

# Epoxy Matrices for Filament-Wound Carbon Fiber Composites\*

ROGER J. MORGAN, *Michigan Molecular Institute, 1910 West St. Andrews Road, Midland, Michigan 48640*, and CONNIE M. WALKUP, *P.O. Box 808, Livermore, California 94550*.

## Synopsis

Epoxyes suitable for filament-winding fibrous composites must be processible at ambient temperatures, nontoxic, chemically simple, undergo full cure at  $\leq 100^{\circ}\text{C}$  and, also, be tough and exhibit a  $T_g > 120^{\circ}\text{C}$ . In this paper, we report the cure characteristics, processibility, toxicity, and mechanical and physical properties of a number of amine-cured diglycidyl ether of bisphenol-A (DGEBA) epoxide candidate systems suitable for filament-wound carbon fiber composites. 2,5-Dimethyl-2,5-hexane diamine (DMHDA)-cured DGEBA epoxy was found to be the most promising candidate. The good processibility and thermal properties, together with the low cure characteristics of the DGEBA-DMHDA epoxy system, are discussed in terms of molecular structure of the amine molecule. The network structural parameters that control epoxy toughness and subsequent embrittlement upon plastic flow are discussed. Evidence is presented for plastic flow-induced thermal and mechanical property deterioration of epoxyes as a result of network chain scission.

## INTRODUCTION

The production of fibrous composites by filament winding has considerable potential to produce monolithic structures efficiently and cheaply. Present and future uses in the aerospace and transportation industry include automobile drive shafts, ship hulls, railroad cars, aircraft fuselages, and rocket-motor cases. Filament winding matrices, such as epoxyes, for composites must fulfill a number of requirements to ensure reliable, durable composites are produced.

Epoxy resins utilized in forming filament-wound composites must exhibit low viscosities ( $\eta$ 's) to efficiently impregnate the fiber bundles and long gel times at  $23^{\circ}\text{C}$ . To minimize unreacted starting materials in the finally cured composite requires the chemical cure reactions of the epoxy system to be simple. Furthermore, the number of chemical starting components in the resin must be small to minimize mixing problems that would result in variable thermal and mechanical properties. The toxicity of the resin chemical starting materials must be low. Also, the epoxy system must attain full cure at relatively low post-cure temperatures,  $< 150^{\circ}\text{C}$ , to minimize the development of fabrication strains in the composite.

The toughness and mechanical performance of a filament-wound composite component is enhanced by crack deflection mechanisms and/or molecular flow

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occurring in the epoxy matrix. The inhibition of crack propagation through a bundle of fibers in a composite can occur by deflection of the crack parallel to the fiber axis by either propagation along the fiber matrix interface and/or through the fiber itself. A poor fiber-matrix interface bond and/or microscopic fiber failure by splitting will both enhance these crack deflection toughening mechanisms. The composite performance can also be enhanced under load by molecular flow occurring in the epoxy matrix. Molecular flow is enhanced as  $T_g$  is approached because the glassy state-free volume is increased. However, the epoxy matrix cannot be too soft otherwise the composite will readily buckle in compression. In the case of filament-wound Kevlar 49-epoxy composites, such as pressure vessels, the poor fiber-matrix interfacial strength, the microscopic splitting of the fibers, and matrix ductility all enhance composite mechanical performance.<sup>1,2</sup> However, for C fiber-epoxy filament-wound composites the fiber-matrix interface is generally stronger than for Kevlar 49 composites and the C fiber fails without longitudinal fiber splitting. Hence, for C fiber-epoxy composites the matrix is the principal component that affects composite toughness, and this matrix must be tough through a wide temperature range and possess a  $T_g > 120^\circ\text{C}$ .

In this paper we report our studies on the cure characteristics, processibility, toxicity, and mechanical and physical properties of a number of amine-cured epoxide candidate systems for filament-wound C-fiber composites. The cure characteristics, temperature, and strain-rate dependence of the mechanical properties and deformation processes of the most favorable epoxy system are reported. The molecular factors that optimize processing, thermal and mechanical response, and stress-induced aging of these epoxy matrices are then discussed.

