Water Absorption in Epoxy Resins: The Effects of the Crosslinking Agent and Curing Temperature

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ABSTRACT: Epoxy systems were prepared with the same epoxide (diglycidyl ether of bisphenol A) with five different hardeners: 4,4′-diaminodiphenylmethane (H1), diethylenetriamine (H2), a cycloaliphatic amine based on isophorone diamine (H3), a polyaminoimidazoline-based hardener (H4), and a polyamidoamine-based adduct hardener (H5). Samples were subjected to four different postcure treatment temperatures (23, 55, 75, and 150°C). Water absorption kinetics were obtained for each material and for each postcure treatment. The water absorption behaviors for the materials with H1, H2, and H3 were similar, whereas those for H4 and H5 were quite different. This is discussed in terms of the molecular structures of the hardeners. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 2544–2549, 2005

Key words: coatings; curing of polymers; diffusion; resins

INTRODUCTION

The absorption and diffusion of water in polymeric materials such as epoxy systems is related to the free volume[1–3] and the polymer–water affinity.[3,4] The amount of free volume depends on the molecular packing and is affected by both the crosslink density (and therefore the extent of curing) and physical aging.[5] The polymer–water affinity is significantly influenced by the presence of hydrogen-bonding sites within the polymer.[6] Water can sometimes be absorbed without causing swelling; when this happens, it is suggested that it remains unbound to the polymer and is effectively accommodated within the free volume.[4] On the other hand, bound water molecules that attach to the polymer through hydrogen bonds disrupt the interchain hydrogen bonds and induce swelling[6,7] and plasticize the polymer.[8,9]

The interaction of water with epoxy resins and its effect on the physical and mechanical properties have been studied fairly extensively.[4,8,10–15] Most of the studies were conducted on materials based on diglycidyl ether of bisphenol A (DGEBA) but used a variety of curing agents to produce the crosslinked network. Van Landingham et al.[4] studied the effect of epoxy–amine stoichiometry on water diffusion in an epoxy system with bis(*para*-amino cyclohexyl)methane as a cycloaliphatic amine curing agent for DGEBA. In this study, a reduction in the glass-transition temperature (T_g) and moisture-induced swelling strains were reported for samples exposed to different conditioning environments. Enns and Gillham[14] studied the water absorption of DGEBA cured with diaminodiphenyl sulfone (DDS) as a function of the extent of cure.[14] They observed that the equilibrium water content (after long exposure times) increased with the extent of room-temperature cure and attributed this to an increase in the free volume occurring upon curing. Diamante et al.[11] studied the water uptake of DGEBA, cured with a stoichiometric mixture of 3,3′ diaminobenzidine and aniline, and discovered that when the proportion of aniline was reduced, the diffusion coefficient (D) and equilibrium water uptake increased. Karasz and coworkers[8,9] showed that sorbed water plasticized epoxy polymer, causing a reduction in T_g in tetraglycidyl 4,4′-diaminodiphenyl methane (TGDDM) cured with DDS. This was attributed to the presence of a strong interaction between the dispersed water and some specific segments or groups in the crosslinked polymer.[9] Evidence for irreversible changes in the epoxy network caused by water absorption has been provided by the study of absorption–desorption cycling; it was found that hygrothermal cycling caused an increase in the sorption capacity in various cases, including DGEBA cured with either di-(1-aminopropyl-3-ethoxy)ether[10] or triethylene tetraamine[12,15] or the TGDDM–DDS system.[15] Maxwell and Pethrick[13] studied the dielectric relaxation of some epoxies with different levels of absorbed water and concluded that the water could exist in clusters in which it was relatively free or could be molecularly dispersed within the resin and bound to it, probably

TABLE I
Material Compositions

Code	Material	Grade	Commercial name	Supplier	Mix ratio (phr)[a]
EP	DGEBA	Commercial	DER 331	Dow Chemical (Midland, MI)	
H1	4,4′-methylenedianiline	Lab	—	Acros Organics (Geel, Belgium)	26[b]
H2	Diethylenetriamine	Commercial	—	Dow Chemical	11[b]
H3	Cycloaliphatic polyamine	Commercial	Aradur 42	Huntsman (Bad Säckingen, Germany)	22[c]
H4	Polyaminoimidazoline	Commercial	Aradur 140 BD	Huntsman	50[c]
H5	Polyamidoamine adduct	Commercial	Aradur 450 BD	Huntsman	60[c]

[a] Parts per hundred parts of EP by weight.
[b] Stoichiometric ratio.
[c] As recommended by the manufacturer.

by hydrogen bonding. The state of dispersion of water will have a very significant influence on the relaxation behavior and associated properties such as diffusion, as well as the fracture properties of the material.

