PHYSICAL AGING OF A TETRAFUNCTIONAL/PHENOL NOVOLAC EPOXY MIXTURE CURED WITH DIAMINE
DSC and DMA measurements

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Abstract

The physical aging of a system containing tetraglycidyl-4-4'-diaminodiphenylmethane (TGDDM), with a multifunctional novolac glycidyl ether resin hardened by 4,4'-diaminodiphenylsulphone (DDS) has been investigated by differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). Samples fully cured were aged at temperatures between 200 and 250°C, during periods of time from 1 to a maximum of 336 h. Furthermore, the dynamic mechanical relaxation behaviour annealed at temperature of 220°C, was studied, aging during 24 and 168 h. The effect of the enthalpy relaxation during DSC heating scan is shown by the presence of an endothermic peak whose position and intensity depends on the aging conditions, both temperature and time. DSC studies suggest that enthalpy relaxation increases gradually with aging time to a limiting value for each temperature where structural equilibrium is reached. DMA results show that the effect of aging is to cause chain stiffening and a decrease in the height of the peak value of the loss factor.

Keywords: DMA, DSC, physical aging, TGDDM epoxy

Introduction

Physical aging is a phenomenon that has recently been shown to be of great importance when considering the behaviour of glassy polymers [1]. The gradual rearrangement of molecular chains that occurs following a quench from above the glass transition temperature, T_g, causes a gradual increase in density towards the equilibrium value. A reduction in molecular mobility also occurs, resulting an increase in the modulus [2].

Another important parameter to be taken into account is the effect of physical aging on the structural organization of a polymer. The changes that can occur in a material with aging can affect its application, perfomance and lifetime, therefore, a study of this effect is very important as it is shown in recent papers [3].

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Enthalpy loss during the aging process is recovered during reheating the aged sample to above T_g, and the enthalpy difference, Δh (enthalpy relaxation), between the original and the annealed glass is a good indication of the structure change on annealing. So, the enthalpy determined by differential scanning calorimetry, DSC, is an adequate property to monitor physical aging. Also, dynamic mechanical analysis, DMA, provides us information on the structure of polymers taking place during the physical aging process. The importance of physical aging studies of glassy polymers can thus be of significant practical as well as academic interest considering their widespread application as structural materials and the need to design such materials with long term durability.

Although in the last years there were some reports on physical aging in networks based on epoxy resins which are specially interesting because they deal with the physical aging process which occurs after the vitrification phenomenon, when the curing temperature is lower than the maximum glass transition temperature of the crosslinked polymer [4, 5], there is little information about this process on epoxy systems cured with diamines, as to that is interesting its research [6].

In this paper, the physical aging of a system based on an epoxy resin cured with a diamine with a controlled thermal history was investigated by DSC and DMA. Previously, we have reported for this epoxy system the kinetics of the cure reaction and the thermogravimetric behaviour [7, 8].

Experimental

Materials and cure procedure

The studied epoxy resin system was a mixture of three components. The main one is tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM), (Ciba-Geigy MY 720). The second component is a multifunctional novolac glycidyl ether resin (Ciba-Geigy EPN 1138) and the third is an aromatic amine hardener, 4,4'-diaminodiphenylsulphone (DDS), purchase from Fluka Chemie. All these components were commercial products, and were used as received, without purification. The masses per epoxy equivalent for TGDDM and EPN were determined in our laboratory by hydrochlorination [9]. The values obtained, respectively, were 130 and 180 g eq^{-1}. The hardener has a molecular mass of 248.31 and purity >96% according to the supplier. The composition of the mixture was 43.3 % of TGDDM, 35.7% of EPN and 21.0% of DDS, yielding an amine/epoxide ratio of 0.64. The material was prepared by mixing the components in an oven at 120°C and stirring continuously until a homogeneous mixture was obtained and then poured into a rectangular mold to obtain a homogeneous sheet of material. The mixture was cured for 2 h at 160°C followed by 2 h at 220°C.

Differential scanning calorimetry

A Perkin Elmer DSC-7, which was calibrated with high purity indium and zinc standards, was used for the measurement of the heat flow, or the specific heat capac-

ity, as a function of temperature. The DSC curves were obtained using about 10 mg of sample with a heating rate of 10°C min^{-1} under a nitrogen flow of 40 ml min^{-1}.

