Mechanical and Thermal Properties of Epoxy Resins With Reversible Crosslinks

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The tensile properties: Young's modulus, ultimate tensile strength, ultimate elongation, the glass transition temperature, and the dynamic mechanical properties (dynamic shear modulus (G'), loss tangent (Tan δ)), of three epoxy resins (Epon 828, Epon 836, Epon HPT 1071) cured with the disulfide-containing crosslinking agent—4.4-dithiodianiline (DTDA) have been characterized. The results show that DTDA is a satisfactory crosslinking agent for the epoxide resins that have been studied as compared to the well-known curing agent methylene dianiline (MDA). There are no significant differences between the properties of Epon 828 cured with DTDA at stoichiometric ratio (2:1) and Epon 828 cured with DTDA at small amine excess ratio (1.75:1). The glass transition temperature of the cured tetrafunctional epoxy resin Epon HPT 1971 (235°C) is significantly higher than that of difunctional epoxy resins such as Epon 828 (T_g–175°C), but the product is too brittle to be used without plasticizer.

INTRODUCTION

In recent years, the recovery or recycling of plastics and composite materials has become increasingly important in order to minimize environmental problems and to develop new technology for energy utilization. Epoxy resins, because of their unique properties, are widely used for engineering purposes. They are used for high-strength adhesives, protective coatings, electronic and electrical applications, and as matrix materials for fiber-reinforced composites. Epoxy resins, after curing with conventional crosslinking agents, cannot be recovered or reprocessed and therefore cannot be recycled. Tesoro and Sastri reported that experimental epoxy resins crosslinked by 4,4'-dithiodianiline (DTDA) can be solubilized by reduction and recovered (1, 2). Reduction has been attained by the cleavage of the disulfide bonds that are present in the crosslinking agent by a reducing agent [Tri-n-butyl phosphine (Bu3P)], to the point of complete solubilization of the thermoset. The recovery of the soluble polymer has been followed by renewing the disulfide linkages by oxidation [e.g. with iodine (I_2)], or by reaction of the thiol groups formed with polyfunctional crosslinking agents. In order to determine whether epoxide resin systems crosslinked with DTDA would be suitable for engineering applications, it was essential to characterize their mechanical properties, glass transition temperatures, and dynamic mechanical responses. The present paper describes the characterization of three epoxy resins cured with DTDA:

A) Liquid Epon 828 cured with a stoichiometric ratio, (2:1 epoxy to crosslinking agent), and with excess amine ratio (1.75:1 epoxy to crosslinking agent). The latter was explored because, in previous work (1, 2), it was shown that in the system Epon 828/DTDA, only the resin with a lower crosslink density (1.75 moles of epoxy to 1 mole of amine) was reduced to the point of complete solubilization under the conditions evaluated.

B) Semi-solid epoxy resin Epon 836 and C) tetrafunctional epoxy resin Epon 1071. It was important to determine the properties of the system Epon 1071/DTDA even though reduction of this system has not yet been proven experimentally, because Epon 1071 is a prototype of a multifunctional epoxy resin developed for use in hot and/or wet environments.

The cured epoxy DTDA systems were tested and compared with equivalent resins cured with the well-known crosslinking agent methylene dianiline (MDA). In this work the following mechanical properties were evaluated: Young's modulus (E), ultimate tensile strength (σu), and ultimate elongation (ϵu). The T_g measurements were done by Dynamic Mechanical Analyzer (DMA). DMA was also used to determine shear modulus (G'), dynamic loss tangent (Tanδ), and the modulus in the rubbery region (E_T).

EXPERIMENTAL

Materials

The epoxy resins and the crosslinking agents used in this work are shown in *Table 1*. The crosslinking agents, Dithiodianiline (DTDA) and methylene dianiline (MDA) obtained from a commercial source (Ald-

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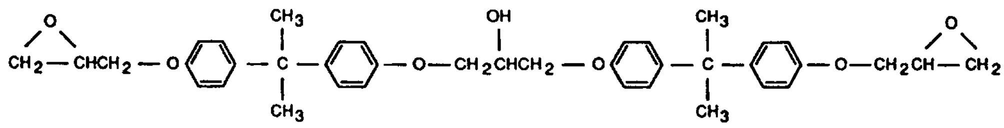
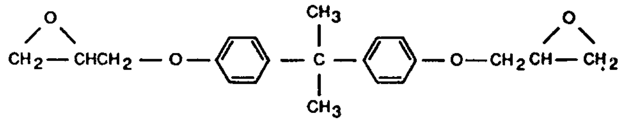
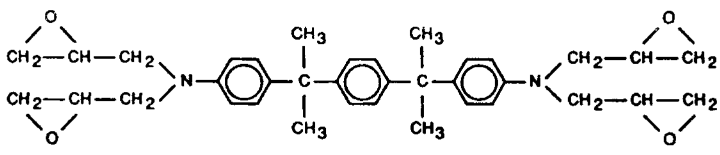
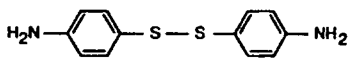
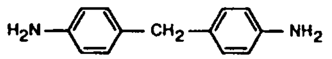
Table 1. Chemical Structure of Epoxy Resins and Crosslinking Agents used for Preparation of Network Polymers.

