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WATER SORPTION IN TETRAFUNCTIONAL PHENOL NOVOLAC EPOXY MIXTURES CURED WITH A DIAMINE

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Abstract

The diffusive and dynamic mechanical behaviour of an epoxy system containing tetraglycidyl-4,4'-diaminodiphenylmethane and a multifunctional Novolac glycidyl ether cured with 4,4'-diaminodiphenylsulfone was studied after water sorption. The diffusion of water was performed at 100% relative humidity, by immersion of specimens in water at 20, 40, 70 and 100°C. In all sorption experiments, the water diffusion followed Fick's law. Diffusion coefficients and saturated water concentrations were estimated for these temperatures. The activation energy for diffusion was determined from the relationship linking the diffusion coefficient and the reciprocal of the absolute temperature. The value obtained was 45.7 kJ mol^{-1}. Dynamic mechanical analysis of samples immersed in water at 25 and 100°C, and with various water contents, showed a shift in T_g (defined by the tanδ peak) to lower temperatures over the glass transition region, and a slight decrease in the dynamic storage modulus in the presence of water as a result of a plasticization effect.

Keywords: diffusion coefficient, DMA, TGDDM epoxy, water sorption

Introduction

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

Epoxy resins and composites based on epoxy resins are widely used in a variety of applications. Tetraglycidyl-4-4'-diaminodiphenylmethane (TGDDM) epoxy is an ideal material for many important usages as a matrix for fiber-reinforced composites. There are some commercial epoxy formulations of great significance in the manufacture of high-performance composites that utilize more than one epoxy to aid in processing or to improve properties. A great number of them are prepared by mixing a TGDDM and a Novolac resin, which are cured

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with 4,4'-diaminodiphenylsulfone (DDS). In the design of these polymers, it is essential to know the effects of water sorption on this class of polymer, and a knowledge of the principles governing the sorption processes is also required for a fuller understanding of the behaviour of these materials.

The nature of the epoxy–water molecule interactions has been investigated by using various techniques [1–3]. Apicella *et al.* [4–6] proposed three different modes for the water sorption of epoxy systems: (a) bulk dissolution of water in the polymer network; (b) moisture sorption onto the surface of holes that define the excess free volume of the glassy structure; and (c) hydrogen bonding between hydrophilic groups of the polymer and water. Moy and Karasz [7], Mikols *et al.* [8] and more recently Pethrick *et al.* [9], have reported that in epoxy compounds the water exists in two distinct forms: the free water that fills the microcavities of the network, and the bound water in strong interactions with polar segments such as epoxy rings, glyceryls or the nitrogen atoms of the amine compound.

In previous work in our laboratory [10, 11], the cure kinetics and the isothermal time–temperature–transformation (TTT) diagram of this TGDDM/Novolac/DDS system were studied by differential scanning calorimetry (DSC). In the present paper, the water sorption kinetics and the changes in the dynamic mechanical properties with varying water content are investigated.

Experimental

The epoxy resin system studied was a mixture of three components. The main one is TGDDM (Ciba-Geigy MY 720), the second is a multifunctional Novolac glycidyl ether resin (Ciba-Geigy EPN 1138), and the third is an aromatic amine hardener, DDS, available from Fluka Chemie.

All these components were commercial products, and were used as received without purification. Since these commercial resins are not pure monomers and contain impurities produced during manufacture [12, 13], the masses per epoxy equivalent for TGDDM and EPN were determined in our laboratory by hydrochlorination [14]. The values obtained, respectively, were 130 and 180 g eq^{-1}. The hardener has a molecular weight of 248.31 and purity >96% according to the supplier. The material was prepared by mixing the components in an oven at 120°C and stirring continuously until a homogeneous mixture was achieved. The composition of the mixture was 43.3wt% of TGDDM, 35.7wt% of EPN and 21.0wt% of DDS, yielding an amine/epoxide ratio of 0.64.

The mixture was cured for 2 h at 177°C, then postcured for 2 h at 220°C. Samples for dynamic mechanical experiments were prepared as cylindrical specimens measuring roughly 19 mm in length and 6.3 mm in diameter.

