D. A., and Huang, T. C., *J. Non-Cryst. Sol.* **120**, 47–60 (1990).
- [8] Bell, J. P., Schmidt, R. G., Malofsky, A., and Mancini, D., *J. Adhes. Sci. Technol.* **5**, 927–944 (1991).
- [9] Guerrica-Echevarria, G., Eguiazabal, J. I., and Nazabal, J., *J. Mater. Sci.* **37**, 4529–4535 (2002).
- [10] Glass, T., Pham, H., and Winkler, M., *Proc. 58th ANTEC*, Detroit, MI, 1813–1817 (2000).
- [11] Narsavage-Heald, D. and Pearson, R. A., *Proc. 24th Annual Meeting of the Adhesion Society*, Williamsburg, VA, 383–385 (2001).
- [12] Blackman, B., Dear, J. P., Kinloch, A. J., and Osiyemi, S., *J. Mat. Sci. Lett.* **10**, 253–256 (1991).
- [13] Ivanova, K. I., Pethrick, R. A., and Affrossman, S., *J. Appl. Polym. Sci.* **82**, 3468–3476 (2001).
- [14] Shen, C. H. and Springer, G. S., *J. Comp. Mat.* **10**, 2–20 (1976).
- [15] Kerr, C. and Walker, P., *Adhesion 11* (Applied Science Publishers, London, 1987), Chap. 12, pp. 17–37.
- [16] Plueddemann, E. P., *Pro. Org. Coatings* **11**, 297–308 (1983).
- [17] Ishida, H. and Koenig, J. L., *J. Colloid Interface Sci.* **64**, 565–576 (1978).
- [18] DeLollis, F. N. and Montaya, O., *J. Appl. Polym. Sci.* **11**, 983–989 (1967).
- [19] Kinloch, A. J., *Adhesion and Adhesives: Science and Technology* (Chapman and Hall, New York, 1987), pp. 90–954.
- [20] Ellis, B., *Chemistry and Technology of Epoxy Resins* (Chapman and Hall, London, 1993), pp. 58–59.
- [21] Walker, P., *J. Adhes. Sci. Technol.* **5**, 279–305 (1991).
- [22] Zanni-Deffarges, M. P. and Shanahan, M. E. R., *Int. J. Adhes. Adhesives* **15**, 137–142 (1995).
- [23] Barrie, J. A., in *Diffusion in Polymers*, J. Crank and G. S. Park (Eds.) (Academic, New York, 1964).
- [24] Wu, W., Orts, W. J., Majkrzak, C. J., and Hunston, D. L., *Polym. Eng. Sci.* **35**, 1000–1004 (1995).
- [25] Commercial Information from the Dow Chemical Company. Form No. 296-01411-0501X SMG, The Dow Chemical Company, Midland, MI, (2001).
- [26] Vaideeswaran, K., Bell, J. P., and Nikles, D. E., *J. Appl. Polym. Sci.* **76**, 1338–1350 (2000).
- [27] Bell, J. P. and Schmidt, R. G., U.S. Patent 4,812,363 (1989).
- [28] Sung, N. H., Kaul, A., Chin, I., and Sung, C. S. P., *Polym. Eng. Sci.* **22**, 637–644 (1982).