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Thermal degradation of a diglycidyl ether of bisphenol A/1,3-bisaminomethylcyclohexane (DGEBA/1,3-BAC) epoxy resin system ☆

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Abstract

The thermal degradation for a system containing a diglycidyl ether of bisphenol A (DGEBA) and 1,3-bisaminomethylcyclohexane (1,3-BAC) has been studied using dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC). The DMA results showed that the peak value of the dynamic loss factor (tan δ), the glass transition temperature (T_g), and the dynamic storage modulus (E') above T_g changed considerably with increasing thermal degradation, while E' below T_g only underwent a moderate change with increased thermal degradation. There was no appreciable change in the β transition temperature (T_β) with thermal aging time. DSC results showed the same trend for T_g as with DMA. A shift of T_g to higher temperature with increasing aging times was found, but a decrease in T_g for longer aging times was also observed. This could be attributed to thermooxidative degradation in the oven. 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, such as further crosslinking and loss of dangling chains in the crosslinked network.

Keywords: Degradation; Epoxy; Resin; Thermal aging

1. Introduction

Recently, a considerable amount of research has been done on the thermal degradation of epoxy resins because this is a major problem in the application of epoxy resins in

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different types of environments [1–4]. In fact, long-term thermal aging stability is required for many of the applications in which epoxy resins are used, such as for structural adhesives, coatings, and composites.

The investigation of a polymer degradation has been traditionally carried out at two different levels. The polymer technologist is primarily concerned with the change in physical properties of the polymer with time, and the polymer scientist is interested in the reasons for these changes. However, these activities cannot be divorced. Indeed, if further major advances are to be made in the improvement of the durabilities of polymers in service, a better scientific understanding of the chemical and physical phenomena involved in polymer degradation and stabilization under technological conditions is necessary [5].

The cure of epoxy resins is a complicated process. For successful application of epoxy resins, it is necessary to select a suitable hardener and then cure the resin to attain a controlled network structure.

This work was part of a larger study on the relationship between structure and physicochemical properties of the DGEBA/1,3-BAC epoxy system. The determination of the activation energies for α and β relaxations, the kinetics of cure reactions, and the mechanical properties for this system have been previously reported [6–8].

The objective of this part of the project was to characterize the thermal degradation of this epoxy system as monitored via DMA and DSC analysis. The loss of mass over the aging time is used as an additional monitor of the degree of thermal degradation.

2. Experimental

The epoxy resin used was a diglycidyl ether of bisphenol A (DGEBA), Epikote 828 of Shell Chemical Co., with an equivalent weight of epoxy groups of 192 g eq^{-1}. The curing agent was 1,3-bisaminomethylcyclohexane (1,3-BAC), from Mitsubishi Gas Chem. Co., with a molecular weight of 142 g mol^{-1}. The reactants were used as-received, with a stoichiometric ratio of amine/epoxy of 1. The formulation is 100 g DGEBA for 18.5 g 1,3-BAC. The epoxy prepolymer and the comonomer were stirred under vacuum at room temperature for ten minutes in order to prevent formation of air bubbles. The mixture was cured for 24 h at room temperature and then postcured for 2 h at 120°C.

For the analysis of the thermal degradation, 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 by DMA and DSC techniques.

Dynamic mechanical measurements were performed with a DMA-7 analyzer connected to a liquid nitrogen cooling accessory CCA-7 from Perkin-Elmer. Samples were prepared as rectangular shapes suitable for the DMA tests. Dimensions of the cut rectangular specimens were 19.0 × 4.3 × 4.3 mm. All the experiments with DMA were carried out in three-point bending mode with a frequency of 1 Hz over the temperature range −100–250°C, under a helium flow of 40 ml min^{-1}. The temperature ramping rate was 5°C min^{-1}.

DSC measurements were carried out with a Perkin-Elmer DSC-7 calorimeter. Dynamic heating experiments were conducted under a nitrogen flow of 40 ml min^{-1} using samples cut into disc shapes of about 10 mg in weight. The instrument was stabilized to 30°C, then the sample pan was placed in the DSC cell and heated over the temperature range up to 180°C and 5°C min^{-1} heating rate.

The mass loss of the samples was measured using a balance with a resolution of 0.1 mg. The average mass of three samples was used for each time.

