The Effect of Thermal History and Strain Rate on the Mechanical Properties of Diethylenetriamine-Cured Bisphenol-A-Diglycidyl Ether Epoxies

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Synopsis

The tensile mechanical properties of diethylenetriamine (DETA)-cured bisphenol-A-diglycidyl ether (DGEBA) epoxies prepared from 9, 11 and 13 phr DETA are reported as a function of thermal history, strain-rate and test temperature. These epoxies exhibit macroscopic yield stresses and >10% ultimate elongations. The mechanical properties of these epoxies exhibit a free-volume dependence as a function of thermal history. Annealing below T_g causes an increase in the macroscopic yield stress and a decrease in the ultimate elongation, whereas quenching from above T_g lowers the yield stress and increases the elongation. These mechanical property modifications are shown to be reversible with reversible thermal–anneal cycles. The activation volumes associated with Eyring's theory for stress-activated viscous flow for the DGEBA-DETA epoxies are within the range of values (9–12 nm³) reported for noncrosslinked polymers. These observations suggest that the DGEBA-DETA epoxies are not as highly crosslinked as would be expected from normal addition reactions of epoxide groups with primary and secondary amines. The formation of lower crosslink density networks is discussed in terms of potential chemical reactions.

INTRODUCTION

The increasing use of epoxies as adhesives and composite matrices has led to a need to predict the durability of these materials in service environments. The durability of epoxies can be predicted with confidence only if their basic structure-property relations are understood.

The structure of epoxies can be complex. The chemical and physical structures depend on specific cure conditions because more than one reaction can occur and the kinetics of each reaction exhibits different temperature dependences. In addition, the structure is affected by such factors as steric and diffusional restrictions of the reactants during cure,[1-6] the presence of impurities which can act as catalysts,[7] the reactivity of the epoxide and curing agent,[8] isomerization of epoxide groups,[9-11] inhomogeneous mixing of the reactants,[12] and cyclic polymerization of the growing chains.[8] These factors can lead to physically and chemically heterogeneous network structures.

Amine-cured epoxies are one of the most common epoxy systems. In these systems, networks are generally assumed to result from addition reactions of epoxide groups with primary and secondary amines. For epoxides and amines with functionalities $\gtrsim 3$, highly crosslinked network structures can be formed. However, recent electron and optical microscopy studies of strained films and fracture topographies of diethylenetriamine (DETA)-cured bisphenol-A-dig-

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lycidyl ether (DGEBA) epoxies indicated that these epoxies deform and fail by a crazing process.[13]   This crazing process involves significant microscopic flow, which is not expected for a highly crosslinked epoxy network structure.

The chemical structures of the DETA and DGEBA molecules are illustrated in Figure 1.   The DGEBA epoxide is difunctional, whereas the DETA amine is pentafunctional if all the amine hydrogens react.   Hence if all amine hydrogens react with epoxide groups in the absence of side reactions, a highly crosslinked network structure should be produced.

The purpose of this paper is to further illustrate that the DGEBA-DETA epoxies are not highly crosslinked glasses, as indicated by their tensile mechanical properties and the effect of thermal history and strain rate on these properties.

EXPERIMENTAL

DER 332 (Dow) pure DGEBA monomer and DETA (Eastman) were used in this study.   Prior to mixing, both the DGEBA and DETA monomers were exposed to vacuum to remove absorbed moisture.   The DGEBA epoxy monomer was also heated to 60°C to melt any crystals present[12] and was then immediately mixed with the DETA at room temperature.   Epoxies with three different epoxy:amine ratios were prepared: 9, 11, and 13 parts per hundred by weight (phr) DETA.   (The stoichiometric mixture for the DGEBA-DETA system contains ~11 phr DETA.[14]   This composition was determined by assuming that all amine hydrogens react with epoxide groups in absence of side reactions.) Sheets, 0.75 mm thick, of each epoxy mixture were prepared between glass plates separated by Teflon spacers.   A release agent (Crown 3070) was used to facilitate the removal of the epoxy sheets from the glass plates.   The epoxy sheets were cured at room temperature for 24 hr in vacuum, then removed from the glass plates, and postcured at 150°C for 24 hr in vacuum.   The glasses were cooled slowly at 2°C/min to room temperature to minimize any stresses caused by thermal gradients.