To perform the isothermal aging experiment, the samples were subjected to the following thermal history to evaluate the enthalpy evolution: TGDDM/EPN/DDS samples were heated at 20°C min^{-1} in the DSC to 260°C, and left at that temperature for several minutes, in order to erase any previous thermal history of each sample. Then, the samples were quenched from 260°C to the aging temperature, T_a. After annealing for times up to 336 h, the samples were quenched to room temperature and then immediately reheated at 10°C min^{-1} through the glass transition region. In order to measure the enthalpy relaxation, a second DSC scan was always made by cooling again to 30°C and immediately reheating at 10°C min^{-1} to provide a zero annealing time reference curve. These experiments gave the dependence of peak temperature, T_p, and enthalpy loss, on log (annealing time). The time/temperature history of the DSC experiments is shown schematically in Fig. 1.
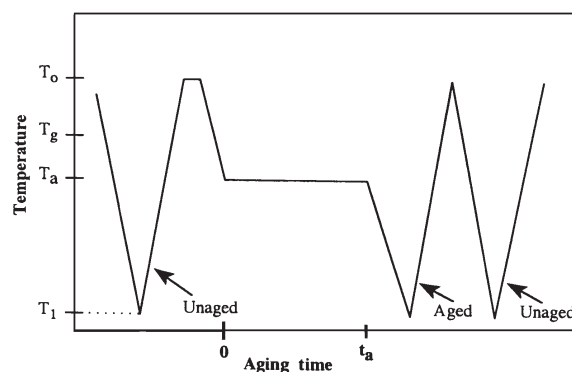

Fig. 1 Scheme of temperature history for DSC experiments

The isothermal processes of aging were between 200 and 250°C for the TGDDM/EPN/DDS system. Aging treatment was performed directly in the DSC cells for samples requiring short aging times, while a temperature controlled oven was used for aging treatment for long times. The aging experiment was designed to be carried out in a dry, dark and inert atmosphere in order to avoid any possible complications that may due to chemical aging.

Dynamic mechanical analysis

A DMA-7 connected to a liquid nitrogen cooling accessory CCA-7 from Perkin Elmer was used to characterize the temperature dependence of the dynamic storage modulus, E', and the loss factor, tanδ, of the samples at various aging extents.

Dynamic mechanical measurements were carried out in three-point bending mode with a frequency of 1 Hz over the temperature range from −100 to 300°C under a helium flow of 40 ml min^{-1}. The rate temperature change was 5°C min^{-1}. The sam-

ples for these experiments were prepared as cylindrical specimens measuring roughly 19 mm in length and 6.4 mm in diameter, these specimens were submitted a similar thermal process of aging in a temperature controlled oven. For each aging time three samples were performed.

Results and discussion

Differential scanning calorimeter studies

Physical aging in polymers can occur at different rates at any fixed temperatures below T_g. The kinetics of aging have been demonstrated to be dependent on both time and temperature. The results of the DSC experiments on TGDDM/EPN/DDS are presented and discussed. The effect of the physical aging on enthalpy relaxation during DSC heating scan is shown by the presence of an endothermic peak whose position and intensity depends on the aging conditions. For each aging condition, several scans were made under identical conditions. The effects of sub-T_g aging for various times at 220°C on DSC curves of TGDDM/EPN/DDS are shown in Fig. 2. This Figure shows that as aging times increase, an endothermic peak appears below the onset of the glass transition inflection, its magnitude and sharpness increase with increasing time.
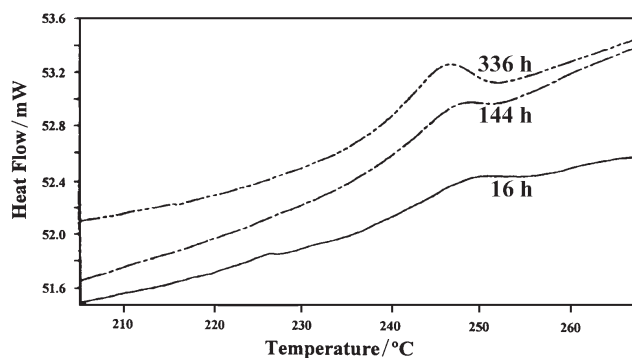