Despite the strong influence of absorbed water on the properties of epoxy systems, there do not appear to be any reports in the literature of studies in which the use of different curing agents was compared. The aforementioned studies that involved different curing agents were conducted in different laboratories with different methodologies and characterization methods, and this makes a comparison of the effects of different curing agents difficult to perform with confidence. The investigation presented in this article compared the behavior of a single epoxy cured with five different agents, using preparation methods and characterization procedures that were standardized as closely as possible. A further motivation for this work was to provide information for a companion study of the curing stresses in the same materials and of the behavior of the curing stresses during aging in air at room temperature at different humidity levels.[16–19]

EXPERIMENTAL

Materials

The epoxy resin (EP) and crosslinking agents used in the experiments reported here along with the mixing ratios are shown in Table I. DER 331 (Dow Chemical Co.) is an undiluted DGEBA-based liquid epoxy resin with an epoxy equivalent mass of 182–192 g/mol, a typical grade for solvent-free coatings. Five different types of amine curing agents were used in this study in conjunction with EP. The curing agents were 4,4′-diaminodiphenylmethane (H1), diethylenetriamine (H2), a cycloaliphatic amine based on isophorone diamine (H3), a polyaminoimidazoline-based hardener (H4), and a polyamidoamine-based adduct hardener (H5). The chemical structures of EP and the curing agents are presented in Figures 1 and 2, respectively.

Mixing procedure

The mixing of EP with curing agents H2–H5 was carried out with 100-g batches *in vacuo* with a mechanical paddle stirrer. The EP–hardener mix ratios are given in Table I. Each batch was mixed *in vacuo* for about 3 min at a moderate speed. Then, the mix was allowed to stand for 5 min before application.

Hardener H1 was a solid at room temperature, and a different mixing technique was required to prepare a mixture suitable for use as a coating at the ambient temperature. A total batch of 100 g was prepared by the melting of H1 at 100°C and mixing with equal parts of EP at that temperature. Then, the mixture was added to the remainder of EP at room temperature and mixed *in vacuo* to obtain the final mix at a temperature of about 35°C. Although the mixed material was at about 35°C at the commencement of the application, the coated substrate reached room temperature
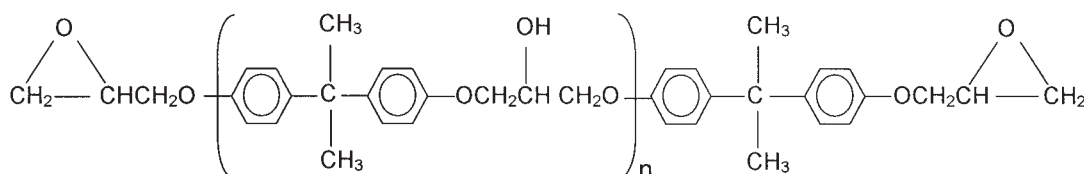
Diglycidyl ether of bisphenol A (DGEBA), n ≤ 1
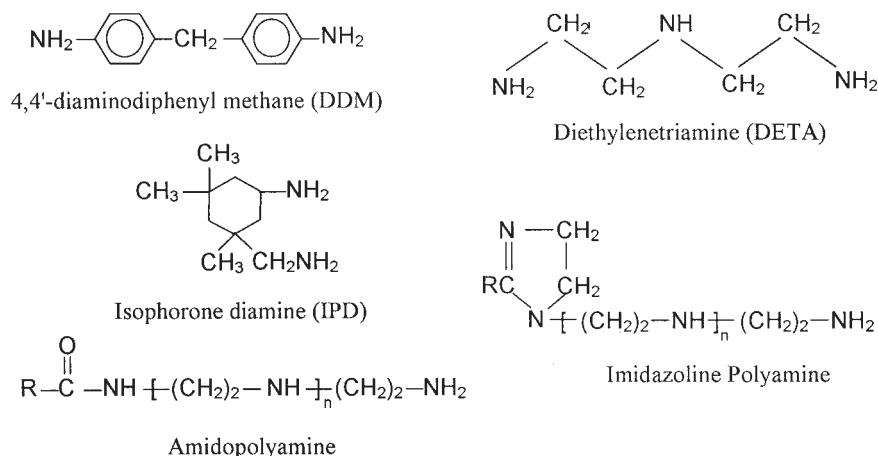
Figure 1 Chemical structure of EP.

