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DYNAMIC MECHANICAL ANALYSIS
Thermal degradation of a diglycidyl ether of bisphenol A and 1,3-bisaminomethylcyclohexane epoxy resin system

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Abstract

Using dynamic mechanical analysis (DMA) we have studied thermal degradation for a system containing a diglycidyl ether of bisphenol A (DGEBA) and 1,3-bisaminomethylcylohexane (1,3-BAC). The changes of dynamic mechanical properties during thermal degradation indicated a shift of the glass transition temperature (T_g) to higher temperatures and a decrease in the peak value of the dynamic loss factor (tan δ) with an increasing of aging time. The value of dynamic storage modulus (E') at the rubbery state showed an increase with aging time, while E' at the glassy state only underwent a moderate change with increased thermal degradation. From these results it can be argued that thermal degradation during the stage prior to the onset of the severe degradation involves structural changes in the epoxy system, as further crosslinking and loss of dangling chains in the crosslinked network.

Keywords: DMA, epoxy resins, thermal degradation

Introduction

Research in thermal degradation of epoxy systems is of great interest because this is an outstanding problem in the application of these systems in different types of environment and for the widely usage of these materials as structural adhesives, coatings, and as matrices in fiber reinforced composites.

The ultimate criterion of the durability of a polymer component is the length of time it continues to perform satisfactorily under service conditions. The design of polymeric materials for durability is therefore just as important a design characteristic as dimensional design and the two are frequently interrelated. The accelerated aging tests have been developed for the analysis of thermal degradation. These intends to accelerate only those elements of the environment that are destructive to the polymer under service conditions without introducing new ones. If accelerated test are to have relevance to real conditions, this de-

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mands an understanding of the physical and chemical phenomena involved in polymer deterioration [1].

There are many papers about thermal degradation of polymers using differential scanning calorimetry (DSC) and thermogravimetry (TG) techniques [2–5], but there are only a few papers describing thermal degradation with DMA technique [6].

The work described here was part of a larger study of the curing characteristics and structure property relationships of DGEBA/1,3-BAC epoxy system. Topics like the activation energies for α and β transitions and the kinetics of cure reaction for this system have been reported previously [7–8]. The objective of this part of the project was to characterize thermal degradation of this epoxy system monitored via DMA analysis.

Experimental

A diglycidyl ether of bisphenol A (DGEBA) epoxy resin, Epikote 828 of Shell Chemical Co., was used, and the curing agent was 1,3-bisaminomethylcyclohexane (1,3-BAC), manufactured by Mitsubishi Gas Chem. Co. These commercial products were used as received without further purification. The formulation is 100 g DGEBA for 18.5 g 1,3-BAC. In order to allow the evacuation of air bubbles the epoxy prepolymer and the comonomer were stirred under vacuum at room temperature for ten minutes. The mixture was cured 24 h at room temperature followed by 2 h at 120°C. Samples were prepared into cylindrical specimens measuring roughly 19 mm length and 6 mm diameter.

For the analysis of thermal degradation the samples were aged in a forced convection oven set at 156°C and then three samples for each time were taken out of the oven at different lengths of aging time, and were measured on a Perkin Elmer DMA-7 analyzer. All the experiments were performed in three-point bending mode with a frequency of 1 Hz over the temperature range of 60–180°C under a helium flow of 40 ml/min. The temperature ramping rate was 5 $\mathrm{deg \cdot min^{-1}}$.

As an additional monitor of the degree of thermal degradation the mass loss of the samples was measured with a balance having a resolution of 0.0001 g.

Results and discussion

In the Fig. 1 is shown the behaviour of dynamic storage modulus (E') in the glass transition region with different lengths of aging time. It can be observed a trend of the increased rubbery state E' with increased time of thermal aging, this trend is quantitatively illustrated in Fig. 2, and it shows changes of E' at 170°C (which is above T_g). Figure 3 shows the change of E' at 100°C (which is below