Fig. 2 DSC scans for TGDDM/EPN/DDS. The aging temperature was 220°C

As the sample is cooled through its glass transition temperature from a temperature over T_g, T_o, to T_a where isothermal aging is applied, some macroscopic properties such as enthalpy decreases, if then the sample is reheated the enthalpy loss of the glass increases slowly according to its temperature dependence. It is proposed that the appearence of the DSC endothermic peak is an indication of that the time and temperature dependent with phenomenon of physical aging, manifested as an enthalpy relaxation, having taken place in the sample prior to the scan. The endothermic peak appears superposed on T_g when T_a is close to T_g, however at low aging temperature, the endothermic peak can be located below T_g [10]. The evolution of the peaks can be seen in Fig. 3, where the endothermic peak does not appear after the glass temperature transition, which proves that the physical aging has place below T_g. We have
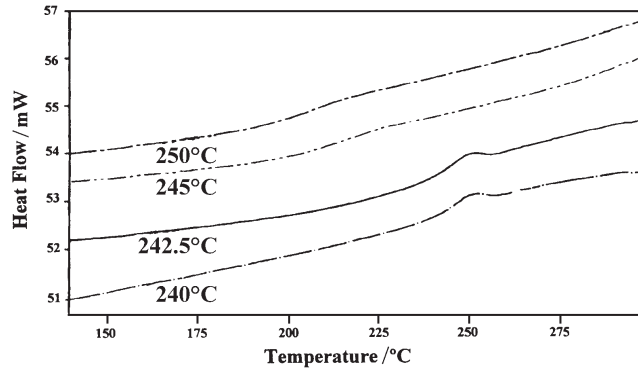
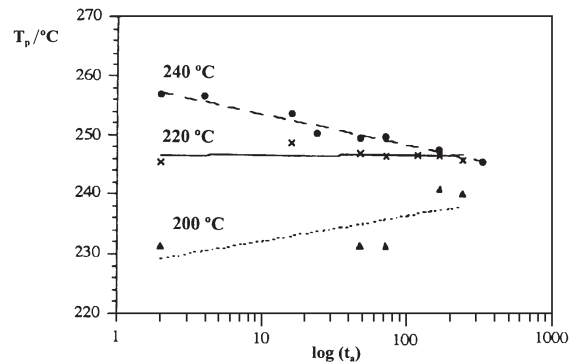**Fig. 3** DSC scans for TGDDM/EPN/DDS. The aging time was 72 h

Fig. 4 Dependence of peak temperature, T_p, *vs.* log annealing time for TGDDM/EPN/
DDS aging at several temperatures

previously determined from the isothermal time-temperature-transformation diagram, TTT, that the value of the maximum glass transition temperature for TGDDM/EPN/DDS is about 242°C corresponding to 92% of conversion [11]. Figure 4 shows that the temperature of the endothermic peak, T_p, shifts to higher temperatures with the aging time, t_a, until approaching the glass transition temperature T_g where decrease slightly.

Considering that during the cooling of the aged sample to room temperature, T_1, there is no appreciable process of relaxation [12] and that the heat capacity C_p of the material is independent of aging time, Δh may be calculated by the following expression

$$\Delta h = \int_{T_1}^{T_o} C_{p,aged} \, dT - \int_{T_1}^{T_o} C_{p,ref} \, dT = \int_{T_1}^{T_o} (C_{p,aged} - C_{p,ref}) \, dT \qquad (1)$$

$C_{p,aged}$ and $C_{p,ref}$ are the specific heat capacities of the aged sample and of the reference sample, respectively.

Assuming that the heating rate of the sample is the same as the heating rate in the furnace, the enthalpy relaxation can be calculated by the equation

$$\Delta h = \frac{1}{m} \int_{t_1}^{t_o} (P_{\text{aged}} - P_{\text{ref}}) \mathrm{d}t \qquad (2)$$

where P_{aged} and P_{ref} are the output powers for the aged specimen and for the reference DSC scan, and t_1 and t_o are the times corresponding to T_1 and T_o, respectively. Figure 5 is aged sample and reference DSC scans (P) and difference between the output signals of the aged and reference scans (ΔP). The change in enthalpy during physical aging can be determined by difference between the aged and unaged scans [13].

The enthalpy of the glass decreases with aging time and consequently the enthalpy relaxation Δh increases as Fig. 6 shows for the aging temperatures of 200, 220 and 240°C.
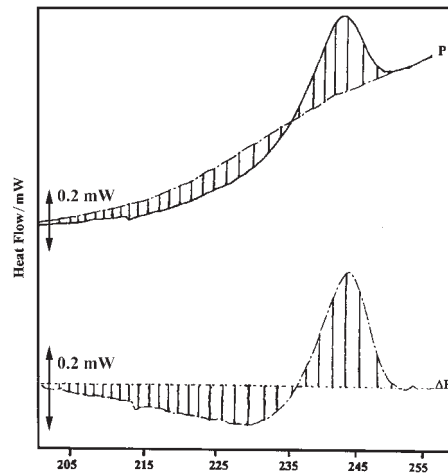

