WATER ABSORPTION OF A DIGLYCIDYL ETHER OF BISPHENOL A/1,3-BISAMINOMETHYLCYCLOHEXANE (DGEBA/1,3-BAC) EPOXY RESIN SYSTEM

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Abstract

The diffusive and dynamic mechanical behavior of the DGEBA/1,3-BAC epoxy resin system was studied during water absorption. The diffusion of water was investigated at 100% relative humidity, by immersion of specimens in water at 60, 80 and 100°C. In all absorption experiments, water diffusion followed Fick's law. Diffusion coefficients and saturated water concentrations are given for these temperatures. The activation energy for diffusion was determined from the relationship between the diffusion coefficient and the reciprocal of the absolute temperature. The value obtained was 31.2 kJ mol^{-1}. Dynamic mechanical analysis of samples immersed in 100°C water and with various water contents showed both a shift of T_g, defined by the $tan\delta$ peak, to lower temperatures and a slight decrease in the dynamic modulus in the presence of water. These effects are probably a result of plasticization.

Keywords: DMA, epoxy resins, water absorption

Introduction

Polymeric materials absorb water at varying rates. This absorption of water affects the mechanical and thermal properties. Accordingly, it is very important to determine the degree of water absorption and the diffusion coefficient of water in polymeric materials. Accelerated water absorption tests of polymers provide a useful means of predicting their long-term properties.

Epoxy resins and composites based on epoxy resins are widely used in a variety of applications. In the design of these polymers, therefore, it is essential to know the effects of the absorption of water on this class of polymer, but a knowledge of the principles governing the absorption processes is also required for a fuller understanding of the behavior of the components in service. The water absorption of epoxy resins can largely be attributed to the water affinity

of the specific functional groups of the cured epoxy resin of a highly polar nature.

The nature of the epoxy-water molecule interactions has been investigated by various techniques [1-3]. Apicella *et al.* [4-6] proposed three different modes for the water absorption of epoxy systems. Moy and Karasz [7] reported that the water in epoxy compounds exists in two distinct forms: the 'free water' that fills the microvoids of the network, and the 'bound water' in interaction with polar segments such as epoxy rings, glyceryls, or the nitrogen atoms of the amine compound.

The present work forms part of a larger study of the curing characteristics and structure-property relationships of the DGEBA/1,3-BAC epoxy resin system [8-10]. The objective of this part was to study the water absorption kinetics and the changes in the dynamic mechanical properties with varying water content for this system.

Experimental

The epoxy resin used was a diglycidyl ether of bisphenol A (DGEBA), Shell Epikote 828, and the curing agent was 1,3-bisaminomethylcyclohexane (1,3-BAC), manufactured by Mitsubishi Gas Chem. Co. Both components were used as received without further purification. The formulation was 100 g DGEBA for 18.5 g 1,3-BAC. In order to allow the evacuation of air bubbles, the resin and the hardener were stirred under vacuum at room temperature for 10 min. The mixture was cured for 24 h at room temperature, followed by 8 h at 60°C, and then postcured for 2 h at 120°C. Samples for dynamic mechanical experiments were prepared as cylindrical specimens measuring roughly 19 mm in length and 6.4 mm in diameter.

At each temperature, the samples used for water diffusion investigations were discs cut from cylindrical specimens with a diameter of 6.4 mm and a thickness of 0.8 mm. After measurement of the initial mass of each sample, these specimens were placed in distilled water at 60, 80 or 100°C, using a constant temperature bath. Periodically, the specimens were removed, dipped in water at room temperature to suppress water desorption, dried with filter paper, immediately weighed on a balance having a resolution of 0.1 mg, and then returned to the water bath. The procedure was repeated until the water diffusion in the specimens reached equilibrium, i.e. no further increase in mass was observed.

Dynamic mechanical analysis (DMA) tests were performed with a DMA-7 analyser connected to a liquid nitrogen cooling accessory CCA-7 from Perkin-Elmer. All experiments were carried out in three point-bending mode with a frequency of 1 Hz over the temperature range −100 to 200°C under a helium flow of 40 ml min^{-1}. The temperature ramping rate was 5°C min^{-1}.

For investigations on the influence of water on the dynamic mechanical properties, dry samples as well as samples immersed in 100°C water so as to have various water contents were used. To prevent water desorption from the samples during dynamic tests, they were coated with silicone vacuum grease. There was no absorption of water by the vacuum grease.

