

Moisture Absorption Behavior of Epoxies and Their S₂ Glass Composites

Amit Chatterjee,^{1*} John W. Gillespie Jr.^{1,2,3}

¹Center for Composite Materials, University of Delaware, Newark, Delaware 19716

²Department of Material Science and Engineering, University of Delaware, Newark, Delaware 19716

³Department of Civil and Environmental Engineering, University of Delaware, Newark, Delaware 19716

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ABSTRACT: The influence of moisture exposure on the behavior of three toughened epoxy-amine systems (scrimp resins SC11, SC15, and SC79, Applied Pleramic, Inc., Benicia, CA) was investigated. Neat resin samples were conditioned by immersion in distilled water at 71°C and in an environmental chamber at 85% relative humidity and 87.8°C until saturation. The equilibrium weight gain ranged from 1.8 to 3.8% for the resins. The long-chain, low-crosslink-density epoxy system (SC11) absorbed the highest amount of water and was saturated first, and it was followed by the medium-crosslink-density (SC15) and high-crosslink-density materials (SC79). The moisture diffusivity decreased with the increasing crosslink density of the resins. The percentage reduction of the glass-transition temperature (T_g) at equilibrium moisture absorption was highest for the low-crosslink molecule. The percentage

reductions for the medium-crosslink and higher crosslink systems were comparable. A net weight loss after drying was observed for the SC11 and SC79 resin systems. Fourier transform infrared analysis confirmed the segment breakage and leaching of molecules from the epoxy-amine network. The effects of moisture cycling on T_g were dependent on the epoxy-amine morphology. During the drying stage, T_g increased to a value higher than that of the unaged dry systems. The S₂ glass composite samples were conditioned under identical conditions for the resin system. Composite systems absorbed less moisture than the neat resins as expected. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 3942–3951, 2008

Key words: ageing; composites; crosslinking; diffusion; glass transition

INTRODUCTION

Epoxy resins are a class of versatile thermoset polymers that are widely used in structural applications.¹ Epoxy-resin-based composites are also often used in applications in which their long-term properties are of primary importance.² It is well recognized that epoxy resins can suffer substantial losses in their mechanical properties due to the absorption of water.^{2–8} Although some studies have found that water absorption induces more or less reversible degradation, prolonged hydrothermal aging may lead to irreversible damage of the resin because of susceptibility of the polymer to hydrolysis, oxidation, and changes in the effective average crosslinked molecular weight.^{3–6} Furthermore, it has been reported that the environmental effects can cause property alterations because of the development of microstresses in the composites.^{1,9} The moisture absorption behavior of epoxy resins has been investigated, but it is still not fully understood.¹⁰ Generally, two forms of absorbed water in an epoxy matrix have been observed

with dielectric relaxation methods: free water and bound water. Free water might reduce the free volume of the networks because it fills this volume. The bound water might reduce the free volume of the networks because it swells the structure. It is still not clearly understood how these retained water forms disperse within the two-phase networks.^{10,11}

Most pure cured epoxy resins are brittle materials having a fracture energy of about 2 orders of magnitude lower than that of engineering thermoplastic resins and 3 orders lower than that of any metals.⁹ Rubber additives are generally used to modify the epoxy resins to improve the fracture properties without a significant reduction of the thermal and mechanical properties.^{12–14} The two-phase epoxy systems having low levels of rubber absorb more water than those with higher levels.^{9–11} Although the diffusion coefficient of moisture is increased with the rubber content, the activation energy and free volume for moisture diffusion barely change until phase inversion occurs. After phase inversion, the free volume is significantly increased, and the activation energy is decreased.

In most applications, the epoxy is used at a temperature well below the glass-transition temperature (T_g). Usually, when the material is exposed in a hydrothermal environment, T_g decreases, and there-

*Present address: Gentex Corporation, Carbondale, PA.

Correspondence to: A. Chatterjee (chatterjeemit@yahoo.com).

fore the service temperature of the material changes. Modification of T_g reflects the degree of resin plasticization and water/resin interactions occurring in the material. Identifying mechanisms responsible for changes in T_g and being able to predict T_g depression are critical for material applications and engineering design. Epoxy resins are not in thermodynamic equilibrium at temperatures below T_g .⁴ As a result of the complexity of epoxy systems, discussions about the interactions between water and epoxy systems at a molecular level remain rather limited, and scientific consensus is quite lacking.⁴

The microstructure plays a large role in the moisture diffusion process in the resin and polymer matrix composite systems. The effects of absorbed moisture on the interphase region could be detrimental to the interfacial strength between the toughener particles, resin, and fiber and thus have an impact on the performance of their composites. Reductions in T_g due to moisture can also degrade the interphase region, particularly if the wet T_g of the interphase is exceeded in service.^{15,16} These types of deleterious effects can lead to a reduction in toughener particle-resin adhesion and failure at the interfaces that leads to the formation and propagation of microcracks and other damage leading to degradation of the composite properties.¹⁵

Vacuum-assisted resin-transfer molding (VARTM) has been identified as an affordable process for manufacturing composite structures. The process is greatly simplified when the part can be infused at room temperature. Many of the epoxy resins have high viscosity and are unsuitable for VARTM processing. Moreover, moisture-induced behavior for two-phase toughened VARTM epoxies has not been well documented. Very limited information is available on the mechanisms of moisture absorption in toughened epoxies, and a consensus on the dominant mechanisms has not been reached.^{10,17-19} A wide range of resins have been developed for this process that offer low viscosity at room temperature. In many emerging applications, service temperature requirements are in the range of 82°C (180°F). Consequently, the wet T_g values of candidate resins will need to be higher than the service temperature to ensure that the elevated-temperature properties are adequate. The SC scrimp resin series by Applied Pleramic, Inc. (API, Benicia, CA), are the VARTM resins under consideration here and have wide multipurpose applications^{20,21} as adhesives, coatings, and structural matrices in composites.