3. Results and discussion

Fig. 1 shows the loss factor (tan δ) over the whole temperature range with different lengths of aging time. It was found that there were no appreciable changes in the position of T_β with thermal degradation, although in the β-transition region, a decrease was observed in the peak value of tan δ between the samples without degradation and the samples with different aging times. In the glass transition region, there was a decrease in the peak value of tan δ and a shift of T_g, defined by the tan δ peak, to higher temperatures with an increasing aging time up to 1000 h. From this aging time, a decrease in T_g was found. We have also observed that secondary peaks appear in tan δ at temperatures higher than T_g. These peaks could correspond to zones with a high

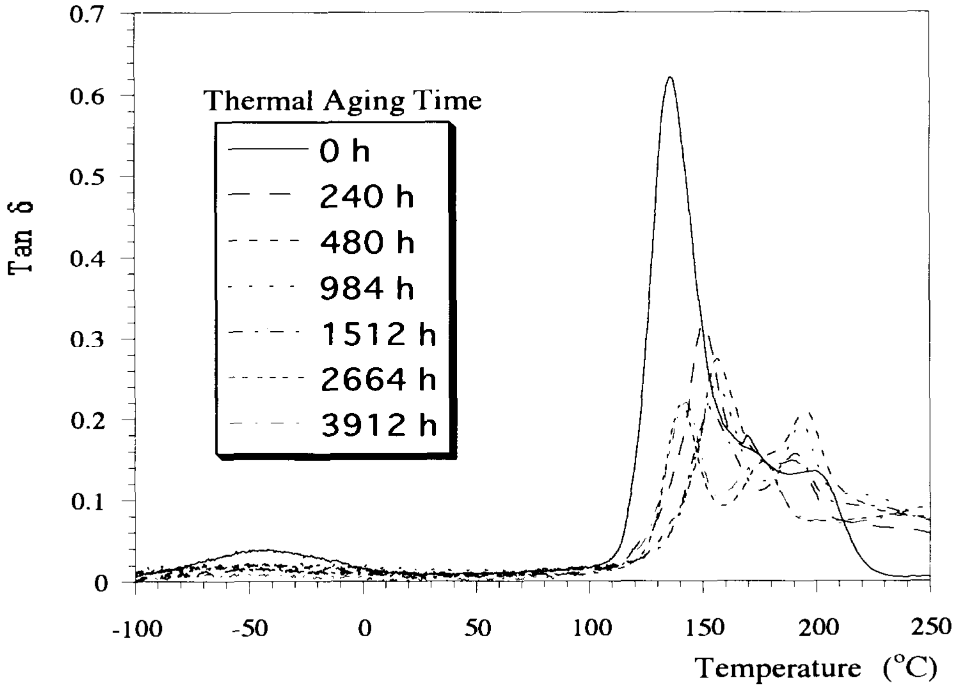

Fig. 1. Tan δ vs. temperature over the whole temperature range.

density of crosslinking inside the epoxy matrix formed during the cure schedule. It was established that low temperature curing leads to a low density of matrix crosslinking; when the cure schedule is carried out at higher temperatures, materials with high local crosslinking densities were obtained [9].

The behaviour of the dynamic storage modulus (*E*′) over the whole temperature range with different amounts of degradation is shown in Fig. 2. A trend in the increased rubbery state *E*′ with increased time of thermal aging can be seen, while *E*′ at the glassy state appears quite scattered with an increasing amount of degradation. These trends are shown in Fig. 3.

Fig. 4 shows the percentage loss of mass over the aging time. Fig. 5 shows some of the dynamic heating experiments with DSC. The midpoint temperature of the baseline slope change was taken as T_g for the DSC measurements following the ASTM DSC method for measuring glass transitions [10]. A shift of T_g to higher temperature is also found with increasing aging time up to 1500 h, and then there is a decrease of T_g with aging time.

Fig. 6 shows the variation of T_g with aging time for DMA and DSC measurements. The values of T_g observed by DMA were higher than those from DSC. In the literature, generally, DMA T_g values, as defined by the tan δ peak, are reported to be higher than T_g values measured by DSC. This difference is due to the difference in measuring frequencies of the techniques and the differences in the analysis [11, 12]. The result obtained by DSC for the value at 0 aging time is higher than the corresponding DMA value. This is because the DSC dynamic heating experiments for these samples showed