Results and discussion

The experimental results on water absorption for the DGEBA/1,3-BAC system at 60, 80 and 100°C are presented in Fig. 1. These curves show Fickian type diffusion, i.e. the water absorption process followed the predictions of Fick's law. The mass of water absorbed increased linearly with the square root of time, and then gradually slowed until an equilibrium plateau, i.e. saturation, was reached.
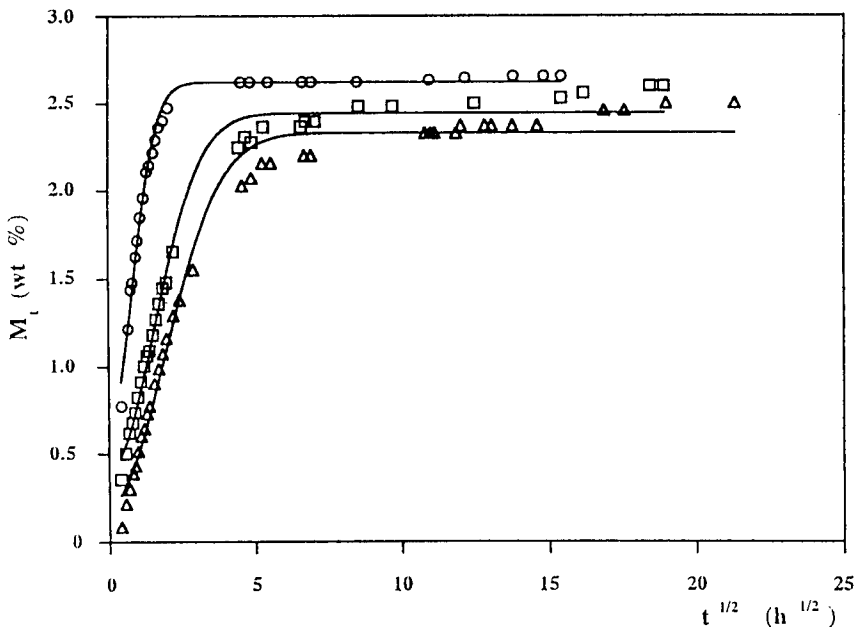

Fig. 1 Plots of M_t vs. $t^{1/2}$ at 60, 80 and 100°C

It has been shown by Crank [11] that for single-phase diffusion the mass gain resulting from water absorption can be expressed in terms of two parameters, the diffusion coefficient, D, and the mass of water absorbed at saturation, M_s, as:

$$\frac{M_t}{M_s} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left[-\left(-\frac{Dt}{h^2}\right)\pi^2(2n+1)^2\right] \qquad (1)$$

where it has been assumed that the initial water content is zero, and h and M_t are the thickness of the sample and the mass of water absorbed in time t, respectively.

For small values of t, Eq. (1) can be replaced by the following approximate expression:

$$\frac{M_t}{M_s} = 4\left(\frac{Dt}{h^2}\right)^{1/2}\left[\frac{1}{\pi^{1/2}} + 2\sum_{n=0}^{\infty} (-1)^n \, ierfc \, \frac{nh}{2(Dt)^{1/2}}\right] \tag{2}$$

A further approximation can be made, involving only the leading term in Eq. (2) as follows:

$$\frac{M_t}{M_s} \approx 4\left(\frac{Dt}{\pi h^2}\right)^{1/2} \tag{3}$$

From Eq. (3), the diffusion coefficient D can be calculated from the initial linear portion of the absorption curve.

It can be seen from Fig. 1 that the initial linear relationship between M_t and $t^{\frac{1}{2}}$ is clearly observed in each case, followed by saturation. Good agreement is obtained between the theoretical prediction of Eq. (1) (shown by solid lines) and the experimental points. The diffusion coefficients obtained from these curves are listed in Table 1. Saturated water concentrations M_s are given in the same Table. While the equilibrium is almost independent of temperature, the diffusion rate is greatly influenced by temperature: as the temperature increased, the time required to reach equilibrium was significantly reduced. The values of diffusion coefficients obtained in the present work are in agreement with the range of values reported by Loos et al. [12] for most polymers and their composites.