## EXPERIMENTAL

### Materials

The five epoxy systems evaluated in this study were as follows:

1. Pure diglycidyl ether of bisphenol-A epoxide (DGEBA), DER 332, Dow, cured with a aliphatic polyethertriamine, Jeffamine T403, Jefferson. This system has been used as a filament-wound resin system for Kevlar 49-epoxy composites and has been well characterized.<sup>3</sup>

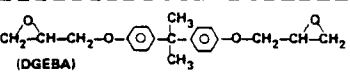
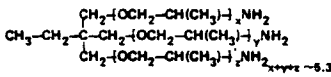
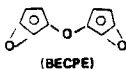

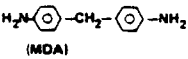
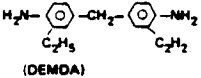
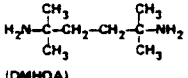
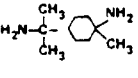
2. A 50 wt % DGEBA and 50 wt % bis(2,3-epoxy cyclopentyl) ether (BECPE), Union Carbide, epoxide mixture cured with a eutectic mixture of 60 wt % methylene dianiline (MDA) and 40 wt % *m*-phenylene diamine (MPDA), Uniroyal. This system has been used as a filament-winding system for glass fiber-epoxy composites.

3. DGEBA cured with an amine curing agent mixture of 60 wt % MDA and 40 wt % diethyl-methylene dianiline (DEMDA), XU205, Ciba Geigy. This aromatic amine curing agent mixture exhibits a lower vapor pressure and does not crystallize compared to the MDA/MPDA curing agent.

4. DGEBA cured with 2,5-dimethyl-2,5-hexane diamine (DMHDA), Aldrich.

5. DGEBA cured with menthane diamine (MNDA), Rohm and Haas.

TABLE I  
The Chemical Structures, Compositions, and Cure Conditions  
of the Epoxy Filament Winding Systems

Chemical structure	Stoichiometric composition in wt%	Cure conditions
(i)  (DGEBA)	68	24h, 23°C 16h, 85°C
 (T403)	32	
(ii) DGEBA	38.3	
 (BECPE)	38.3	8h, 23°C 3h, 93°C 2h, 163°C
 (MPDA)	9.4	
 (MDA)	14.0	
(iii) DGEBA	75.8	
MDA	14.5	8h, 23°C
 (DEMDA)	9.7	2h, 160°C
(iv) DGEBA	82.5	
 (DMHDA)	17.5	16h, 23°C 1h, 60°C 3h, 130°C
(v) DGEBA	80.1	
 (MNDA)	19.9	8h, 23°C 2h, 150°C

The chemical structure of the starting components, their stoichiometric composition [assuming cure occurs exclusively by primary amine-epoxide (P.A.-E) and secondary amine-epoxide (S.A.-E) reactions] and cure conditions are documented in Table I. To modify the 23°C  $\eta$  and gel times of some of the epoxy systems an epoxide diluent diglycidyl ether of 1,4-butanediol (DGEBD), Ciba Geigy was used.

### Methods

A rotating spindle viscometer (Brookfield) was used to determine the 23°C  $\eta$ 's of the epoxy systems as a function of time at 23°C. (An epoxy system that exhibited an  $\eta$  below  $10^3$  cP after 8 h at 23°C was considered acceptable for filament winding.)

A differential scanning calorimeter (DSC) (DuPont 910) was used to monitor the  $T_g$ 's of the epoxies at a heating rate of  $10^\circ\text{C min}^{-1}$ .

For the mechanical property tensile tests, dogbone-shaped specimens with a gauge length of 7.5 cm and a width of 1.3 cm were cut from cast epoxy sheets. Tensile tests were carried out in the 23–125°C range on a mechanical tester (Instron, TTDM) in the crosshead speed range of 0.02–20 cm/min range.

Moisture sorption characteristics of the epoxies were ascertained from weight increases in boiling water as a function of exposure time. After exposure times of 120 h, the moisture sorption approached equilibrium.

The deformation modes in the epoxies were monitored with a polariscope (Photoelastic, Inc.).