Dogbone-shaped specimens, suitable for tensile mechanical property studies, were machined to a 2.5-cm gauge length and a width of 0.3 cm within the gauge length from the cured sheets; the edges were polished along the gauge length. For T_g measurements a portion of the epoxy sheets were filed to produce a powder suitable for DSC measurements.

$$CH_2 — CH — CH_2 — O —⟨O⟩— \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}} —⟨O⟩— O — CH_2 — CH — CH_2$$
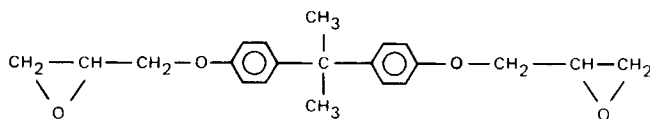
bisphenol-A-diglycidyl ether epoxy

DGEBA

$$H_2N — CH_2 — CH_2 — NH — CH_2 — CH_2 — NH_2$$

diethylene triamine

DETA

Fig. 1. The DGEBA-DETA epoxy system.

Some of the dogbone-shaped specimens were exposed to various thermal histories by annealing in a preheated tube furnace in He. These specimens were quenched in ice water when removed from the furnace.

For the room-temperature tensile mechanical property studies, dogbone-shaped specimens were fractured in tension in a tensile tester (Instron TM-S-1130) at crosshead speeds of 0.05–5.0 cm/min. DSC analyses to determine the T_g's of the epoxy specimens were performed with a differential scanning calorimeter (Rigaku model M 8075) using a heating rate of 5°C/min.

RESULTS AND DISCUSSION

The T_g's of the DGEBA-DETA epoxy systems are shown in Table I. The T_g exhibits a maximum at the stoichiometric composition. Maxima in T_g as a function of composition have been previously reported for a number of epoxy systems.[6,15–20] For amine-epoxide addition reactions in the absence of side reactions, Bell[16] has theoretically shown that excess amine increases the molecular weight between crosslinks, which lowers the T_g relative to an epoxy prepared from the stoichiometric mixture. Bell also noted that excess epoxy systems would possess approximately a similar molecular weight between crosslinks. However, unreacted epoxide groups could plasticize the system. Also, excess of one component in the system enhances the possibility of unreacted molecules which act as plasticizers. Furthermore, steric and diffusional restrictions can limit the chemical reactions, which further accentuates the number of unreacted species.

The effect of thermal history on the tensile room-temperature mechanical properties of DGEBA-DETA epoxies are illustrated in Table II. These epoxies exhibit macroscopic yield stresses and >10% ultimate elongations. Lee and Neville[21] report higher ultimate elongations for these DGEBA-DETA epoxy systems. These types of mechanical responses suggest that these glasses are not highly crosslinked.

Furthermore, the mechanical properties of these epoxies exhibit a free-volume dependence as a function of thermal history, which indicates that these glasses consist of regions of lightly or noncrosslinked material. A typical volume-temperature plot for a polymer is illustrated in Figure 2. Changes in free volume, or local order, in the glassy state can occur as a result of the extension to temperatures below T_g of packing changes associated with the liquid state. The liquid-volume temperature plot extrapolated to below T_g in Figure 2 represents the lower free-volume, equilibrium state of the glass. The time necessary to achieve the equilibrium state at a given temperature below T_g depends on the glassy-state mobility. Below a specific temperature, the glassy-state mobility is too small to allow any changes in free volume. A decrease in free volume that

TABLE I
T_g's of DGEBA-DETA Epoxies

Composition	T_g, °C
DGEBA-DETA (9 phr DETA) epoxy	116
DGEBA-DETA (11 phr DETA) epoxy	130
DGEBA-DETA (13 phr DETA) epoxy	107

TABLE II
Effect of Thermal History on the Tensile Room-Temperature Mechanical Properties (Strain
Rate ~10^{-2} min^{-1}) of DGEBA-DETA Epoxies

Thermal history	Yield (Y) or fracture (F) stress,[a] MPa ±1	Ultimate elongation,[a] % ±1
DGEBA-DETA (9 phr DETA) epoxy		
Unannealed	(Y) 84	11
111°C, 1 day	(Y) 87	11
111°C, 2 days	(Y) 88	11
111°C, 4 days	(F) 77	9
Quenched in ice water from 171°C after 10 min	(Y) 77	14
DGEBA-DETA (11 DETA) epoxy		
Unannealed	(Y) 76	13
125°C, 1 day	(Y) 80	11
Quenched in ice water from 185°C after 10 min	(Y) 75	15
DGEBA-DETA (13 phr DETA) epoxy		
Unannealed	(Y) 81	14
102°C, 1 day	(Y) 84	14
102°C, 3 days	(Y) 84	13
102°C, 6 days	(Y) 84	12
102°C, 17 days	(Y) 86	11
Quenched in ice water from 162°C after 10 min	(Y) 75	15
A-1: 102°C, 1 day	(Y) 84	14
A-2: quenched in ice water from 162°C after 10 min	(Y) 74	17
A-3: 102°C, 1 day	(Y) 84	14