Table 1 Water absorption parameters of DGEBA/1,3-BAC

Temp./°C	Water diffusion coefficient/$\times 10^{-12}$ m^2/s	Mass of water absorbed at saturation/wt%
60	2.70	2.50
80	5.16	2.60
100	9.02	2.66

When the diffusion is Fickian and a function of temperature only, the diffusion coefficient is related to temperature by the Arrhenius relationship, given by

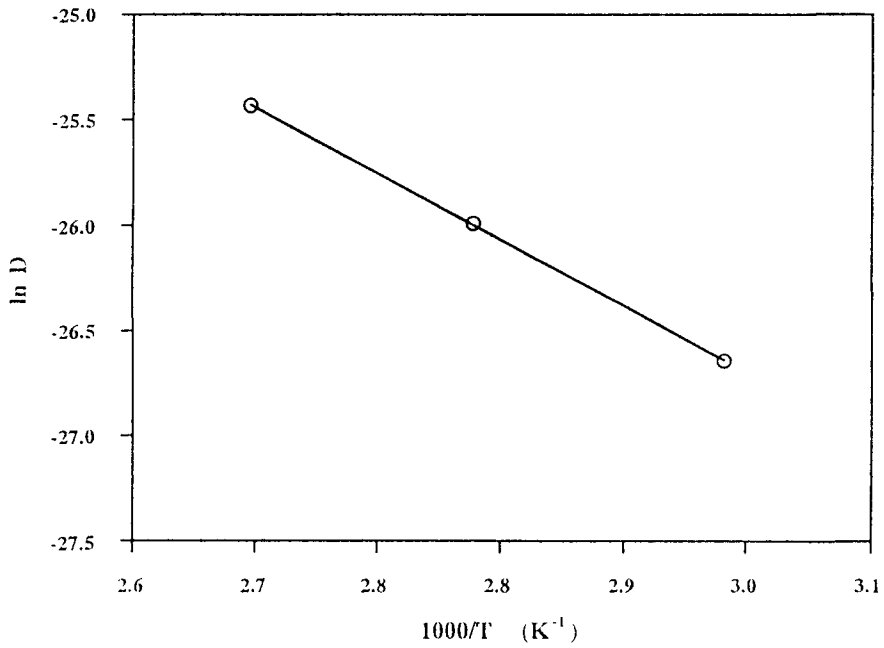$$D = D_o \exp\left[-\left(\frac{E}{RT}\right)\right] \tag{4}$$
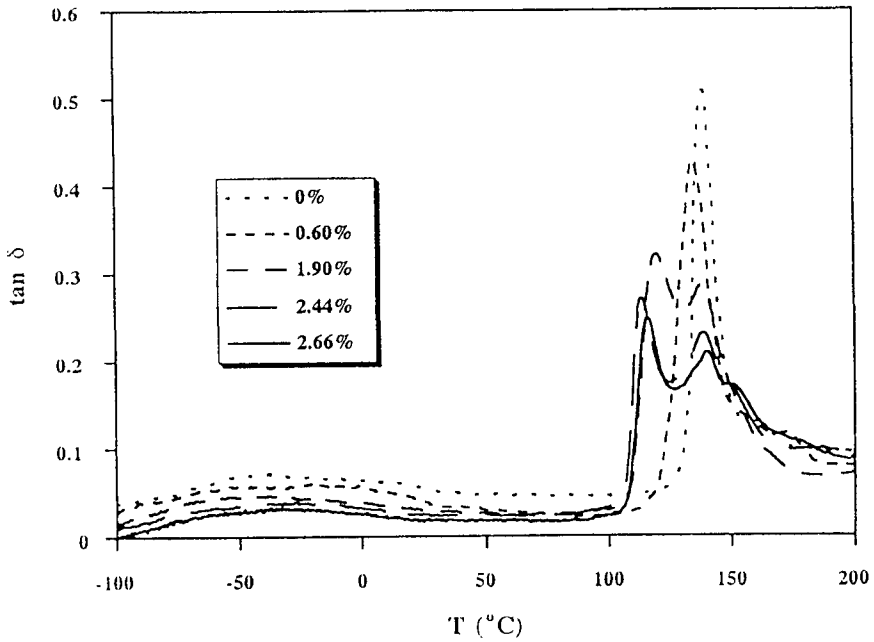
Fig. 2 Arrhenius plot to determine the activation energy

Fig. 3 *Tan*δ of DGEBA/1,3-BAC with various water contents as a function of temperature

where D_o is the pre-exponential coefficient, R is the gas constant, T is the absolute temperature, and E is the activation energy for diffusion. A plot of $\ln D$ vs. the reciprocal of absolute temperature, T, is shown in Fig. 2. The value of the activation energy for this system is 31.2 kJ mol^{-1}.