Near-infrared spectroscopy (Cary 14 spectrometer) was used to study the degree of cure in the epoxy systems by monitoring the absorbances of the epoxide ( $A_e$ ) and phenyl ( $A_p$ ) groups at 2.205 and 2.160  $\mu$ m, respectively. As the phenyl group does not participate in any of the chemical reactions, the absorbance of this group was utilized as an internal standard. The epoxide group consumption was determined by monitoring the changes in the  $A_e : A_p$  ratio with cure conditions.

## RESULTS AND DISCUSSION

### Properties of Epoxy Filament Winding Systems

The properties of the epoxy filament winding systems investigated in this study are documented in Table II, and are now critically discussed.

The DGEBA-T403 fulfills all the requirements for a filament-wound epoxy system and its structure–property relations are well established, but the  $T_g$  of 92°C is too low for C fiber–epoxy composites.

The mechanical and thermal properties of the DGEBA–BECPE–MPDA–MDA meet the requirements; however, component mixing problems

TABLE II  
Properties of Epoxy Filament Winding Systems

Epoxy system	$T_g$ , °C	Wt% H <sub>2</sub> O Sorption	23°C Mechanical prop		Processing	Carcinogenicity <sup>4-7</sup>
			Tensile strength (MPa)	Failure strain (%)		
(i) DGEBA–T403	92	2.6	55.2	15.0	O.K.	DGEBA–weak
(ii) DGEBA–BECPE–MPDA–MDA	148	4.7	110.3	6.5	$\eta$ O.K.; homogeneous mixing difficult	BECPE–weak BECPE–DGEBA–Synergistic effect MPDA–poss MDA–mod/severe
(iii) DGEBA–MDA–DEMDA	120	2.0	82.8	12.0	15 wt% DGEBD	DEMDA–mod
(iv) DGEBA–DMHDA	143	2.3	94.8	8.7	O.K.	DMHDA–O.K.
(v) DGEBA–MNDP	130	2.5	96.6	7.0	10 wt% DGEBD	MNDA–O.K.

as a result of amine crystallization and resultant phase separation together with the carcinogenicity of the amines are negatives.

Compared to the MPDA-MDA amine curing mixture, the MDA-DEMDA is less of a problem from a carcinogenic (low vapor pressure) and mixing (no recrystallization) viewpoint. However, to attain the desirable 23°C  $\eta$  requires the addition of 15 wt % DGEBD diluent which lowers the  $T_g$  to 120°C.

The DGEBA-DMHDA system fulfills the processing, thermal, and mechanical requirements and is a physically and chemically simple system that is noncarcinogenic. Furthermore, full cure can be attained at low post-cure temperatures (i.e., 3 h, 100°C<sup>7</sup>) which minimizes fabrication strains in the composite.

For the DGEBA-MNDA system our studies indicated that to attain desirable processing and attain full cure < 150°C requires the addition of 10 wt % DGEBD diluent. In the absence of DGEBD, Donnellan and Roylance<sup>8</sup> report that only 80% epoxide consumption occurs after 1 h at 154°C. Indeed full cure is not attained even after 12 h at 150°C. Consistent with these observations Chiu et al.<sup>9</sup> report DGEBA-MNDA epoxies that have been post-cured 2 h, 150°C exhibit mechanical property modifications upon subsequent exposure to 125°C (Argon atmosphere), which is indicative of further crosslinking. Our attempts to cure at higher post-cure temperatures of 200°C for 3 h in the absence of the DGEBD diluent resulted in a lower  $T_g$  than attained after a 8 h, 150°C post-cure, which suggests degradation occurs at these higher post-cure temperatures. Lee and Neville<sup>10</sup> report substantial deterioration and outgassing occurs when the DGEBA-MNDA system is exposed to temperatures in the 160–200°C range. The DGEBA-MNDA system exhibits better short-term, high-temperature mechanical properties than the DGEBA-DMHDA system<sup>9</sup>; however, such properties deteriorate if the epoxy is exposed to temperatures near 100°C because of further crosslinking and/or network chemical degradation.

From the data documented in Table II, we conclude that the DGEBA-DMHDA epoxy system offers the best potential as a filament-winding resin for C fiber-epoxy composites, and as such we investigated its cure characteristics and mechanical response in more detail.

