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DETERMINATION OF THE ACTIVATION ENERGIES FOR α AND β TRANSITIONS OF A SYSTEM CONTAINING A DIGLYCIDYL ETHER OF BISPHENOL A (DGEBA) AND 1,3-BISAMINOMETHYLCYCLO-HEXANE (1,3-BAC)

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Abstract

Using dynamic mechanical analysis (DMA) we have studied the variation with the frequency of the dynamic mechanical properties (storage modulus, *E*'; loss modulus, *E*'' and loss tangent or tan δ) for a system containing a diglycidyl ether of bisphenol A (DGEBA) and 1,3-bisaminomethylcyclohexane (1,3-BAC). These properties were measured both in the glass transition and β transition regions. An increase in frequency caused a shift of tan δ peak positions in both regions toward higher temperature. Finally, we report the activation energies of a DGEBA/1,3-BAC epoxy system for α and β transitions.

Keywords: activation energies, α and β transitions, epoxy resins

Introduction

Dynamic mechanical properties are the mechanical properties of materials as they are deformed under periodic forces. The dynamic modulus, the loss modulus and a mechanical damping or internal friction express these properties.

A dynamic mechanical analyzer subjects a material to controlled mechanical oscillation and measures the in-phase and out-of-phase response of the sample, from which one calculates the storage modulus *E*' and the loss modulus *E*'' respectively. *E*' is a measure of the elastic energy stored and *E*'' is a measure of the energy lost as heat. The loss tangent or tan δ is given by *E*''/*E*' and represents the ratio of energy dissipated to energy stored per cycle.

The dynamic mechanical technique can provide valuable information about all changes in the state of molecular motion as temperature is scanned. Therefore, this technique is considered to be one of the most effective for studying the

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influence either of molecular structure or of phase morphology on the physical properties of natural and synthetic polymers [1].

Dynamic mechanical studies usually indicates the presence of different transitions like the α transition or glass-rubber transition and the β transition.

In the glass transition region the damping is high because of the initiation of micro-Brownian motion in molecular chains. A frozen-in segment can store much more energy for a given deformation than a free-to-move rubbery segment. Every time a stressed, frozen-in-segment becomes free to move its excess energy is dissipated as heat. Micro-Brownian motion is concerned with the co-operative diffusional motion of the main chain segments.

The β transition is associated with motion about the chain backbone of a relatively small number of monomer units or with motion of side groups. Thus the activation energy of this transition is generally lower than the α transition activation energy since it corresponds to a segment motion which is smaller than the micro-Brownian motion of the main chain [2].

The aim of this work is to study the variation with the frequency of the dynamic mechanical properties for the DGEBA/1,3-BAC epoxy system and to report the activation energies for the α and β transitions. No literature values were found for dynamic mechanical analysis of a DGEBA/1,3-BAC system like the one used in this work.

(a)

(b)

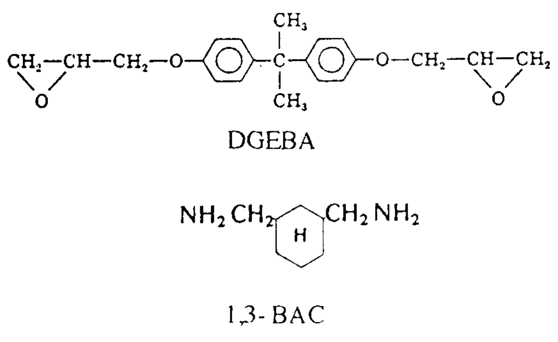

Fig. 1 Chemical structure of the diglycidyl ether of bisphenol A (a) and 1,3-bisaminomethylcyclohexane (b)

Experimental

The epoxy resin used was a diglycidyl ether of bisphenol A (DGEBA), Shell Epon 828, and the curing agent was 1,3-bisaminomethylcyclohexane (1,3-BAC), manufactured by Mitsubishi Gas Chem. Co. Chemical structures of both compounds are shown in Fig. 1. Chemicals were used as received, with a stoichiometric ratio amine/epoxy of 1. The formulation is 100 g DGEBA for

18.5 g 1,3-BAC. The mixture was cured 24 h at room temperature followed by 2 h at 110°C. Samples were prepared into cylindrical specimens measuring roughly 19 mm length and 5 mm diameter.

Dynamic mechanical properties were measured by employing a Perkin Elmer DMA7 analyzer connected to a liquid nitrogen cooling accessory over the temperature range of −100 to 200°C at six different frequencies: 1, 5, 8, 10, 20 and 30 Hz under helium atmosphere (40 cm^3 minute). The temperature ramping rate was 5 deg·min^{-1}.

Results and discussion

Figure 2 illustrates a typical experiment at the standard frequency of 1 Hz. The storage modulus, *E*', loss modulus *E*'' and tan δ for DGEBA/1,3-BAC are given over a temperature range of −180 to 230°C.

The drop in the storage modulus and the corresponding maximum in the loss modulus and tan δ curves of the polymers are due to the transitions associated with increases in internal friction such as long range segmental motions at the α transition and localized motions of chain segments or side groups at the β transition temperature.