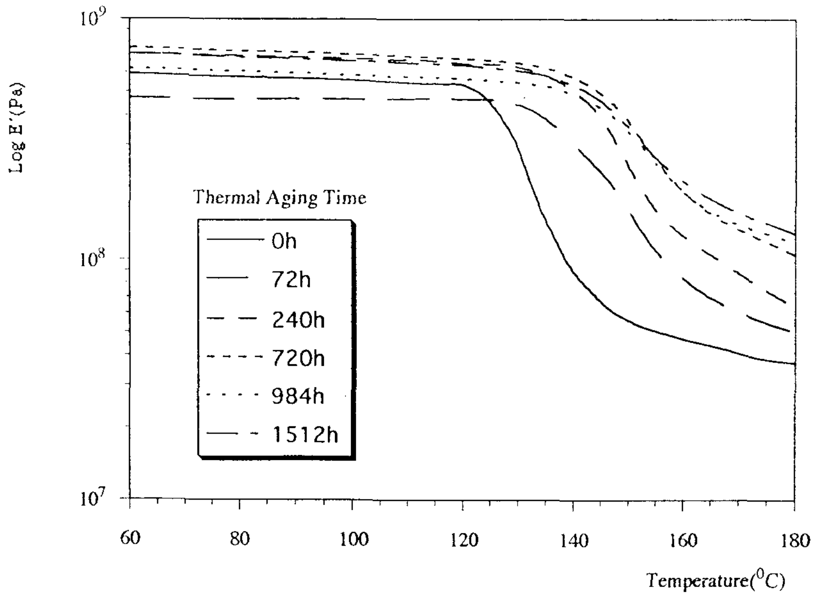

Fig. 1 E' *vs.* temperature with different lengths of aging time

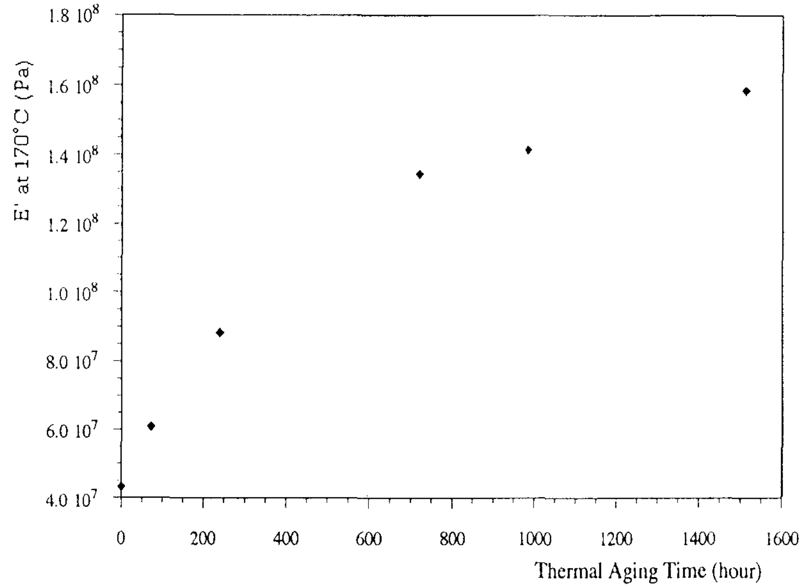

Fig. 2 Change of E' above T_g *vs.* aging time

T_g) with aging time, only a moderate change with measured thermal degradation is observable.

Figure 4 illustrates the loss factor (tan δ) in the glass transition region with different lengths of aging time. It can be observed a decrease in the peak value of the loss factor and a shift of T_g to higher temperatures with increasing aging, time. These trends are shown respectively in Figs 5 and 6.

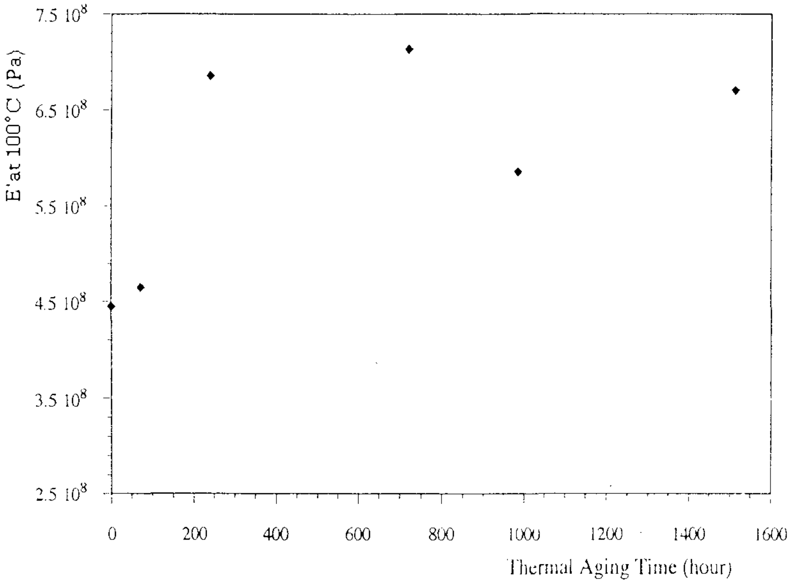

Fig. 3 Change of E' below T_g *vs.* aging time

From the theoretical relationships between E' above T_g with the crosslink density [9]:

$$E' = \frac{3\Phi dRT}{M_C} \tag{1}$$

where E' is the elastic modulus in the rubbery state; d, density; R, the gas constant; T, the absolute temperature; M_c, the molecular weight between crosslinks; and Φ, the front factor which value is close to unity. If the effect of dangling is neglected, then

$$M_C = \frac{d}{\alpha} \tag{2}$$

where α is the crosslink density. Thus, (Eq. (1)) changes to

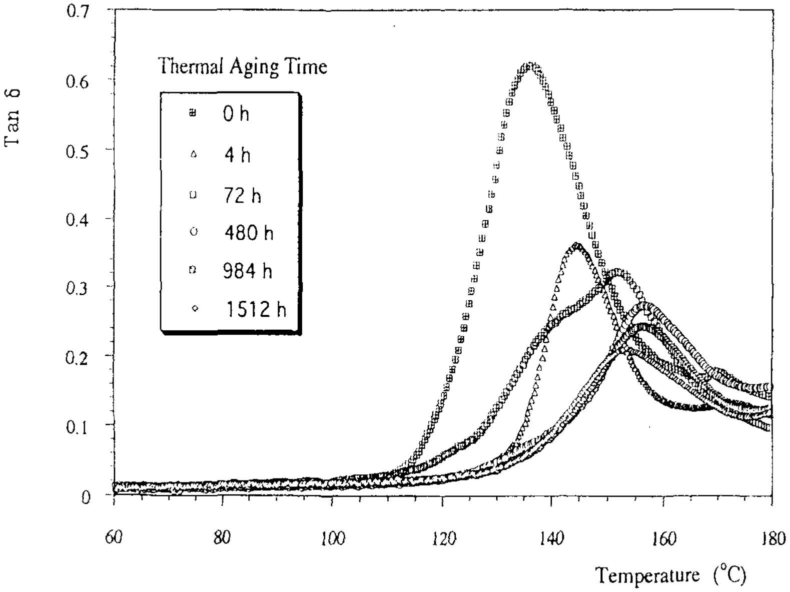

Fig. 4 Tan δ *vs.* temperature with different lengths of aging time

$$E' = 3\Phi\alpha RT \tag{3}$$

This equation shows that an increase of crosslink density will cause an increase in E', so we can conclude that the increased E' in the rubbery state during thermal degradation must result from an increased crosslink density because the other parameters in (Eq. (3)) should remain unchanged.

The relationship between T_g and α [10]:

$$T_g = K_1 \log K_2 \alpha \tag{4}$$

where K_1 and K_2 are constants for the same groups of resins, it also predicts an increase in T_g if crosslink density is increased, so we can conclude too, that the increased T_g during thermal degradation must result from an increased crosslink density.

Figure 7 shows the percentage loss of mass over the aging time for our epoxy system. The decreasing peak value of tan δ like other authors have mentioned [6], seems to support the fact of the lost part was mainly the dangling chains in the crosslinked network.

From the analysis of these results for the thermal degradation it can be concluded that further crosslinking and loss of dangling chains in the crosslinked