### Properties of the DGEBA-DMHDA Epoxy System

Rinde et al.<sup>7</sup> first reported the potential of the DGEBA-DMHDA epoxy system as a good candidate for a wet filament-winding resin. They report the P.A.-E reaction is 50 times faster than the S.A.-E reaction for the sterically crowded DMHDA molecule and that full cure can be attained within 3 h at 100°C. We have conducted further cure studies and determine this system can be > 90% cured at 60°C after 120 h (Fig. 1). We found the incorporation of 2 wt % H<sub>2</sub>O into the amine prior to the curing did not affect the cure chemistry and full cure was still attained after a 3 h, 130°C post-cure.

The tensile mechanical properties of the DGEBA-DMHDA epoxy system are illustrated in Figure 2 as a function of test temperature (23–125°C) and strain rate (0.02–20 cm/min). The rupture strain, which is related to the molecular flow and toughness of the resin, is > 8% for the temperatures and strain rates investigated. Indeed, > 75°C at strain rates  $\leq$  0.5 cm/min, the

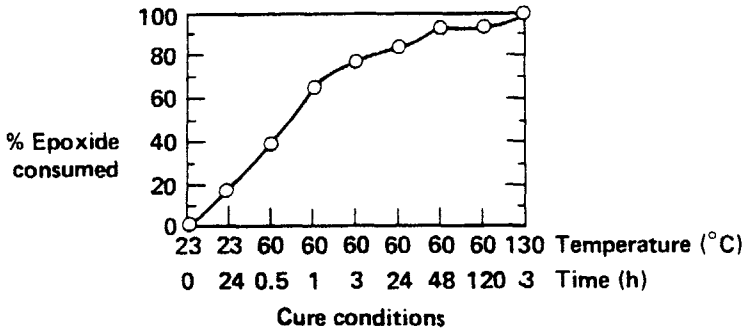


Fig. 1. Epoxide consumption of DGEBA-DMHDA epoxy vs. cure conditions.

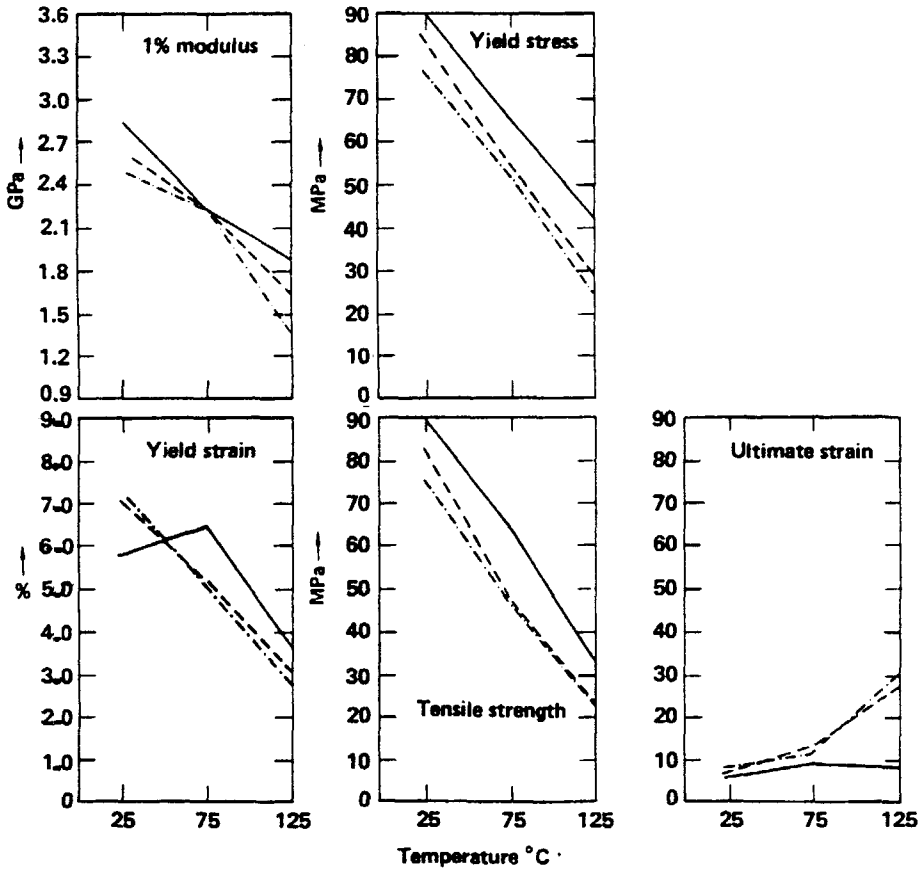


Fig. 2. Mechanical properties of DGEBA-DMHDA epoxy as a function of temperature and strain rate (cm/min): (—)20.0; (---)0.5; (-·-)0.02.

