

STUDY OF THE INFLUENCE OF WATER ABSORPTION ON DIFFERENT EPOXY-DIAMINE SYSTEMS BY DSC

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The diffusive, calorimetric and thermal degradation behavior of different epoxy-amine systems was investigated during water sorption at different temperatures (23, 40 and 70°C). Experimental results showed that the water absorption at these temperatures fitted well to Fick's law. Influence of water immersion during different periods of time on the glass transition temperatures was studied by differential scanning calorimetry. Thermal degradation of saturated samples was studied by thermogravimetric analysis. Dependence on the selected curing cycle was also checked.

Keywords: diffusion, DSC, gravimetry, TG, water absorption

Introduction

The presence of water in a polymer (e.g., epoxy resin) can lead to marked changes in the resin chemical and physical state. Morgan *et al.* [1] Pryde *et al.* [2] and Apicella *et al.* [3] have reported that absorbed water in an epoxy can lower T_g (by as much as 20°C). In fact, sorption water may act as a plasticizer and crazing agent for epoxies.

For this study, we chose different epoxy-diamine systems consisting of an epoxy resin, diglycidyl ether of bisphenol A (DGEBA, $n=0$) and 1, 2 diamine cyclohexane (1, 2 DCH) or *m*-xylylenediamine (mXDA) as curing agents. These systems were chosen because of its high reactivity in a wide range of temperatures. In previous articles [4, 5] the *TTT* diagram of these epoxy-diamine systems were obtained. Two different curing cycles for the DGEBA/1,2 DCH system were selected in order to study the influence of the curing schedule on the final properties. In previous papers, the influence of the curing cycle on the thermal stability and on the thermodegradation activation energies of similar systems were studied [6, 7].

Experimental

Materials

DGEBA ($n=0$) was the epoxy resin used (Resin 332, Sigma Chemical Co. St. Louis, USA), and 1, 2-diamine cyclohexane (1, 2 DCH, Fluka) and *m*-xylylenediamine 99% (m-XDA) (Aldrich) were the curing agents. The equivalent epoxy molecular mass

of the resin was 173.6 g eq^{-1} , as determined by wet analysis [8, 9] and that of the 1, 2-DCH was taken as 28.5. All of them were used as received.

Sample preparation

The epoxy resin and the curing agents were carefully and homogeneously mixed, at stoichiometric ratios, before being introduced into a cylindrical frame. Curing reactions were programmed according to the *TTT* diagrams previously described for these materials [4, 5].

For the DGEBA ($n=0$)/1, 2-DCH system, two curing cycles were selected. One of them consists of two stages: a first step at 23°C during 7.5 h and a second one in a stove, at 70°C during 24 h. The system cured through this sequence will be named B/DCH B system, and the other one, cured through an 'old' curing cycle (because it was the first system studied) will be named B/DCH A system. The 'old' curing cycle consisted also of two stages: a first step at 23°C during 24 h and a second one in a stove at 70°C during 16 h. As can be seen in [4], both sequences are very similar, because our aim was to check if a small change in the curing cycle implies a significant difference on the water diffusion and on the effect on its thermal properties. After curing, the samples were removed from the frame. Checking the *TTT* diagram [4] it can be seen that, at the end of the first step of each cycle, curing conversions of the material differ in 20%, being 80 and 60% for the old and new cycles, respectively. For the old system during the first step of the curing, the sample gels and vitrifies, while the second one (B system) only gels after the first

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step. Our question is to know if those differences will affect to the effect of water diffusion of our system.

For the DGEBA ($n=0$)/mXDA system [5], the curing cycle consists of a first step at 40°C during 2 h and 28 min and a second step at 70°C during 24 h. After curing, the samples were removed from the frame.

For diffusion experiments, samples were prepared in the form of cylinders that were introduced in flasks containing water, and were kept there for different periods of times, at different temperatures (23, 40 and 70°C), before being studied. For calorimetric analysis (DSC), samples in the form of discs were 20 to 25 mg in mass and 6-mm in diameter.

Methods

Gravimetric measurements

Periodically, sample mass were determined using a Sartorius R200D balance with a sensitivity of 0.001 mg. The relative mass increase in each sample was calculated as:

$$M_t = \frac{m_t - m_0}{m_0} \cdot 100$$

M_t (%) values represented in Fig. 1 were obtained from the water uptake of three samples after exposure to identical conditions.

Differential scanning calorimetry

A Perkin-Elmer DSC7 unit, under control of a 1020 system controller, was used for calorimetric measurements. The experiments were carried out in a temperature range from 5 to 250°C at a heating rate 10 K min⁻¹.

