

EFFECT OF WATER EXPOSURE CYCLES ON PHYSICAL PROPERTIES OF A PARTICLE-FILLED, EPOXY-BASED ADHESIVE

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ABSTRACT

The effect of cyclic hydrothermal aging on a particle-filled, epoxy-based adhesive was studied using a sequence of water absorption, desorption and reabsorption at different temperatures. Moisture sorption characteristics were explored by measuring the mass uptake of water and 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 which 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 hydrothermal aging temperature and history 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.

KEY WORDS: water absorption, reabsorption, epoxy, T_g depression, swelling

1. INTRODUCTION

The excellent mechanical properties of epoxy resins have led to their use as adhesives for bonding applications, including many in the construction, electronic packaging, aerospace and automotive industries. However, the wider application of adhesive materials requires greater understanding of material performance and the ability to withstand environmental effects during long-term use [Chiang and McKenna, 1996]. 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 the investigation of 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. A cycle of water absorption/desorption/reabsorption (ADR) in the adhesive has been conducted to mimic environmental exposure in typical applications.

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 found [Lee and Rockett, 1992] 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 Knaebel (1997) 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 Koenig (1992) 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 [Hilton and Yi, 1993; Yi and Hilton, 1995], 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. In addition, the relation of swelling and T_g depression to the apparent free volume under ADR conditions was investigated.

Many techniques are available for measuring water ingress [Saenger and Tong, 1991; Schadt and VanderHart, 1995; Nguyen et al., 1995; Luo et al., 1995]. The present study utilized a gravimetric sorption technique to characterize the adhesive under hygrothermal aging (from 30 °C to 45 °C) in distilled water. This work suggests that water sorption of this particle-filled and epoxy-based adhesive has a dual nature. 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 stage of hydrogen bond formation in the adhesive. The hygrothermal aging temperature and history do not alter the apparent free volume of the adhesive system. Therefore, the depression of T_g proceeds to a definite value which is governed by the water fraction in the apparent free volume but not by the final equilibrium water content of the system.

2. MATERIALS AND EXPERIMENTS¹

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 structure applications [Yorkgitis and Marhevka, 1994]. Adhesive films, nominally 300 μm thick, have been produced by curing the adhesive between Teflon blocks in a pressure vessel at 130 $^{\circ}\text{C}$ and 1.38 MPa (200 psi) for 13 h. The samples were then slowly cooled to room temperature. Such a procedure enables us to overcome the critical issue of preparing thin films with uniform thickness and no voids. DSC experiments showed that the adhesive has a dry T_g of 86 $^{\circ}\text{C}$ (the standard uncertainty for all the T_g measurements is 3 $^{\circ}\text{C}$), 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. The temperature of cure was considerably lower than the (150 to 205) $^{\circ}\text{C}$ range that could be expected in an automotive body structure application. After curing, the film was cut to dimensions of ca. 40 mm x 6 mm x 0.3 mm. The initial mass fraction of water in samples was less than 0.05 % (the standard uncertainty is 0.01 %), and their initial dimensions were obtained using electronic calipers.

Specimens were hygrothermally exposed in distilled water baths at constant temperatures of 30 $^{\circ}\text{C}$, 35 $^{\circ}\text{C}$, 40 $^{\circ}\text{C}$ and 45 $^{\circ}\text{C}$. Nominally, there were 150 to 200 specimens in each bath. Specimens were taken from the baths at different times (about 3-5 specimens per bath each time) for mass uptake measurements. After the specimens were saturated, a desorption (drying) procedure was conducted on them at the same temperature used in the absorption procedure. The drying 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. By only drying the specimen at the initial hygrothermal aging temperature, we know that the water cannot be dried out completely; consequently, a small amount of water was retained in each specimen. Subsequently, these specimens were completely dried at 100 $^{\circ}\text{C}$. Afterwards, the specimens with near 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 were taken periodically from the bath for water uptake measurements, and then returned to the bath for subsequent measurements.

3. RESULTS AND DISCUSSION

Results from the sorption experiments were plotted as mass uptake fraction ($\Delta M/M_0$, $\Delta M = M_t - M_0$) versus the square root of time ($t^{1/2}$), where M_t is the current and M_0 is the original sample mass, respectively. Fig. 1 shows the mass uptake of the virgin adhesive films submerged in a water bath at constant temperatures ranging from 30 $^{\circ}\text{C}$ to 45 $^{\circ}\text{C}$. The desorption

¹ 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 necessarily that they are the best available for the purpose.

results for saturated specimens dried at aging temperatures of 30 °C, 35 °C, 40 °C and 45 °C are presented in Fig. 2. It is shown that, after drying to an equilibrium value at the initial aging temperature (up to 540 h), the specimens still retained a small amount of water. Subsequently, after further drying at 100 °C for another few hours, a negligible amount of water was retained by each specimen. This suggests that some of the water forms strong interactions with adhesive components. Results from the reabsorption experiments are plotted in Figure 3. Each point in these figures represents the average of 3-5 specimens; the standard uncertainty of the mass fraction of water measurement is 1.0×10^{-4} .