Environmental durability data are limited for these types of API epoxy resin systems. In this study, three VARTM epoxy resins, denoted SC11, SC15, and SC79, were characterized as a function of environmental conditioning. A comprehensive study was conducted on the influence of water and temperature on the

behavior of the two-phase epoxy resin systems. The effects of absorbed moisture on the polymer properties for the epoxies were characterized. The correlations of the microstructures with the water absorption properties were evaluated. These effects are extremely important in determining the potential effects of moisture on the fiber-matrix interphase region in polymer composites. The irreversible degradation effects were studied for these three epoxy resin systems. Identical conditioning was also performed for the S₂ glass composites system.

EXPERIMENTAL

Materials

Three epoxy prepolymers (SC11A, SC15A, and SC79A from API) and three hardeners (SC11B, SC15B, and SC79B) were used (the stoichiometric ratio of amino hydrogen to epoxy was 1). The details for the chemistry and formulations are described in the material data sheet from API.¹¹ The cure schedules for the three different systems were as follows. For SC11 (A + B), parts A and B (100/40 w/w) were mixed and placed in a mold and were cured at 74°C for 2 h; for SC15 (A + B), parts A and B (100/30 w/w) were mixed and placed in a mold and were cured at 43°C for 14 h and postcured at 93°C for 30 min and at 127°C for 90 min; and for SC79 (A + B), parts A and B (100/40 w/w) were mixed and placed in a mold and were cured at 43°C for 14 h and postcured at 121°C for 4 h and at 177°C for 2 h.

Sample preparation

Composite panels [30 cm × 30 cm (12 in. × 12 in.)] with S₂ glass (eight layers, 4463 sizing, 24 oz/yd² plane-weave fabric; SBA240, Mahogany Co., Mays Landings, NJ) were infused at room temperature with the VARTM process. The panels were cured and postcured according to the cure cycles mentioned previously. The neat resin polymer specimens were prepared by simple mixing of the resin in a mold, curing, and postcuring as described previously. The postcured samples were surface-ground, polished, and cut into dynamic mechanical analysis (DMA) sample dimensions of 60 mm × 13 mm × 3 mm. The DMA samples from the composite panels were prepared in the same manner. Before aging, the samples were dried in a desiccator at 25°C and weighed periodically until a constant weight was obtained. The dimensions were measured for each dried sample.

Absorption

The DMA samples were aged under two different conditions: (1) in water at 71°C in an oven until satu-

ration and (2) in an environmental chamber at 87.7°C and 85% relative humidity for 1600 h. Periodically, samples were removed, and weight gains were measured with a Mettler (Columbus, OH) AT250 analytical balance until the weight was constant.

Desorption

After aging under these two different conditions, some samples were taken out and dried at 50°C in an oven. The weight loss was measured during the drying cycle. Drying was stopped after the final equilibrium weight was obtained between two successive measurements.

Swelling experiments

For the swelling experiments, the sample volume was calculated from length, thickness, and width measurements made with micrometers accurate to ± 0.01 mm. For each specimen, the thickness and width were calculated as the average of five measurements, one near each end and three measurements at approximately equidistant positions along the length. The length was determined from the average of the three measurements.

DMA

A DMA-2980 from TA Instruments (New Castle, DE) was used to thermally characterize the samples under a nitrogen atmosphere. The DMA apparatus was operated in a double-cantilever mode under a 1-Hz frequency to measure the temperature dependence of the viscoelastic properties (storage and loss moduli) from -100 to 250°C . A heating ramp of $1-5^\circ\text{C}/\text{min}$ was used. T_g of the polymer was reported as the loss modulus peak. The values presented for aged and nonaged samples were the averages of three samples.

Apparent diffusivity

The apparent diffusivity (D_a) values for the neat resins samples were calculated from the initial slope (F) of a plot of the percentage moisture content (M_t) as a function of time^{1/2}:

$$D_a = (\pi/16)(FL/M_{\text{sat}})^2 \quad (1)$$

where L is the thickness and M_{sat} is the percentage effective moisture equilibrium content. More detailed information about diffusivity measurements is presented elsewhere.^{15,16,22} A square sample having a length-to-thickness ratio of 100 : 1 must be used to get accurate diffusivity measurements according to the ASTM standard.²² The rationale for the 100 : 1

aspect ratio comes from the derivation (from one-dimensional theory) of correction factors accounting for moisture ingress through the edges of a rectangular specimen. However, we used rectangular samples having an aspect ratio of $\sim 22 : 1$ for the water saturation measurements. Therefore, the calculated diffusivity should be considered an apparent diffusivity, but the results will allow a comparison of the three resins and their composites.