Figure 2 Chemical structures of the epoxy curing agents.

$(23 \pm 1°C)$ within a period of less than 2 min (confirmed with an IR thermometer). This means that the vitrification stage took place at room temperature, as in the case of the mixtures based on the liquid curing agents.

Sample preparation

Samples were prepared for the study of the water absorption kinetics according to ASTM D 570-81.[20] After the completion of mixing, the epoxy systems were cast in the form of discs 50.8 mm in diameter and 3.0 ± 0.1 mm thick. Polyethylene molds were employed to avoid the use of release agents. The samples were given an initial 24-h cure at room temperature in a desiccator (0% relative humidity). They were then postcured according to one of the schedules given later followed by storage at 0% relative humidity until they were required for the water absorption experiments.

Postcure conditions

Four different postcure conditions were applied to samples of each of the five epoxy systems:

C1: Continued curing at 23°C in a dry atmosphere for 4 weeks.
C2: 24 h at 55°C.
C3: 12 h at 75°C.
C4: 4 h at 150°C.

The postcuring treatments at an elevated temperature were conducted in an air-circulating oven accurate to $\pm 1°C$. At the end of the postcuring period, cooling was conducted in the oven; the rate of cooling in the region of T_g was $-2.0 \pm 0.5°C/min$.

Details of the curing characteristics are given elsewhere.[18,19]

Measurements of the water absorption kinetics

The water absorption kinetics were obtained after a period of 4 weeks for samples cured under condition C1 and after 24 h for samples cured under conditions C2, C3, and C4. At the end of this curing period, the samples were immersed fully in distilled water at $23 \pm 1°C$. The samples were removed at intervals, one at a time, for weighing. All surface water was removed, and the samples were wiped with a dry cloth. Weighing was performed on an analytical balance to ± 0.1 mg. Sample weight changes were plotted versus the square root of the time in anticipation that Fick's law would be obeyed. The moisture content was calculated with the following expression:

$$M_t \ (\%) = 100 \times \left(\frac{W - W_0}{W_0} \right)$$

where M_t is the moisture content at time t, W is the weight of the sample at the time of measurement, and W_0 is the weight before immersion in water. Three samples were used for each measurement, and the error bars representing the standard deviation are smaller than the symbols used in the graphs showing the results (Figs. 3–6).

RESULTS AND ANALYSIS

Water absorption data are given in Figures 3–6. The data are arranged according to the cure schedule, so that all five epoxy systems are compared on each graph. The amount of absorbed water increased gradually and leveled off at the equilibrium water absorption (M_∞), which depended on the material and on the postcure conditions. The values of M_∞ are summarized in Figure 7 for all materials and postcure combinations.

Figure 3 Sorption of water by the epoxy systems following the postcure under condition C1.
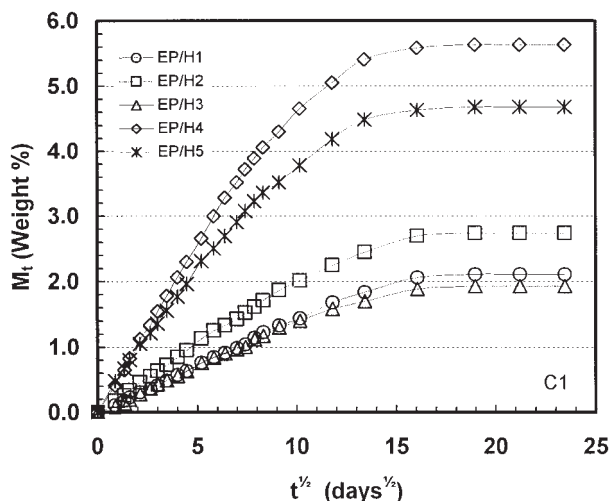

Figure 5 Sorption of water by the epoxy systems following the postcure under condition C3.