Structure	Identification
	**EPON 836**
	**EPON 828**
	**EPON HPT 1071**
	**4.4 Dithiodianiline DTDA**
	**Methylenedialline MDA**

rich), were used as received. The commercial resins: Epon 828, Epon 836, and Epon HPT 1071, all from the Shell Development Company, were used as received.

Preparation of Samples

The preparation of the samples was done by using an aluminum mold which had been treated with a mold release agent (Mold Release, Frekote 33.Hysol (Co)).

The procedure for curing the liquid epoxy prepolymer, Epon 828 was as follows: Heating the resin and the curing agent separately to 80°C, applying vacuum for 15 min to remove bubbles, mixing the resin and the crosslinking agent. The mixture was placed in a heated vacuum oven (80°C) and degassed at this temperature for 10 min; then the mixture was poured into the aluminum mold (which also had been heated to 80°C) and placed again in a heated oven for curing. A cure profile of 100°C for 2 h followed by 150°C for 2 h was employed. After curing, the samples were allowed to cool slowly to room temperature in the oven.

The procedures for curing the solid epoxy resins, Epon 836 and Epon HPT 1071, were the same as for the liquid epoxy (Epon 828), except that the solid resins were melted prior to use. The cure profile for Epon 836 was also 100°C for 2 h followed by 150°C for 2 h.

The cure profile for Epon HPT 1071 was 150°C for 2 h followed by 200°C for 4 h.

After curing and cooling, the samples were taken out of the mold and prepared for mechanical testing by polishing with fine sandpaper.

Materials Characterization

Tensile measurements were made using an Instron tester at room temperature, according to ASTM, test D-638-68, type IV with a crosshead speed of 5mm/min. Young's modulus, E. ultimate tensile strength, σu, and ultimate elongation, ϵu, were determined. Each result is an average derived from at least four specimens per sample. Values of E, σu, and ϵu were within ±5 percent of the average. Measurements of T_g, shear modulus, G', and loss tangent, Tanδ, were made using a Dynamic Mechanical Analyzer (DMA Du Pont 982) in a resonance mode at a heating rate of 5°C/min. The measurements were made over a temperature range from 40°C to about 20°C above T_g. The average molecular weight between crosslinks Mc, was calculated according to Murayama (3):

$$Mc = \frac{RT}{E} \cdot 1$$

where R is the gas constant, T, the absolute temperature, and E is the modulus in the rubbery region (in this case 20°C above T_g). Finally, the theoretical value of *Mc*, was calculated from the molar ratio of epoxy resin to the crosslinking agent.

RESULTS AND DISCUSSION

Mechanical Properties

Tensile data of the epoxy resin cured with the crosslinking agents DTDA and MDA are presented in *Table 2*. As can be seen from the *table*, the values of: Ultimate tensile strength, *u*, and Young's modulus *E*, are higher for the epoxy resins cured with DTDA than for the equivalent resins cured with MDA.

Although in most cases the differences are not significant, the results indicate that the tensile properties of these epoxy resins cured with DTDA are comparable to those of resins cured with MDA as the crosslinking agent.

Another advantage of DTDA is the differences between the stress-strain behavior of the epoxy resins cured with DTDA and the same resins cured with MDA (*Fig. 1*). While the systems cured with MDA show only elastic deformation, the epoxy resins cured with DTDA are more ductile and have elastic and plastic deformation as well. These differences in the stress-strain behavior are probably caused by the more flexible disulfide bonds in the thermoset network.

For the system Epon 828/DTDA, differences between the tensile properties of resin cured at stoichiometric ratio and at excess amine ratio, are not significant. These results were expected because, as noted by others (4, 5), a small excess of amine (in this case 14 percent) has little effect on the mechanical properties at room temperature.

Epon 836 cured with either MDA or DTDA has a higher ultimate elongation than Epon 828 cured with these crosslinking agents, probably due to lower crosslink density in the case of cured Epon 836 resin.

The low values of ultimate tensile strength, σu, and ultimate elongation, ϵu for the systems Epon 1071/MDA and Epon 1071/DTDA indicate that the two systems are too brittle for use without plasticizer.

