

Effect of Hygrothermal Aging History on Sorption Process, Swelling, and Glass Transition Temperature in a Particle-Filled Epoxy-Based Adhesive

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ABSTRACT: The effects of hygrothermal aging history and initial water content on sorption behavior and the physical properties of a commercial particle-filled epoxy-based adhesive were studied by the analysis of the water reabsorption process. ATR-FTIR analysis was performed to characterize the hydrogen bond interactions among the water and either resin or fillers. Swelling behavior and the depression of the glass transition temperature (T_g) under different hygrothermal aging histories were related to the water in the apparent free volume of the adhesive. The results show that the water diffusion of the adhesive is a non-Fickian process. It is also observed that swelling (which is reversible and consistent with hydrogen bond formation) and the rate of diffusion are not only dependent on the hygrothermal temperature but also the hygrothermal history. In addition, the swelling observed on the reabsorption process does not alter the apparent free volume of this adhesive system, and T_g depression is independent of the final equilibrium water content of the system. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 1581–1591, 2002; DOI 10.1002/app.10447

Key words: hygrothermal aging history; epoxy resin; reabsorption

INTRODUCTION

The excellent mechanical properties of epoxy resins have led to their use as adhesives for structural bonding applications. However, the durability of adhesives can be affected by environmental exposure. Humidity, ionic contaminants, and temperature are all factors for degradation of structural bonding.^{1–3} Water absorption and exposure to other environments degrade the mechanical strength and physical properties of the adhesives. The degradation may be strongly af-

ected by the presence and nature of fillers within the adhesives, because the filler–resin interface can be preferentially attacked by a particular environmental agent. Therefore, a knowledge of the behavior of adhesives under adverse conditions is necessary to predict their long-term performance. This work continues the investigation of a preliminary study⁴ on the water sorption characteristics and measurements of swelling and the depression of the glass transition temperature (T_g) of a particle-filled epoxy-based structural adhesive. In the present study, a cycle of water absorption/desorption/reabsorption (ADR) in a commercial adhesive has been conducted to mimic environmental exposure in typical applications. Consequently, the absorption of water by adhesives will generally not reach the saturation level, nor is desorption completed to the fully dry condition.

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Although the mechanisms of diffusion of water into neat or filled polymer resins are still not completely understood, the problem is even more complex when the material is subjected to several water exposure cycles (ADR cycles). It has been found⁵ in unsaturated polyester, vinyl ester, and acrylic resins that the diffusion coefficients, D , calculated for absorption were much higher than those for desorption and reabsorption, because the D of absorption was calculated using the "observed water content," which was lower than the "true water content." Lee and Knaebel⁶ performed experiments on fluoropolymers exposed to toluene and benzene solutions. Their results show that the diffusion coefficient in repeatedly exposed specimen appears to be consistently smaller than that of fresh samples. However, in a study of methanol diffusion into poly(methyl methacrylate), Grinsted and Koenig⁷ found that the diffusivity increased with the number of cycles. All these investigations have been generally performed in neat resins (thermosets) or polymers (thermoplastics) without consideration of fillers. There are also some studies on the effect of hygrothermal cycles on the viscoelastic response of polymeric composites,^{8,9} but the cycle effect on the diffusion of moisture into the material was not analyzed.

This work attempts to give some insight to the ADR behavior of a particle-filled epoxy-based commercial adhesive. The gravimetric technique was used to characterize the sorption under hygrothermal aging. Fourier transform infrared (FTIR) spectra were recorded for a qualitative analysis of water sorption as well as hydrogen bond interactions among the water and either resin or fillers. Two reabsorption processes have been performed with different hygrothermal histories and levels of initial water content in the adhesive. The effects of hygrothermal aging history and initial water content on the structure and physical properties were examined. In addition, the relation of swelling and T_g depression to the apparent free volume under ADR conditions was investigated.

MATERIAL AND EXPERIMENTAL PROCEDURES*

The adhesive used in this study is an epoxy-based structural adhesive to fit the requirements of au-

*Certain commercial materials and equipments 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.

Table I Components of the Adhesive as Given by Manufacturer

Ingredient	Percent (wt)
Alumina trihydrate	10–20
Epoxy resin	10–20
Bisphenol A–epichlorohydrin copolymer	10–20
Methyl methacrylate–butadiene–styrene polymer	5–15
Barium Metaborate	3–8
Dimethyl siloxane (reaction product with silica)	2–8
Dicyandiamide	1–5
Aluminum	1–5
Silica gel	1–5
Organo nickel complex	0.5–3

tomotive vehicle structure applications.¹⁰ It was supplied by the 3M Company (3M 5042). The components of the adhesive are presented in the Table I. Adhesive films, nominally 300 μm thick, were obtained by curing the adhesive between Teflon blocks in a pressure vessel at 130°C and at 1.38MPa (200 psi) for 13 h. The samples were then slowly cooled to room temperature. Such a protocol enables us to overcome the essential achievement of preparing thin films with uniform thickness and less voids. After curing, the film was cut to dimensions of ca. 40 \times 6 \times 0.3 mm. Specimens were then dried to an equilibrium state in a vacuum oven at 60°C. The mass of each specimen was measured using an analytical balance (OHAUS Analytical Plus, measuring ± 0.01 mg). Measurements showed that the initial mass fraction of water in the samples was less than 0.05%, the standard uncertainty being 0.01%.