Crosslink density

The crosslink density was calculated on the basis of the Flory–Rehner equation^{23,24}:

$$v = -[\ln(1 - V_r) + V_r + \chi V_r^2]/2(V_r^{1/3} - 0.5V_r)\rho V_0 \quad (2)$$

where v is the crosslink density, V_r is the volume fraction of the resin in the swollen state, V_0 is the volume fraction of the solvent, and ρ is the polymer density. χ is the polymer–solvent interaction parameter:

$$\chi = (\delta_s - \delta_r)^2 V_0 / RT \quad (3)$$

where δ_s is the solubility parameter of the solvent and δ_r is the solubility parameter of the epoxy resin. R is the universal gas constant, and T is the absolute temperature. The volume fraction of the resin was calculated as follows:

$$V_r = [(W_d - W_f)/\rho] / \{[(W_d - W_f)/\rho] + [(W_s - W_d)/\rho_s]\} \quad (4)$$

where W_d is the weight of the dry sample, W_s is the weight of the swollen sample, ρ_s is the density of the solvent, and W_f is the weight of the second-phase material.

Fourier transform infrared (FTIR) spectroscopy

FTIR analysis of the polymer samples was carried out with a Nicolet (Waltham, MA) Magna-IR 860 spectrometer with a deuterated triglycine sulfate detector. The leached water sample was sandwiched between two ZnSe crystals (25 mm \times 2 mm) that were separated by a Teflon spacer 0.1 mm thick. The spectra were recorded between 400 and 4000 cm^{-1} at a resolution of 1 cm^{-1} . The average spectra were recorded after 400 scans. The gain on the instrument was set to 1.0, and the spectra of all the leached polymer segments were background-subtracted with the spectrum of pure Milli-Q (Millepore, Billerica, MA) water to get the actual spectrum for the sample.

TABLE I
Percentage Weight Gain at Saturation, Apparent Diffusivity, and β of Three VARTM Epoxy Systems and Their S₂ Composites

System	M_{sat} (%)		Apparent diffusivity $\times 10^{-9}$ (cm ² /s)	β (wt % ⁻¹)
	71°C immersion in water	85% relative humidity at 88°C		
Neat resin				
SC11	3.85	2.43	12.6	0.34
SC15	3.07	1.75	6	0.31
SC79	2.78	1.65	3	0.29
S ₂ glass composites				
SC11	2.12	1.17	16.3	0.12
SC15	1.14	0.85	11	0.10
SC79	1.10	0.77	7	0.06

RESULTS AND DISCUSSION

Moisture absorption and desorption

Water absorption measurements can be difficult to interpret because water absorption is understood to be a measure of both the efficiency of the structural packing of the epoxy network and the polarity of the network structure (the ability of the groups to form hydrogen bonds with water). The results of the moisture absorption for the neat resins and the S₂ glass composites (the nominal fiber volume fraction is 50%) are summarized in Table I. In the case of SC11, the conditioning temperatures exceeded the dry T_g of this resin. However, this resin has been used in applications requiring services temperature greater than the dry T_g , and the data are therefore relevant. The results in Table I show that the percentage weight gains for SC11, SC15, and SC79 are 3.85, 3.07, and 2.78%, respectively, for the case of water immersion at 71°C. The weight gain at saturation for 85% RH at 88°C is lower, as expected (2.43, 1.75, and 1.65% for SC11, SC15, and SC79, respectively). The same trend is observed for the composite specimens (Table I), except that the percentage weight gain is lower because approximately 50% of

the volume is glass fibers, which do not absorb moisture. A general overall observation is that SC79 absorbs less moisture at saturation than SC15, which in turn absorbs less moisture than SC11 in both the neat resin and composite samples.

The transient percentage weight gain for the resins immersed in water at 71°C is shown in Figure 1. The curves initially increase linearly with the square root of the aging time as expected. The water uptake increases rapidly during the early stages and then levels off, although not completely, even after 1600 h have elapsed. SC11 absorbs moisture more rapidly and achieves saturation in less time (ca. 225 h) in comparison with SC15 and SC79, which take approximately 900 h. In Figure 2, the transient percentage weight gain for SC79 resins and S₂ glass/SC79 is presented to illustrate the effects of the conditioning and fiber volume on the moisture uptake. These results are used to cross-correlate the reduction of T_g with the moisture content in a later section. In Figure 3, the drying of the S₂ glass composites immersed in water at 71°C is presented for the three epoxy resins. At a time equal to zero, the weight gain is equal to the saturation level attained during absorption. The results are normalized via the original dry weight. In

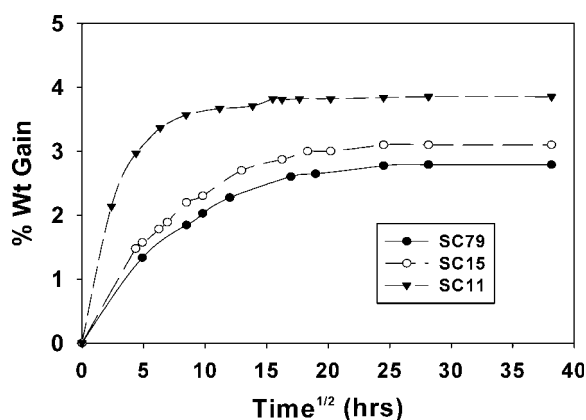


Figure 1 Water absorption profiles for the neat epoxy systems with exposure time.