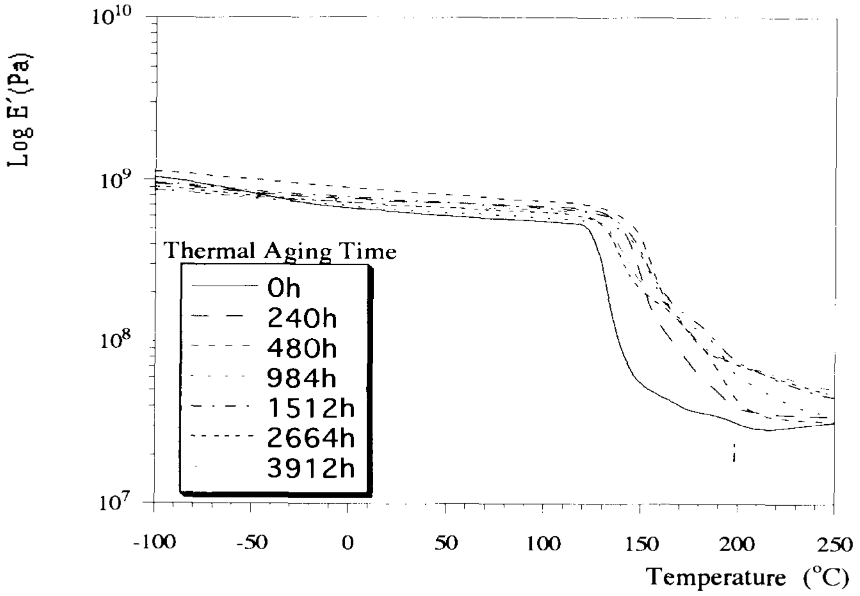

Fig. 2. *E*′ vs. temperature over the whole temperature range.

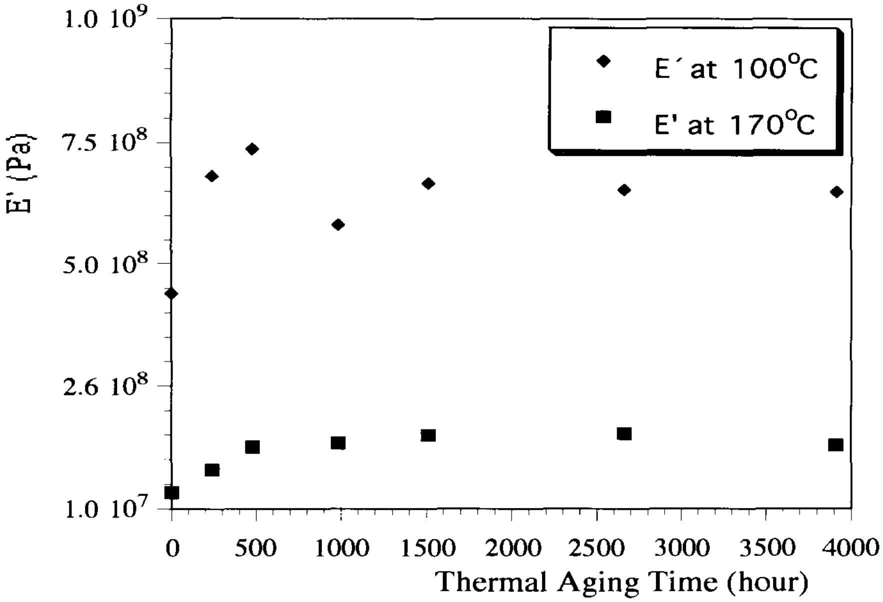

Fig. 3. Change of E' at 100°C and 170°C with aging time.