rupture strain is in the 10–30% range. This ductility is caused by molecular flow via inhomogeneous and/or homogeneous plastic deformation. Birefringence studies reveal that residual homogeneous plastic deformation in fractured specimens is enhanced with increasing temperature and decreasing strain rate. These birefringence studies indicate the enhanced ductility of the epoxy at higher temperatures is primarily a result of homogeneous plastic

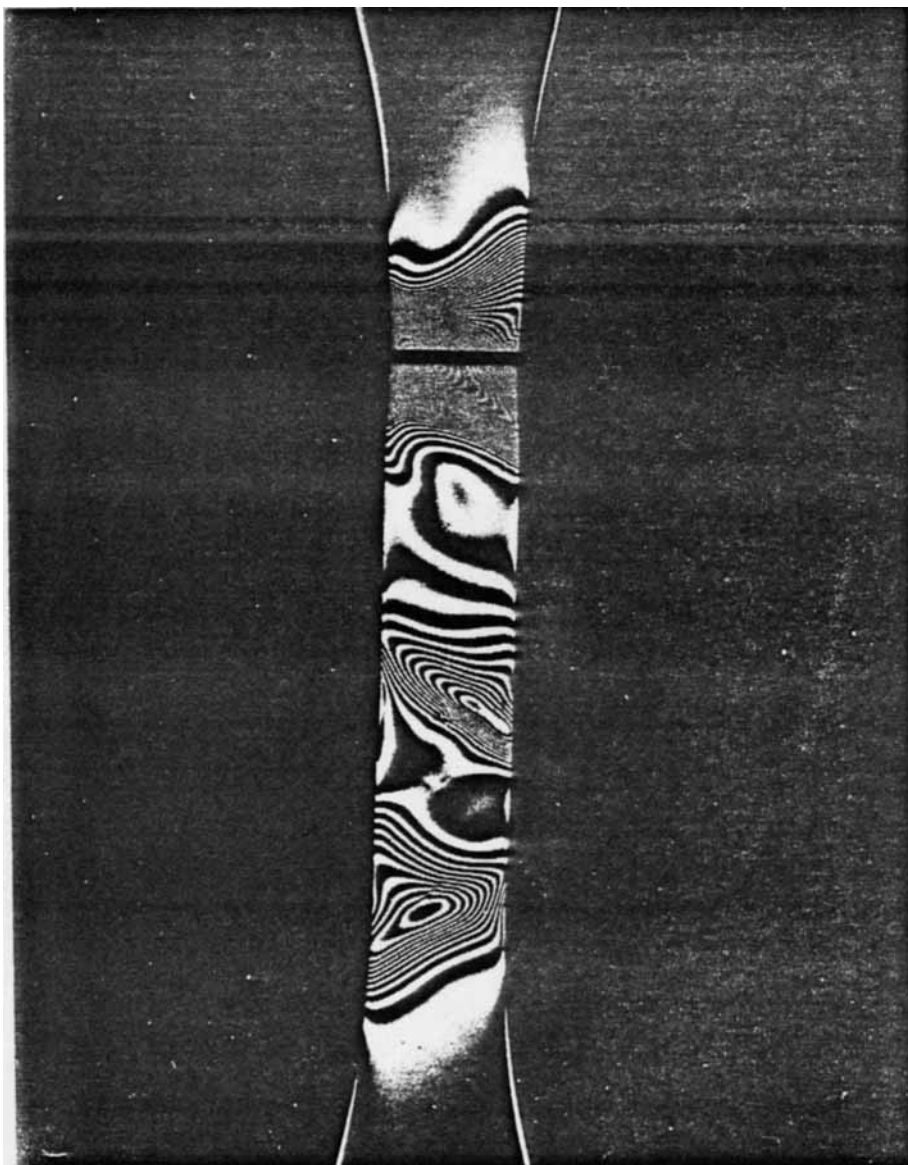


Fig. 3. Residual plastic flow in DGEBA-DMHDA epoxy fractured at 125°C at a strain rate of 0.5 cm/min.

flow. The birefringence patterns associated with inhomogeneous plastic flow in a DGEBA-DMHDA glass is illustrated in the micrograph in Figure 3.