At each temperature, the samples used for water diffusion investigations had identical properties and curing history. Discs cut from cylindrical specimens with a diameter of 6.3 mm and a thickness of 0.7 mm were used. After measurement of the initial mass of each sample, these specimens were placed in deionized water at 20, 40, 70 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 Perkin Elmer AD4 balance having a resolution of 0.01 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 –120 to 300°C under a helium flow of 40 ml min^{-1}. The scanning rate was 5°C min^{-1}.

For investigations of the influence of water on the dynamic mechanical properties, dry samples and also samples immersed in water at 25 and 100°C so as to afford various water contents were used. To prevent water desorption from the samples during dynamic tests, they were coated with silicone vacuum grease.

Results and discussion

The experimental results on water sorption for the TGDDM/Novolac/DDS system at 20, 40, 70 and 100°C are presented in Fig. 1. These curves show Fickian-type diffusion, i.e. the water sorption process follows the predictions of Fick's law. The mass of water absorbed increased linearly with the square root of time until saturation was reached. In fact, although the sorption processes of liquids and vapor in glassy polymers follow complex mechanisms, water diffusion in epoxy resin matrices has frequently been represented by Fickian behaviour [8, 15, 16].

It has been shown by Crank [17] that, for single phase diffusion, the mass gain resulting from water sorption can be expressed in terms of two parameters, the diffusion coefficient, D, and the mass of water absorbed 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.

A simplified form of Eq. (1) [17]:

$$\frac{M_t}{M_s} = 4\left(\frac{Dt}{\pi h^2}\right)^{\frac{1}{2}} \qquad (2)$$

For gravimetric analysis, Eq. (2) is a valid representation of the time dependence of the water uptake, and D can be calculated from the initial linear portion of the sorption curve.

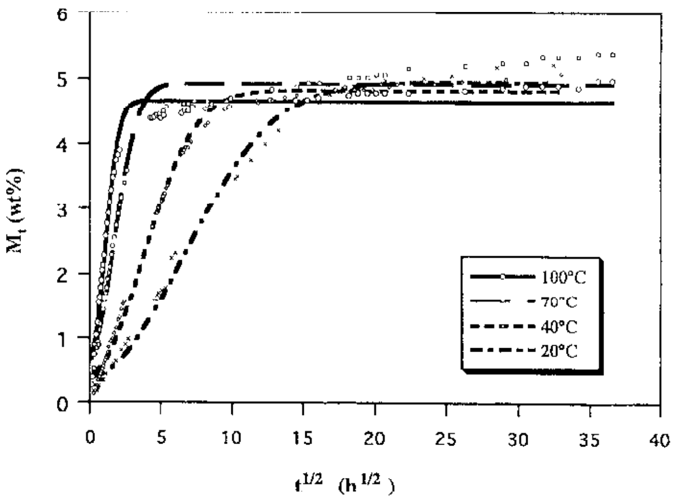

Fig. 1 Plots of M_t *vs.* $t^{1/2}$ at different temperatures

It can be seen from Fig. 1 that an initial linear relationship between M_t and $t^{1/2}$ 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. Diffusion coefficients obtained from these curves are summarized in Table 1. Saturated water concentration M_s are given in the same Table.

Table 1 Water sorption parameters of TGDDM/Novolac/DDS

Temperature/ °C	Water diffusion coefficient $D/\times10^{-12}$ m^2 s^{-1}	Mass of water absorbed at saturation M_s/wt%
20	0.13	5.22
40	0.41	5.09
70	1.68	5.38
100	7.74	4.99

While the equilibrium concentration is almost independent of temperature, the diffusion rate is influenced greatly by temperature: as the temperature increased, the time required to reach equilibrium was significantly reduced. The D values obtained in the present work are in agreement with the range of values reported by Loos and Springer [18] for most polymers and their composites.

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

$$D = D_0 \exp\left(-\frac{E}{RT}\right) \tag{3}$$

where D_0 is the preexponential 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, $1/T$ (K^{-1}), is shown in Fig. 2. The value of the activation energy for this system is 45.7 kJ mol^{-1}.