Specimens were initially hygrothermally exposed in distilled water baths at different constant temperatures: 30, 35, 40, and 45°C. Nominally, there were from 150 to 200 specimens in each bath. Specimens were taken out from the baths at different times (about three to five specimens per temperature bath each time). Water on the surface of specimens was taken off by using a dry clean paper towel, and then the mass uptake was determined. Samples were not put back into the bath for subsequent mass uptake measurements after their removal from the water bath. Therefore, the measurement at each time was a result of a continuous absorption process.

The desorption process was conducted after saturation. About 40 specimens were left in each

bath for these experiments. Desorption process was continuously carried out in an oven at ambient pressure and humidity. The specimens were dried at the initial aging temperature used in the absorption process. The mass of each specimen was periodically measured until reaching the final equilibrium state.

In the current study two reabsorption procedures were adopted. The first one, named as Case A, was applied after the removal of specimens (hygrothermally exposed in distilled water baths at 30, 35, 40, and 45°C, as mentioned above) from the baths at different times and subsequent desorption. The desorption (drying) procedure was conducted as commented in the previous paragraph. By only drying the specimen at the initial hygrothermal aging temperature, water could not be completely taken out. Consequently, a small amount of water was retained in each specimen. Subsequently, these specimens with remaining "initial" water content were placed back into the distilled water bath for the reabsorption process at the same aging temperature than their former absorption and desorption processes. The initial water content depends on the hygrothermal absorption aging time. During this reabsorption process, specimens were taken out from the bath for water uptake measurements at the same time used in the absorption process.

The second procedure, called Case B, was conducted on specimens that were completely dried after reaching saturation in the absorption process. These specimens were continuously exposed in distilled water baths at constant temperatures of 30, 35, 40, and 45°C during the absorption process. After specimens were saturated, they were completely dried in a vacuum oven at 60°C. Afterwards, the specimens with zero water content were put back into distilled water baths at the same temperature used in absorption procedure for reabsorption. During the reabsorption procedure, specimens of Case B were taken periodically from the bath for water uptake measurements, and then returned to the bath for subsequent mass uptake measurements.

Glass transition temperatures were measured using a Differential Scanning Calorimeter, Perkin-Elmer DSC/TA7DX, PC series with an Intracooler. Samples (~10 mg) were weighed and quenched from room temperature at the maximum cooling rate to -40°C and then scanned at 10°C/min under dry nitrogen (20 cm³/min). The T_g values are an average for several measurements.

DSC measurements showed that the dried adhesive has a T_g of 86°C (the standard uncertainty for all the T_g measurements is about 1°C), and also showed that the long curing time (being much longer than recommended by the manufacturer) causes no alteration, such as degradation, in chemical structure.

The linear swelling strain was calculated from measurements (with electronic calipers) of sample length, both performed before immersion and after saturation was 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 strain was taken to be three times the linear swelling strain. To avoid potential problems arising from 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 was attempted. The uncertainty of the swelling strain measurement is about 0.02 to 0.03%.

To elucidate chemical changes in adhesive structure due to the water uptake, Fourier transform infrared (FTIR) analysis was used with attenuated total reflection (ATR) technique. The FTIR spectra were recorded from 4000 to 650 cm⁻¹ using a Nicolet 550 spectrometer. The ATR accessory used a KSR-5 substrate at 45°.

RESULTS AND DISCUSSIONS

Sorption Processes

Some results from a previous study⁴ of the absorption and desorption processes for this epoxy-based adhesive are presented in Figures 1 and 2. Results from the sorption experiments are plotted in Figure 1 as mass fraction of water absorbed ($\Delta M/M_o$, $\Delta M = M_t - M_o$) vs. the square root of time ($t^{1/2}$), where M_t is the mass at time t , and M_o is the original sample mass, respectively. Each point represents the average of three to five specimens. The standard uncertainty of the mass fraction of water measurement is 1×10^{-4} . It has been established that for considering a diffusion behavior as linear Fickian diffusion, the plot of $\Delta M/M_m$ against $t^{1/2}$ has to be linear up to values of $\Delta M/M_m$ equal to 0.6 or higher, where the M_m is the maximum mass uptake at the aging temperature considered.¹¹ Reduced sorption plots in the previous study showed that water absorption in

