

Relation of Swelling and T_g Depression to the Apparent Free Volume of a Particle-Filled, Epoxy-Based Adhesive

Martin Y. M. Chiang, Marta Fernandez-Garcia

Polymers Division, National Institute of Standards and Technology (NIST), Gaithersburg, Maryland 20899

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ABSTRACT: The effect of hygrothermal aging on a particle-filled, epoxy-based adhesive was studied using a gravimetric sorption technique. This study has explored moisture sorption characteristics as well as the associated behaviors of swelling and the depression of the glass transition temperature (T_g). We observed that the diffusion of water in this adhesive has a non-Fickian behavior, and the depression of T_g proceeds to a definite value that is independent of the final equilibrium water content of the system. Our observations suggest that water diffuses into the polymer in a dual-sorption mode, in which water resides in two populations. In one population, water is considered to occupy apparent free volume of the adhesive, and the second population

water infiltrates polymer structure and forms hydrogen-bonded clusters. Our results show that hygrothermal aging temperature and swelling do not alter the apparent free volume of this adhesive. We conclude that the constant value of T_g depression at saturation implies that only water in the apparent free volume is responsible for the T_g depression, whereas the swelling proceeds through the formation of hydrogen bonds in the adhesive. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 1436–1444, 2003

Key words: hygrothermal aging; swelling; glass transition temperature; absorption; particle; fillers; adhesive

INTRODUCTION

The mechanical properties of adhesives are of great interest in a variety of technological applications, including many in the construction, electronic packaging, aerospace, and automotive industries. The wider application of adhesive materials requires greater understanding of material performance and the ability to withstand environmental effects during long-term use.¹ This understanding involves the disciplines of polymer science and applied mechanics, where the former addresses effects on the microscopic level (moisture sorption characteristics) and the latter is related to the macroscopic level (mechanical response). This paper presents an investigation of sorption characteristics and measurements of swelling and the depression of the glass transition temperature (T_g) of a particle-filled, epoxy-based structural adhesive. The sorption, swelling, and T_g depression are related to the apparent free volume of adhesive. An understanding of such effects on the adhesive is clearly a

necessary step for correlating water uptake and the associated behaviors with mechanical performance.

Most epoxy-based commercial adhesives are formulated with fillers, which are employed to improve properties and reduce costs. However, most studies of adhesive materials exposed to moisture (such as measurements of mechanical and physical properties, sorption characteristics, and chemical degradation of adhesive) have concentrated on model epoxies and neglected the effect of fillers.^{2–7} Although those studies have provided useful insight, they still cannot represent a complete and proper picture of the effect of moisture on commercial particle-filled adhesives. In fact, including fillers in adhesives increases the difficulty in characterizing the moisture sorption and the degradation mechanisms of the adhesives. There are some reports in the literature investigating the mechanical performance of adhesive joints and effect of fillers on their durability.^{8–10} In Minford's report,⁸ a large number of adhesives were investigated and their shear strengths compared under equivalent conditions to determine effects of various test parameters (such as aggressive environments like seacoast and industrial atmospheres). The effect of moisture ingress on adhesively bonded joints were evaluated via stress relaxation and fracture analysis by Hand et al.⁹ Bowditch¹⁰ investigated the effect of water on the mechanical properties of a particle-filled adhesive itself and also the nature of the interface or interphase that exists between adhesive and substrate. Also, in his study, treated and untreated silica powders were used to fill

Correspondence to: M. Y. M. Chiang (martin.chiang@nist.gov).

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a model epoxy adhesive formulation to study the tensile strength after immersion in water. The current experimental investigation was undertaken to determine the effect of moisture on the structure and physical properties of a particle-filled adhesive used for structural bonding applications. Acquiring an unfilled version of the adhesive from the manufacturer was not possible; therefore, a comparative investigation could not be conducted in this study.

Many techniques are available for measuring water ingress in polymers.^{4,11–13} The present study utilized a gravimetric sorption technique to characterize the adhesive under hygrothermal aging (from 30 to 70°C) in distilled water. The results of this study suggest that the water uptake of this particle-filled and epoxy-based adhesive has a dual-sorption mode, in which water resides in two populations. One population of water is considered to occupy apparent free volume of the adhesive, and other one infiltrates polymer structure and forms hydrogen-bonded clusters. It also suggests that, for this adhesive, the moisture contained in the apparent free volume is the decisive factor for the depression of T_g , and that the swelling due to water uptake proceeds through the formation of hydrogen bonds in the adhesive. The hygrothermal aging temperature and swelling do not alter the apparent free volume of the adhesive system. Therefore, the depression of T_g proceeds to a definite value that is governed by the water fraction in the apparent free volume but not by the final equilibrium water content of the system.

MATERIALS AND EXPERIMENTS*

The adhesive used in this study is an epoxy-based one-part structural adhesive supplied by 3M Company (3M 5042) to fit the requirements of automotive vehicle body structure applications.¹⁴ The ingredients of the adhesive are listed in Table I. It is a one-component adhesive with good flame retardance, and is suited for weld-bonding applications. The manufacturer suggests that the minimum curing temperature for 5042 is 120°C, but that it can be cured within 20 min at temperatures from 150 to 205°C, though a longer time should be considered when the temperature is lower than the 150°C.