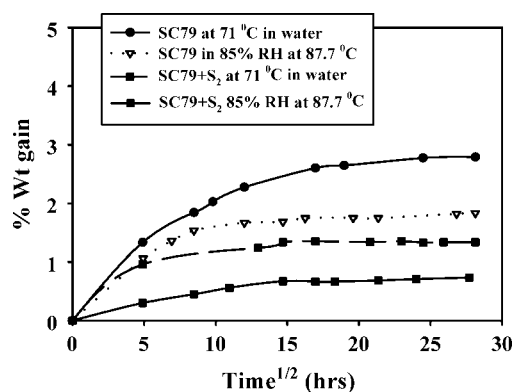


Figure 2 Water absorption profiles of SC79 epoxy resin and its S₂ glass composite systems.

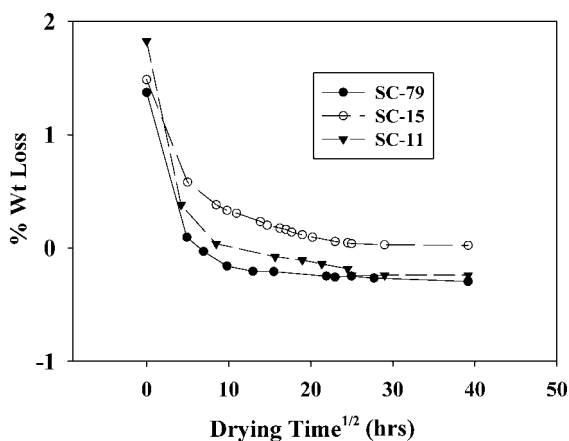


Figure 3 Water desorption profiles of three epoxies and their S_2 glass composite systems.

the case of SC15, no net change in weight is observed after drying. However, a net weight loss of approximately 0.25% has been measured for both SC11 and SC79 resins.

It has been reported that hydrothermal aging induces oxygen-containing groups in the Di-Glycidyl Ether of Bisphenol A/bis (p-aminocyclohexyl) methane (DGEBA/PACM) epoxy resin.³ As a result, the polymer absorbs water; and a fraction of water reacts chemically, causing the addition of oxygen-containing groups to the backbone of the polymer molecule that can break the chain. In the initial stages, these reactions lead simply to the chemical addition of water, which is unable to leave upon drying, and a corresponding net weight increase results. This is not observed in any of the conditioned epoxy resins studied. However, after the number of chemical reaction sites has been increased, the probability of a given intercrosslinked chain being cleaved (i.e., the chain splits at two or more places) increases. Thus, this facilitates the separation and subsequent leaching of the detached segments from the network and leads to weight loss during aging and drying. This is one possible explanation for the weight loss observed in SC11 and SC79 resins (Fig. 3).

To correlate this with the weight loss due to decomposition of the polymer after environmental aging, we have performed an FTIR analysis. Figure 4 shows the FTIR spectra of three different water samples present in the container after aging at 71°C. The spectra clearly show that the epoxy backbone chains break during water immersion at 71°C, and then segments leach out. The leached substances contain the —OH, —NH, and —C=O groups. We have seen a significant difference between the pure water and the water samples after immersion of SC11 and SC79 resins. The leached concentration is highest for SC11, which is followed by SC79. The peaks' absorption between 3000 and -3500 cm^{-1} is due to —OH and

—N—H stretching. In correlating these findings with the weight loss results during the desorption study (Fig. 3), we clearly find that hydrothermal aging leads to the loss of some segments from the backbone polymer systems along with the scission of some crosslinked chains. Irreversible molecular and structural changes in the behavior of water absorption and desorption are observed for these epoxy systems. We have not seen any weight loss for the SC15 system after drying. The FTIR spectra of the water sample present in the container after aging at 71°C for SC15 show no significant peaks (Fig. 4). This clearly indicates that the SC15 resin does not decompose during environmental aging under these conditions.

Effects of moisture conditioning on T_g

The conditioned samples (SC11, SC15, and SC79) were analyzed by DMA, and T_g was measured with the loss modulus peak. The values are presented in Table II. After approximately 300 h, the change in T_g with the immersion time is almost constant. Water in the epoxy resin systems has different bonding states. The engaged water molecules that disrupt the interchain hydrogen bonds depress T_g , whereas water that forms clusters or hydroxyl–water groupings has no measurable effect on T_g . Hence, after saturation, T_g is almost constant for the aged samples (Fig. 5).

Figure 6 shows the decrease in T_g with increasing water absorption for the different epoxy resin systems. It can be observed that the decrease in T_g is directly related to the water absorption (Figs. 6 and 7) of the epoxy network. SC11 has the highest water absorption and highest percentage decrease in T_g , and it is followed by the SC15 and SC79 epoxy resin systems.

Figures 5 and 8 show the effects of the aging time (in water at 71°C) on T_g of the SC11, SC15, and SC79 epoxy resin systems before and after drying. Before drying, T_g initially decreases with the aging time

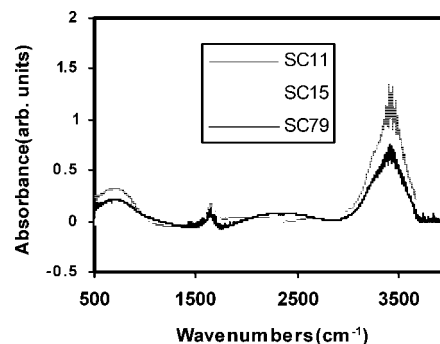


Figure 4 FTIR spectra for segmented polymer molecules in conditioning water at 71°C for three epoxy systems.