Samples containing various amounts of water were prepared to investigate the influence of water on the dynamic mechanical properties. Both dry samples and samples immersed in 100°C water for 1, 24, 264 or 2640 h and containing 0.60, 1.90, 2.44 or 2.66 wt.% water, respectively, were used for the experiments.

In Fig. 3, the changes in $tan\delta$ for the DGEBA/1,3-BAC epoxy resin system containing various amounts of water are given over the temperature range −100 to 200°C. The dry sample exhibits a peak centered at 140°C, the α-transition peak or T_g, and a low-temperature β-transition peak at about −40°C. This low-temperature peak is quite broad, indicating that a wide spectrum of motion types and/or activation energies contribute to the transition [4]. Water absorption induces a slight decrease in the intensity of the β peak, but this β-transition is still appreciable at high water contents; however, the position of the peak does not alter significantly with variation in the amount of water. A decrease in the peak value of $tan\delta$ and a shift in T_g, defined by the $tan\delta$ peak, to lower temperatures with an increase of water content can be seen in the glass transition region. Secondary peaks appear in $tan\delta$ at temperatures higher than T_g. These
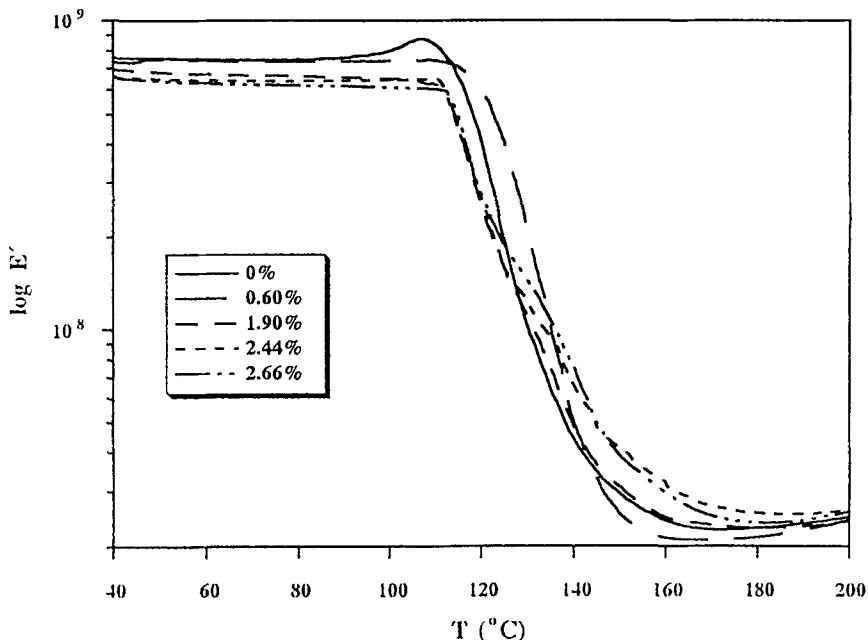

Fig. 4 Dynamic storage modulus of DGEBA/1,3-BAC with various water contents as a function of temperature

peaks could correspond to high crosslink density zones included inside the epoxy matrix, formed during the cure schedule. It has been established that low-temperature curing leads to a low cross-link density matrix and, when the cure schedule is carried out at higher temperatures, high local cross-link densities materials are obtained [13].

The behavior of the dynamic storage modulus, E', over the glass transition region with various amounts of water is shown in Fig. 4. Only a slight decrease in the value of E' in the glassy state can be observed with change of the water content. These effects observed due to water absorption in Figs 3 and 4 are probably a result of plasticization of the DGEBA/1,3-BAC epoxy resin system.

Conclusions

Water absorption at 60, 80 or 100°C has been studied for the DGEBA/1,3-BAC epoxy resin system. The kinetics of water absorption at these temperatures could be fitted well by a Fickian diffusion model. Good agreement was observed between the experimental and theoretical values. The activation energy for diffusion was determined as 31.2 kJ mol^{-1}. Changes in dynamic mechanical properties were observed for samples containing absorbed water. The absorbed water caused a plasticizing effect in this system by the shift of T_g to lower temperatures and by a slight decrease of dynamic modulus.

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