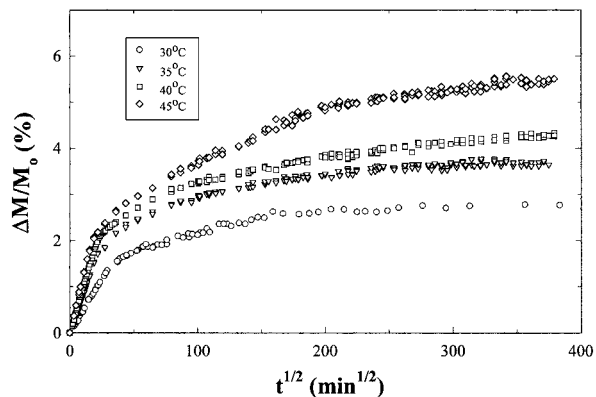


Figure 1 Mass uptake history of the adhesive films submerged in a water bath at constant temperatures ranging from 30 to 45°C.

this adhesive does not follow the prediction of linear Fickian diffusion. There are numerous physical and chemical mechanisms that could be considered responsible for non-Fickian transport kinetics. In the present work the observed deviations have been attributed to the well-known time-dependent viscoelastic response of polymers¹² as well as the retardant moisture uptake process produced by the presence of fillers/matrix interphase.¹³

The desorption results for saturated specimens tested at aging temperatures of 30, 35, 40, and 45°C are presented in Figure 2. The kinetics of desorption process at the temperatures studied follow a Fickian behavior. After drying to an equilibrium value at the initial aging temperature (up to 540 h), the specimens still retain a small amount of water. Subsequently, after a further

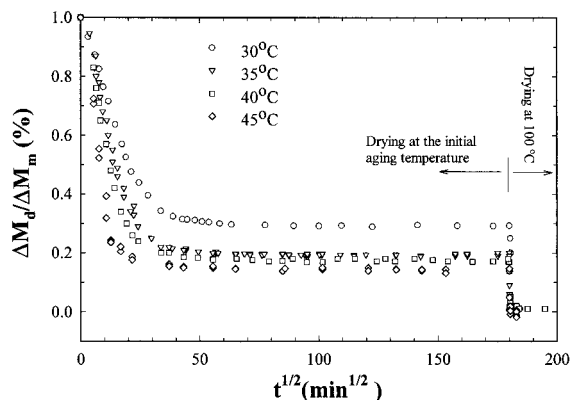


Figure 2 Fraction of mass change during desorption process ($\Delta M_d/\Delta M_m$, $\Delta M_d = M_m - M_t$) vs. the square root of time.

drying at 100°C in an oven at ambient pressure and humidity for another 100 h, a negligible amount of water was retained by each specimen. This feature suggests that some amount of the water originates strong interactions with adhesive components. It is also possible that voids might exist in the deteriorated (or disrupted) resin–filler interface after the absorption process, and such voids may retain some water. However, VanderHart et al.¹⁴ in a study of a filled resin by NMR concluded that water prefers the resin over the voids.

Figure 3 shows the ATR-FTIR spectra of unexposed and hygrothermally aged specimens (at 35 and 45°C). The band assignments of the spectra are listed in Table II. A quantitative measurement of the amount of absorbed water in the adhesive by ATR-FTIR requires a reference band, which has to remain unaffected by water uptake. However, none of the bands could be used as a reference for quantitative determination of the water uptake with the possible exception of the

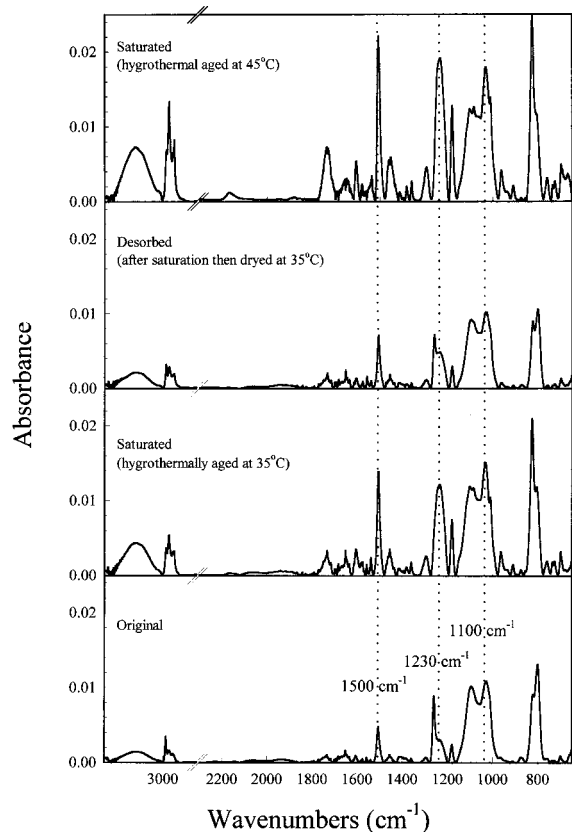


Figure 3 ATR-FTIR spectra for samples (a) unexposed, (b) hygrothermally aged at 35°C (c) dried at 35°C (d) hygrothermally aged at 45°C.