TABLE II
 T_g , β , Crosslink Density, Activation Energy, Free Volume, and Other Volumetric Parameters for the Toughened VARTM Epoxy Systems

Parameter	Resin system		
	SC79	SC15	SC11
Dry T_g ($^{\circ}\text{C}$)	170	96	52
T_g ($^{\circ}\text{C}$) for samples saturated with water at 71°C	143	83	28
T_g ($^{\circ}\text{C}$) for saturated samples dried at 50°C for 900 h	177	99	53
% T_g increase after drying	4.12	3.01	2.91
% swelling increase (saturated at 71°C)	2.23	3.08	3.75
Density (g/cm^3)	1.15	1.14	1.11
Activation energy (kJ/mol)	32	28	11
$\Delta l/l_0$ (%)	0.74	0.82	1.18
Crosslink density (mol/g)	0.023	0.015	0.0011
Free volume (V_f/V^*)	0.087	0.101	0.247
Dry T_g ($^{\circ}\text{C}$) for the S_2 glass composite	181	100	52

and then approaches an asymptotic value (Fig. 5, Table II). With drying, T_g increases and finally rises above the initial dry T_g value of the neat resin system (ranging from 3 to 4%, as shown in Table II and Fig. 8). The increase in the aging time may facilitate transient water diffusion into the resin system and/or facilitate the chemical reaction between the water and the epoxy network. However, increases in T_g of the desorption samples are due to the branched polymer chain orientation and the coupling with each other, which ultimately increases the crosslink density of the epoxy polymer. This observation is quite different from the results reported in the literature.^{23–27} The interchain bond breakage increases chain mobility with transient water diffusion. During desorption, the broken chains may interlink with themselves and with the main network system. This may increase the network system rigidity. Therefore, the crosslink density may increase with desorption, and the trend is SC79 > SC15 > SC11 for the epoxy resin systems. The increased T_g value is ultimately higher than that of the fully cured unaged materials (Table II). The bound water in the aged epoxy net-

work² also promotes secondary crosslinking with hydrophilic groups such as hydroxyls and amines in the epoxy network.²⁵ This increased crosslink density contributes to the lowering of T_g in epoxy resins after saturation. More details about the crosslink density are discussed later.

Morphology of the epoxy systems [transmission electron microscopy (TEM) analysis]

To correlate the morphological characteristics with the moisture diffusion properties of the networks, the microstructure of the cured resins was analyzed with TEM. The systems contain two distinct phases of networks: globular particles dispersed in a continuous epoxy matrix. The water absorption property depends on the second-phase architecture and on the concentration.²⁸ In the case of SC11, the particles are small at 65–120 nm and more uniformly dispersed than those in the SC15 and SC79 systems. Figure 9 shows the morphology. A higher number of the toughened particles per unit of area having a lower size will absorb more moisture in the system

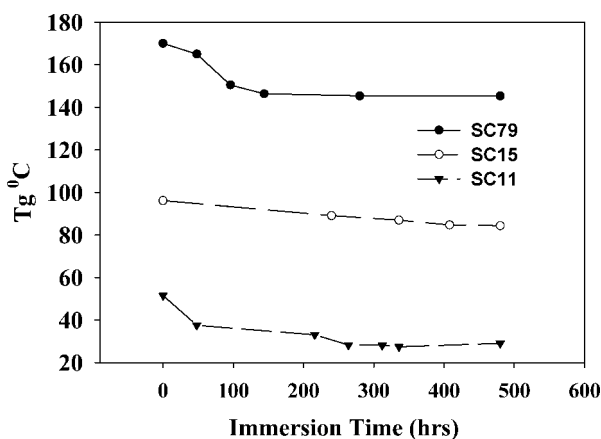


Figure 5 Variation of T_g as a function of water immersion time for the neat epoxy resin systems.

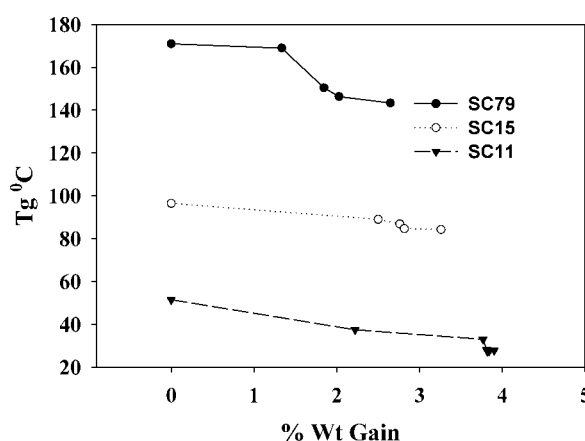


Figure 6 Variation of T_g as a function of percentage weight gain for the neat epoxy resin systems.

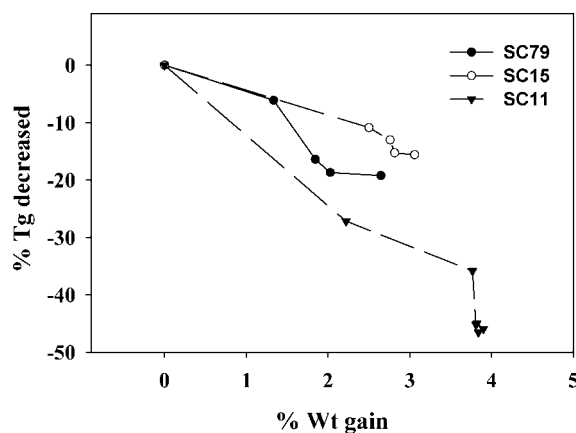


Figure 7 Variation in the percentage T_g decrease as a function of percentage weight gain for the neat epoxy resin systems. Samples were immersed in water at 71°C .

because of an increase in the free volume, which increases the moisture diffusion rate.²⁸ This phenomenon explains the highest moisture absorption of SC11 followed by SC15 and SC79.