The solid line in the Figures 1 and 3 is the fit to the experimental data based on a non-Fickian diffusion model used in previous work [Chiang and Fernandez-Garcia, 1999], which used a time-dependent boundary condition

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

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, $\hat{\alpha}_i$ 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. The kinetics of desorption at the temperatures studied follow a Fickian behavior.

Figure 4 presents the comparison of mass uptake history between absorption and reabsorption for the hygrothermal aging temperature 30 °C. General observations regarding these data also apply to the other hygrothermal aging temperatures studied. The difference in sorption kinetics between the absorption and reabsorption is considerable from the very beginning of the sorption process. We interpret this result to mean that the structure of samples has been significantly modified prior to the reabsorption. The saturation level increases markedly between the absorption and reabsorption. This significant difference in the saturation level we attribute to hydrogen bond formation during the previous hygrothermal aging 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 even though the water has been extracted during the desorption process. Thus, during the reabsorption, the hydrogen bond formations are, in a sense, re-developed to a greater extent at the interface between the fillers and the resin.

Table 1 lists the diffusion coefficient (D) obtained from the fit to the experimental data by using the non-Fickian diffusion model presented in eqs. (1) and (2). Also, in Table 1, the maximum water uptake (M_m , the maximum water content at the saturation level) for different sorption processes with different hygrothermal aging temperatures are listed.

Sample swelling is compared to the maximum volume of water uptake in Fig. 5, for absorption and reabsorption at different aging temperatures. Each point corresponds to a specific aging temperature, and is the average of six specimens measured. The relative volume increase after saturation ($\Delta V_4/V_0$) due to swelling is plotted versus the volume fraction of water uptake (V_w/V_0) which is calculated from the measured mass gain:

$$\frac{\Delta V_{\infty}}{V_0} = 0.01 M_4 v \quad (3)$$

where M_4 is the mass gain at the saturation, ρ is the dry resin density (equal to 1.1 g/cm³ for this resin) and v is the specific volume of water. The dashed line in Fig. 5 is the curve fit to experimental results. The general behavior is similar to that observed by other authors [e.g., El-Sa'Ad, 1989], in that the swelling of the resin is less than the volume of water absorbed. The volume of water absorbed is indicated in Fig.5 by a solid line with slope 1.0 (based on the ideal mixing law). Various researchers [e.g., Chang et al., 1974; Adamson, 1980; Diamant et al.; Moy and Karasz,1980] 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 the 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 swelling. Accordingly, the difference between the solid and dotted lines in Fig.5 represents the amount of apparent free volume probed by the water molecules at the indicated hygrothermal aging temperature.

From Figure 5, a linear relationship (dashed line -- a linear regression) between the swelling of samples at saturation and the amount of water absorbed at saturation is noted. Also, 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 ($T \leq 45$ °C) in the two sorption cases. 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 the sorption processes, the volumetric changes of the occupied volume and the rearrangement of the polymer network occur simultaneously. The finding of this constant fraction (percentage) indicates that apparent free volume of this adhesive is not only independent of hygrothermal aging temperature but also hygrothermal aging history. This result also suggests water molecules exist in this adhesive system in either of two states, one in which water is considered to occupy apparent free volume of the adhesive, and the second in which water forms hydrogen-bonded clusters.

As described earlier, although water retained in the apparent free volume is relatively mobile, some interaction with the epoxy resin is possible through the disruption of the hydrogen

bond between polymer chains (interchain hydrogen bond). This disruption is caused by the strong affinity between the water and polar hydroxyl groups in the cured resin. Also, the disruption could participate in the plasticization of the polymer with other water retained in the apparent free volume. Based on the results in Fig. 2, the amount of this water that interacts with the epoxy in the apparent free volume is about a mass fraction of 0.72 % (Note, that data in Fig.2 are normalized by the saturated mass).

Figure 6 and Table 2 present the variation of glass transition temperature with hygrothermal temperature in the absorption and reabsorption processes. As shown in Figure 6, T_g values for saturated samples from the two processes exhibit practically identical values. It is also shown in the figure that the T_g value obtained for the saturated samples in absorption is almost same as that in the reabsorption case, although the specimens have different saturation levels. This is 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.

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 [Kelly and Bueche, 1961; Ellis and Karasz, 1984]. The T_g depression by water for this adhesive is about 24 °C regardless of hygrothermal aging temperature and history. Since we believe that only the water content contained in the apparent free volume fraction (≈ 2 %) is responsible for the T_g depression, 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. 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 retained in those samples after the drying is about 0.72 %, all in “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.

