Moisture Diffusion in Epoxy Systems

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ABSTRACT: The moisture diffusion process of an epoxy system is studied as a function of epoxy-amine stoichiometry and the resulting microstructure. Differences in diffusion behavior are related to the relative importance of diffusion through the low-density and high-density microstructural phases for different stoichiometries. Also, changes in saturation level with stoichiometry are explained by competing effects of free volume *versus* the content of the low-density phase. Increasing the humidity level causes a corresponding increase in saturation level, while increasing the temperature causes more pronounced non-Fickian behavior. The effects of absorbed moisture on the thermomechanical properties of the epoxies are also investigated. Reductions in the glass transition temperature, T_g , and moisture-induced swelling strains are measured after exposure of samples to the three conditioning environments. Moisture-induced swelling strains increase with increasing moisture content. The reductions in T_g range from 5 to 20°C and are generally larger for amine-rich samples than for epoxy-rich and stoichiometric samples. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 787–798, 1999

Key words: moisture diffusion; epoxy microstructure; glass transition temperature; moisture-induced swelling; fiber-matrix interphase

INTRODUCTION

Moisture transport in polymer systems is related to the availability of molecular-sized holes in the polymer structure and the polymer–water affinity.^{1–4} The availability of holes depends on the polymer microstructure, morphology, and crosslink density, which are functions of degree of cure, stoichiometry, molecular chain stiffness, and the cohesive energy density of the polymer.² The polymer–water affinity is related to the presence of hydrogen bonding sites along the polymer chains, which create attractive forces between the polymer and water molecules. The water molecules that are free to move through the holes, or free volume, are often referred to as unbound molecules. Because this unbound moisture is filling free volume, it does not cause dimensional changes of the polymer. In contrast, the water molecules that attach to the polymer chain *via* hydrogen bonding, referred to as bound molecules, disrupt the interchain hydrogen bonding, inducing swelling, and plasticize the polymer.^{2–4}

In the case of epoxies, significant amounts of free volume exist, particularly at temperatures $50-150^{\circ}$ C below the glass transition temperature, T_g , that are often used in moisture absorption studies.^{2,5,6} Also, the epoxy–water affinity is relatively strong because of polar hydroxyl (—OH) groups created by the epoxide ring-opening reaction with primary and secondary amines.¹⁻⁴ Because these hydroxyl groups retain a certain amount of steric freedom, they can hydrogen bond with similar groups located on nearby segments.³ However, the polar water molecules can hydrogen bond with these hydroxyl groups, thus disrupting the interchain hydrogen bonding. The molecular structure is thus altered to conform with the pres-

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ence of the moisture, the results of which are often observed as dimensional changes and reductions in T_{σ} .^{3,4}

For many polymer systems, the free volume of the resin tends to dominate the diffusion process.^{1,7} This observation is due, at least in part, to the inaccessibility of hydrogen bonding sites.^{4,6} In two studies, the amount of volume change due to moisture-induced swelling was significantly less than the volume of moisture absorbed, indicating that a large portion of the absorbed water resides in the free volume.^{3,8} This unbound moisture content was found to account for weight gains of 2.0-2.5% for epoxy-amine systems that absorbed 3.0-3.5% moisture by weight.^{1,2,6} If each hydroxyl group attracted a single water molecule, the bound moisture content at saturation would be approximately 8% by weight, yielding a total weight gain in excess of 10%,⁶ which is not generally observed experimentally.

The inaccessibility of sorption sites is thought to be related to the two-phase morphology often observed in epoxy systems.⁹⁻¹⁴ This two-phase microstructure generally consists of a high crosslink density nodular or microgel phase surrounded by a low-density phase that is composed of unreacted and/or partially reacted material. In a related study,¹⁴ atomic force microscopy (AFM) phase images were used to study epoxy microstructure. An example of such an image is shown in Figure 1 for a sample prepared with a stoichiometric mixture of EPON 828 epoxy and PACM 20 amine curing agent (see the Experimental Section for a description of these materials) and cured for 2 h at 80°C. AFM phase images correspond to changes in the phase of the oscillating cantilever probe, and the contrast is a result of changes in energy dissipation across the sample surface.¹⁵ In Figure 1, the harder, less viscoelastic microgel phase appears as brighter areas compared to the softer, more viscoelastic phase, which are the very dark regions. Further, the phase contrast between white and black in this figure is 90°, which is an extremely large range. Therefore, the property differences between the two phases are quite significant. After postcuring this sample for 2 h at 160°C, the low-density phase had disappeared because the conversion of epoxy and amine species approached 100%. However, for nonstoichiometric samples, the two-phase microstructure remained after postcuring due to the presence of unreacted excess epoxy or excess amine species.