Moisture-induced swelling

Dimension measurements were taken for the dry and apparent moisture saturation samples. The length was increased from 0.31 to 0.66 mm in the length direction for most of the specimens. The swelling strain $[A (\%)]$ was calculated with the change in length divided by the dry length:

$$A(\%) = (\Delta l/l_0) \times 100 \quad (5)$$

where l_0 is the initial dry dimension and Δl is the change in that dimension due to moisture absorption at saturation. The observed dimensional changes result in swelling strains of 0.74–1.20%. In general, swelling increases linearly with the moisture saturation level. The moisture expansion coefficient (β) was calculated with the following equation:

$$\beta = (\Delta l/l_0)/M_t \quad (6)$$

where M_t is the moisture level (%) at a given time. β was determined from a linear fit of the moisture-induced strain as a function of the moisture level. Figure 10 shows the resulting curve for SC79. In Figure 10, the M_t values are the average moisture levels at the time at which specimen dimensions were measured. β is a function of a resin's morphology and microstructure. Similar curves were obtained for SC15 and SC11. β was calculated and is presented in Table I. β is highest for SC11 and lowest for SC79 (0.34, 0.31, and 0.29 for SC11, SC15, and SC79, respectively). Figure 11 shows the strain– M_t curve for the SC11 S_2 glass composite in the longitudinal

direction. Again, similar curves were drawn for SC15 and SC79, and β was calculated. The values are also presented in Table I. The range of the strain in the S_2 glass composite is 0.06–0.12% in the length direction. As discussed previously, the S_2 glass composites absorb less moisture, and the swelling strains are further reduced in comparison with the neat resin systems because of the fiber constraint.

Apparent diffusion, activation energy, crosslink density, and free volume

The apparent diffusivity values for the neat resins and the S_2 glass composite samples were calculated from F of a plot of M_t as a function of time^{1/2} with eq. (1), where L is the thickness and M_{sat} is the percentage effective moisture equilibrium content, as described previously in the Experimental section. The values are presented in Table I. SC11 has the highest apparent diffusion and is followed by SC15 and SC79. Using Arrhenius plots [eq. (7)], that is, logarithmic plots of diffusion coefficient (D) versus the reciprocal of the temperature, we have calculated the activation energy (E_0) for the moisture diffusion:

$$D = D_0 \exp(-E_A/RT) \quad (7)$$

where D_0 , the diffusion coefficient of moisture at $T = \alpha$ (infinity), is constant (the coefficient value from the curve); E_A is the activation energy; R is the gas constant; and T is the absolute temperature. The estimated E_A values for the epoxy resins are given in Table II. The resin that has a high number of particles separated out in the second phase with a lower size will have lower E_0 values. The E_0 value is higher for SC79, indicating that the two-phase morphology should have a lower number density of larger particles. This is consistent with the TEM picture (Fig. 9).

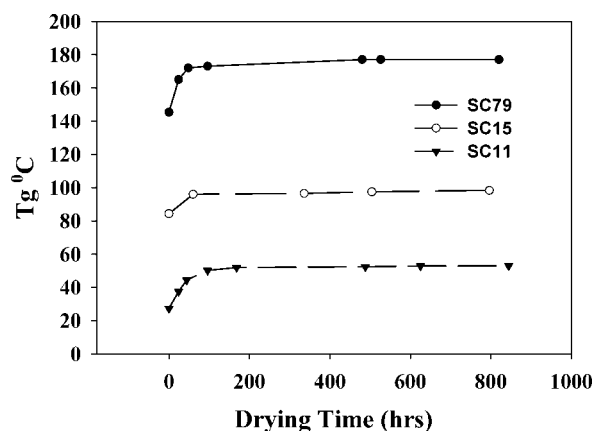


Figure 8 Change in T_g with drying time for the neat epoxy resin systems. After saturation, samples were dried in an oven at 50°C .