Table II IR Bands for Original Sample

Region	Peaks	Groups
3700–3100		OH and NH stretching vibration (epoxy resin) SiO ₂ stretching vibration (silica)
3100–2800	3040	Al ₂ O ₃ stretching vibration (alumina) =CH stretching vibration (epoxy resin, methyl methacrylate–butadiene–styrene polymer)
	2965, 2915, 2880	CH—, CH ₂ — CH ₃ asymmetric and symmetric stretching vibration (methylmethacrylate–butadiene–styrene polymer, epoxy resin, organo nickel complex)
	2850	CH ₃ —symmetric stretching vibration (dimethylsiloxane)
2300–2100	2270, 2200, 2160	C—N stretching vibration (dicyandiamide) multiple bands because of the resonance
1800–1300	1730	C=O stretching (epoxy resin, methylmethacrylate–butadiene–styrene polymer)
	1600	C=C aromatic ring stretching vibration (epoxy resin, methylmethacrylate–butadiene–styrene)
	1500	CH— aromatic ring stretching (epoxy resin, methyl methacrylate–butadiene–styrene polymer, aluminum)
	1450	CH ₃ —, CH ₂ — deformation (epoxy resin, methyl methacrylate–butadiene–styrene polymer, dimethyl–siloxane, organo nickel complex) CH ₂ —O deformation (epoxy resin) B—O (barium metaborate)
1300–650	1290	C—C stretching vibration aromatic ring (epoxy resin, methylmethacrylate–butadiene–styrene polymer)
	1260	C—O—C aromatic ether stretching deformation (epoxy resin) bridge between benzene rings (epoxy resin)
	1180	Si—O asymmetric stretching (silica and dimethyl siloxane)
	1100	C—O—C out of plane stretching deformation (epoxy resin), Si—O—C asymmetric stretching (dimethylsiloxane)
	1025	CH—out of plane deformation in aromatic rings, 2H adjacent- <i>para</i> - or unsymmetrical trifunctional (epoxy resin)
	825	CH— aromatic rings, monofunctional (methyl methacrylate–butadiene–styrene polymer)
	800	Si—O—rocking (silica and dimethylsiloxane)

aromatic band at 1500 cm⁻¹, which would remain invariant for an unfilled resin sample. Even for this band, the intensity can change because some fillers can contribute to this band. Therefore, we report only qualitative changes.

In Figure 3, the band around 2200 cm⁻¹, which is assigned to the curing agent (dicyandiamide), appears in spectra before and after aging. Therefore, an excess of curing agent is used in the formulation, and consequently, it can be said that the adhesive formulation under study is not stoichiometric. After hygrothermal aging, the water contributes to broaden bands in the range 3600–3000 cm⁻¹ as well as at 1640 cm⁻¹, the former correspond to H—O—H stretching, and the latter to the bending mode. These bands appear in all the exposed samples, and their intensities de-

crease as the water content diminishes. The intense CH stretching bands between 3000 and 2800 cm⁻¹, which arise from aliphatic hydrocarbons, are also changing with the water absorption. In addition, a difference in the spectra for unexposed and exposed samples is observed in the 1500 and 825 cm⁻¹ bands, assigned to C=C stretching of the benzene ring and the out-of-plane bending of aromatic rings, respectively. The IR absorption near to 1600 cm⁻¹, due to the stretching vibration of C=C aromatic rings, also appears to increase with water uptake. The quaternary carbon between the aromatic rings shows a band at 1180 cm⁻¹, which also increases with the absorption of water. The bands at 1260 and 1025 cm⁻¹ are due to the aromatic and aliphatic ether stretching in the epoxy. The aromatic band

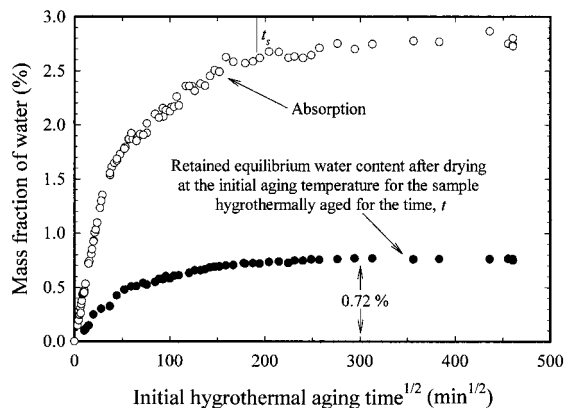


Figure 4 Retained equilibrium water content after drying at initial hydrothermal aging temperature for the specimen hydrothermally aged at 30°C. The mass uptake history of the specimen during the absorption is also shown.

is shifted at 1230 cm^{-1} , and its intensity increases when the bonded water is present. All these features mentioned above have demonstrated the water absorption by the polymeric matrix. However, water has been also absorbed by fillers. For instance, the band at 1100 cm^{-1} , due to the Si—O asymmetric stretching in the silica, changes with moisture uptake.

The spectrum of a desorbed sample is also included in Figure 3, showing that water is still retained in the adhesive. This retention can be seen through the band at 1260 cm^{-1} , which is shifted down to 1230 cm^{-1} because of the strong bond between the water and the resin. However, this band is less intense than in saturated samples. Also, after desorption, the band corresponding to the interaction of water and silica at 1100 cm^{-1} becomes less intense compared with the saturated specimen. This observation indicates that, after the desorption process, the water retained in the sample is sorbed by the resin but not by the silica.