Adhesive films, nominally 300 μm thick, were produced by placing the adhesive between Teflon blocks. The blocks clamped with binder clips were cured under hydrostatic pressure in a vessel at 1.38 MPa (200

TABLE I
The Ingredients of the Adhesive

Ingredient	Mass fraction
Alumina trihydrate	0.1–0.2
Epoxy resin	0.1–0.2
Bisphenol A–epichlorohydrin copolymer	0.1–0.2
Methyl methacrylate–butadiene–styrene polymer	0.05–0.15
Barium metaborate	0.03–0.08
Dimethyl siloxane (reaction product with silica)	0.02–0.08
Dicyandiamide	0.01–0.05
Aluminum	0.01–0.05
Silica gel	0.01–0.05
Organo nickel complex	0.005–0.03

psi) and 130°C for 13 h. The samples were then slowly cooled to room temperature. Such a procedure enabled us to overcome the critical issue of preparing thin films with uniform thickness and no voids.¹⁵ The clamping pressure is much lower than the hydrostatic pressure. The specimen is quite thick (300 μm) compared to the polymer dimensions, therefore, it is unlikely that the specimen would possess any preference for molecular orientation under such condition (there is no confinement effect on molecular orientation). DSC experiments showed that the adhesive has a dry T_g of 86°C (the standard uncertainty for all the T_g measurements is about 3°C), and also showed that the long curing time (being much longer than recommended by the manufacturer) causes no alteration in chemical structure, such as degradation. After curing, the film was cut to dimensions of ca. 40 \times 6 \times 0.3 mm. The initial mass fraction of water in samples was less than 0.05% (the standard uncertainty is less than 0.01%), and their initial dimensions were obtained using electronic calipers.

Specimens were hygrothermally exposed in distilled water baths at constant temperatures of 30, 35, 40, 45, 50, and 70°C. Nominally, there were 150–200 specimens in each bath. The specimens were taken from the baths at different times (about 3–5 specimens per bath each time) for water uptake measurements. The water on the surface of specimens was removed by using a dry, clean paper towel. After removal from the water bath, the sample was not put back into the bath for subsequent mass uptake measurements. Therefore, the measurement at each time was a result of a continuous absorption process. The mass of each specimen was measured using an analytical balance (OHAUS Analytical Plus, measuring to 0.01 mg), and finally the mass uptake determined. The standard uncertainty of the mass fraction of water uptake measurement is 1×10^{-4} .

The linear swelling strain was calculated from measurements (with electronic calipers) of the length of the samples both before immersion and after saturation.

*Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology (NIST), nor does it imply that they are necessarily the best available for the purpose.

tion had been reached. In each sample, the length was determined from the average of three measurements at different locations across the specimen. It was assumed that the swelling was isotropic, so the volumetric swelling was taken to be three times the linear swelling. In order to avoid nonuniformity in swelling within the sample caused by concentration gradients during early stages of sorption, no measurement of the time-dependent (or moisture dependent) swelling were attempted. The uncertainty of the swelling measurement is about 0.02–0.03%.

Subsequently, the desorption process was conducted after saturation. About 40 specimens were left in each bath for these experiments. The specimens were dried at the initial aging temperature used in the absorption process. The drying process was continuously conducted in an oven at ambient pressure and humidity, and the mass of each specimen was periodically measured until reaching the apparent equilibrium value. Then, these dried specimens were taken for a reabsorption study. The detailed information on desorption and reabsorption is reported in a separate publication.¹⁶

Soxhlet extraction was used to collect residuals out of the adhesive samples. Water was used as the extraction solvent. These samples were hygrothermally treated by steaming at atmospheric pressure and a temperature near 100°C for several hours in the extractor. Fourier transform infrared (FTIR) spectra were recorded for the extracted substances using a Nicolet 550 spectrometer with KBr pellets. Subsequently, scanning electron microscopy (SEM) was performed on the adhesive sample that had been extracted.

RESULTS AND DISCUSSION

General characteristics of sorption

Results from the sorption experiments were plotted as mass uptake fraction ($\Delta M/M_o$, $\Delta M = M_t - M_o$) vs the square root of time ($t^{1/2}$), where M_t is the current and M_o is the original sample mass. Figure 1(a) shows results of mass uptake fraction history of the adhesive films submerged in a water bath at constant temperatures ranging from 30 to 70°C. Each point represents the average of 2–4 specimens; the standard uncertainty of the mass fraction of water measurement is about 0.01%. Figure 1(a) indicates that the diffusion rate is temperature dependent while the relationship between the time to reach the equilibrium value and temperature is not clear. Such an occurrence also was presented in a previous study on an epoxy-based adhesive containing fillers.¹⁷ The absorption observed in the current study was not accompanied by any visible damage to the material except color changes (whitening) in the case of 50 and 70°C.