4. CONCLUSIONS

The study shows that the water diffusion in this particle-filled epoxy-based structural adhesive exhibits a non-Fickian behavior for absorption and reabsorption. In addition, the diffusivity of water into the adhesive is dependent on the hygrothermal aging temperature and history. We observed that 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 system. The hygrothermal aging temperature and history do not alter the apparent free volume of this particle-filled adhesive system. The results suggest that the water sorption of this adhesive has a dual-sorption mode, in which one population of water is considered to occupy apparent free volume of the adhesive, and the second population forms hydrogen bonded cluster. We are able to relate the swelling and T_g depression to water associated with the apparent free volume of the adhesive. Consequently, we conclude that 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, we suggest that one might overestimate

the T_g depression if conventional wisdom on the magnitude of T_g depression (about 10 °C to 15 °C for every 1 % (mass fraction) of water) is used.

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Table 1. Diffusion coefficients (D) and maximum mass fraction of water uptake (ΔM_x) for adhesive at each temperature and process.

Hygrothermal Aging Temperature (°C)	Absorption		Desorption		Reabsorption	
	D ($10^{-13}\text{cm}^2/\text{s}$)	ΔM_x (%)	D ($10^{-13}\text{cm}^2/\text{s}$)	ΔM_x (%)	D ($10^{-13}\text{cm}^2/\text{s}$)	ΔM_x (%)
30	2.18	2.80	3.35	1.97	9.18	3.25
35	4.50	3.70	4.64	2.98	11.82	4.18
40	5.03	4.35	6.47	3.58	19.22	4.64
45	7.28	5.42	9.36	4.63	24.79	6.23

* D is calculated based on the mean value of ΔM_x .

Table 2. Glass transition temperature for each process (T_g for unexposed sample is 86.2 °C) □

Hygrothermal Aging Temperature (°C)	Absorption T_g (°C)	Desorption T_g (°C)	Reabsorption T_g (°C)
30	64.0	75.8	60.3
35	62.2	77.7	61.7
40	62.7	76.2	61.5
45	64.5	77.9	62.2

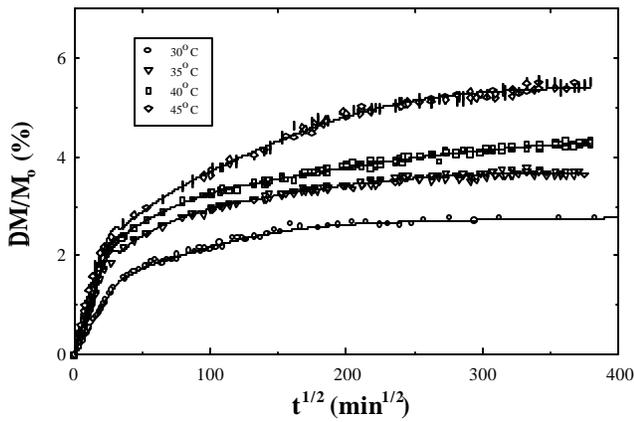


Fig.1 Mass uptake history of the adhesive films submerged in a water bath at constant temperatures ranging from 30 to 45 °C. The solid line is the fit to the experimental data based on the eqs. (1) and (2).

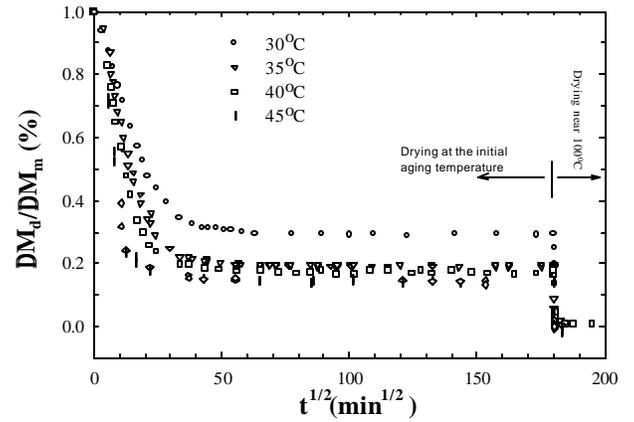


Fig.2. Fraction of mass change from desorption ($\Delta M_d/\Delta M_m$, $\Delta M_d = M_m - M_t$) versus the square root of time, where M_t is the current and M_m is the saturated mass.