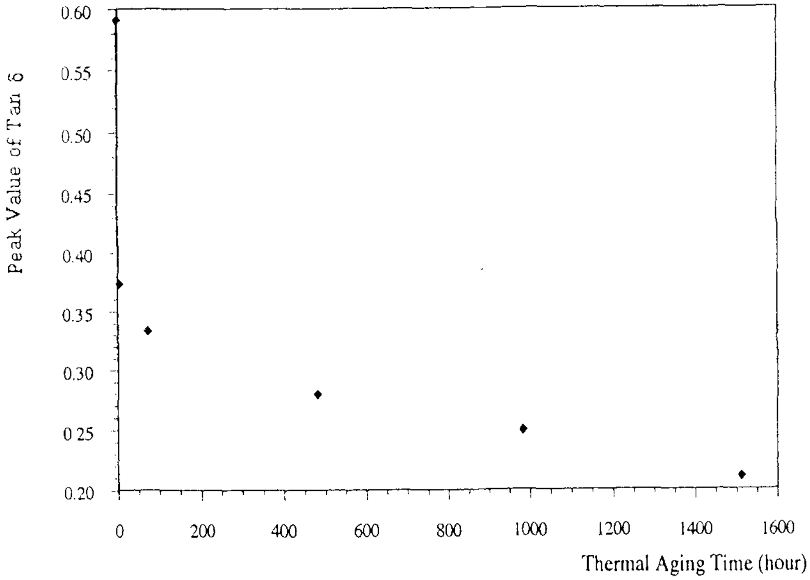

Fig. 5 Decrease of tan δ peak value *vs.* aging time

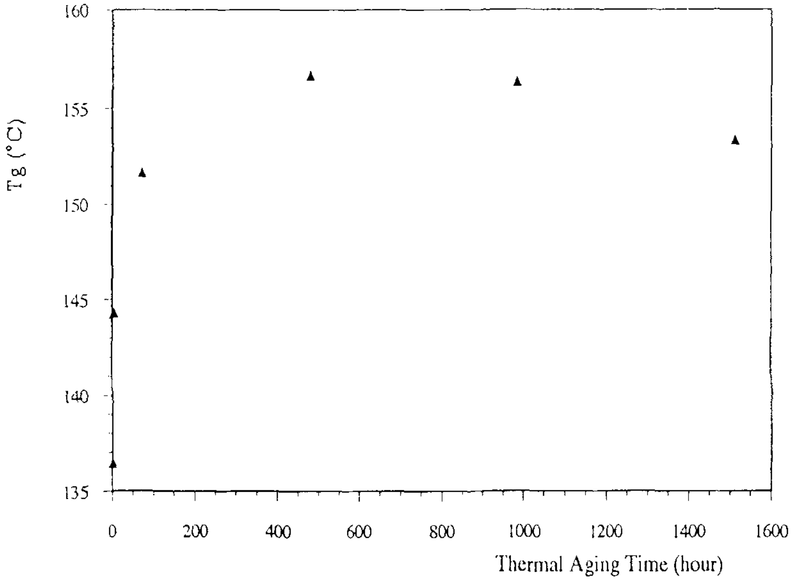

Fig. 6 Increase of T_g *vs.* aging time

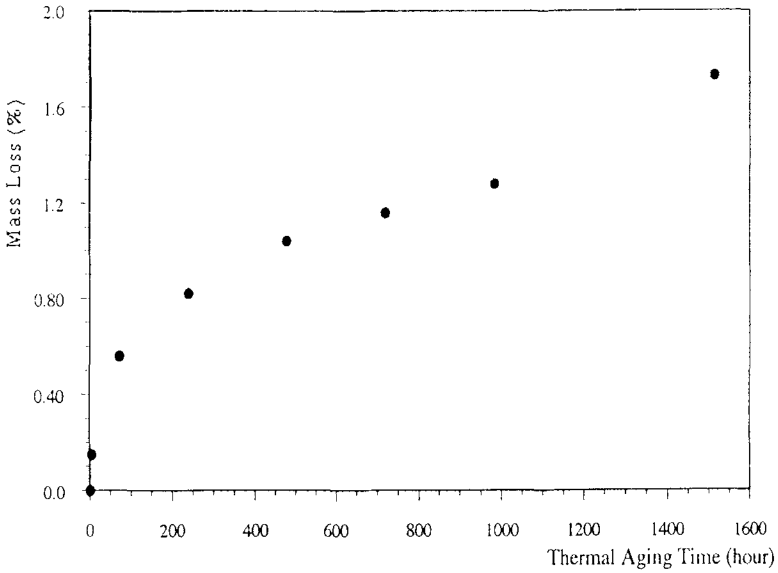

Fig. 7 Mass loss *vs.* aging time

network are occurring during the stage prior to the onset of the severe degradation and these structural changes can be identified by the DMA technique.

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Zusammenfassung — Mittels Dynamischer Mechanischer Analyse (DMA) wurde der thermische Abbau eines Systemes mit Gehalt an Diglycidylester von Bisphenol A (DGEBA) und 1,3-Bisaminomethylcyclohexan (1,3-BAC) untersucht. Die Änderungen der dynamischen mecha-

nischen Eigenschaften während des thermischen Abbaues zeigen eine Verschiebung des Glasumwandlungspunktes (T_g) in Richtung höherer Temperaturen und eine Abnahme des Peakwertes von tan δ bei zunehmender Alterungszeit. Der Wert von E' im gummiartigen Zustand zeigt eine Zunahme mit der Alterungszeit, während E' im glasartigen Zustand mit zunehmendem thermischen Abbau nur einer mäßigen Änderung unterliegt. Anhand dieser Ergebnisse kann darauf geschlossen werden, daß der thermische Abbau während des Zustandes vor Einsetzen des starken Abbaues strukturelle Veränderungen im Epoxysystem umfaßt, wie zum Beispiel Vernetzung und der Verlust von freien Ketten im Netzwerk.