Figure 1 Atomic force microscopy phase image of a stoichiometric sample.¹⁴ The difference between white (hard) and black (soft) regions represents a 90° difference in the phase response of the oscillating cantilever probe.

Changes in epoxy microstructure will likely impact the moisture diffusion behavior in these materials. For example, the high crosslink densities associated with the microgel phase might severely hinder moisture diffusion such that the rate of diffusion into the lower density phase is much higher than that of the nodular phase. Also, in several experimental studies of epoxies, certain reacting species have been shown to preferentially adsorb onto various surfaces using several techniques.^{16–18} This preferential adsorption phenomenon can result in the formation of interphase regions in composite materials, altering the local stoichiometry, microstructure, and properties of the material adjacent to the fiber. Because microstructure plays a large roll in the moisture diffusion process, the effects of absorbed moisture on these interphase region could be detrimental to the interfacial strength between the fiber and the epoxy matrix and thus to the performance of the composite. Moisture-induced swelling can reduce mechanical interlocking between the fiber and matrix that evolves during cool down because of the differences in thermal expansion between the two constituent materials. Thus, swelling could cause significant changes in the internal stress state in the interphase region. Reductions in T_g due to absorbed moisture could also degrade the interphase region, particularly if the wet T_g of the interphase is exceeded in service. These types of deleterious effects can lead to reductions in fiber–matrix adhesion and even failure at the fiber–matrix interface,^{19–22} which could then cause the formation and propagation of microcracks and other damage and lead to reductions in composite performance.

In this article, the effect of stoichiometry on the moisture diffusion process as well as the effects that absorbed moisture can have on polymer properties for different stoichiometries are characterized. These effects will be extremely important in determining the potential effects of moisture on the fiber-matrix interphase region in polymer composites.

THEORY OF DIFFUSION IN POLYMERIC MATERIALS

The classical limiting case of diffusion can be described using Fick's second law with a constant diffusion coefficient or diffusivity, D^{23} such that

$$\frac{\partial c}{\partial t} = D\nabla^2 c \tag{1}$$

where c is the moisture concentration and t is time. For one-dimensional diffusion through an infinite plate of thickness L, this equation reduces to²⁴

$$\frac{\partial c}{\partial t} = D_x \frac{\partial^2 c}{\partial x^2} \tag{2}$$

where D_x is the diffusivity through the thickness of the material. The diffusion of moisture into glassy polymers generally follows this law when the moisture transport is completely controlled by diffusion, that is, when diffusion mechanisms related to degradation, molecular relaxation, or insufficient curing, for example, are not active.¹ Further, D_x often exhibits a dependence on temperature that follows an Arrhenius relationship²⁵ given by

$$D_x = D_0 \exp\left(\frac{-A_0}{RT}\right) \tag{3}$$

where D_0 is a constant coefficient, A_0 is the activation energy for diffusion, R is the universal gas

constant, and T is the temperature measured on an absolute scale.

For most practical applications, changes in the percentage of moisture content, M, can be measured gravimetrically, that is, as changes in the weight or mass of the polymer specimen²⁶ as in

$$M = \frac{w - w_d}{w_d} \cdot 100 \tag{4}$$

where w is the weight or mass of the material at any time, t, and w_d is the weight or mass of the dry material. The total weight or mass of moisture in the specimen at any time is given by

$$w - w_d = \frac{1}{L} \int_0^L c dx \tag{5}$$

For an initially dry material, the value of D_x can be calculated from the initial slope, F, of a plot of M(t) as a function of $t^{1/2}/L$ using the following relation²⁷:

$$D_x = \left(\frac{\pi}{16}\right) \left(\frac{F}{M_{\text{sat}}}\right) \tag{6}$$

where $M_{\rm sat}$ is the equilibrium moisture saturation level for a particular environment. Such a plot should be linear up to $M = 0.6 M_{\rm sat}$ with less than 2% deviation for true Fickian diffusion.²⁷