Thermogravimetric analyzer

The thermogravimetric study was carried out using a Thermogravimetric Analyzer (TGA7) from Perkin Elmer controlled by a 1022 computer. The system was operated in the dynamic mode in the temperature range from 40 to 400°C, at a heating rate 10 K min⁻¹. All the experiments were carried out under a dry nitrogen atmosphere.

Results and discussion

Water diffusion study, thermogravimetric analysis

Water diffusion in epoxy resin matrices has frequently been represented by a Fickian behavior (Fick's second law) [10]. Diffusion behavior of the three systems at different water temperatures is shown in Fig. 1, where experimental measurements of $M_t(t)$ vs. $t^{1/2}$ are shown. As it can be seen, the be-

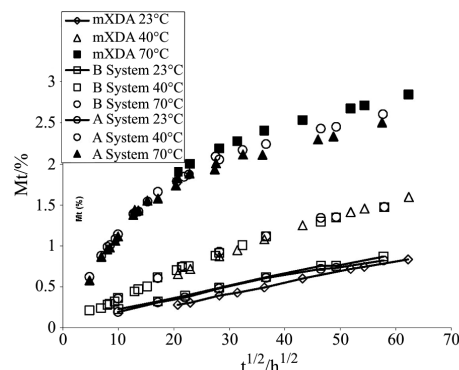


Fig. 1 Diffusion behavior of DGEBA ($n=0$)/1,2-DCH A and B systems and DGEBA ($n=0$)/mXDA system at different water temperatures

havior is similar to that predicted by Fick's law. The features of Fickian diffusion have been described by Fujita [10]: (1) sorption curves are linear in the initial stages; (2) above the linear portions, sorption curves are concave to the abscissa axis; and (3) reduced sorption curves, plotted for films of different thickness, are superimposables. Our experimental results reasonably fulfilled these criteria, although they are more clear for high temperatures.

In the first steps, the diffusion behavior is strongly influenced by temperature; as conditioning temperature is increased, the diffusion process speeds up. It can be seen that at low temperatures, the saturation value is around 1.5%. Moy *et al.* [11] and Jelinski *et al.* [12] have predicted that water is essentially bound water below this value. The increase of excess water uptake caused by microvoiding has been found to be progressively more relevant as the temperature is increased. This observation is in line with the low energies for craze formation required at high temperatures.

DGEBA ($n=0$)/mXDA samples gain less water than DGEBA ($n=0$)/1,2-DCH samples at 23 and 40°C, but they took the higher water uptake at 70°C. This can be related to some postcuring effects on the mXDA system that increase the crosslinking and glass transition temperature.

Following Loos *et al.* [13] and Moy *et al.* [11] works, we checked if diffusion behavior is sensitive to curing conditions. But these differences between A and B systems were only outstanding at 70°C (no differences between diffusion curves for 23 and 40°C were observed). Differences between B/DCH and B/mXDA systems are logic; although the epoxy resin is the same, curing agent are different, causing a different morphology that involves, in general, different final properties, such as T_g , water absorption, etc.

An increase of the conditioning temperature significantly reduces the time required to reach the equilibrium moisture content. Barral *et al.* [14], Moy *et al.*

[11] and Loos *et al.* [13] checked the same behavior for similar systems.

Calorimetric analysis

To study the effect of water uptaken by the DGEBA ($n=0$)/1,2-DCH and DGEBA ($n=0$)/mXDA systems, several samples were immersed in water at 23, 40 and 70°C during different periods of time. Normalized calorimetric curves obtained in dynamic DSC scanning for these three systems are shown in Figs 2 and 3. In all DSC curves, exothermic events are in downward direction and endothermic events correspond to upward direction peaks.

Samples immersed and not immersed in water at 40°C show relaxation peaks around 100°C. This peak appears at lower temperatures for the immersed systems, but in these cases its position does not depend on time of immersion, as it can be seen in Figs 2a–c. A different behaviour is observed for samples immersed in water at 70°C. These relaxation peaks appear at higher temperatures compared to the not immersed systems, although these peaks keep almost same positions regardless of time of immersion, as it can be seen in Figs 3a–c.

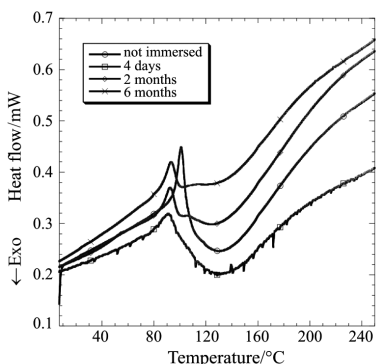


Fig. 2a DSC curves from dynamic experiments of the B/DCH A system after immersion in water at 40 °C during different periods of time