The initial parts of the M_t–$\sqrt{t}$ graphs were straight, up to at least $M_t = 0.5M_\infty$, and this confirmed Fickian behavior. It therefore follows the standard equation for the diffusion of a penetrant:[21]

$$\frac{M_t}{M_\infty} = \frac{4}{h}\left(\frac{Dt}{\pi}\right)^{1/2}$$

where h is the thickness of the sample. This relationship was used to calculate D. The results of this analysis for all materials and postcure conditions are given in Figure 8.

The measurements of T_g for all five materials following curing at all of the temperatures used were made by differential scanning calorimetry.[18,19] The results for cure condition C1 are given in Figure 7, and
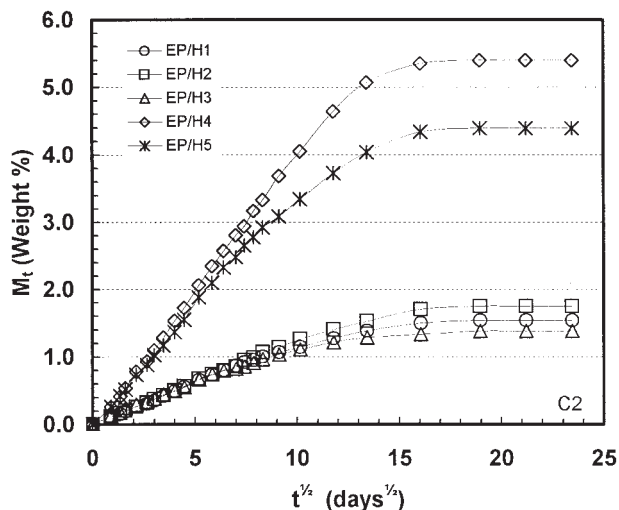
the results for cure condition C4 are given in Figure 9. More results and details of the measurement procedure are given elsewhere.[18,19]

DISCUSSION

The selection of epoxy hardeners used in this study included a wide range of amine curing agents covering the commonly used examples, such as aromatic amine, aliphatic amine, cycloaliphatic amine, polyaminoimidazoline, and polyamidoamine. The water absorption characteristics of the materials thus formulated were found to separate into two distinct classes. Figure 7 shows that EP/H1, EP/H2, and EP/H3 form one group and that EP/H4 and EP/H5 form another. M_∞ for the EP/H1, EP/H2, and EP/H3 group was lower than that for EP/H4 and EP/H5 for all postcure

Figure 4 Sorption of water by the epoxy systems following the postcure under condition C2.
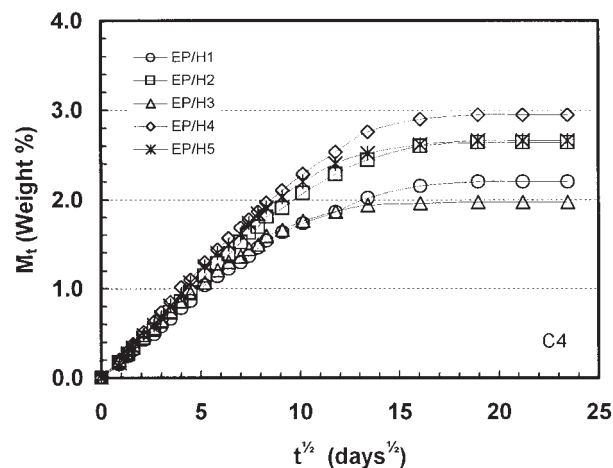