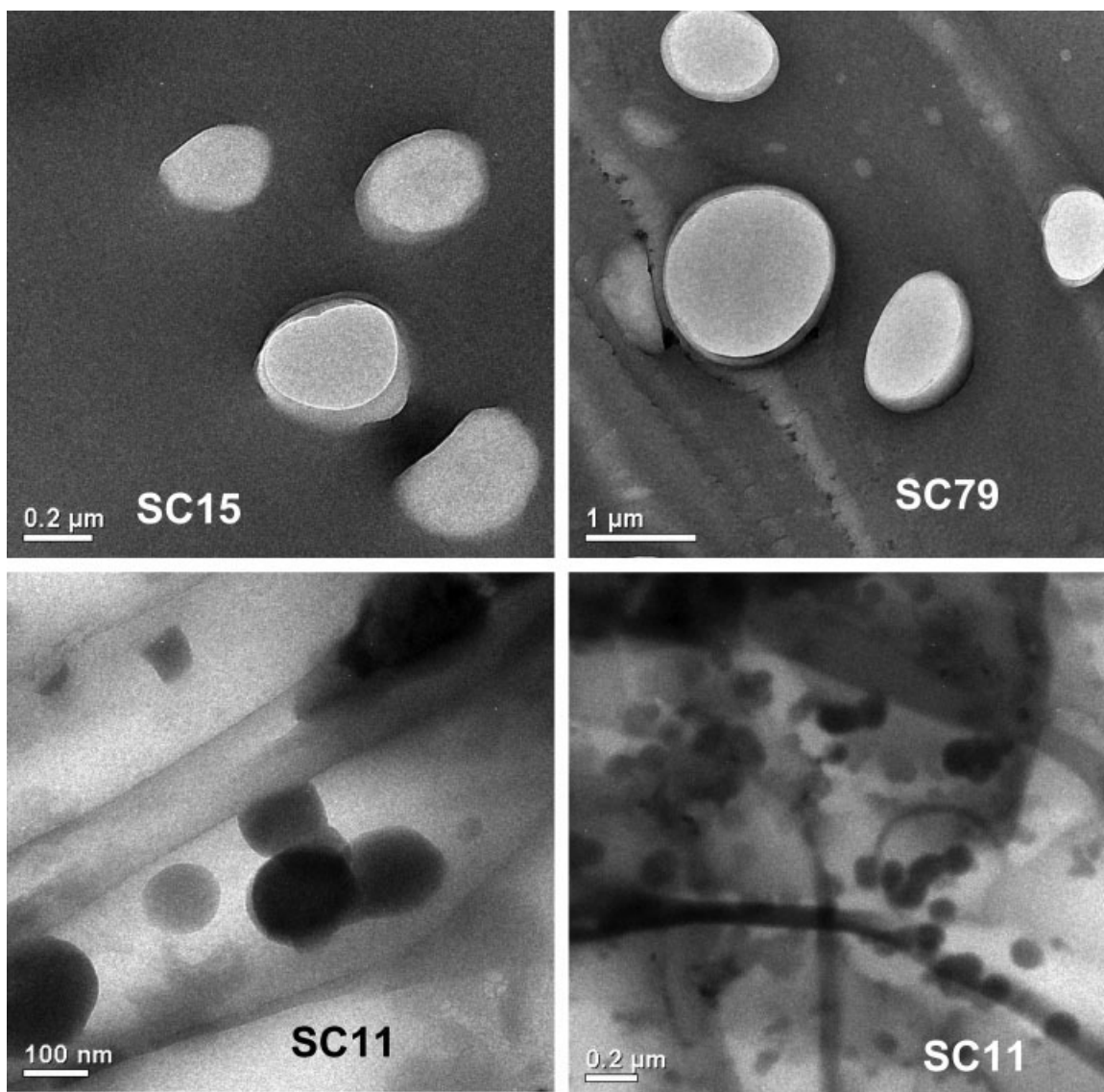


Figure 9 TEM micrographs for three toughened epoxy systems indicating two-phase morphologies.

The crosslink density was measured and is presented in Table II. SC79 has the highest crosslink density and is followed by SC15 and SC11. The molecular weight between crosslinks (M_c) was measured for the three different systems. SC11 has the highest chain length (858 g/mol), and SC79 has the

lowest one (44 g/mol), as shown in Figure 12. M_c was normalized with M_c of SC79 and plotted with the normalized activation energy of the resin for SC79, as shown in Figure 13. This clearly indicates

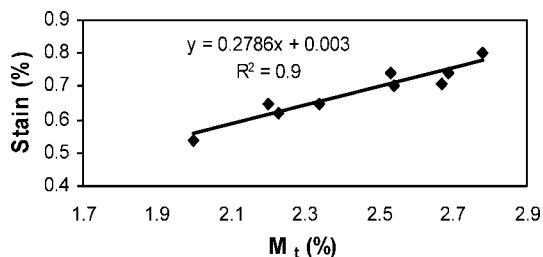


Figure 10 Percentage strain change with moisture saturation percentage (M_t) for the SC79 resin system.

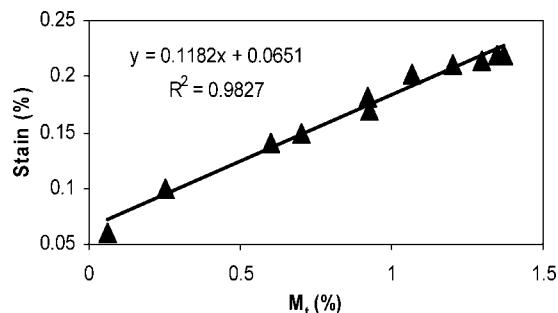


Figure 11 Percentage strain change with moisture saturation percentage (M_t) for the SC11-S₂ glass composite system.

that a decrease in the activation energy of 67% increases M_c by approximately 1900%, and that in turn increases the moisture absorption by 68%. SC79, with the highest crosslink density, has the highest activation energy, which causes a lower moisture rate of absorption in comparison with SC15 and SC11. The long-chain polymer epoxy system (SC11) requires less energy for the water molecule to move from one place to another. The lower chain length between the crosslinks of SC79 increases the crosslink density, and that requires more energy for the water molecule to penetrate the polymer molecule. It has been reported that samples with $M_c < 200$ g/mol act as a brittle matrix, whereas those having $M_c > 1000$ g/mol should show a rubbery-type response.²⁶ These two extremes are separated by a rather large intermediate range, and the transition from a brittle resin to a tougher resin can be predicted. On the basis of the aforementioned result, SC11 shows the highest toughness, and this correlates well with our experimental findings and with the TEM pictures. The variation in the epoxy resin cured phase morphology also changes the moisture absorption properties.²⁸ We have correlated this with the crosslink density of the polymer and β . It shows a similar trend; that is, the higher the crosslink density is, the lower β is. Epoxy resins contain significant amounts of free volume, so the moisture absorption phenomenon is important as it has an impact on the structural integrity of epoxy composites. The free volume of the resin tends to dominate the diffusion process for many resin systems. This is due to the inaccessibility of the hydrogen-bonding sites. Thus, moisture diffusion is dependent on the free volume (V_f) of the resin networks, as indicated by the Doolittle equation²⁹:

$$D = D_0 \exp(-BV^*/V_f) \quad (8)$$

where B is usually considered to be unity and V^* is the critical amount of free volume for a water mole-