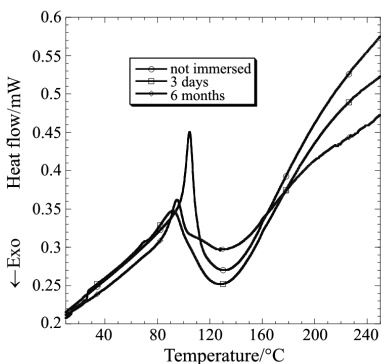


Fig. 2b DSC curves from dynamic experiments of the B/DCH B system after immersion in water at 40°C during different periods of time

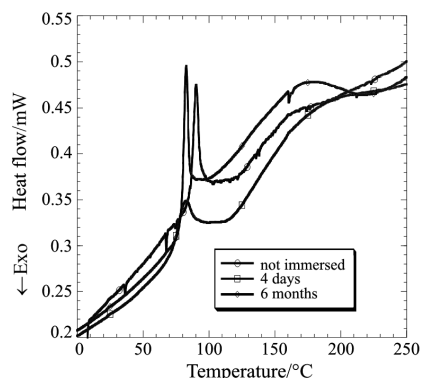


Fig. 2c DSC curves from dynamic experiments of the B/mXDA system after immersion in water at 40°C during different periods of time

According to other authors a postcuring effect owing to the immersion in water can be assumed [15]. This effect obviously depends on immersion time and water temperature. For not immersed samples and for those immersed not much time in water, an exothermic peak after the relaxation peak can be observed in Figs 2a–c. This can be related to the postcuring effect provoked by this DSC scans. The area of these peaks becomes smaller as the time of immersion increases. This

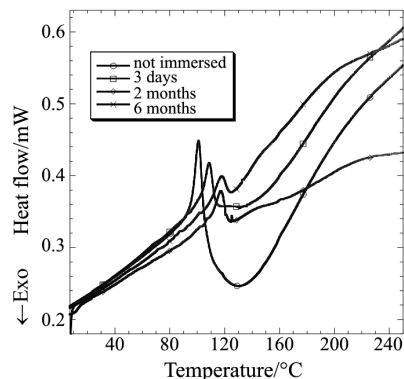


Fig. 3a DSC curves from dynamic experiments of the B/DCH A system after immersion in water at 70°C during different periods of time

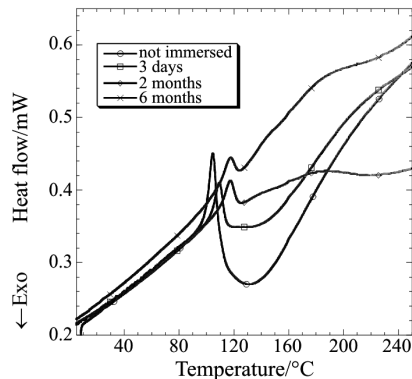


Fig. 3b DSC curves from dynamic experiments of the B/DCH B system after immersion in water at 70°C during different periods of time

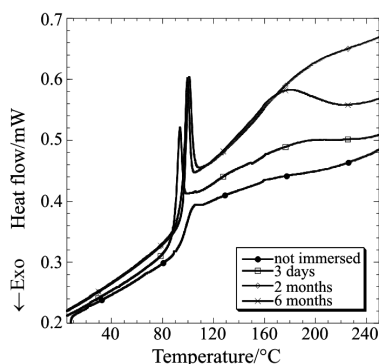


Fig. 3c DSC curves from dynamic experiments of the B/mXDA system after immersion in water at 70°C during different periods of time

can be explained because as the immersion time increases, a postcuring effect due to the water temperature can be more pronounced. At the same time, the absorbed water during this immersion is evolved during DSC scans, and the endothermic peak related to that released water overlaps with the exothermic peak due to the postcuring, making this latter smaller. As we can see in Figs 2a–c, the postcuring effect due to the immersion in water at 40°C is not as high as that corresponding to the samples immersed in water at 70°C (Figs 3a–c). For the former, DSC scans show exothermic peaks, whose area decrease as the immersion time increases. This can be due to the increase of postcuring effect and/or to the increase of evolved water (as immersion time increases, water uptake does also). In case of immersion time was enough to provoke a total postcuring effect, no curing residual heat (exothermic) should be detected. For samples immersed at 70°C, a different behavior can be observed. Exothermic peaks were only detected for systems immersed up to two months. For samples immersed up to six months not only no exothermic peaks were detected, but also endothermic heat has been observed. This can be related to the evolved water during DSC experiments. In the case of samples immersed up to two months this endothermic effect was overlapped by the exothermic peak corresponding to the postcuring. In the case of B/mXDA systems, even for those immersed in water at 40°C the postcuring effect during immersion was detected (Fig. 2c)

From second DSC scans, glass transition temperatures were determined. In Fig. 4, T_g values for the