Figure 6 Sorption of water by the epoxy systems following the postcure under condition C4.
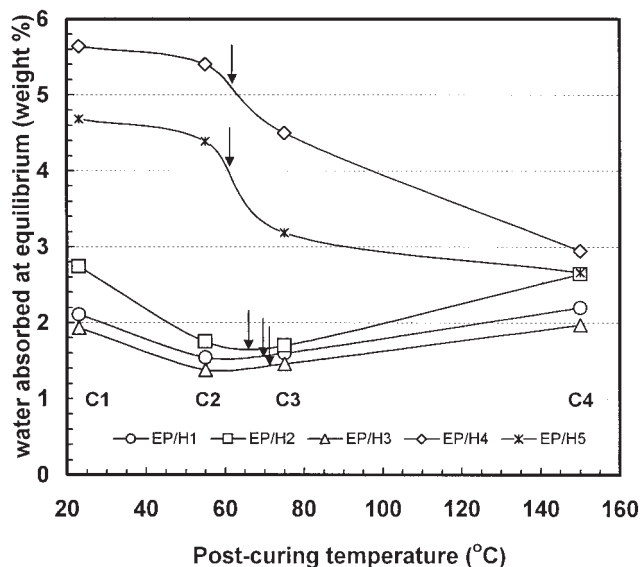
Figure 7 Equilibrium water uptake for samples treated at different postcure temperatures. The arrows indicate the T_g values of samples cured under condition C1.

Figure 9 T_g values of samples cured with different epoxy hardeners under condition C4.

conditions. Although advancing the postcure temperature from 55 to 75°C caused the value of M_∞ to fall significantly with EP/H4 and EP/H5, it hardly changed at all in EP/H1, EP/H2, and EP/H3. When the postcure temperature was increased to 150°C, M_∞ fell still further with EP/H4 and EP/H5, whereas it increased with EP/H1, EP/H2, and EP/H3. As a result of these changes, the values of M_∞ obtained for postcure condition C4 were relatively closely bunched (in the range of ~2–3%), in comparison with the ranges obtained for C1 (1.9–5.6%) and C2 (1.4–5.4%).
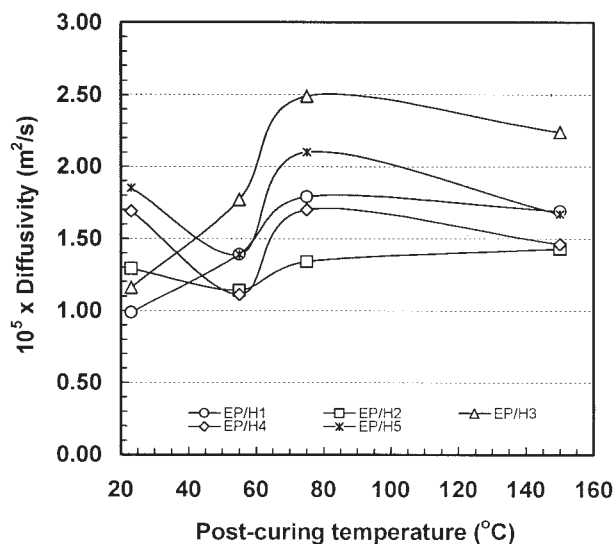