It has been suggested that, for the behavior to be considered as linear Fickian diffusion, the plot of $\Delta M/$

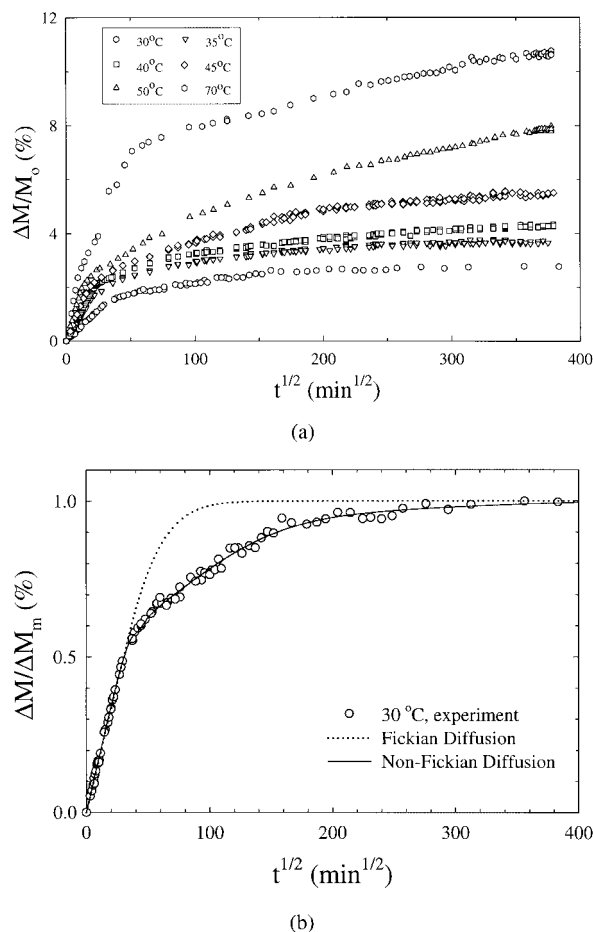


Figure 1 (a) Mass uptake history of the adhesive films submerged in a water bath at constant temperatures ranging from 30 to 70°C. (b) A typical reduced absorption plot at 30°C. The solid line is the fit to the experimental data based on a model for non-Fickian diffusion [eqs. (1) and (2)]. Dotted line is the fits of Fickian diffusion based on the saturation level from the experimental result.

ΔM_m against $t^{1/2}$ should be linear up to $\Delta M/\Delta M_m > 0.6$, where the ΔM_m is the mass uptake at equilibrium for the aging temperature considered.¹⁸ From a typical reduced sorption plot in Figure 1(b), it is noted that absorption data do not appear to follow Fickian diffusion (particularly at $\Delta M/\Delta M_m > 0.5$). The solid line is the fit to the experimental data based on a model, which is discussed later, for non-Fickian diffusion—an immediate high rate of water uptake, followed by a slow evolution toward an equilibrium value. The dotted line is the fit of Fickian diffusion based on the saturation level from the experimental results.

There are numerous physical and chemical mechanisms that are deemed responsible for non-Fickian transport kinetics. However, the departure from the linear Fickian behavior of this adhesive can be attributed to the inherent time-dependent response of polymers,¹⁹ or retardant water uptake process by the exis-

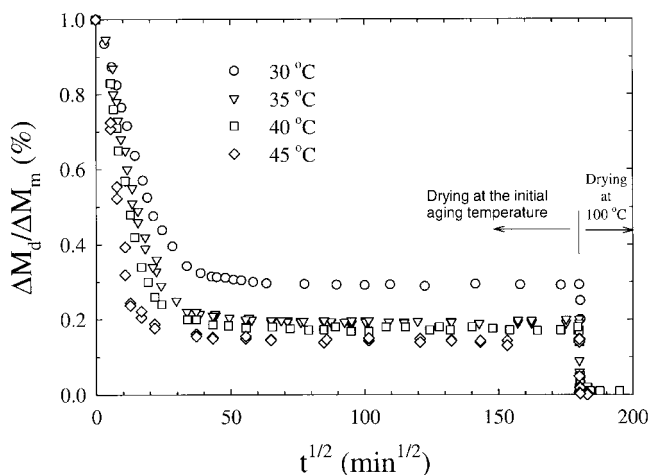


Figure 2 Fraction of mass change from desorption ($\Delta M_d / \Delta M_m$, $\Delta M_m = M_m - M_t$) vs the square root of time, t , where M_t is the current and M_m is the saturated mass, respectively.

tence of filler/matrix interface²⁰ or the voids in matrix.²¹ One way to model this non-Fickian diffusion is to use a time-dependent concentration boundary condition²²:

$$C(\pm l, t) = C_o + \sum_{i=1}^{\infty} C_i [1 - \exp(-\beta_i t)] \quad (1)$$

in the classic diffusion equation:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} \quad (2)$$

where C is moisture content at time t , C_o is the instantaneous concentration, and the summation is the concentration contributed by retardation processes. The t is the time, β_i constants associated with material retardation time, z the coordinate through the thickness of the adhesive film, l the half thickness of the adhesive film, and D the diffusion coefficient. Upon integration of the distribution of moisture content across the thickness due to the boundary condition, eq. (1),

the total mass uptake is obtained. This model retains a constant diffusion coefficient, and the non-Fickian aspect is contributed from the time-dependent concentration boundary condition. Since the adhesive structure is assumed to be macroscopically homogeneous and isotropic, and the equilibrium levels of sorption in the polymer solid are low relative to the volume of polymer at hygrothermal aging temperature below 50°C, it has been assumed that the diffusion coefficient is independent of water concentration in the adhesive.