Figure 4 shows the equilibrium water content after desorption as a function of initial hydrothermal aging time for specimens aged at 30°C. It can be seen from the figure that the retained water content depends upon the hydrothermal aging time during the absorption up to $t < t_s$, and a constant value is achieved if $t > t_s$. t is the hydrothermal aging time during the absorption process and t_s is the time required to reach saturation during the process (shown in the figure). The retained equilibrium water content for the specimen hydrothermally aged at 35, 40, and 45°C

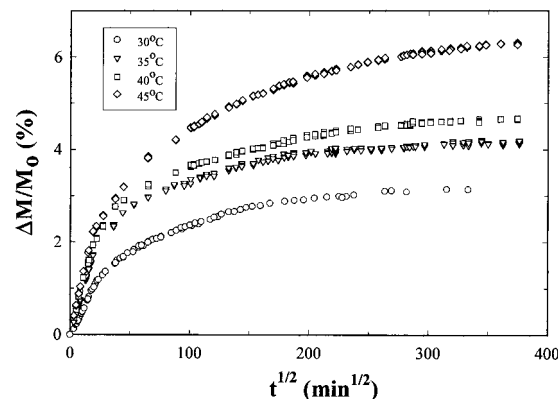


Figure 5 Mass uptake fraction vs. the square root of time for Case A reabsorption at temperature ranges from 30 to 45°C.

coincides with those aged at 30°C. Therefore, it can be said that under our empirical conditions the amount of water reacting with hydrophilic groups is independent of aging temperature. A mass fraction of about 0.72% is associated with tightly bonded water, as determined from Figure 4. The water hydrogen bonded to hydrophilic groups of the polymer resin cannot be removed unless specimens are dried at temperatures higher than the water absorption temperature.

Results from the Case A and Case B reabsorption experiments are plotted in Figures 5 and 6, respectively, as mass fraction of water ($\Delta M/M_0$, $\Delta M = M_t - M_0$) vs. the square root of time ($t^{1/2}$). Each datum on the plots in Figure 5 (Case A) results from a different sample with its own hydrothermal aging history. Figure 6 displays the

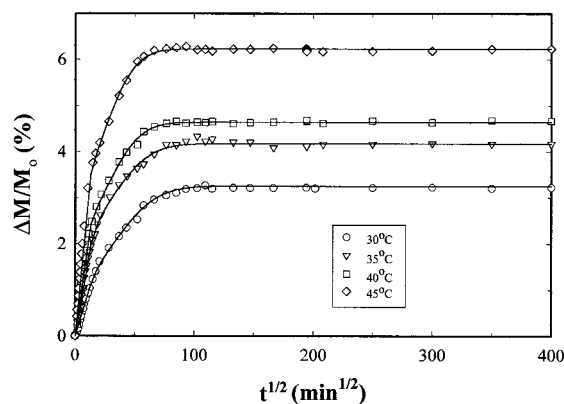


Figure 6 Mass uptake fraction vs. the square root of time for Case B reabsorption at temperature ranges from 30 to 45°C. The solid line is the fit to the experimental data based on eqs. (1) and (2).

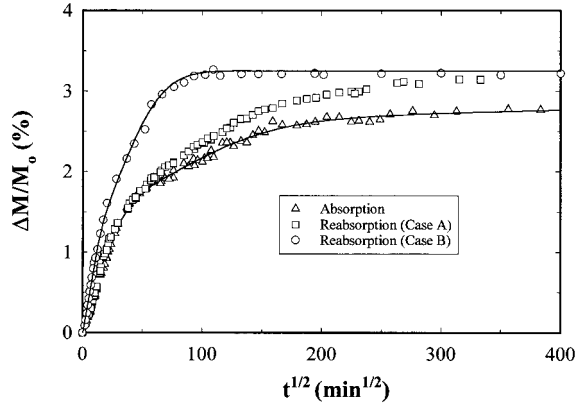


Figure 7 Comparison of mass uptake history among three sorption processes (absorption, reabsorption Cases A and B) for specimens hygrothermally aged at 30°C.

water uptake content measured for Case B reabsorption in which the samples were completely dried, after reaching saturation in the absorption process of the virgin adhesive. Based on the data presented in these figures a non-Fickian behavior is observed for both Case A and Case B reabsorptions. However, Case B shows a sorption behavior closer to a Fickian process. The deviations from the Fickian behavior for this resin are interpreted as a consequence of the inherent time-dependent response of polymers and also the retarded moisture uptake process by the existence of fillers.

Figure 7 presents the comparison of mass uptake history among three sorption processes (absorption, reabsorption Cases A and B) for the hygrothermal aging temperature at 30°C. General observations regarding these data also apply to the other hygrothermal aging temperatures studied.

