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Relaxations in Thermosets. 11. Solvent Effect on the Cross-Link Network in an Epoxide–Amine Thermoset

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ABSTRACT: Thermosets of the diglycidyl ether of Bisphenol A cured with 4,4′-diaminodiphenylmethane were prepared by mixing the components first in a methyl ethyl ketone solution and second in their pure states. These were studied by differential scanning calorimetry. The T_g of the thermoset prepared by the first procedure is 30 °C lower in the initial stages of curing than of that prepared by the pure components. This difference is reduced to 15 °C at full cure. The presence of solvent molecules during the early stages of chemical reactions decreases the cross-link density in the ultimately formed network structure, which in turn, as shown in an earlier paper (*Polymer* 1987, *28*, 2023), decreases the rubber modulus of the thermoset.

Introduction

The probability that two molecules, or two segments of a macromolecule, would react to form a condensation product is expected from hydrodynamic considerations to depend on the local diffusion coefficient, or internal viscosity, and the spatial or conformational degrees of freedom of the macromolecule. This probability is therefore expected to generally decrease when the temperature of the reactants is decreased and/or the reactants are diluted by a solvent. In particular, when the reactants form a cross-linked network, as during the curing of a thermoset, the viscosity, the cross-link density, and the number of accessible conformations for the network all change with time, and the properties of the network formed depend upon the conditions under which the reactions occurred. In an earlier study of the dynamic mechanical relaxation of epoxide thermosets, we had found[1] that the rubber modulus of the thermoset was decreased by a factor of about 2 when it was prepared by mixing methyl ethyl ketone solutions of its components and the strength of its sub-T_g, mechanical relaxations increased. Thus the thermoset prepared by mixing the components in the solvent was tougher.

The main purpose of our study is to investigate the changes in the calorimetric glass transition temperature of the thermosets prepared when its constituents are initially dissolved in a weakly interacting solvent. The study reveals a significant effect of the presence of the solvent, during the initial stages of the cure, on the cross-link density of the ultimate network of covalent bonds formed in the thermoset.

Experimental Procedure

Diglycidyl ether of Bisphenol A (DGEBA) was obtained under the trade name Epon-828 from Shell Chemical Co. It has been characterized by LeMay et al.[2] and has M_n = 380, n = 0.14, T_g = 259 K, and f = 2.0. 4,4′-Diaminodiphenylmethane (DDM) was purchased from Aldrich Chemical Co., and methyl ethyl ketone was obtained from Fisher Chemical Co. All chemicals were used as such. Two moles of DGEBA was mechanically mixed with 1 mol of DDM for 2–3 min at 353 K. The liquid sample thus obtained is called thermoset here. To obtain a fully cured sample, the thermoset was kept for 5 h at 363 K followed by 3 h at 443 K.

A solution of DGEBA–DDM in methyl ethyl ketone (MEK) was prepared by mixing a solution of 1 g of DDM/mL of MEK with the stoichiometric amount of DGEBA at 348 K for 2 min. A fully cured sample was obtained by evaporating the solvent by pumping at 358 K for 1 h (p = 0.05 Torr), followed by heating at 363 K for 4 h and at 443 K for 3 h.

A Perkin-Elmer differential scanning calorimeter (DSC-4) with TADS computer-assisted data acquisition was used for all studies. Curvature of the scans was eliminated with the SAZ function, which subtracts during scanning the base line obtained with empty sample pans. Open aluminum pans containing 20–45-mg samples were used under the flow of argon gas, and curing was carried out inside a convection oven, where the temperature was held constant to ±1 °C.

Results

Chemical reactions between the DGEBA and DDM molecules occur at all temperatures, but the rate of reactions rapidly increases with the temperature of the reactants. The result of the reactions is the formation of a macroscopic gel with an infinitely interconnected covalent-bond network with unreacted or partly reacted DGEBA and DDM molecules contained within the network. It is known that, during curing, the uncatalyzed reaction of a primary amine with an epoxide first forms a secondary amine, which in turn reacts with another epoxide group to form a tertiary amine.[3,4] The reactions are autocatalyzed by hydroxyl groups that are generated in the reactions. For aromatic amines, the reactions occur concomitantly with two rate constants. The network develops on cross-linking of linear molecules, when the epoxy group opens to form a hydroxyl group, leading eventually to a fully connected network at the gel point (this may be reached before the solvent is completely removed under vacuum). The reactions continue to occur but thereafter become diffusion controlled when the internal viscosity of the gel becomes very large, and this ultimately leads to the formation of a glass. The extent of reaction at the time when a thermoset is macroscopically rigid depends upon the temperature of the cure, but its value is typically between 80 and 100%.[3,4] As the glassy thermoset is now aged, its amorphous structure relaxes toward a lower energy state as a result of slow diffusion of segments within the network. This is known as physical aging. The densification of the structure may in turn facilitate further chemical reactions between the remaining unreacted components. This is known as postcure. In an incompletely cured thermoset both physical aging and postcure occur simultaneously, but in a fully cured sample only the former occurs.