The desorption results for specimens tested at aging temperatures of 30, 35, 40, and 45°C are presented in Figure 2. Desorption was not measured for the 50 and 70°C specimens because the equilibrium moisture content had not been reached in over three months. The kinetics of the desorption at the temperatures studied follows Fickian behavior. After drying to an equilibrium value at the initial aging temperature (up to 540 h), the specimens still retained a small amount of water (Table II). Subsequently, after further drying near 100°C in an oven at ambient pressure and humidity for a few hours, a negligible amount of water mass was retained by each specimen. This suggests that some of the water may be bound more strongly by adhesive components than other water molecules. Based on the results in Figure 2, the amount of this bond water that interacts with the epoxy is about a mass fraction of 0.72% (see Table II; note that data in Figure 2 are normalized by the maximum mass uptake).

Figure 3 displays the variation of saturated moisture content and diffusivity of moisture in the adhesive corresponding to different hygrothermal aging temperatures. Shen and Springer²³ mentioned that the water saturation value attained in a resin they studied depends significantly on the relative humidity of its environment, but is essentially insensitive to the temperature. In their study, the temperature only affects the kinetics of water uptake. Conversely, the maximum water content measured for the adhesive studied here increases markedly with increasing temperature (Table II). This increase has been also observed in neat epoxy-based resins,^{24,25} and it could be a result of

TABLE II
Water Content at Different Hygrothermal Temperatures

Hygrothermal aging temperature (°C)	Water content		
	Absorption, volume fraction, % (at saturation)	Water not participating the depression of T_g (i.e., subtracting the apparent free volume fraction, 2.03%, from the absorption)	Remaining mass fraction after desorption at hygrothermal aging temperature
30	3.08	1.05	0.76
35	4.07	2.04	0.72
40	4.79	2.76	0.72
45	5.96	3.93	0.72

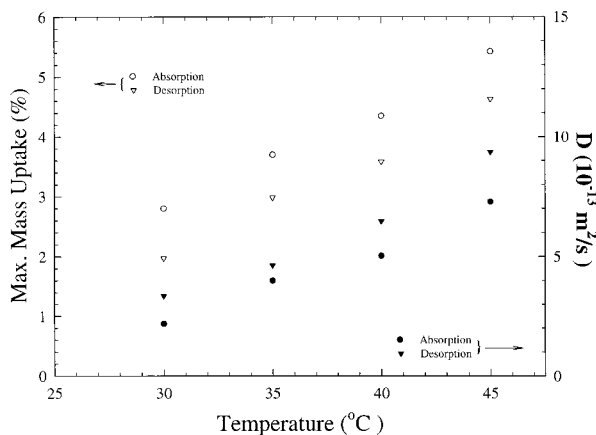


Figure 3 The variation of saturated moisture content and diffusivity of the adhesive corresponding to different hygrothermal aging temperatures.

polymer structure relaxation caused by swelling stress, shift in the glass transition temperature, or water interacting with fillers in the adhesive.

Table III lists the activation energy obtained from the Arrhenius relationship, $D = D_0 \exp(-E/RT)$ based on the diffusivity of different hygrothermal aging temperatures, where D_0 is a permeability index, E the activation energy, R the universal gas constant, and T the temperature. It seems to have a good agreement with results (from 43.1 to 59.8 kJ/mol) reported for some neat epoxy resins.²⁶

Swelling and apparent free volume

Results comparing the swelling of samples to the volume of water uptake at different aging temperatures are presented in Figure 4. The relative volume increase ($\Delta V/V_0$) due to swelling is plotted vs the volume fraction of water uptake, as calculated from the measured mass gain. Data are shown for saturation (or for maximum mass uptake for 50 and 70 °C). Each point corresponds to a specific aging temperature studied. The dotted line is the curve fit to experimental results not including 50 and 70°C. Also, it was observed that the swelling approached equilibrium with that of water uptake. The general behavior is similar to that observed by other authors,²⁷ in that the swelling volume of the resin is less than the volume of water uptake—the latter being indicated in Figure 4 by a solid line with slope 1.0 (based on the ideal mixing