[a] Average values for five specimens measured at each specific thermal history.

occurs in the glassy state results in inhibition of the flow processes that occur during deformation and a more brittle mechanical response. Rapid cooling from above T_g, however, produces a glass with a larger free volume.

For each DGEBA-DETA epoxy in Table II, annealing 5°C below T_g causes an increase in the macroscopic yield stress and a decrease in the ultimate extension as the equilibrium states of these glasses are approached. Quenching from 55°C above T_g for each epoxy composition produces lower macroscopic yield stresses because of the high free volume frozen into these glasses. Prior to deformation, DGEBA-DETA (13 phr DETA) epoxy specimens designated A-1, A-2, and A-3 in Table II were exposed to the same thermal history as the preceding samples in this series. After initially annealing at 102°C for 1 day (A-1), quenching from 55°C above T_g (A-2) produces a lower macroscopic yield stress. Subsequent annealing of the quenched specimen in the glassy state 5°C below T_g (102°C) (A-3) produces essentially reversible changes in the macroscopic yield stress and ultimate elongation. These reversible changes in the mechanical properties suggest that little change occurs in the crosslink density in the regions controlling the flow processes as a result of the annealing conditions. Furthermore, the modifications of the macroscopic yield stress and ultimate elongation with thermal history indicate that the flow processes in DGEBA-DETA epoxies are controlled free-volume-dependent regions. Such regions must consist of lightly or noncrosslinked material.
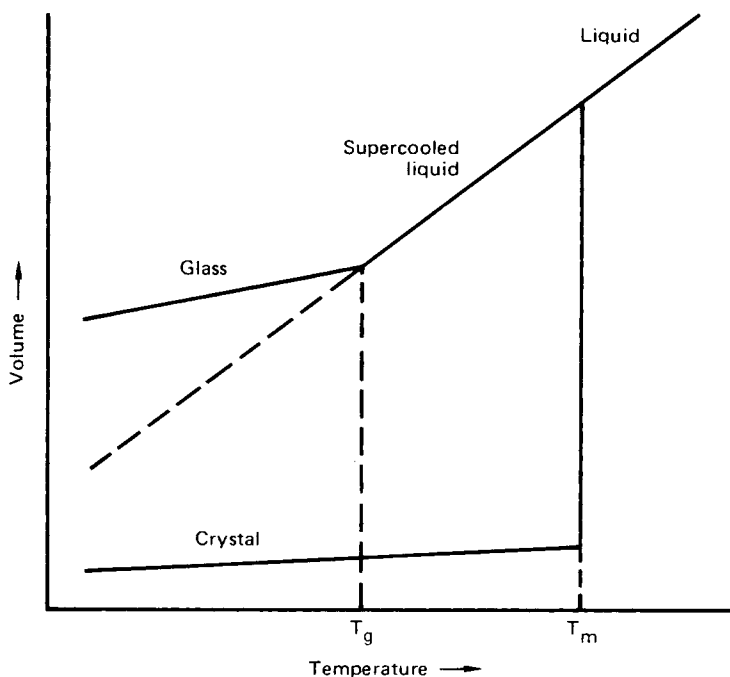
Fig. 2. A schematic volume-temperature plot for a polymer.

Figure 3 illustrates the effect of annealing [5°C below T_g (125°C)] on the temperature and strain-rate dependence of the macroscopic yield stress of DGEBA-DETA (11 phr DETA) epoxy relative to the unannealed epoxy. The general increase in the yield stress at all temperatures and strain rates on annealing below T_g further illustrates the free-volume dependence of these epoxies.