#### **Molecular Factors That Enhance Filament-Winding Epoxies**

To ensure long gel times at 23°C for filament-winding epoxy systems requires that the P.A.-E > S.A.-E reaction rate and that the S.A.-E reaction does not occur at low temperatures. The incorporation of CH<sub>3</sub> groups on the C atom adjacent to the NH<sub>2</sub> groups in amine molecules such as DMHDA and MNDA inhibits the S.A.-E reaction at 23°C. To attain low 23°C  $\eta$ 's and low

post-cure temperatures (to achieve full cure), the amine molecule must be relatively flexible. In this regard molecular models indicate the DMHDA molecule is considerably more flexible than MNDA and, therefore, DMHDA-DGEBA systems exhibit lower  $23^{\circ}\text{C}$   $\eta$ 's and post-cure temperatures to achieve full cure. The combination of a relatively flexible amine molecule with a sterically crowded C atom adjacent to the  $\text{NH}_2$  group produces epoxies with  $T_g$ 's in the  $125$ – $150^{\circ}\text{C}$  range. To produce higher  $T_g$  systems would require stiffer amine molecules which would compromise the resin processibility capabilities.

For epoxies to exhibit tough, crack-blunting characteristics, these glasses must be capable of undergoing plastic flow prior to and/or during crack propagation. Deformation can occur in these glasses by homogeneous plastic flow or inhomogeneously via shear banding and/or crazing.<sup>3,11-14</sup> The ability of epoxies to undergo plastic flow depends on (1) the glassy-state free volume and (2) the deformability of the basic network ring structures and their ability to undergo cooperative motion.<sup>3</sup> The glassy-state free volume depends on the thermal history of the epoxy, the proximity to  $T_g$ , and the molecular shape and packing ability of the constituent epoxide and amine portions of the network and the geometric constraints imposed on their packing by the crosslinked network geometry.

The ability of one-phase epoxies to exhibit significant glassy-state toughness over a wide temperature range is limited by the temperature dependence of the yield stress. Toughness will be limited when macroscopic defects

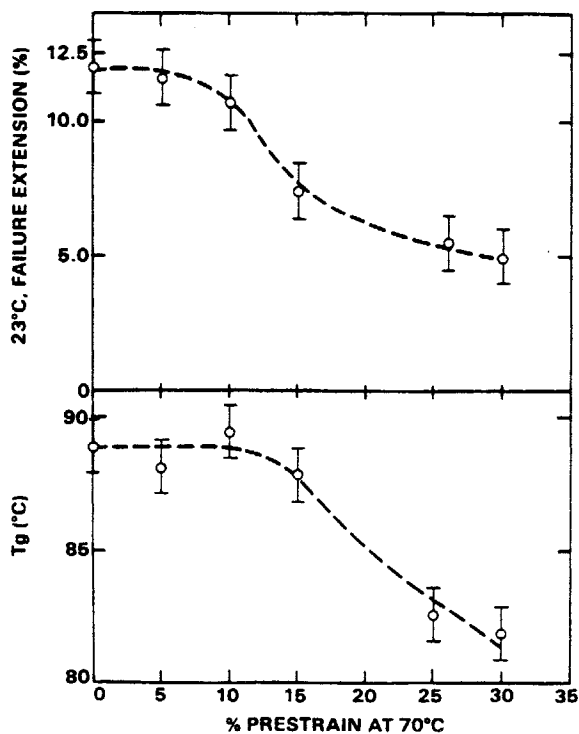


Fig. 4. (a) Tensile failure extension,  $23^{\circ}\text{C}$  and (b)  $T_g$  vs. prestrain at  $70^{\circ}\text{C}$  for subsequently annealed DGEBA-T403 epoxies.



produced during processing and/or network defects cause failure prior to the development of plastic flow. Network defects can result from unreacted groups or impure starting compounds.