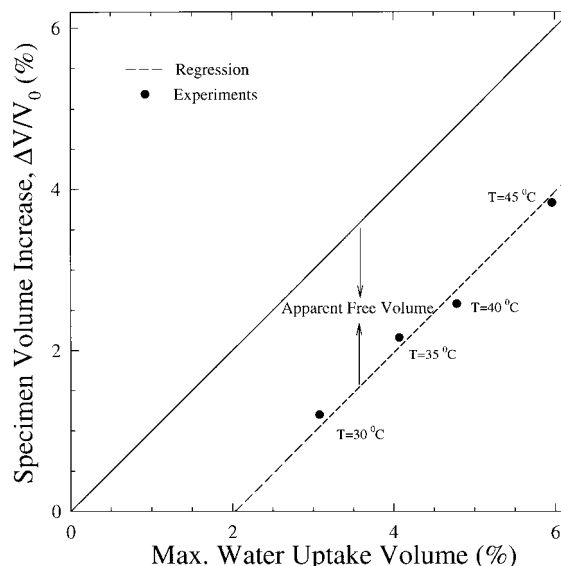


Figure 4 The volume increase of sample (swelling) vs the volume of water uptake at different hygrothermal aging temperatures. Experimental data (symbols) are shown for saturation. Dotted line is the curve fit to the data not including 50 and 70°C. Solid line with slope 1.0 is based on ideal mixing law.

law). Various researchers^{2,28} have suggested that water molecules can exist in the polymer in either of two states (dual mode). In one state, water molecules fill the apparent free volume that is present in the polymer in the dry state and are relatively mobile within the apparent free volume voids. Since the water fills volume that already exists, it does not cause swelling. In the second state, water infiltrates the polymer molecular structure through hydrogen bonding, becomes immobilized, and causes to swelling. Accordingly, in this study the difference between the solid and dotted lines in Figure 4 represents the amount of apparent

TABLE III
Activation Energy

Process condition	Activation energy (kJ/mol)	Diffusion coefficient at infinite temperature, D_0 ($10^{-3} \text{ m}^2/\text{s}$)
Absorption	59 ± 4	1.30
Desorption	56 ± 2	3.85

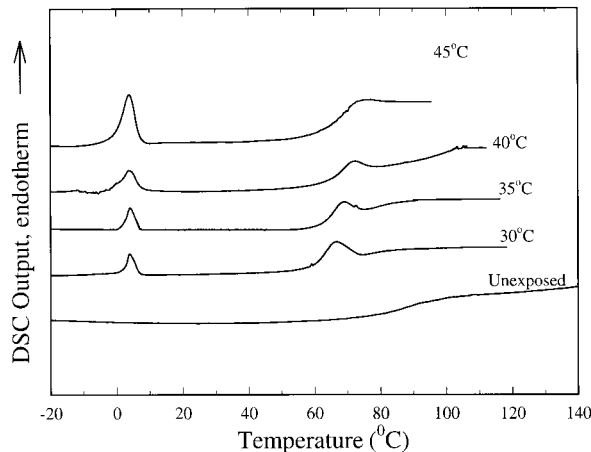


Figure 5 DSC output for saturated samples at different hygrothermal aging temperatures. The lowest curve represents the output of dry sample.

TABLE IV
Glass Transition Temperature

Bath temperature (°C)	T_g (°C)		
	Saturated (measured at 2000 h after the immersion)	Desorption at hygrothermal aging temperature	Desorption at 100°C
30	64.0	75.8	89.7
35	62.2	77.7	87.9
40	62.7	76.2	86.0
45	64.5	77.9	86.8

^a Dry T_g (Unexposed) = 86.1°C (Fig. 5).

free volume probed by the water molecules at the indicated hygrothermal aging temperature.

From Figure 4, a linear relationship (dotted line) between the swelling of sample at saturation and the amount of water uptake at saturation is noted. Also, the two lines (solid and dotted lines) are parallel. This indicates that the apparent free volume fraction occupied by the water in this adhesive remains constant at 2.03% (with standard uncertainty 0.06%) for the aging temperatures discussed ($T < 45^\circ\text{C}$). The finding of this constant fraction (percentage) implies that the swelling of the adhesive at the aging temperatures discussed may have negligible effect on the change of apparent free volume. Or, conversely, during the swelling, the volumetric changes of the occupied volume and the rearrangement of the polymer network occur simultaneously. Furthermore, it is worthwhile to note that after drying to equilibrium at the initial aging temperature (see Fig. 2), a reversible swelling (no net increase in volume) was observed. This suggests that the water retained after drying was held in the apparent free volume of the adhesive.

Depression of T_g

Figure 5 shows the investigation of T_g by DSC for saturated samples at different hygrothermal aging temperatures. In all cases, samples were heated after cooling them to -40°C with a constant cooling and heating rate of $10^\circ\text{C}/\text{min}$. The T_g is defined in this work as the midpoint of the transition of DSC output at temperatures between 60 and 80°C in Figure 5. The lowest curve in Figure 5 represents the output of a dry sample. The transition of curves near 4°C indicates water that melted near 0°C and did not participate in the depression of T_g .²⁸ In other words, the transition can be attributed to the melting of ice formed from clustered water in the sample during the cooling below freezing point, and the unclustered water participated in the depression of T_g . We believe this formation of clustering is associated to hydrogen bonds of water with fillers (debonding at matrix–filler interfaces in wet environment). A previous study¹⁸ shows that bonds between epoxies and some fillers used in

this adhesive system (such as silica and aluminum) are thermodynamically unstable in the presence of water, and that water is capable of displacing adhesive from fillers. This interfacial debonding between adhesive and fillers may act as a nucleus for the formation of hydrogen-bonded cluster. Furthermore, it is anticipated that the clustered water can be more easily desorbed than that trapped in the apparent free volume of the system. Therefore, the diffusivity of water desorption is higher than that of the absorption for the adhesive studied. However, this dual-mode absorption process is quite different from what was reported on an epoxy-based resin,¹² where the water was mainly dispersed on a molecular basis rather than aggregated into regions to form clusters. The major difference is that fillers were involved in this study.