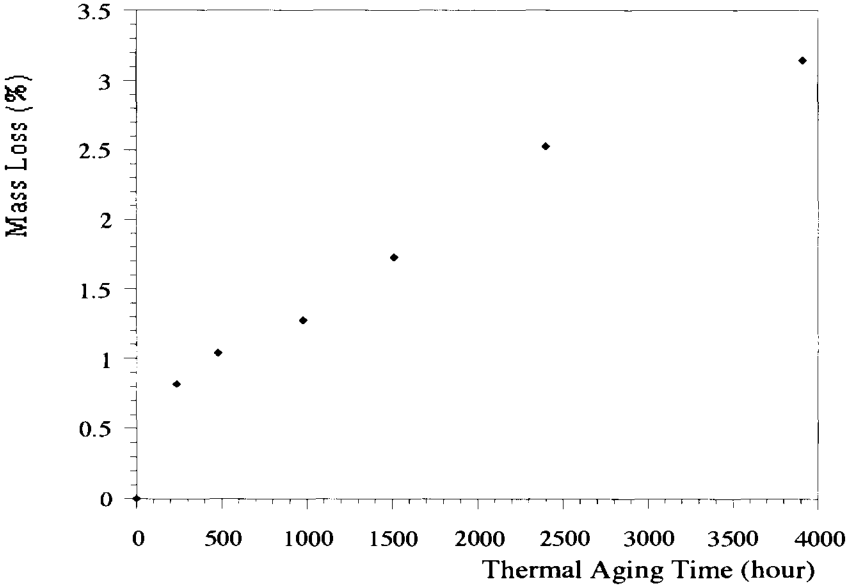

Fig. 4. Mass loss with aging time

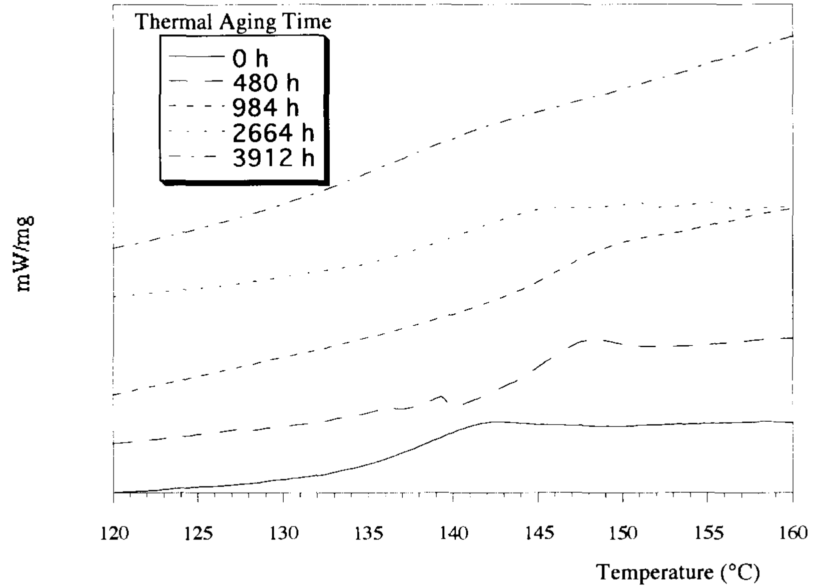

Fig. 5. DSC dynamic heating experiments.

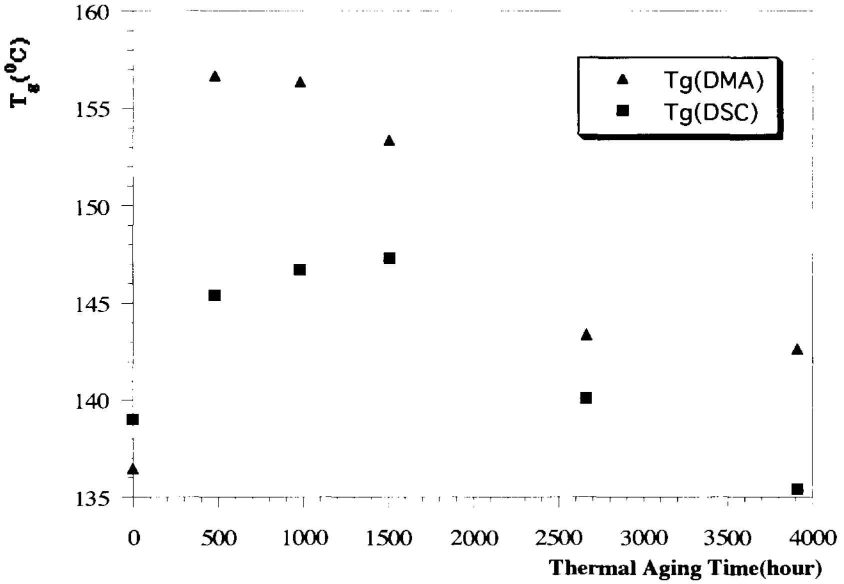

Fig. 6. Variation of T_g with aging time (DMA and DSC measurements).

a residual heat of reaction, which masked the T_g value; therefore it was necessary to run a second scan.

From all these results it can be argued, as other researches have found from studies of similar epoxy systems [13], that during thermal degradation structural changes such as further crosslinking and loss of dangling chains occur slowly during the stage prior to the onset of severe degradation. However in our experiments with DSC, no exothermal peaks were detected in the temperature range up to 180 °C. This means that the speed of further crosslinking during the degradation could be several orders lower than during the resin curing stage.

However, the observed decrease in T_g for high aging times, confirmed by DMA and DSC measurements, has been found previously by others [14, 15]. This could be attributed to thermooxidative degradation in the oven [16].

Further investigations of the properties of the DGEBA/1,3-BAC epoxy system are being carried out by our group to understand these results more fully and to study the evolution of both physical and mechanical properties with different curing schedules.

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