The DSC scans for the DGEBA–DDM thermoset prepared by mixing neat components at 353 K were first obtained by heating from 373 and 473 K at 10 K/min. The thermoset was immediately cooled to 358 K and cured at 358 K for 60 min and then further cured at 403 K for 30,

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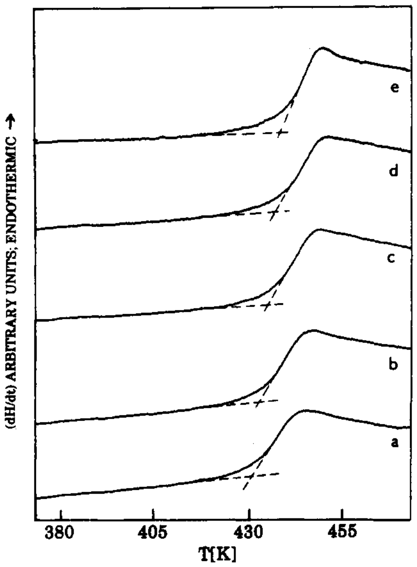

Figure 1. DSC scans for the DGEBA-DDM thermoset first held for 1 h at 358 K and then further cured at 403 K for 30 (a), 60 (b), 120 (c), and 1200 min (d). Curve e is a scan obtained after curing for 3 h at 358 K and then 5 h at 443 K. All are rescans obtained after first heating from 323 K to 473 K at 10 K/min and then immediately cooling the sample to 323 K at 300 K/min.

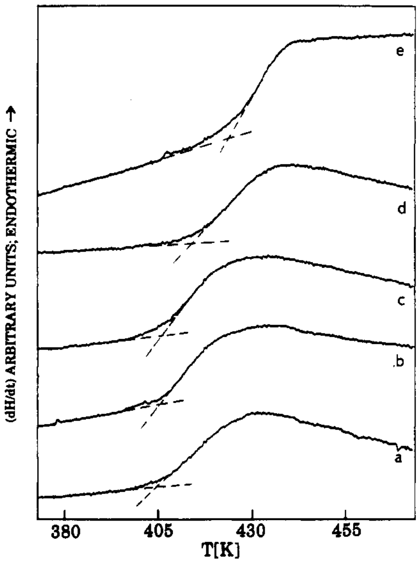

Figure 2. DSC scans for the DGEBA-DDM thermoset prepared from the methyl ethyl ketone solutions, first pumped for 1 h at 353 K at a pressure of 0.05 Torr and then further cured at 403 K for 30 (a), 60 (b), 120 (c), and 1200 min (d). Curve e is a scan obtained after pumping for 1 h at 358 K (0.05 Torr) and then heating at 358 K for 2 h and 443 K for 5 h. All are rescans obtained after first heating the samples from 323 K to 473 K and then immediately cooling the sample to 323 K at 300 K/min.

60, 120, and 1200 min. The DSC scan obtained after each cure is shown in Figure 1 as curves a–d. For comparison, a DSC scan obtained for the same heating rate for a fully cured sample, which was obtained by curing at 358 K for 3 h and at 443 K for 5 h after scan d in Figure 1, is shown as curve e. Curves a–d in Figure 2 show the DSC scans obtained at a heating rate of 10 K/min for the thermosets prepared by mixing MEK solutions of the components after pumping for 1 h at 353 K (p = 0.05 Torr) and further curing for 30, 60, 120, and 1200 min at 403 K. Curve e is the scan of a fully cured sample, which was heated in a vacuum (0.05 Torr) at 358 K for 1 h, then at 358 K for 2 h at 1 atm, and finally at 443 K for 5 h. All DSC scans in both figures are rescans after first heating the samples to 473 K at 10 K/min and then cooling them at 300 K/min.

Table I
Glass Transition Temperatures of DGEBA-DDM Thermosets Prepared from the MEK Solution and from Neat Components at Different Curing Times and at Full Cure

time, min	T_g(neat), K	T_g(MEK solution), K
30	431.0	404.5
60	433.0	405.0
120	435.5	405.0
1200	436.5	415.0
full cure	438.0	423.0

This procedure did not appreciably affect the value of T_g but excluded all effects of physical aging on the DSC scans. The value of T_g was determined by drawing tangents to the slopes of the endotherms, as illustrated by broken lines in both figures. This is a widely used and accepted procedure for determining the onset temperature of the glass → liquid transition for a given heating rate.

At the initial stages of the cure, i.e., 30, 60, and 120 min (curves a–c), the T_g of the thermoset prepared from MEK solutions is about 30 K lower than the T_g of that prepared from neat components. After curing at 403 K for 1200 min, this difference decreased to 20 K, and on full curing it ultimately decreased to 15 K. The T_g of thermosets prepared in MEK solutions and from neat components at different curing times are summarized in Table I.