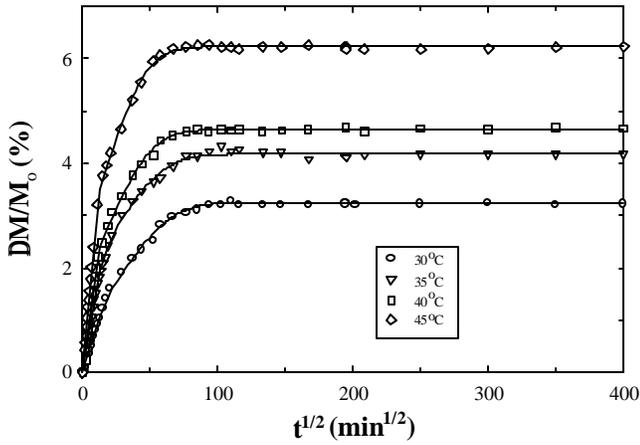


Fig.3 Mass uptake fraction versus the square root of time for reabsorption at temperatures ranging from 30 to 45 °C. The solid line is the fit to the experimental data based on the eqs. (1) and (2).

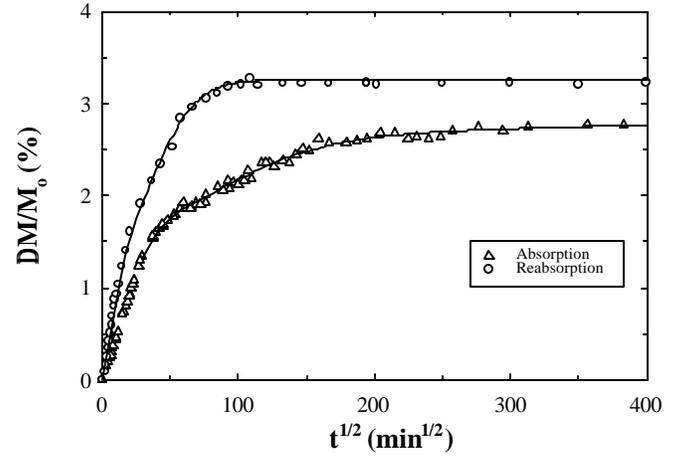


Fig. 4. Comparison of mass uptake history between absorption and reabsorption for specimens hydrothermally aged at 30 °C

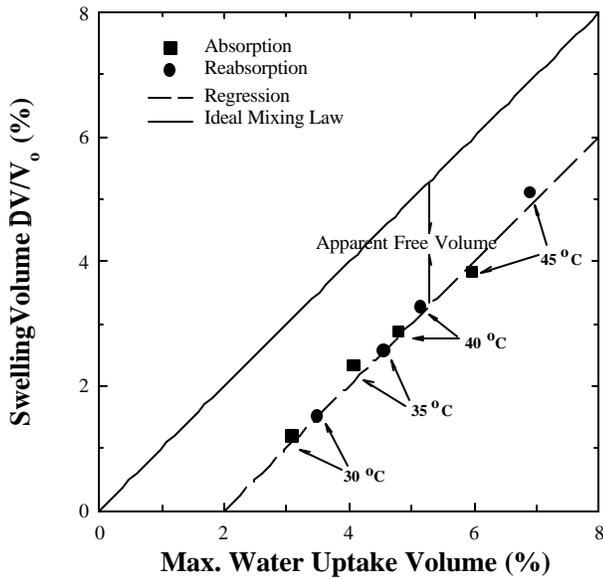


Fig. 5. Swelling of samples versus the volume of saturated water uptake fraction at different aging temperatures for samples in absorption and reabsorption processes

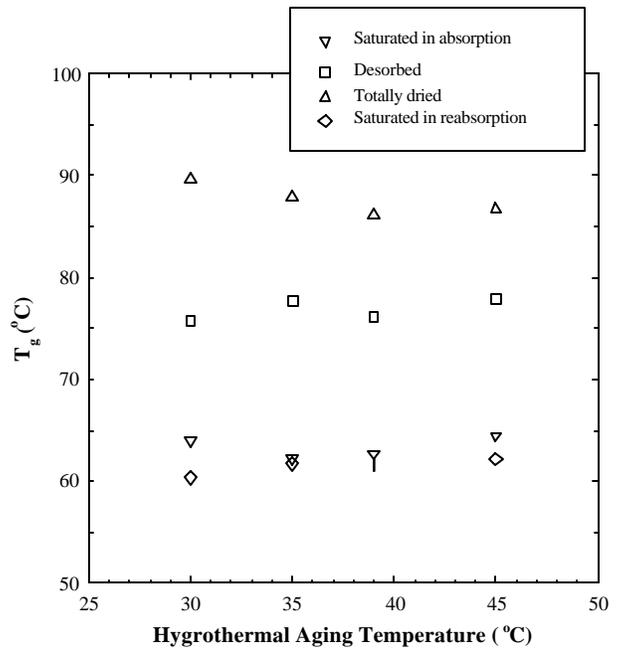


Fig. 6. Variation of glass transition temperature with hydrothermal aging temperature in all the sorption processes