Fig. 5 Aged sample and reference DSC scans (P) and difference between the output signals of the aged and reference scans (ΔP), respectively
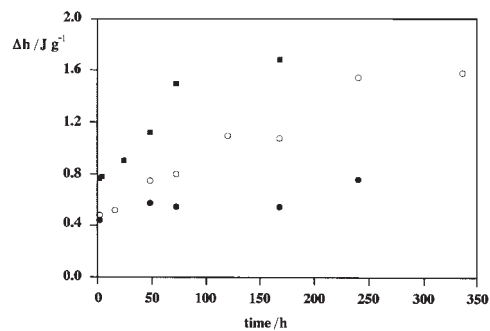

Fig. 6 The variation of the experimentally determined relaxation enthalpy with aging time. ● – 200°C; ○ – 220°C and ■ – 240°C

Dynamic mechanical study

The DMA is essentially able to detect all changes in the state of molecular motion in a viscoelastic solid as temperature is scanned [14]. These changes can affect at the application, perfomance and lifetime of the system. The dynamic mechanical relaxation behaviour of TGDDM/EPN/DDS annealed at 220°C during 24 and 168 h and unaged have been studied. The dynamic storage modulus, E', and the loss factor, $\tan\delta$, measured as a function of temperature are shown in Fig. 7. This unaged sample scan shows two peaks in the $\tan\delta$ trace; a lower temperature peak (at around –50°C) corresponding to the secondary relaxation, T_{β}, and a much more distinct higher temperature peak corresponding to the glass transition temperature, T_{g}.
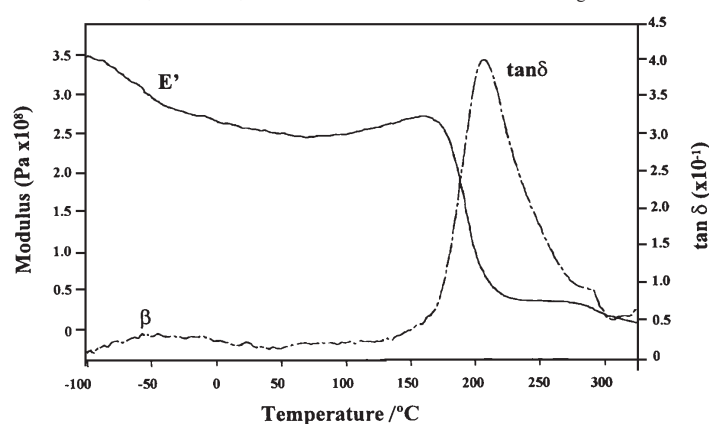

Fig. 7 DMA scan of TGDDM/EPN/DDS of an unaged sample

Figure 8 reports a comparison of the dynamic storage modulus curves as a function of temperature, between –100°C and 270°C for the samples isothermally aged at 220°C for 24 and 168 h, respectively. It is apparent that aging caused chain stiffening, which expectedly resulted in a higher modulus for TGDDM/EPN/DDS aged for longer times.

Table 1 exhibits the variations observed in the aged samples at 220°C for 0, 24 and 168 h. In the glass transition region, the $\tan\delta$ peak value decrease with the aging time. The temperature of this main peak shifts at higher temperatures, if the aging time is short, whereas if the aging time is longer, the position decreases slightly. The dynamic storage modulus was measured at 100°C.

Table 1 The $\tan\delta$ peak temperature, its intensity and dynamic storage modulus aging at 220°C

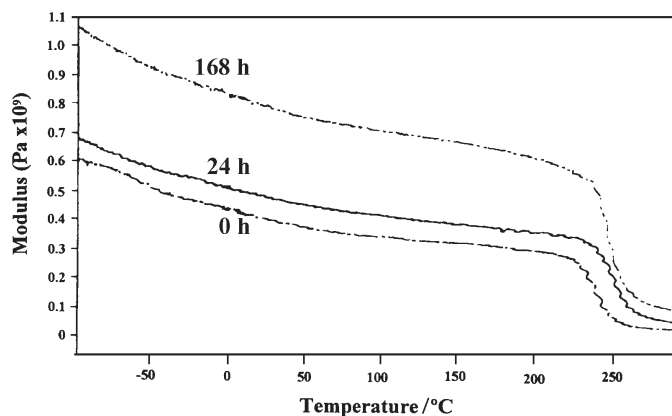| Time/h	Temperature/°C	$\tan\delta$	Storage modulus/Pa
0	246.6	0.397	$2.7 \cdot 10^{8}$
24	256.9	0.292	$4.8 \cdot 10^{8}$
168	249.5	0.286	$7.3 \cdot 10^{8}$