The T_g depression of the adhesive is listed in Table IV. It is noted from the table that after drying samples at 100°C for a few hours; the T_g recovered to its original value. This implies that the process below 50°C is reversible; consequently, the T_g depression should be attributed to the plasticizing effect of water on T_g . For the 50 and 70°C cases, where the material leaching was involved, the DSC analyses have not been performed at this moment. Within experimental uncertainty the depressed T_g seems independent of the saturation amount of water uptake. However, in previous stud-

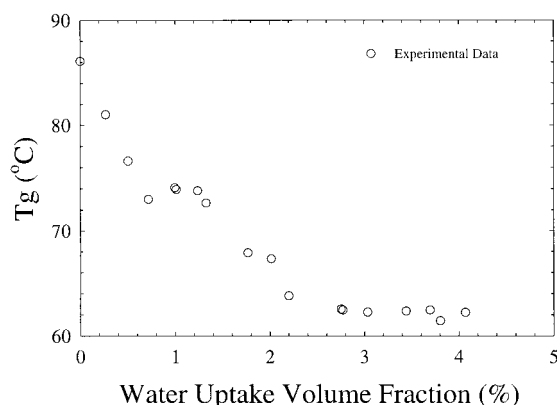


Figure 6 The T_g depression vs progressive water uptake for the sample under a hygrothermal aging of 35°C .

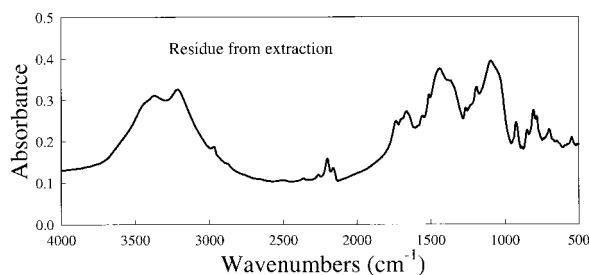


Figure 7 FTIR spectra of the materials extracted from the adhesive sample.

ies on the water-induced plasticization of epoxy,^{30,31} the depression of T_g was found increasingly dependent on the saturation amount. In the study of McKague, Jr., et al.,³⁰ a neat Narmco 5208 epoxy resin was used. A high performance epoxy resin ($T_g > 200^\circ\text{C}$) based on a tetrafunctional epoxy monomer cured with an aromatic diamine was investigated by Moy and Karasz.³¹

In this study, the independence of T_g depression on saturation amount demonstrates the plasticizer (water) acts as a poor solvent of the adhesive; only a limited amount of water participates in the change of the macromolecular structure. Such a plasticizer is known as an interstructural plasticizer.³² It is characterized by a drop in T_g to a definite value; a further introduction of the plasticizer does not affect the position of T_g . It also can be shown that the ratios of the area under the peak near 4°C in Fig. 5 are almost identical to the ratios of the third column in Table II (i.e., 1.05 : 2.04 : 2.76 : 3.93; the column lists the difference between the saturation and the apparent free volume fractions of the adhesive). In other words, the water melting in the DSC trace is comparable to the relative volume increase less the apparent free volume fraction. This implies that only water in the apparent free volume affects the mobility of chains and increases chain flexibility, while the rest of the water is not associated with the depression of T_g . Since the macroscopic swelling does not alter the apparent free volume fraction of the adhesive, the T_g depression at

saturation is not only independent of aging temperature and saturation level, but also swelling.

The data in the fourth column of Table II and the third column of Table IV represent the water content remaining in samples, and the T_g values from DSC analysis, respectively, after drying the samples to an equilibrium stage at an initial aging temperature. In these cases, the water remaining in the adhesive seems to have a constant volume fraction for the aging temperatures considered (i.e., $\approx 0.72\%$ for $30\text{--}45^\circ\text{C}$), and the T_g has recovered to a nearly constant value (i.e., $\approx 76^\circ\text{C}$). Also, the peak near 4°C in DSC output has vanished (not shown in this report), which indicates that water remaining in the adhesive system has fully participated in the depression of T_g . Therefore, from a previous argument that only the water in apparent free volume should be taken into account for the plasticization process, i.e., water remains in the apparent free volume after drying.

Figure 6 shows the T_g change of the adhesive due to progressive water uptake during hygrothermal aging at 35°C . It can be seen from the figure that experimentally the T_g has been depressed to around 64°C at the water uptake volume fraction of about 2%, which is nearly equal to the apparent free volume fraction of the adhesive (2.03%) probed in this study, and no further depression in subsequent water uptake was observed. This result provides the evidence to support our previous statement that only the water contained in the apparent free volume affects the mobility of polymer chains and increases chain flexibility, while the rest of the absorbed water is not associated with the depression of T_g .