Each of the DGEBA-DETA epoxy systems exhibited a linear dependence of the yield stress (σ_y) with the logarithm of the strain rate ($\dot{\epsilon}$) at constant temperature. These data are consistent with Eyring's theory of stress-activated viscous flow for polymers.[22] This theory predicts[23] that the yield stress is a linear function of the logarithm of the strain rate at constant temperature T, i.e.,

$$\frac{d\sigma_y}{d \ln \dot{\epsilon}} = \frac{2kT}{v} \tag{1}$$

where k is Boltzmann's constant and v is the activation volume, which is associated with that volume displaced when a chain segment jumps when acted on by an applied stress. The values of the activation volumes for each DGEBA-DETA epoxy system in the room-temperature-($T_g - 30$°C) range are 9–12 nm³. These values are within the range of those reported for noncrosslinked polymers[24–30] and two epoxy systems.[6,31] These observations suggest that either regions of low and/or noncrosslink density control the flow processes of the DGEBA-DETA epoxies and/or the rupturing of crosslinks does not significantly affect the values of the activation volumes.

Hence the effects of thermal history and strain rate on the mechanical response of DGEBA-DETA epoxies indicate that regions of low or noncrosslink density
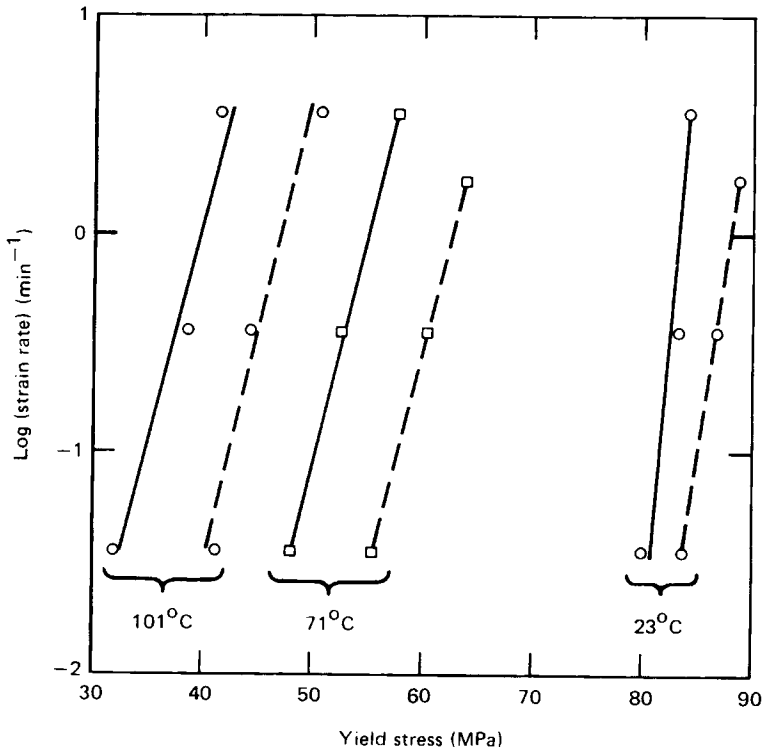
Fig. 3. Yield stress vs log(strain rate) of a DGEBA-DETA (11 phr DETA) epoxy as a function of temperature and thermal history for (- - -) annealed 24 hr at 125°C and (—) unannealed samples.

control the flow processes that occur under the influence of stress in these glasses. Such observations are consistent with the reported microscopic deformation and failure processes of these systems and their morphology.[13] (From straining DGEBA-DETA epoxy films directly in the electron microscope, these epoxies were found to consist of crosslinked molecular domains embedded in a lower crosslinked density matrix, with the latter controlling the flow processes.[13]) These observations suggest that chemically either (1) few epoxide secondary-amine reactions occur in DGEBA-DETA epoxies, thus limiting the number of crosslinks and/or (2) polyether linkages are formed by trans etherification through a ring-opening homopolymerization of the epoxide.[7,10,14,32] The epoxide-amine reactions are controlled by the presence of H-bond donors such as OH groups, which are necessary to open the epoxide rings.[2,3,7] The trans etherification reaction requires a tertiary amine as a catalyst and a H-bond donor as a cocatalyst.[7,10,32] For the DGEBA-DETA system, sufficient quantities of tertiary amines are only formed above 120°C.[10] Hence the final chemical structure of the DGEBA-DETA epoxy system can be complex, because it will depend on such parameters as (1) the relative rates of the chemical reactions at room temperature and the final postcure temperature, (2) the concentrations of catalysts such as sorbed moisture in the system, and (3) the steric restrictions inhibiting reactions at secondary amine sites.

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