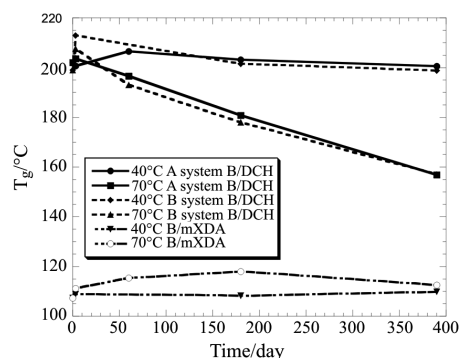


Fig. 4 T_g values for the three systems after immersion in water at different temperatures after 13 months

three epoxy-diamine systems after several immersion times in water at different temperatures are shown.

For A and B B/DCH systems, T_g values reach a maximum at low times, but after two months those values decrease with time, that can be attributed to a plasticizer effect [15]. This effect is more pronounced for the samples immersed in water at 70°C. At 40°C, the effect is almost negligible. The reason can be that even for long immersion times, 40°C is not high enough to produce a plasticizer effect. We can also observe that this effect does not depend on the curing cycle selected. In Table 1, T_g values corresponding to samples after immersion during 13 months in water at different temperatures are shown. After 13 months, the plasticizer effect is reflected in a decrease in T_g .

For B/mXDA system, the influence on the T_g value is different. At 40°C, same behavior than that for B/DCH systems is observed. But at 70°C, not only T_g does not decrease, but also there is a small increase, that can be associated to a postcuring during immersion in water at this temperature.

Thermogravimetry

Using TG, thermal behavior of samples after immersion in water during 13 months was studied. As it can be observed in Figs 5a–c, before the typical beginning of the thermal decomposition corresponding to the epoxy groups (at around 300°C), there is a previous step corresponding to the evaporation of the uptaken water (between 100 and 300°C). This step is higher as the water content increases, that means as the water temperature increases. The temperature interval corresponding

Table 1 T_g , in(°C), for the three different systems after 13 months in water at different temperatures, obtained from second DSC scans

Water temperature/°C	B/DCHA system	B/DCHB system	B/mXDA system
Not immersed	202.08	199.02	107.37
23	204.74	200.55	106.41
40	200.55	198.83	109.85
70	156.92	157.12	112.53

to this first step is the same observed in DSC experiments corresponding to the postcuring and/or releasing of water.

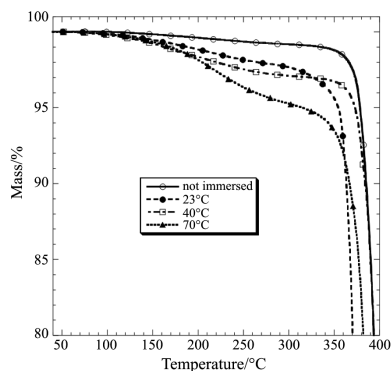


Fig. 5a Thermal degradation curves for the B/DCH A system at 10 K min^{-1} after immersion in water at different temperatures during 17 months

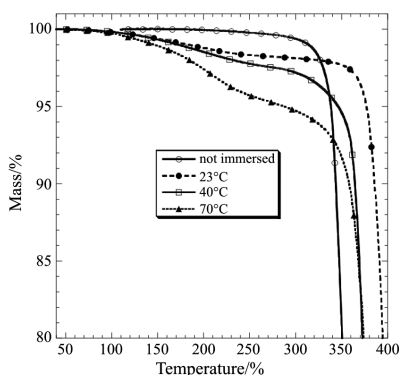


Fig. 5b Thermal degradation curves for the B/DCH B system at 10 K min^{-1} after immersion in water at different temperatures during 17 months

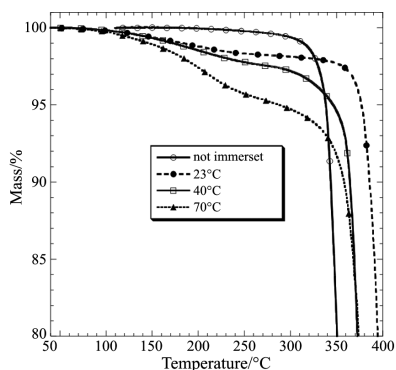


Fig. 5c Thermal degradation curves for the B/mXDA system at 10 K min^{-1} after immersion in water at different temperatures during 17 months

Conclusions

The water absorption by three epoxy systems was studied by means of a gravimetric analysis. The water uptaked temperature and water uptaked curing conditions dependences were checked.

A dynamic calorimetric analysis on several samples that had been immersed in water over different periods of time was performed. Relaxation peaks as well exothermic peaks associated to a postcuring effect were observed. From second DSC scans, the influence of water, temperature and time on T_g values was checked.

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