Discussion

As evident in Figures 1 and 2 and Table I, the effect of the MEK used in the preparation of the thermoset is to reduce the T_g of the thermoset. In our earlier studies, careful examination for traces of MEK solvent in the thermoset by infrared spectroscopy had shown that the solvent was completely removed from the thermoset after vacuum treatment at 353 K, as done here. A possible plasticization effect, i.e., a decrease in T_g accompanied by a decrease in the elastic modulus, based on the interaction of the MEK with the polymer chains in the cross-linked network therefore seems to be ruled out. Therefore, the effect observed here should be considered in terms of the cross-link density of the thermosets.

The change in the glass transition temperature of a cross-linked polymer can be interpreted in terms of the number of cross-links per unit mass in the polymer. For this analysis, we follow the Gibbs–Di Marzio theory[5,6] for the viscous flow and glass transition phenomenon in terms of the configurational entropy of amorphous polymers. Accordingly, T_2, the second-order thermodynamic transition temperature at which the temperature-dependent configurational entropy becomes formally zero, increases as the number of cross-links in a polymer increases. The ratio of the glass transition temperature to this temperature, i.e., T_g/T_2, is typically in the range 1.15–1.25 and remains constant[5,6] with a change in the cross-link density, as both T_g and T_2 are expected to increase in the same proportion with an increase in the cross-link density. The relation given by Di Marzio[6] may be written as

$$\frac{T_g(x) - T_g(0)}{T_g(0)} = \frac{Ax}{1 - Ax} \tag{1}$$

$$A = KM/\gamma \tag{2}$$

where, $T_g(x)$ refers to the T_g of a polymer with x number of cross-links per gram and $T_g(0)$ to that with no cross-links. K is a constant with a value of $(1.3 \pm 0.1) \times 10^{-23}$ as given in ref 8, which we use here. M is the molecular weight of a monomer, and γ is the number of flexible bonds per monomer. $T_g(0)$ is the glass transition temperature of the polymer before cross-linking by DDM occurs, and this would be equal to the hypothetical case of the ultimately formed polymer but with all the cross-links removed, which is of course not attainable experimentally. One possibility for resolving this dilemma is by substituting for $T_g(0)$ the temperature of the gelation point of the thermoset, which was determined as 383 K using a measurement frequency of 1 Hz by Babayevski and Gillham.[7] With $T_g(x) = 423$ K, $M/\gamma = 45$, and $K = 1.3 \times 10^{-23}$, we obtain $x = 1.6 \times 10^{20}$ g^{-1} for the thermoset prepared from MEK solution. Similarly, from $T_g(x) = 438$ K for the thermoset prepared from neat components, we obtain $x = 2.2 \times 10^{20}$ g^{-1}. Alternatively, $T_g(0)$ may be regarded as the T_g of the unreacted or uncured DGEBA–DDM mixture. Using the value of 259 ± 2 K, obtained by Choy and Plazek,[8] we obtain $x = 6.6 \times 10^{20}$ g^{-1} for the thermoset prepared from MEK solution and $x = 7.0 \times 10^{20}$ g^{-1} for that prepared from neat components. For either choice of $T_g(0)$, the cross-link density of the network is lower in the thermoset prepared from MEK solutions than in that prepared from neat components. In the first case the relative decrease is 37% whereas in the second case it is 6%.

The rubber modulus G_R of a cross-linked polymer is given by[9]

$$G_R = \rho RT/M_e \tag{3}$$

where ρ is the density and M_e is the molecular weight between the cross-links, R is the gas constant, and T is the temperature. Therefore, a decrease in the cross-link density decreases the rubber modulus by about the same proportion because the density of the thermoset prepared with or without the solvent differs by less than 1%, and our earlier studies[1] have shown that the rubber modulus of the DGEBA–DDM thermoset prepared from MEK solutions is nearly half of that of the thermoset prepared from neat components. We conclude that, within the approximations of the configurational entropy theory and given the discussed uncertainty in using the T_g of the uncross-linked polymer network, the effect of the MEK solvent on the G_R of the DGEBA–DDM thermoset can be qualitatively understood in terms of a decrease in the T_g of the thermoset. In molecular terms the decrease in the cross-link density implies that the presence of MEK in the initial states of the cure decreases the probability of complete chemical bonding of DGEBA with DDM.

Conclusions

The calorimetric glass transition temperature of an epoxy thermoset prepared from solutions of the components in methyl ethyl ketone is substantially lower than that prepared from the neat components. While aging of the thermosets raises the T_gs of both thermosets, the difference between the respective T_gs of the two variously prepared thermosets decreases from an initial value of 30 K in the early stages of the cure to 15 K for the fully cured samples. The lower T_g of the thermoset prepared from the MEK solution is attributed to a lower cross-link density of the ultimately formed network structure.

References and Notes

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