Extraction, FTIR, and SEM

Figure 7 presents the FTIR spectra for the materials extracted from the adhesive samples. With Table V, the result indicates that at higher aging temperatures (50°C and above) silica gel and the dicyandiamide (curing agent) were leaching from the specimen. The loss of dicyandiamide may be attributed

TABLE V
Infrared Absorptions Reported in the Range of Wavenumbers from 550 to 3800 cm^{-1}

Region (cm^{-1})	Peaks (cm^{-1})	Chemical groups
3800–2800	3400	Si—O stretching vibration (silica)
	3370, 3200	NH ₂ stretching vibration (dicyandiamide)
2300–2100	2270, 2200, 2160	C/N stretching vibration (dicyandiamide) multiple bands (due to resonance)
2000–950	1730	C=O stretching
	1660	NH ₂ scissors deformation (dicyandiamide)
	1570	C=N scissors deformation (dicyandiamide)
	1440	CH ₃ —, CH ₂ — (methylmethacrylate–butadiene–styrene polymer, dimethylsiloxane, organo nickel complex), B—O (barium metaborate)
	1090	Si—O—Si rocking (silica and dimethylsiloxane)
950–550	925	NH ₂ wagging (dicyandiamide)

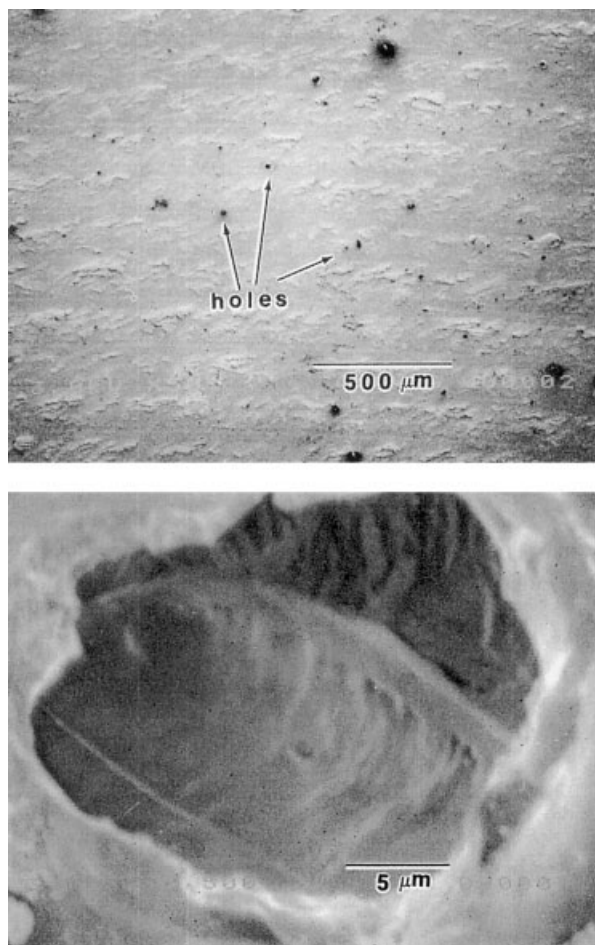


Figure 8 SEM photographs of the extracted adhesive specimen.

to the excess of the curing agent left in the adhesive. Based on the similarity in the whitening characteristics between the extracted material and the hygrothermal aging specimens (50 and 70°C), it is possible that dicyandiamide and fillers leached from samples aged at 50 and 70°C. Subsequently, the water replaced the space that used to be occupied by the silica gel. The density of silica is 2.2 g/cm³ (137 pounds per cubic foot), but the porosity of silica gels makes their density less than the density of water; a common commercial form has a bulk density of about 0.7 g/cm³. Therefore, instead of seeing a net mass loss in the case of material leaching for samples aged at 50 and 70°C, a continuous increase in the net mass of specimen at lower pace has been noted [Fig. 1(a)]. Consequently, the mass uptake for these samples cannot reach equilibrium for the time studied. Figure 8 shows typical SEM photographs of these specimens being dried after extraction. Holes were observed on the sample surface consistent with leaching materials recovered, which appeared to be particle fillers. The result provides further evidence to support the leaching of materials at higher hygrothermal aging temperatures ($\geq 50^\circ\text{C}$).

CONCLUSIONS

The diffusion of water into this epoxy-based, particle-filled adhesive does not follow a Fickian process, but the desorption is Fickian. The classic diffusion equation with a time-dependent concentration boundary condition seems adequate for modeling the non-Fickian aspect of the water uptake process. This work suggests the water uptake of the adhesive has a dual sorption mode. This dual mode segregates the water into two populations. One population of water is considered to occupy the apparent free volume of the adhesive, and the second population forms a hydrogen-bonded water cluster in the adhesive.