The amount of plastic flow and the toughness exhibited by a crosslinked epoxy is limited by the network extensibility. The crack resistance of the network can decrease during plastic deformation as a result of network chain scission. The segments with the lowest extensibilities at any given time in the failure process will carry a significant portion of the load and will undergo scission, resulting in a process of progressive scission of the least extensible segments. We investigated the effect of plastic strain on the epoxy network structure deterioration. DGEBA-T403 epoxies were strained up to 30% at 70°C; then the load was removed, and this strain completely annealed out at 100°C. The ductility of such epoxies decreased by 50% and their  $T_g$ 's were lowered 8°C (Fig. 4) compared to reference specimens that were exposed to the same thermal history but were not stressed at 70°C. Such deterioration in the mechanical response and  $T_g$  are consistent with network deterioration via chain scission. In more direct evidence we deformed thin DGEBA-T403 epoxy films directly in the Fourier transform infrared spectrometer and from difference spectra found permanent chemical changes occur at 23°C after 10% deformation and subsequent removal of the load. Also, Brown and Sandreczki<sup>14</sup> have detected free radicals, indicative of network chain scission, by electron paramagnetic resonance studies after ballmilling these epoxies.

Hence, a defect-free network with segments of equal extensibilities would be the most desirable network for optimizing the toughness of filament winding epoxies over a wide temperature range.

## CONCLUSIONS

To ensure long gel times and low  $\eta$ 's at 23°C for amine-cured DGEBA epoxies suitable for filament winding requires a flexible amine molecule with a sterically crowded carbon atom adjacent to the  $\text{NH}_2$  group, such as in DMHDA. The flexibility of the DMHDA amine molecule also allows utilization of low post-cure temperatures ( $\leq 100^\circ\text{C}$ ) to attain full cure but still produce an epoxy with a  $T_g$  of  $> 140^\circ\text{C}$  suitable for filament-wound C fiber-epoxy composites.

Epoxy networks can deteriorate during plastic flow as a result of network chain scission of the least extensible network segments. A defect-free epoxy network with segments of equal extensibility would be the most desirable network for optimizing the toughness of filament-winding epoxies over a wide temperature range.

## References

1. R. J. Morgan, E. T. Mones, W. J. Steele, and S. B. Deutscher, Proc. of the 12th National SAMPE Tech. Conf., Seattle, WA, (1980), pp. 368-379.
2. C. O. Pruneda, R. J. Morgan, F. M. Kong, J. A. Hodson, R. P. Kershaw, and A. W. Casey, Proc. of the 29th National SAMPE Symp., Reno, NV, (1984), pp. 1213-1222.
3. R. J. Morgan, F. M. Kong, and C. M. Walkup, *Polymer*, **25**, 375 (1984).
4. W. B. Deichmann, W. E. MacDonald, M. Coplan, F. Woods, and E. Blum, *Toxicology*, **11**, 185 (1978).
5. J. M. Holland, D. G. Gosslee, and N. J. Williams, *Cancer Res.*, **39**, 1718 (1979).

6. OSHA Carcinogen List, Category III, The Bureau of National Affairs, Washington, DC, 1979.
7. J. A. Rinde, I. L. Chiu, E. T. Mones, and H. A. Newey, *Compos. Technol. Rev.*, 1(2), 4 (1979).
8. T. Donnellan and D. Roylance, *Polym. Eng. Sci.*, 22, 821 (1982).
9. I. L. Chiu, J. R. Kolb, and H. A. Newey, *Compos. Technol. Rev.*, 5(1), 18 (1983).
10. H. Lee and K. Neville, *Handbook of Epoxy Resins*, McGraw-Hill, New York, 1967, Chap. 7.
11. R. J. Morgan and J. E. O'Neal, *J. Mater. Sci.*, 12, 1966 (1977).
12. R. J. Morgan, J. E. O'Neal, and D. B. Miller, *J. Mater. Sci.*, 14, 109 (1979).
13. R. J. Morgan, E. T. Mones and W. J. Steele, *Polymer*, 23, 295 (1982).
14. I. M. Brown and T. C. Sandreczki, McDonnell Douglas Research Laboratories, St. Louis, personal communication.

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