Although the diffusivity does not, in general, depend on the moisture concentration of the surrounding environment, the moisture saturation level is often observed to depend on relative humidity according to the relationship²⁶

$$M_{\rm sat} = a(\rm RH)^b \tag{7}$$

where a and b are constant parameters, and RH is the percentage of relative humidity. $M_{\rm sat}$ has been observed to be both dependent^{28,29} and independent²⁷ of temperature for different polymer systems. These seemingly contrasting observations have been explained through thermodynamic arguments.²⁸ For water in epoxy, the heat of solution, ΔH_s , is negative. This factor is opposed thermodynamically by the heat of vaporization of water, ΔH_v . If $\Delta H_s = -\Delta H_v$ then $M_{\rm sat}$ will not be a function of temperature. For some systems, this equality does not hold and a tem-



Figure 2 Chemical structures of (a) EPON 828 epoxy, where n = 0.2, and (b) PACM 20 amine.

perature-dependent saturation level is observed. In this article, thin epoxy samples are exposed to two temperatures and two humidity levels to characterize one-dimensional diffusion through these materials.

EXPERIMENTAL

Materials

The resin system used throughout this work is a thermally cured epoxy consisting of EPON 828 epoxy, manufactured by Shell Corp., and PACM 20 amine curing agent, manufactured by Air Products, Inc. The EPON 828 epoxy is based on the oligomeric prepolymer diglycidyl ether of bisphenol A (DGEBA), while the PACM 20 amine is a cycloaliphatic diamine with a chemical name of bis(para-amino cyclohexyl) methane. The chemical structure of the two components are shown schematically in Figure 2, where n = 0.2 for EPON 828. This particular polymer system was chosen because it is easy to process, relatively safe to handle, and its thermal and mechanical properties, reaction characteristics, and interaction with solid surfaces have been studied extensively.^{30–37} For this system, a ratio of 28 parts of amine per 100 parts epoxy yields one epoxide group for each amine hydrogen and, thus, is the stoichiometric composition.

Moisture Diffusion Studies

To study moisture diffusion in the EPON 828-PACM 20 polymer system, thin rectangular specimens were processed using homemade molds. Seven to ten specimens were processed for epoxyamine compositions of 14, 20, 28, 50, and 70 parts amine per 100 parts epoxy, as listed in Table I. (Here in, parts of amine per 100 parts epoxy will be abbreviated as pph amine, and samples will be designated by stoichiometry in the following manner: 14 pph amine samples are designated 100-14, 28 pph amine samples are designated 100-28, etc.). The molds consisted of flat plates of stainless steel with damming material pressed firmly to the steel surface to form the boundaries of several mold cavities. The tops of the mold cavities were open to allow air bubbles to escape. Each mold was sprayed with three separate treatments of a nonstick release agent and allowed to air-dry prior to processing. After careful weighing and mixing of the appropriate amounts of epoxy and amine in glass beakers, each mixture was placed in an oven at 80°C for 2 min to decrease viscosity. Portions of each mixture were then drawn into a plastic disposable syringe and injected into the mold cavities. Note that the molds were preheated to 80°C prior to the injection of epoxy. The mold was then placed in an 80°C oven for 2 h. After cooling to room temperature, specimens were removed from the mold cavities and placed in a desiccator.

Moisture samples were made in a variety of shapes and sizes. In general, these samples were approximately square with length and width dimensions ranging from 36–56 mm and thicknesses ranging from 1.2–2.0 mm. Because of the homemade nature of the molds, each as-processed specimen had some slight variations in thickness, length, and width dimensions. To reduce these dimensional variations, the edges and faces of each sample were sanded using 600-grit silicon carbide polishing paper. Each sample was then rinsed off with tap water to remove excess debris. All samples were then dried in a vacuum oven at 50°C for approximately 2 weeks. During the drying period, the weights of several of the thickest

Table ISample Designation andCorresponding Amounts of Epoxy and AmineUsed to Make Samples for the Study ofMicrostructure and the MeasurementThermomechanical Properties, MoistureDiffusion, and Moisture-Related Properties

Sample Designation	Mass (g) EPON 828	Mass (g) PACM 20	Amine (pph)
100-14	48.9	7.0	14.3
100-20	32.3	6.4	19.8
100-28	33.5	9.5	28.4
100-40	29.8	12.1	40.6
100-50	31.9	16.0	50.2
100-60	35.0	21.2	60.6
100-70	21.2	14.9	70.3

specimens were monitored to ensure that equilibrium dryness had been reached prior to immersion in humid environments. Initial dry weights and dry thickness, length, and width dimensions were measured and recorded.