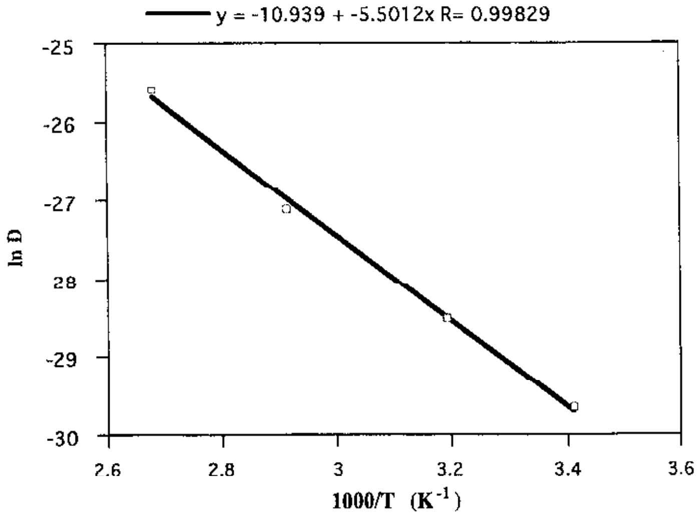

Fig. 2 Arrhenius plot to determine the activation energy

Samples containing various amounts of water were prepared to investigate the influence of water on the dynamic mechanical properties. Dry samples and samples immersed in 25°C water for 24, 525, 960 or 1900 h and containing 0.5, 2.3, 3.0 or 3.9 wt% water, respectively, and also samples immersed in water at 100°C for 15, 24 or 220 h and containing 1.3, 2.8 or 4.6 wt% water, respectively, were used for the experiments.

Figure 3 depicts the changes in tanδ for the TGDDM/Novolac/DDS system at 25°C containing various amounts of water over the temperature range –120 to 300°C, while Fig. 4 illustrates these changes when experiments were performed at 100°C. A zoom of the low-temperature range was made in these Figures for a better presentation of the β-relaxation peak.

The dry sample exhibits a peak centered at 252°C, the α-relaxation peak or T_g, and a low temperature β-relaxation peak at about –50°C. This low temperature peak is quite broad, indicating that a wide spectrum of motion types and/or activation energies contribute to this relaxation [4].

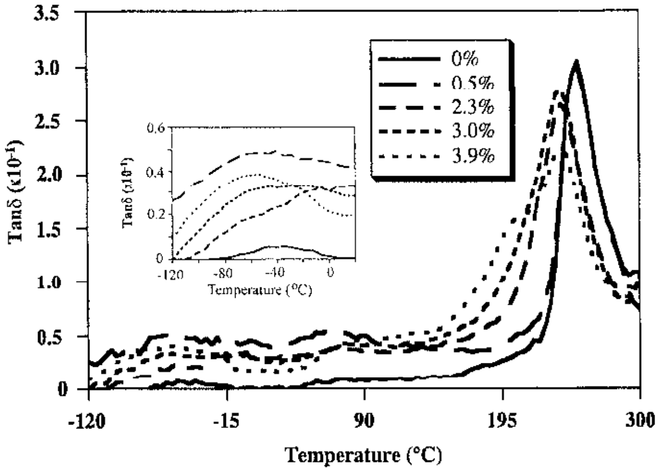

Fig. 3 tanδ *vs.* temperature for TGDDM/Novolac/DDS with various water contents at 25°C

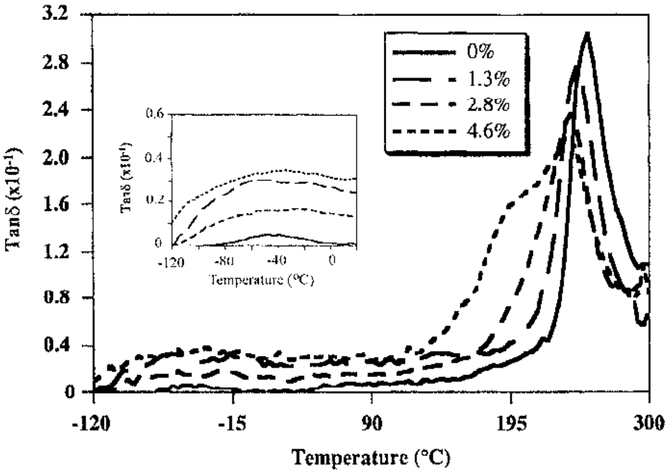

Fig. 4 tanδ *vs.* temperature for TGDDM/Novolac/DDS with various water contents at 100°C