Different models have been proposed to describe the kinetic behavior of water diffusion, from the simplest model given by the linear Fick's law^{15,16} to non-Fickian models.^{12,17–20} In the present study the solid line in the figures is the fit to the experimental data based on a non-Fickian diffusion model,^{4,12} which used a time-dependent boundary condition

$$C(\pm l, t) = C_0 + \sum_{i=1}^{\infty} C_i (1 - \exp(-\beta_i t)) \quad (1)$$

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, C_0 is the instantaneous concentration, and the summation is the concentration contributed by polymeric retardation processes, respectively. t is the time, β_i are constants associated with material retardation time, z is the coordinate through the thickness of the adhesive film, l is the half thickness of the adhesive film, and D is 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. There is no curve fit for Case A because each datum in the case has its own hygrothermal aging history.

In the Case A reabsorption procedure, samples (previously hygrothermally aged for a specific period of time t_a —time duration for absorption from virgin condition) were taken out from the reabsorption process water bath at different times (t_r , time during reabsorption) for the water uptake measurement. It has been observed that if two samples with different aging history (different t_a , called t_{a1} and t_{a2} , and $t_{a2} > t_{a1}$, as well as both t_{a1} and $t_{a2} < t_s$), their water uptake fractions during absorption are the same as long as $t_r \leq t_{a1}$. However, a deviation was found in the water uptake for these two samples when $t_r > t_{a1}$.

At the beginning of the process (the linear part in Fig. 7), the difference in kinetics between absorption and Case A reabsorption is not significant. However, as the diffusion proceeds, this difference becomes significant. The degree of structure modification has grown with the reabsorption time in Case A. On the other hand, the difference between the absorption and Case B reabsorption is considerable from the early stages. The structure has been fully modified in the Case B reabsorption, because the samples have reached saturation, and then water has been completely removed. The water uptake behavior of Case A approaches that of Case B as the reabsorption time increases beyond $t_r > t_s$. After time t_s , the only difference between Case A and Case B samples is the initial water content, where the samples for Case B study have been completely dried. Consequently, absorption and Case A reabsorption require similar time to reach saturation, while saturation is reaching in specimens under Case B protocol at a faster pace.

The saturation level increases markedly between the absorption and Case B or Case A reabsorptions. This significant difference in the saturation level is attributed to hydrogen bond formations during the previous hygrothermal aging

Table III Diffusion Coefficients for Adhesive at Each Temperature and Process

Hygrothermal Aging Temperature (°C)	Absorption		Desorption at Initial Hygrothermal Temperature		Reabsorption Case A		Reabsorption Case B	
	D (10^{-13} cm ² /s)	M_m (%)	D (10^{-13} cm ² /s)	M_m (%)	D (10^{-13} cm ² /s)	M_m (%)	D (10^{-13} cm ² /s)	M_m (%)
30	2.18	2.80	3.35	1.97	a	3.16	9.18	3.25
35	4.50	3.70	4.64	2.98	a	4.14	11.82	4.18
40	5.03	4.35	6.47	3.58	a	4.65	19.22	4.64
45	7.28	5.42	9.36	4.63	a	6.32	24.79	6.23

^a D is calculated based on the mean value of M_m , D is not calculated for the Case A reabsorption because each datum in the case has a different hygrothermal aging history.

history. Once hydrogen bonds have been created during the initial hygrothermal aging process within specimens, the bonding strength between the filler and the resin is disrupted. Thus, during the following reabsorptions, the hydrogen bond formations are, in a sense, redeveloped to a greater extension at the interface between the fillers and the resin. Samples used in Case A and Case B reabsorptions have the same hygrothermal histories but different initial conditions if the reabsorption time is beyond the t_s . In such a situation, the results show that Case A and Case B attain the same reabsorption saturation level.

Table III lists the diffusion coefficient (D) obtained from the fit to the experimental data (mean value of M_m) by using the non-Fickian diffusion model presented in eqs. (1) and (2). In Table III, the maximum water uptake (saturation level) for different sorption processes with different hygrothermal aging temperatures is listed. Figure 8 shows the $\ln D$ vs. $1/T$ and lists the apparent activation energy obtained from the Arrhenius relationship, $D = D_o \exp(-E/RT)$ based on the diffusivity of different hygrothermal aging temperatures, where D_o is a permeability index, E the activation energy, R the universal gas constant, and T the temperature. For the reabsorption cases studied, there is a good agreement with results (43.1–59.8 kJ/mol) reported for some neat resins.²¹ Figure 8 also exhibits the results for absorption and desorption.