Two to four specimens of each epoxy-amine ratio were placed in each of three environments. These environments included 20°C (room temperature) and 75% relative humidity (RH), 20°C and 85% RH, and 50°C and 85% RH. The room-temperature environments were created by placing a saturated salt solution with excess salt in distilled, deionized water at the bottom of a closed desiccator, as recommended by ASTM E104.³⁸ For 75% RH, sodium chloride was used, and for 85% RH, potassium chloride was used. An environmental chamber was used to create the 50°C 85% RH environment. Each set of samples was removed for 10-15 min periodically for weighing. To establish whether the moisture diffusion process is completely reversible for this epoxy system, some of the samples were dried under vacuum at 50°C after 2500-3500 h of conditioning. For these desorption studies, the samples were removed from the vacuum oven and weighed periodically. A digital balance with an accuracy of ± 1 mg was used for all weight measurements.

Moisture-Induced Swelling Studies

Samples used for the moisture diffusion studies were also used to measure moisture-induced swelling. After drying samples to an equilibrium dryness, initial dry thickness, length, and width dimensions were measured and recorded. After moisture samples reached saturation, length and width dimensions were measured again to estimate the amount of moisture-induced swelling. Dimensions of the desorption samples were also measured after all samples had reached an equilibrium dry weight. All dimensional measurements were made using digital calipers that were accurate to ± 0.01 mm.

Studies of Epoxy Properties as a Function of Absorbed Moisture

Concurrent with the processing of moisture diffusion samples, several samples of each epoxyamine stoichiometry listed in Table I were processed with the following approximate dimensions: length = 52-56 mm, width = 8-13 mm, and thickness = 1.2-2.5 mm. These samples were used for dynamic mechanical analysis (DMA). For each stoichiometry, two to six samples were tested; at least one of these samples was processed using the standard 80°C cure followed by a 160°C postcure, while the remainder of the samples received just the standard cure. Each sample was then tested with the DMA using a three-point bend loading configuration, a temperature ramp rate of 2°C/min, and a loading frequency of 1 Hz. Each sample was tested 3 times, as follows: in the dry state prior to exposure to a humid environment; after exposure to humid environments for time periods sufficient for moisture saturation; and after being dried out at 50°C in a vacuum oven for 2 weeks. For standard-cure samples, testing was stopped immediately after T_g was reached so that postcuring reactions would not convolute the results of subsequent DMA testing. The storage modulus E', the loss modulus E'', and tan δ were recorded as a function of temperature, T. The glass transition temperature, T_{g} , was taken as the peak in E''.

RESULTS AND DISCUSSION

The Effects of Temperature and Humidity Level on Moisture Diffusion

For many samples, the moisture absorption of the EPON 828-PACM 20 system was observed to exhibit Fickian behavior only during the initial stages of diffusion. Weight gain due to moisture absorption, M(t), increased proportionally to $t^{1/2}$ before beginning to level off to a saturation level. Instead of continuing to decrease towards zero, however, the diffusion rate either reached a constant level or, in some cases, increased. These types of non-Fickian anomalies are shown for each of the three environments in Figures 3, 4, and 5, respectively. In each of these figures, none of the samples has reached a stable saturation level, even after 3000-4000 h of exposure. Similar behavior has been reported for epoxy systems for which absorption levels continued to rise slowly but steadily after the initial linear increase of M(t) with $t^{1/2}$.^{1,3,7,29,39} These deviations from Fickian behavior are certainly more pronounced in the elevated temperature environment. Thus, the mechanism or mechanisms responsible for this behavior might depend on temperature.

Deviations from Fickian behavior were not observed in all samples, however. In fact, the majority of samples exhibiting non-Fickian moisture uptake were epoxy-rich and stoichiometric sam-



Figure 3 Sorption plot for samples conditioned in the 20°C, 75% RH environment that exhibited non-Fickian absorption.

ples. Of the amine-rich samples, only absorption by the 100-40 samples and one of the 100-60 samples conditioned in the 50°C, 85% RH environment deviated significantly from Fickian diffusion. The deviation observed in the 100-60 sample, however, was most likely due to damage, as will be discussed in a subsequent section. The 100-50 and 100-70 samples and the other two 100-60 samples conditioned in the 50°C, 85% RH environment reached stable saturation levels after approximately 2000–2500 h, as shown in Figure 6. Similarly, all amine-rich samples exposed to the two room-temperature environments have exhibited Fickian absorption up to stable saturation levels that were reached after 3500-4000 h.