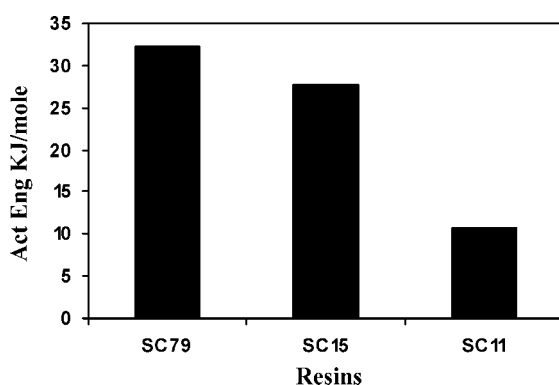


Figure 12 Variation in activation energy of three different epoxy resin systems.

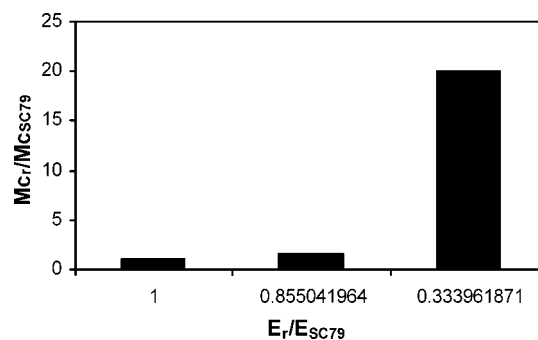


Figure 13 Variation of normalized M_c (molecular weight between the crosslinks) of the epoxy resin with respect to SC79 and the activation energy of the epoxy resin with respect to SC79.

cule to jump to a new position. Therefore, the calculated V_f/V^* values in this equation as a function of the resin networks are given in Table II. The free volume increases with the crosslink density. It is lowest for SC79, which is followed by SC15 and SC11.

The free volume concept is very useful for the transport of small molecules such as solvents or ions through a polymer matrix. The basic concept is that sufficient free volume in the polymer system is required before molecular diffusion of a given size can occur. When there is a large amount of free volume in the system, molecules can move through the polymer matrix relatively unhindered. However, the lowering of the free volume decreases the molecular diffusion. Therefore, the polymer chain segments are crowded by the neighboring chains, and the motion is inhibited. For a molecule to migrate, a free volume hole of sufficient size must occur, and the molecule must have adequate energy to jump into the voids. The rate of migration is the product of the probability that a hole of sufficient size will occur and the probability that the molecule will have the required activation energy. For our specific cases, the specimens with a two-phase morphology with a higher number of separated particles have more free volume than those with a lower number of phase-separated particles.¹⁰ The specimens having a higher number of particles require less activation energy for the water molecule to migrate. SC11 has 3 times more free volume than SC79, and this is correlated to the water diffusion properties. In the case of SC11, the separated particles are homogeneously distributed throughout the resin system. Because the resin free ends are larger in number per unit of area for SC11, that creates more free volume in the networking system. However, for SC15 and SC79, the second phase separates with a larger size, which causes less free volume.²⁸ As free ends of the polymers are less for SC15 followed by SC79, the mois-

ture absorption property will be low compared to that of SC11, and this correlates well with our results (Table II). M_c can be correlated with the density of the neat resin system presented in Table II. SC79 has the highest crosslink density and is followed by SC15 and SC11. The moisture diffusivity for the composite sample is higher compared to that of the neat resin system. However, the total moisture absorption is lower than that of the neat resin (Table I). This may be due to the fiber–matrix interface region, in which the fiber–matrix two-phase system compatibility is an issue.

CONCLUSIONS

The hydrothermal aging of three different epoxy systems induces reversible and irreversible changes in the molecular structure of epoxy networks. The diffusivity, water absorption, swelling coefficients, free volume, and crosslink density are determined for the epoxy systems. The moisture absorption behavior for the epoxy–amine systems very much depends on the resin phase morphology. The circular, uniform particle shape and distribution increase the free volume, and that ultimately increases the moisture absorption of the resin. However, a nonuniform particle distribution of a micrometer size decreases the free volume and the moisture absorption property. The crosslink density very much depends on the epoxy types. The long-chain, low-crosslink-density system absorbs more moisture and has high β and moisture diffusivity. On the other hand, a low M_c value means a lower diffusion coefficient. Irreversible changes are found because of moisture diffusion in the epoxy system, and this has been confirmed by FTIR analysis. The chain is segmented. Segmented molecules leach out from the system with aging. T_g decreases with moisture absorption. The highest percentage decrease in T_g has been observed for the lowest crosslink system. The diffusion coefficient increases exponentially with M_c of the resin systems. The same trend has been observed for the free volume and diffusion coefficient. The S_2 glass composite systems absorb less water than the pure resins. However, the diffusion coefficient of the polymer

S_2 glass composite is higher than that of the neat resins.

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