We observed that the hygrothermal aging temperature and swelling does not alter the apparent free volume of the adhesive system, and the depression of T_g proceeds to a definite value. We were able to relate the swelling and T_g depression to water associated with the apparent free volume of the adhesive. The study suggests that the water in the apparent free volume is the decisive factor for the depression of T_g but not the final equilibrium water content of the system, and the swelling due to water uptake proceeds through the formation of hydrogen bonds in the adhesive. The increase of saturated water content for different hygrothermal aging temperatures is not correlated to the T_g depression. Results presented here may be useful to further develop our understanding of water interaction processes in particle-filled adhesives, and develop a theoretical model for the depression of T_g . Finally, it is concluded that the hygrothermal aging of this particle-filled structural adhesive leads only to reversible plasticization of the polymer and does not cause any chemical degradation at the aging temperatures studied.

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References

1. Chiang, M. Y. M.; McKenna, G. B. *J Res Natl Inst Stand Technol* 1996, 101, 803.
2. Adamson, M. J. *J Mater Sci* 1980, 15, 1736.
3. Apicella, A.; Tessieri, R.; De Cataldis, C. *J Membr Sci* 1984, 18, 211.
4. X. W.; Luo, Yun, Z. Y.; Li, S. J. *Macromol Rapid Comm* 1995, 16, 941.
5. Chin, J. W.; Nguyen, T.; Aouadi, K. J. *Compos Tech Res* 1997, 19, 205.
6. Xiao, G. Z.; Shanahan, M. E. R. *J Polym Sci Polym Phys* 1997, 35, 2659.

7. Xiao, G. Z.; Delamar, M.; Shanahan, M. E. R. *J Appl Polym Sci* 1997, 65, 449.
8. Minford, J. D. In *Treatise on Adhesion and Adhesives*; Patrick, R. L., Ed.; Marcel Dekker: New York, 1973; Vol 3, Chap 2.
9. Hand, H. M.; Arah, C. O.; McNamara, D. K.; Mecklenburg, M. F. *Int J Adhesion Adhesives* 1991, 11, 15.
10. Bowditch, M. R. *Int J Adhesion Adhesives* 1995, 16, 73.
11. Saenger, K. L.; Tong, H. M. *Polym Eng Sci* 1991, 31, 432.
12. Schadt, R. J.; VanderHart, D. L. *Macromolecules* 1995, 28, 3416.
13. Nguyen, T.; Bentz, D.; Byrd, E. *J Coat Technol* 1995, 67, 37.
14. Yorkgitis, E. M.; Marhevka, V. *Proc International Body Eng Conference* 1994, 3.
15. Han, W. H.; Purohit, V.; McKenna, G. B. *Proc Twenty-Fifth North American Thermal Analysis Society Conference* 1997, 382.
16. Fernandez-Garcia, M.; Chiang, M.Y. M. *J Appl Polym Sci* 2002, 84, 1581.
17. De Neve, B.; Shanahan, M. E. R. *J. Adhesion* 1995, 49, 165.
18. Kinloch, A. J., Ed. *Durability of Structural Adhesives*; Applied Science Publishers: England, 1983.
19. Weitsman, Y. *J Phys Chem* 1990, 94, 961.
20. K. P.; Hoh, H.; Ishida, Koenig, J. L. *Polym Comp* 1990, 11, 192.
21. Carfagna, C.; Apicella, A. *J Appl Polym Sci* 1983, 28, 2881.
22. Cai, L. W.; Weitsman, Y. *J Comp Mater* 1994, 28, 130.
23. Shen, C. H.; Springer, G. S. *J Comp Mater* 1976, 10, 2.
24. Schultheisz, C. R.; Schutte, C. L.; McDonough, W. G.; Macturk, K. S.; McAuliffe, M.; Kondagunta, S.; Hunston, D. L. In *Fiber, Matrix, and Interface Properties*; Spragg, C. J., Drzal, L., Eds.; ASTM STP 1290; 1996; p 103.
25. Xiao, G. Z.; Delamar, M.; Shanahan, M. E. R. *Polymer* 1998, 39, 3253.
26. Deiasi, R.; Whiteside, J. B. In *Advanced Composites Materials—Environmental Effects*; Vinson, J. R., Ed.; ASTM STP 658; 1978; p 2.
27. El-Sa'Ad, L.; Darby, M. I.; Yates, B. *J Mater Sci* 1989, 24, 1653.
28. Chang, Y. J.; Chen, C. T.; Tobolsky, A. V. *J Polym Sci: Polym Phys Ed* 1974, 12, 1.
29. Johnson, G. E.; Bair, H. E.; Anderson, E. W. In *Corrosion Control by Organic Coating*; Leidheiser, H., Jr., Ed.; National Association of Corrosion Engineers: Houston, TX, 1981.
30. McKague, E. L., Jr.; Reynold, J. D.; Halkias, J. E. *J Appl Polym Sci* 1978, 22, 1643.
31. Moy, P.; Karasz, F. E. in *ACS Symposium Series 127 (Water in Polymers)*, S. P. Rowland, Ed. , American Chemical Society: Washington, DC, 1980.
32. Tager, A. *Physical Chemistry of Polymers, English Translation*, 2nd ed.; Mir Publishers: Moscow, 1978.