In Figure 7, curves corresponding to Fickian behavior are shown along with data from two samples, one exhibiting Fickian behavior, and the other exhibiting non-Fickian behavior. The Fickian curves were generated using a finite difference model⁴⁰ with measured diffusivities D, sample thicknesses L, and saturation levels $M_{\rm sat}$, of



Figure 5 Sorption plot for samples conditioned in the 50°C, 85% RH environment that exhibited non-Fickian absorption.

the two samples as inputs. Deviations from the fitted curve of the 100-70 sample data [see Fig. 7(a)] are within experimental error caused by uncertainties in weight measurements of ± 1 mg and thickness measurements of ± 0.01 mm, and variations in thickness across a single sample of 0.1– 0.3 mm. Significant deviations from Fickian behavior are observed for the 100-14 sample, as shown in Figure 7(b). This type of non-Fickian behavior has been explained in terms of relaxation phenomena.³⁹ The viscoelastic nature of polymers is often described using relaxation times that are characteristic of a response to a change in an internal or external variable at a given temperature. Thus, changes in humidity level and in the internal moisture concentration during hygrothermal conditioning could induce polymer relaxation, which causes the slow changes in saturation level observed in the present study. Except for the one 100-60 sample, however, non-Fickian absorption has only been observed in samples with amine contents of 40



Figure 4 Sorption plot for samples conditioned in the 20°C, 85% RH environment that exhibited non-Fickian absorption.



Figure 6 Moisture sorption plot for 50°C, 85% RH conditioning of 100-50, 100-60, and 100-70 samples, for which diffusion follows Fick's second law.



Figure 7 Comparison of (a) Fickian and (b) non-Fickian diffusion. The fitted curves represent Fickian moisture absorption and were generated using a finite difference model. The 100-70 sample was conditioned in the 20°C, 75% RH environment, while the 100-14 sample was conditioned in the 50°C, 85% RH environment.

pph or less. If a relaxation effect is the controlling mechanism causing non-Fickian behavior, then the diffusion time scales for the 100-50, 100-60, and 100-70 samples would have to be significantly different compared to that of the other samples for the diffusion and relaxation processes not to interact. However, as is discussed in the following subsection, the rate of moisture absorption did not change significantly with stoichiometry.

For most polymer systems, the moisture saturation level $M_{\rm sat}$ depends strongly on the RH of the environment. This trend was observed for the EPON 828-PACM 20 system, although only two humidity levels were used. Comparing data from samples exhibiting Fickian behavior, the moisture levels for samples in the 85% RH environments were approximately 15–25% higher than the samples in the 75% RH environment. Comparing data from samples in the two room-tem-

perature environments, a 15–25% difference in moisture level is again observed for samples exhibiting non-Fickian behavior when the comparisons are made at similar values of $t^{1/2}/L$.

The effect of temperature on $M_{\rm sat}$, however, does not appear to be significant for samples exhibiting Fickian absorption. However, temperature increases the rate of diffusion and might change the relative rates of diffusion through the low-density and high-density phases, thus causing more pronounced non-Fickian anomalies at 50°C than at 20°C. Also, the moisture levels for the 100-14 samples in the 50°C, 85% RH environment greatly exceeded moisture levels for similar samples in the 20°C, 85% RH environment. This increase in saturation level with temperature is most likely due to the reduction of interactions between water and polymer molecules as temperature increases to near $T_g.$ Note that the T_g of the 100-14 samples was measured to be approximately 56°C in the moisture-saturated state. This effect reduces the enthalpy required for a water molecule to move into free volume in the polymer network such that the saturation level increases sharply.

In contrast to the dependencies of the saturation level, the diffusivity, D, is generally independent of humidity level but extremely dependent on temperature. For the EPON 828-PACM 20 system, diffusivities for the room-temperature environments ranged between 4 imes 10⁻¹⁰ and 3 \times 10⁻⁹ cm²/s depending on stoichiometry. These values were the same within experimental error for both the 75 and 85% RH environments, indicating that D is not a function of humidity level for this system. For the 50°C environment, Dvalues were almost an order of magnitude higher than for the 20°C environments, ranging from 2 \times 10⁻⁹ to 8 \times 10⁻⁹ cm²/s. Note that the errors involved in calculating D are large for samples exhibiting non-Fickian diffusion, because choosing an appropriate saturation level is difficult. However, the relative differences in D between samples of different stoichiometry, presented in the next section, are still significant relative to the errors involved.