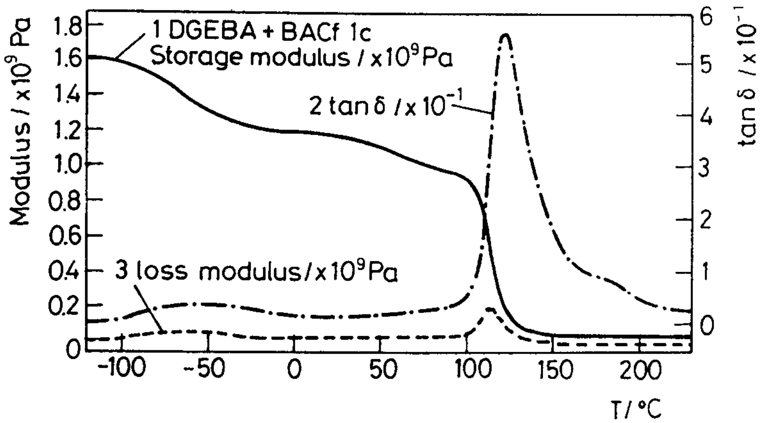

Fig. 2 *E*', *E*'' and tan δ for DGEBA/1,3-BAC at 1 Hz

Figure 3 shows the effect of frequency on the tan δ magnitude in the glass transition and in the β transition regions.

The α and β transition peak positions shifted toward higher temperature with increasing frequency. Values obtained of T_α and T_β are shown in Table 1 where the α transition and β transition temperatures are defined as the temperatures at which the tan δ reaches a maximum in the glass transition and β transition regions respectively.

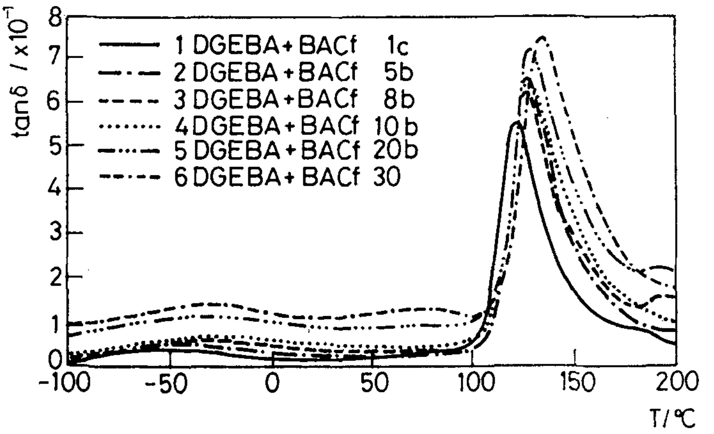

Fig. 3 Tan δ *vs.* temperature for DGEBA/1,3-BAC at f: 1, 5, 8, 10, 20 and 30 Hz

Table 1 Variation of T_{α} and T_{β} with the frequency

Frequency / Hz	T_{α} / °C	T_{β} / °C
1	120.5	–53.0
5	127.0	–48.5
8	128.0	–43.0
10	128.5	–32.0
20	132.0	–28.0
30	134.0	–27.5

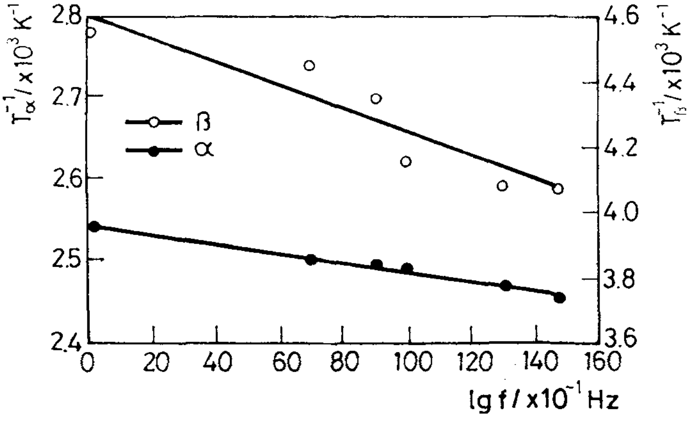

Fig. 4 Arrhenius plot for the α and β transitions

The shift of T_α and T_β in relation to change in the frequency allows the activation energy of the glass transition and β transition temperatures to be determined (3) as

$$\Delta H = - R\left[\frac{\mathrm{d}(\ln f)}{\mathrm{d}(1/T)}\right]$$

where $R = 8.314\cdot10^{-3}$ kJ·mol^{-1}·K^{-1} and T(K) = T_α or T_β. Thus, from the slopes of the plots of $1/T$ *vs.* lg f shown in Fig. 4 the activation energies of the T_α and T_β processes for the DGEBA/1,3-BAC were derived.

The value obtained for the activation energy at T_α is 345.5 kJ/mol and for the activation energy at T_β is 53.4 kJ/mol. These values agree fairly well with those reported by different authors for systems involving a DGEBA resin cured with several diamines.

* * *

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Zusammenfassung — Mittels DMA wurde für ein System aus einem Diglycidylether von Bisphenol A (DGEBA) und 1,3-Bisaminomethylcyclohexan (1,3-BAC) die Abhängigkeit der dynamischen mechanischen Eigenschaften (Speichermodul E' Verlustmodul E'' und Verlusttangens oder tan δ) von der Frequenz untersucht. Diese Eigenschaften wurden sowohl in der Glasumwandlungs- als auch in der ß-Übergangsregion gemessen. Die Erhöhung der Frequenz verursacht in beiden Regionen ein Verschieben des tan δ Peaks zu höheren Temperaturen. Letztlich beschreiben wir die Aktivierungsenergie des Epoxysystems DGEBA/1,3-BAC für die α- und β-Übergänge.