Swelling and the Depression of Glass Transition Temperature

In the current swelling analysis, as commented on in the Experimental section, the time-dependent swelling phenomena have been not measured, although such phenomena exist.²²

Sample swelling is compared with the maximum volume of water uptake in Figure 9, for Case B reabsorption at different aging temperatures. Each datum point corresponds to a specific aging temperature, and is the average of six specimens measured. The relative volume increases after saturation ($\Delta V_\infty/V_o$) due to swelling is plotted vs. the volume fraction of water uptake

$$\frac{\Delta V_\infty}{V_o} = 0.01 M_\infty \rho v \quad (3)$$

where M_∞ is the mass gain at the saturation, ρ is the dry resin density ($\rho = 1.1$ g/cm³ for this resin) and v is the specific volume of water. The dashed line in Figure 9 is the curve fit to experimental results. The general behavior is similar to that previously observed.^{4,23} The swelling of the resin

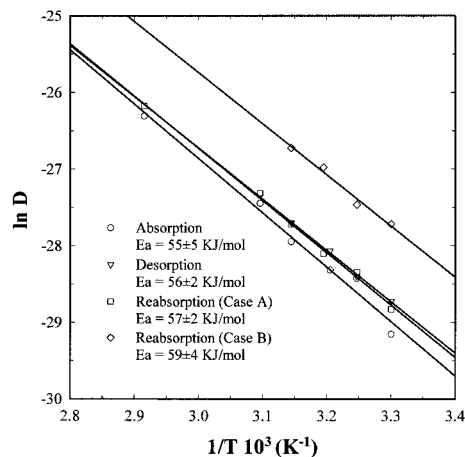


Figure 8 Plots of the $\ln D$ vs. the inverse of the hygrothermal aging temperature for each sorption process.

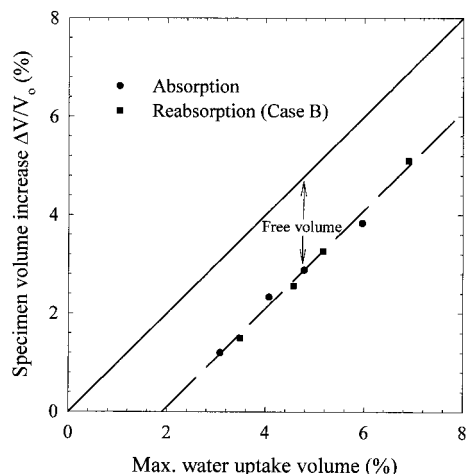


Figure 9 Swelling of samples vs. the volume of saturated water uptaken at different aging temperatures for samples in absorption (■) and Case B reabsorption processes (●).

is lower than the total volume of water absorbed. The volume of water absorbed is indicated in Figure 9 by a solid line with slope 1.0 (based on the ideal mixing law). Various researchers^{24–27} have suggested that water molecules can exist in the polymer in two states. In one state, water molecules fill the free volume that is present in the adhesive in the dry state and are relatively mobile within such a free volume. Swelling is not produced because the water fills volume that already exists. In the second state, water infiltrates the polymer molecular structure through hydrogen bonding. Hence, it becomes immobilized, and swelling is caused. Accordingly, the difference between the solid and dotted lines in Figure 9 represents the amount of apparent free volume probed by the water molecules at the indicated hygrothermal aging temperature. This apparent free volume includes the conventional “free volume” of polymers, region unwetted by polymer matrix and cavities due to the porous nature of silica gel. There is evidence that the conventional “free volume” is greater than the free volume in microvoids (unwetting and cavities). A study using proton NMR by VanderHart et al.¹⁴ showed that the volume fraction of these microvoids in a commercial compound was estimated to be $0.20 \pm 0.03\%$. Therefore, it is assumed that the volume fraction of these microvoids does not contribute much to the apparent free volume of the adhesive here studied.

A linear relationship (dashed line) between the swelling of samples at saturation and the amount

of water reabsorbed at saturation (Case B reabsorption) is noted from Figure 9. Besides, the two lines (solid and dashed lines) are parallel. This indicates that the apparent free volume fraction occupied by the water in this structural adhesive remains constant at 2.00% (with standard uncertainty 0.09%) for the aging temperatures discussed ($T \leq 45^\circ\text{C}$) in the reabsorption Case B. The constant fraction implies that the swelling of the adhesive at aging temperatures below 45°C may have a negligible effect on the change of the apparent free volume. Or, conversely, during the swelling in Case B reabsorption, the volumetric changes of the occupied volume and the rearrangement of the polymer network occur simultaneously. In addition, this constant value is almost the same as the apparent free volume fraction (2.03%, with standard uncertainty 0.09%) probed by the same procedure in the absorption process for virgin samples. This identification indicates that the apparent free volume is not only independent of hygrothermal aging temperature but also hygrothermal aging history. Finally, this result is consistent with the previous argument⁴ that two states of water molecules exist in this adhesive system; one, in which water is considered to occupy apparent free volume of the adhesive, and the second one in which water forms hydrogen-bonded clusters.

Some interaction with the epoxy resin could be possible through the disruption of the hydrogen bond between polymer chains (interchain hydrogen bond), as described earlier, although water retained in the apparent free volume is relatively mobile. This disruption could be caused by the strong affinity between the water and polar hydroxyl group in the cured resin. Also, the disruption could participate in the plasticization of the polymer with other water retained in the apparent free volume. The amount of this water that interacts with the epoxy in the apparent free volume is about a mass fraction of 0.72%, based on the results in Figure 4.