The Effect of Stoichiometry on Moisture Diffusion

The non-Fickian diffusion behavior appears to be restricted to certain stoichiometries and thus might be related to the two-phase microstructure. As discussed previously, the two microstructural phases could be characterized by entirely differ-



Figure 8 Moisture saturation levels, normalized with respect to the saturation levels of the stoichiometric samples, plotted as a function of amine content for each of the three conditioning environments. Each data point represents an average of two to four samples. Data scatter is on the order of the size of the symbols representing the average data.

ent diffusivities due to the large difference in crosslink density. The 100-50, 100-60, and 100-70 samples are composed of higher amounts of lowdensity phase and lower amounts of the microgel phase compared to samples with less amine content.^{14,40} Further, the size of microgel clusters decreases with decreasing amine content,9,14,40 thus increasing the surface area of the microgel phase. Therefore, as amine content decreases, moisture absorption into the microgel phase will become more important. For samples exhibiting non-Fickian behavior, the following two distinctly different diffusion processes could occur: first, moisture follows the path of least resistance through the low-density phase; second, moisture diffuses into microgels but at a much slower rate. For samples with relatively poor connectivity of the low-density phase, the diffusion process might depend more on the second process than for samples with good connectivity of the low-density phase. This explanation could account for the non-Fickian changes in absorption rate during diffusion in the 100-14, 100-20, 100-28, and 100-40 samples.

Changes in epoxy-amine stoichiometry significantly effect moisture saturation levels and diffusivities. For amine-rich samples, $M_{\rm sat}$ values increase monotonically with increasing amine content from 20 to 70 pph amine, as shown in Figure 8. Decreasing the amine content to 14 pph, however, did not cause a further decrease in saturation levels; but rather, $M_{\rm sat}$ values were higher for the 100-14 samples compared to the

100-20 samples. In one study, $M_{\rm sat}$ was observed to increase with decreasing density for stoichiometric samples cured for different times.⁴¹ However, this decrease in density is related to an increase in free volume caused by an increase in T_g with extent of cure but also corresponds to a decrease in the amount of the low-density phase with increasing extent of cure. In the present study, however, the variation in $M_{\rm sat}$ does not correspond directly to the variation in density with amine content. For samples that differ in composition, free volume will decrease and the amount of the low-density phase will increase as T_g decreases away from the stoichiometric point. Thus, the increase in $M_{\rm sat}$ with increasing amine content for amine-rich samples correlates with an increase in the amount of low-density material. However, as amine content decreases from 28 to 14 pph, the decrease in free volume apparently dominates from 28 to 20 pph amine, resulting in a decrease in $M_{\rm sat}$; from 20 to 14 pph amine, the increase in the content of the low-density phase again dominates, resulting in an increase in $M_{\rm sat}$.

The diffusivity values decreased with stoichiometry, as shown in Figure 9. The diffusivity is proportional to the initial slope of M versus $t^{1/2}$ divided by $M_{\rm sat}$, as given by equation 6. Therefore, this trend is partially a reflection of the increase in $M_{\rm sat}$ with stoichiometry. Although only two temperatures were used for these studies, Arrhenius relationships between diffusivity and temperature, given by equation 3, did reveal important trends. The coefficient values, D_0 , followed a similar variation to $M_{\rm sat}$ with amine content, decreasing from 14 to 20 pph and then increasing monotonically from 20 to 70 pph. Thus, D_0 appears to be dominated by changes in $M_{\rm sat}$.



Figure 9 Moisture diffusivity *D*, plotted as a function of amine content. Each data point represents an average of two to four samples.



Figure 10 Moisture permeability *P*, plotted as a function of amine content. Each data point represents an average of two to four samples.

The activation energies, A_0 , followed a much different trend. For the 100-14, 100-20, and 100-28 samples, $A_0/R = 2900 \pm 200$ K; for the 100-40, 100-50, and 100-60 samples, A_0/R = 3950 ± 100 K; and for the 100-70 samples, $A_0/R = 5000$ K. Thus, increasing temperature has a larger effect on moisture diffusivity for amine-rich samples than for epoxy-rich or stoichiometric samples. This result might be a direct function of the microstructure. As discussed previously, moisture diffusion in the epoxy-rich and stoichiometric samples, which are characterized by poor connectivity of the low-density phase, might depend more on diffusion through microgel regions than the amine-rich samples. Most likely, temperature will effect mobility in the low-density regions more than in the microgel regions. Thus, increasing temperature would have a larger effect on moisture diffusion in samples with higher contents of low-density material, as is observed.