Figure 8 D for water in epoxy compositions versus the postcure temperature.
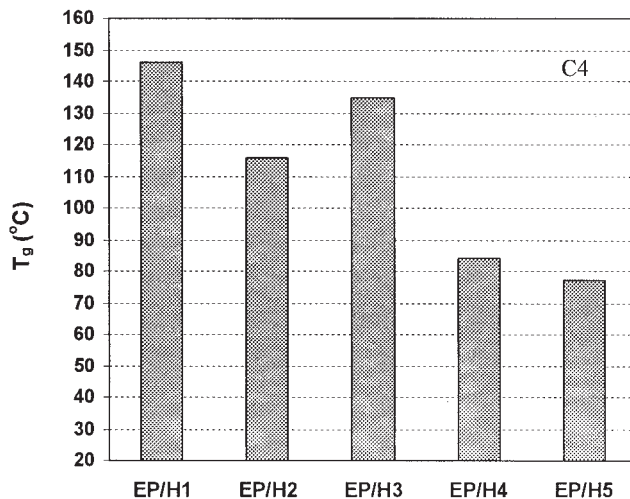
The higher levels of water absorption observed in EP/H4 and EP/H5 after postcure treatment C1 are probably related to an imperfect cure of the materials, which allows easier ingress of water into the relatively loose network structure. The imperfect state of cure was confirmed by FTIR measurements, by which it was found that EP/H4 and EP/H5 still contained small but significant amounts of unreacted epoxy groups even after 200 days under this condition.[18,19] This is attributed to the bulky nature of the hardener molecules H4 and H5, which are fairly immobile at room temperature, especially when sufficient reaction has occurred to form a network with a T_g above room temperature.[18,19] Higher temperature treatments (C3 and C4) mobilized these molecules, allowing further crosslinking, and also accelerated physical aging, reducing the free volume. That closed the gap between the M_∞ values of EP/H4 and EP/H5 and those of the EP/H1, EP/H2, and EP/H3 group (Fig. 7). To account for the increase in M_∞ observed with EP/H1, EP/H2, and EP/H3 when cure treatment C4 was used (150°C), the explanation formulated by Enns and Gillham is invoked.[14] They worked with a DEGBA–DDS epoxy–amine composition and observed that, after curing at 175°C, the water uptake increased with the curing time. They found that the density fell as the curing time increased, and this gave more free volume and facilitated the increase in the water absorption. In these experiments, T_g of the material was below the heat-treatment temperature; for the fully cured material, T_g was higher than that of the partially cured material. Therefore, upon cooling, the fully cured material enters the glassy state at a higher temperature than the partially cured material and then proceeds to increase the density at a lower rate. As a result, the specific-volume-versus-temperature characteristics of the fully cured and partially cured samples may cross,

and the partially cured material has a higher density at room temperature than the fully cured material. In this case, the fully cured material will have more free volume than the partially cured material. In the experiments described here, comparisons were made of samples cured at different temperatures (rather than for different times, as used by Enns and Gillham[14]). Nevertheless, it appears that materials EP/H1, EP/H2, and EP/H3 may have been in this regime when postcured at the highest temperatures (C3 and C4). Presumably, EP/H4 and EP/H5 postcured at condition C3 had not reached a sufficiently advanced state of cure for this phenomenon to be observed as the treatment temperature increased to 150°C (C4). Another relevant observation can be noted from Figure 9. T_gs of EP/H4 and EP/H5 (~84 and ~77°C, respectively) were very much less than the C4 postcure temperature, whereas for EP/H1, EP/H2, and EP/H3, they lay much closer to the postcure temperature (116–146°C); this is an indication that in EP/H4 and EP/H5, the higher molecular mobility contributed to the completion of the crosslinking process.[18,19]

The D data appear to be more complex than those for M_∞ (Fig. 8). It appears that groupings with some correlation with those identified previously emerge, however, because advancing the cure temperature from 23 (C1) to 55°C (C2) caused a sharp drop in D for materials EP/H4 and EP/H5 and a sharp increase with EP/H1 and EP/H3. This time, EP/H2 did not clearly replicate the behavior of either of the other pairs of compositions, showing merely a small fall in D. All five materials showed an increase in D when postcure C3 (75°C) was used. Increasing the postcure temperature to 150°C caused a significant fall in EP/H3, EP/H4, and EP/H5, a small fall in EP/H1, and a modest increase in EP/H2. D depends on many factors, including the free volume, the morphology, and the chemical affinity of the penetrant and host. It is evident that more than one controlling influence is present in the materials studied here. The T_gs of each material showed a monotonic, quasilinear relationship with the postcure temperature,[18,19] and it is clear by an inspection of Figure 6 that there is therefore no correlation of D with T_g for a single material, let alone a general correlation covering all materials.

CONCLUSIONS

The water absorption kinetics followed the prediction of Fick's law. D was found to lie in the range of 1.0–2.5 × 10^5 m²/s for all compositions. The curing agent species used in the epoxy formulations had a significant effect on the water absorption characteristics of the cured resin within this range. The state of cure also had a significant effect and was influenced by the curing agent used. The results were consistent with the hypothesis that the water absorption behavior was strongly influenced by physical aging as well as the degree of crosslinking in the network.

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