From Figs 3 and 4 it can be seen that there is decrease in the peak value of tanδ and a shift in T_g, defined by the tanδ peak, to lower temperatures with an increase of the water content in the glass transition region. The shoulder that appears in the tanδ curves for high water contents could be explained by the increase in the free volume of the network. Free volume changes permit the mobility of polar segments, so it is possible to find a new dynamic mechanical transition. This transition was previously reported and explained [4].

From the zooms of these Figures, it is clear that water sorption induces a slight increase in the intensity of the β-peak respect to the β-peak of the dry sample. However, there is no appreciable trend in the evolution of this peak with the increase of the water content, and the position of the peak is not significantly changed with variation of the amount of water.

The behaviour of the dynamic storage modulus, *E*, over the glass transition region with various amounts of water at 25 and 100°C, respectively, is shown in Figs 5 and 6. Only a slight decrease in the value of *E* in the glassy state can be observed with change of the water content.

The effects observed due to water sorption in Figs 3–6 are a result of plasticization of the TGDDM/Novolac/DDS epoxy resin system.

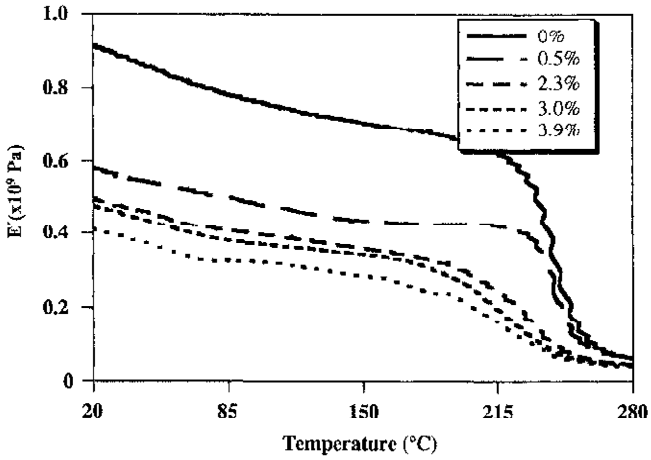

Fig. 5 Dynamic storage modulus *E'*, *vs.* temperature for TGDDM/Novolac/DDS with various water contents at 25°C

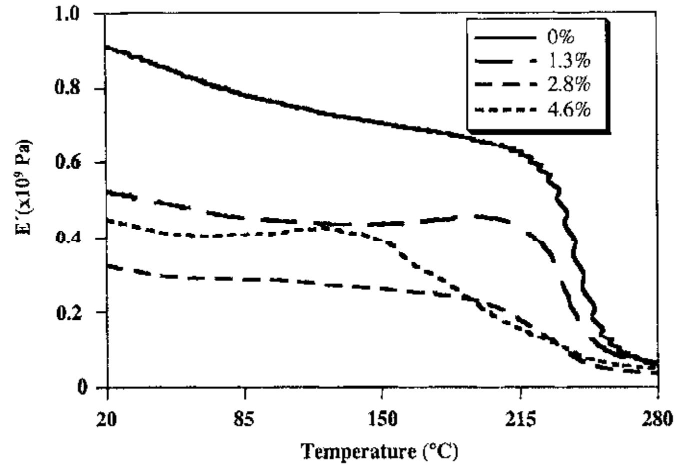

Fig. 6 Dynamic storage modulus *E'*, *vs.* temperature for TGDDM/Novolac/DDS with various water contents at 100°C

Conclusions

Water sorption at 20, 40, 70 and 100°C has been studied for this TGDDM/Novolac/DDS epoxy system. The sorption kinetics of water 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 45.7 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. This effect is particularly obvious over the glass transition region in consequence of a shift in T_g to lower temperatures, a decrease in the peak value of tan δ, and also a slight decrease in the dynamic storage modulus.

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