For the room temperature environments, the permeability, P, which is the product of D and $M_{\rm sat}$ and is given by the slope of M versus $t^{1/2}$, did not change significantly with stoichiometry. This result is shown in Figure 10. At 50°C, the permeability of the 100-20 and 100-28 samples were lower than that of the amine-rich and 100-14 samples, but overall, the changes in P with stoichiometry are not large.

Desorption Studies

One sample of each stoichiometry exposed to each of the three conditioning environments was removed after 2500–3500 h of conditioning for desorption studies. These samples were placed in an oven at 50°C under vacuum for approximately 6 weeks. Several interesting trends have been observed. First, visible cracking occurred during the first 24 h of desorption in the 100-60 sample, which had been conditioned in the 50°C, 85% RH environment. This sample had exhibited non-Fickian diffusion, and the increase in moisture absorption rate for this sample as saturation was approached was similar to other samples that exhibited non-Fickian absorption. Unlike the other samples, however, a stable saturation level was eventually reached, and this saturation level was slightly higher than the other two 100-60 samples conditioned in the same environment. This type of non-Fickian diffusion anomaly has been linked to the development of microcracks in several polymer and polymer composite systems.^{25,42} Thus, some microcracking might have occurred due to some internal flaw in the sample, and during drying, these microcracks formed larger cracks that propagated through the material. No other samples have cracked during absorption or desorption of moisture.

Desorption rates at 50°C were consistent with absorption rates at 50°C. However, two of the samples did not reach the same dry weight, as was measured prior to immersion in humid environments. Both of these samples were epoxy-rich samples, one 100-14 and one 100-20, conditioned in the 50°C, 85% RH environments for approximately 2500 h. In the 100-14 sample, approximately 0.55 wt % of moisture remained after desorption, while for the 100-20 sample, 0.12 wt %of moisture did not desorb. The weights of all other samples returned to their original dry weight within ± 1 mg during these desorption studies. These results indicated that elevatedtemperature exposure to moisture of epoxy-rich samples could result in much stronger interactions between the unreacted epoxy molecules and the absorbed water molecules. Similar results have been observed for other systems.^{7,29}

Effects of Absorbed Moisture on Viscoelastic Response

For each of the stoichiometries, absorbed moisture reduced the T_g by 5 to 20°C, as shown in Figure 11. In general, the reductions in T_g appear to be larger for amine-rich samples than for epoxy-rich and stoichiometric samples. This result correlates with the increased effect of temperature on the diffusivity as measured by the activa-



Figure 11 Reduction in glass transition temperature T_g , due to moisture absorption as a function of stoichiometry.

tion energies, A_0 . The relatively small differences in moisture uptake between samples exposed to 75 and 85% RH environments apparently has a negligible effect on the reduction in T_g . Upon removal of the moisture, the T_g values returned to within $\pm 2^{\circ}$ C of initial dry values for all samples except the stoichiometric samples. For each of the stoichiometric samples, the final T_g values after desorption were 3-5°C higher than the original dry values. Thus, the reductions in T_g for these samples might be underestimated because of the possible occurrence of postcuring reactions during the initial DMA run. In any case, these results indicate that for each of the stoichiometries, absorbed moisture acts merely as a plasticizing agent. The reversibility of this effect indicates that no significant chemical interactions occur between water molecules and the reacted and unreacted epoxy-amine components. Thus, the minute amounts of moisture that could not be removed from samples during desorption are not significant enough to permanently alter the T_g .

The Effect of Stoichiometry on Moisture-Induced Swelling

After reaching moisture levels that were considered to be at or near saturation levels, length and width dimensions increased by 0.1-0.3 mm for the majority of the specimens. Original (dry) sample dimensions in length and width ranged from 36 to 54 mm for specimens used in the moisture-induced swelling studies. Thus, the measurement error of ± 0.01 mm translates into a 3-10% error in the measured dimensional change. Also, because of the significant variations in length and

width dimensions for each individual sample compared with these relatively small dimensional changes, the experimental scatter was quite large for each stoichiometry. Calculating the swelling strain as the change in length or width divided by the dry length or width, the observed dimensional changes result in swelling strains ranging from 0.1 to 0.6%. In general, swelling strains increased with moisture saturation level, as shown in Figure 12. Thus, the change in swelling strain as a function of stoichiometry was similar to the change in moisture saturation level with stoichiometry. Thus, the more moisture absorbed by the sample, the higher the swelling strain.