Fig. 8 Comparison of the storage modulus as a function of temperature for
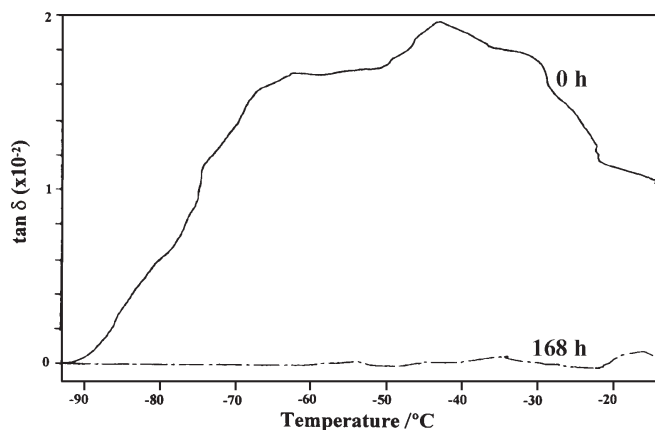TGDDM/EPN/DDS samples aged isothermically at 220°C for 0, 24 and 168 h

Fig. 9 Comparison of tanδ for β-peak of an aging sample at 220°C during 168 h with
the unaged sample

DMA study has reported a broad β-relaxation peak, T_β, about at –50°C, for an unaged samples with the magnitude of relaxation being depressed upon aging treatment. The height peak in the sample aged 168 h is not significant (Fig. 9).

In addition, changes in E' can be attributed to stiffening of the polymer chains in approaching the equilibrium glassy state with reduced free volume and the decrease of the height of the loss factor can be explained by a relaxation in which the epoxy network loses mobility and free volume during its approach toward the equilibrium glassy state and, as a result, the ability to dissipate energy is reduced. This behaviour was reported by other authors [4, 15].

Conclusions

The effect of physical aging on DSC scans between 200 and 250°C, and DMA scans at 220°C of the epoxy system containing tetraglycidyl-4-4'-diaminodiphenylmethane (TGDDM), with a multifunctional novolac glycidyl ether resin (EPN) hardened by 4,4'-diaminodiphenylsulphone (DDS) have been studied. It was proved that the enthalpy relaxation increases gradually with the aging time and to a limiting value for each temperature where structural equilibrium is reached. These limiting values Δh_∞ were calculated experimentally.

DMA studies reflect that good information about the physical aging process can be obtained with this technique. In fact, from the measurable changes in the dynamic storage modulus and in the loss factor can be followed the process of approaching the equilibrium glassy state. DMA technique is a useful approach for the studies of physical aging.

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References

1 L. C. E. Struik, 'Physical Aging in Amorphous Polymers and Other Materials,' Ed. Elsevier, Amsterdam 1978, Chap. 1.
2 C. Bauwens-Crowet and J. C. Bauwens, Polymer, 23 (1982) 1599.
3 L. Guadagno, C. Fontanella, V. Vittoria and P. Longo, J. Polym. Sci., Polym. Phys. Ed., 37 (1999) 173.
4 E. S. W. Kong, Adv. Polym. Sci., 80 (1986) 125.
5 S. Montserrat, J. Polym. Sci., Polym. Phys. Ed., 32 (1994) 509.
6 L. Barral, J. Cano, J. López, I. López-Bueno, P. Nogueira, M. J. Abad and C. Ramírez, European Polym. J., 35 (1999) 403.
7 L. Barral, J. Cano, J. López, P. Nogueira, M. J. Abad and C. Ramírez, J. Thermal Anal., 50 (1997) 409.
8 L. Barral, J. Cano, J. López, I. López-Bueno, P. Nogueira, M. J. Abad and C. Ramírez, J. Therm. Anal. Cal., 51 (1998) 489.
9 H. Jahn and P. Goetzky, Epoxy Resins Chemistry and Technology, 2nd ed., Ed. Clayton A. May, Marcel Dekker, New York 1988, Chap. 13.
10 C. Ramírez, PhD Thesis, University of Santiago, Spain, 1997.
11 L. Barral, J. Cano, J. López, P. Nogueira, M. J. Abad and C. Ramírez, Polym. International, 42 (1997) 301.
12 R. R. Lagasse, J. Polym. Sci., Polym. Phys. Ed., 20 (1982) 279.
13 S.E. B. Petrie, in 'Physical Structure of the Amorphous State,' Ed. Marcel Dekker, New York 1977, p. 225.
14 R. P. Griffiths, PhD Thesis, University of Brunel, UK 1988.
15 E. M. Woo and S. M. Kuo, Polym. Eng. Sci., 37 (1997) 173.