Figure 10 and Table IV present the variation of glass transition temperature with hygrothermal temperature in the two cases of reabsorption process. Some results from the previous study on absorption and desorption are also presented in Figure 10 and in Table IV. T_g values for saturated samples from two reabsorption processes exhibit practically identical values. This fact should be expected because almost the same saturation water content is measured in both reabsorption processes. It is also shown in the figure that the T_g

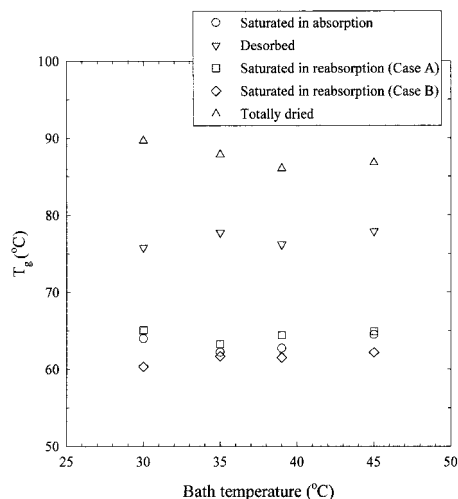


Figure 10 Variation of glass transition temperature with hygrothermal temperature for all the sorption processes. Saturated in absorption, desorbed, saturated in reabsorption (Case A), saturated in reabsorption (Case B).

value obtained for the saturated samples in absorption is almost the same as that found in both reabsorption cases, although the specimens have different saturation levels. Because the T_g depression depends on the water inside the apparent free volume but not the maximum amount of water uptake. And, this apparent free volume is a constant regardless of hygrothermal aging temperature and history. Consequently, the T_g depression is independent of the saturation amount.

The DSC output presented in Figure 11 for saturated samples in both reabsorption processes show peaks near 4°C, which corresponds to the melting of frozen water. This frozen water mainly exists in a bulk water form in the voids due to debonding between fillers and the polymer matrix, because the volume fraction of voids caused by the un wetting of polymer matrix and the po-

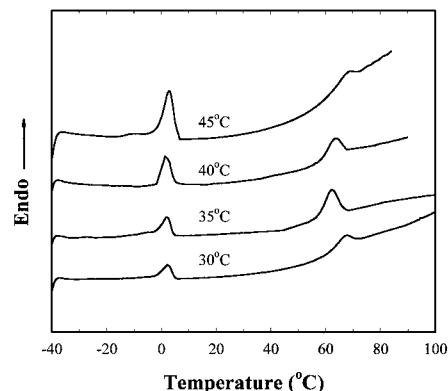


Figure 11 DSC output for saturated samples in Case B reabsorption at different hygrothermal aging temperatures.

rous nature of silica gel is relatively minimal. The intensity of this peak increases with the hygrothermal temperature. Similar peaks were also observed in the saturated samples of the absorption process. This water was explained as the water-forming hydrogen-bonded clusters, which is not contributing to the glass transition depression.⁴

It is widely accepted that the rate of T_g depression is about (10 to 15°C) for every percent of mass fraction water, or even more for some polymers.^{28,29} The T_g depression by water for this adhesive is about 24°C, independent of hygrothermal aging temperature and history, as mentioned above. The rate of T_g depression for this adhesive system (12°C for each 1% mass fraction of water) is in a good agreement with the literature, because it is assumed that only the water content contained in the apparent free volume fraction ($\approx 2\%$) is responsible for the T_g depression. Also, the T_g depression for the samples after drying at their initial hygrothermal aging temperature is about 9°C, and the mass fraction of water re-

Table IV Glass Transition Temperature for Each Sorption Process (T_g for Unexposed Sample is 86°C)

Hygrothermal Aging Temperature (°C)	Absorption T_g (°C)	Desorption at Initial Hygrothermal Temperature T_g (°C)	Reabsorption Case A T_g (°C)	Reabsorption Case B T_g (°C)
30	64	76	65	60
35	62	78	63	62
40	63	76	64	62
45	65	78	65	62

tained in those samples after the drying is about 0.72%, all in the "apparent free volume." Thus, the rate of depression is about 12°C for each increase in the mass fraction water of 1%. This is consistent with that of the saturated samples, and is linearly dependent on the water content in the apparent free volume.

CONCLUSIONS

The study shows that the water diffusion in this particle-filled epoxy-based structural adhesive exhibits a non-Fickian behavior for the cases of absorption and reabsorption processes. In this work, the interactions of water with resin and fillers were analyzed by ATR-FTIR spectra. The analysis identifies that the water retained in the adhesive, after desorption, is bonded to the resin not to the fillers. It has been found that the reabsorption saturation level for this adhesive is independent of the initial water content but dependent on the hygrothermal history. The diffusivity of water into the adhesive is dependent on their hygrothermal aging temperature and history. This study confirms results from a previous study⁴ 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. Furthermore, it is confirmed by a reabsorption process that swelling does not alter the apparent free volume of this adhesive. Therefore, the depression of T_g proceeds to a definite value, which is independent of the hygrothermal aging history and the final equilibrium water content of the adhesive but dependent on the water fraction contained in the apparent free volume.

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