The moisture expansion coefficient, β , is defined as

$$\beta = \frac{\Delta l/l_0}{M_{\rm sat}} \tag{8}$$

where l_0 is the initial dry dimension, and Δl is the change in that dimension due to moisture absorption at saturation. In Figure 12, β is determined from a linear fit of the moisture-induced strain as a function of moisture level. In this figure, $M_{\rm sat}$ values are representative of the moisture levels at the time the dimensions were measured and, thus, should not be dependent on whether the moisture diffusion process was Fickian or non-Fickian. Because of the experimental scatter in the swelling measurements, β values did not show a clear trend for β as a function of stoichiometry. From Figure 12, a β value of 0.22 mm per mm per wt % appears to satisfactorily describe



Figure 12 Moisture-induced strain as a function of moisture saturation level. Data points shown are for individual samples of all the epoxy-amine compositions used in this study. The linear fit yielding β has a correlation coefficient of $R^2 = 0.91$.

CONCLUSIONS

The moisture diffusion process for the EPON 828-PACM 20 system is complicated by non-Fickian effects that were linked to microstructural differences. Amine-rich samples generally exhibited Fickian diffusion. Diffusion rates for epoxy-rich and stoichiometric samples changed during absorption such that Fickian diffusion was not obeyed. For these samples, a slow, steady increase in moisture level was observed after the initial linear increase of M(t) with $t^{1/2}$ such that a stable saturation level was not reached. These differences in diffusion behavior were related to the relative importance of diffusion through the low-density and high-density phases for the different stoichiometries. Increasing the humidity level only caused a corresponding increase in saturation level. Increasing the temperature, however, caused more pronounced non-Fickian behavior. Also, from Arrhenius relationships between temperature and diffusivity, activation energies for diffusion were observed to be higher for amine-rich samples than epoxy-rich and stoichiometric samples. These effects were related to the effects of temperature on the relative rates of diffusion through the low-density and high-density phases.

Saturation levels increased monotonically with increasing amine content from 20 to 70 pph amine but decreased from 20 to 14 pph amine. The competing effects of free volume and content of the low-density phase on the saturation level were used to explain this result. Diffusivity decreased monotonically with increasing amine content. From Arrhenius relationships between temperature and diffusivity, changes in the coefficient D_0 were dominated by changes in $M_{\rm sat}$, while activation energies increased in almost a quantized fashion with increasing amine content. Absorption rate or permeability P, given by the initial slope of the sorption curves or by the product of Dand $M_{\rm sat}$, was not significantly affected by changes in stoichiometry.

Because postcuring is not expected to effect the microstructure significantly, it should not have a significant effect on moisture diffusion. One exception might be the stoichiometric samples. For these samples, the T_g increases dramatically, increasing the free volume and, thus, the saturation

level. Also, the amount of soft phase will approach zero and the crosslink density will increase. This effect might cause a decrease in the diffusion coefficient because the holes in the network through which the moisture must move will be smaller; that is, the activation energy will increase. If the saturation level increases and the diffusivity decreases, then the permeability will remain relatively unchanged after postcuring.

Reductions in the glass transition temperature T_{σ} , due to moisture absorption and moisture-induced swelling strains, were measured after 3000-4000 h of exposure of samples to the three conditioning environments. These reductions in T_g ranged from 5 to 20°C and were generally larger for amine-rich samples than for epoxy-rich and stoichiometric samples. After desorption, T_g values returned to with $\pm 2^{\circ}$ C of their original dry values, except for stoichiometric samples for which values were consistently 3-5°C higher than initial dry values due to postcuring reactions occurring during the first DMA tests. Moisture-induced swelling strains increased with increasing moisture content. Because the dimensional changes were very small, significant error and scatter in the data prevented a correlation between swelling data and stoichiometry from being made. For the swelling coefficient, β , a value of 0.22 mm per mm per wt % adequately describes the EPON 828-PACM 20 system, regardless of stoichiometry.

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