Glass Transition Temperature (T_g)

Table 3 shows the T_g values obtained by DMA for the fully cured epoxide systems. The T_g values for resins cured with DTDA are slightly lower than for resins cured with MDA but the differences (0 to 3°C) are not significant. These results indicate that epoxide resins cured with DTDA can be used at comparable temperatures as resins cured with MDA.

The T_g for Epon 828 cured with DTDA at stoichiometric ratio is slightly higher than for Epon 828 cured with DTDA at excess amine, but the difference (6°C) is not significant. This result is believed to be of practical importance because (as mentioned above) the cured epoxy resin can be reduced to the point of complete solubilization only when DTDA is in excess.

As expected, the T_g for the cured tetrafunctional epoxy resin Epon 1071 is significantly higher (60 to 80°C) than the T_g for the cured difunctional epoxy resins Epon 828 and Epon 836.

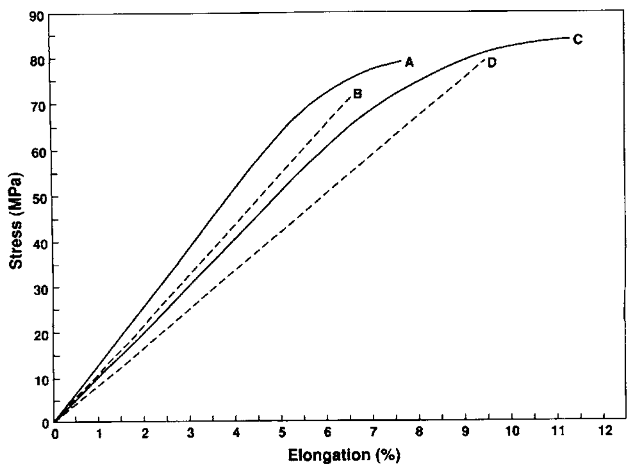


Fig. 1. Stress strain curves for epoxy resins cured with DTDA (———) and MDA (– –). A: Epon 828/DTDA, B: Epon 828/MDA, C: Epon 836/DTDA, D: Epon 836/MDA.

Table 2. Tensile Properties for the Epoxy Resins Cured with the Crosslinking Agents DTDA and MDA.

System	δu (MPa)	E (MPa)	ϵu (%)
Epon 828/DTDA 2:1	79	1291	7.6
Epon 828/MDA 2:1	71	1070	6.5
Epon 828/DTDA 1.75:1	67	1209	5.7
Epon 828/MDA 1.75:1	60	993	6.7
Epon 836/DTDA 2:1	84	1016	11.2
Epon 836/MDA 2:1	79	832	9.4
Epon 1071/DTDA 1:1	37	2105	2.1
Epon 1071/MDA 1:1	35	1642	2.1

Table 3. Glass Transition Temperatures (DMA) for the Cured Epoxy Systems.

System	T_g (°C)
Epon 828/DTDA 2:1	172
Epon 828/MDA 2:1	175
Epon 828/DTDA 1.75:1	166
Epon 828/MDA 1.75:1	167
Epon 836/DTDA 2:1	154
Epon 836/MDA 2:1	154
Epon HPT 1071/DTDA 1:1	235
Epon HPT 1071/MDA 1:1	232

Average Molecular Weight Between Crosslinks (*Mc*)

Table 4 shows the values of average molecular weight between crosslinks, (*Mc*), for the cured epoxy systems studied. As can be seen from the *table*, the values of *Mc* calculated by *Eq 1* are in good agreement with the theoretical values calculated from the molar ratio of epoxy resin to crosslinking agent. The value of *Mc* for Epon 828 cured with DTDA in excess is significantly higher than the *Mc* value for Epon 828 cured with DTDA at stoichiometric ratio. In a subsequent reduction step, the lower cross-link density of the former system makes it possible for reducing agent (like Tri-n-butyl phosphine) to penetrate the crosslinked network and solubilization can thus be attained.

Dynamic Mechanical Properties

Dynamic mechanical responses of the cured epoxy systems that have been studied, are presented in *Figs. 2* and *3* and *Table 5.*

Table 4. Average Molecular Weight (*Mc*) Between Crosslinks for the Cured Epoxy Systems.

System	*Mc* (*Eq 1*)	*Mc* (theoretical)
Epon 828/DTDA 2:1	376	336
Epon 828/MDA 2:1	342	320
Epon 828/DTDA 1.75:1	528	—
Epon 828/MDA 1.75:1	481	—
Epon 836/DTDA 2:1	599	496
Epon 836/MDA 2:1	564	474
Epon HPT 1071/DTDA 1:1	474	458
Epon HPT 1071/DTDA 1:1	457	433

Table 5. Shear Storage Modulus (G'), at Different Temperatures, as Measured by DMA.

System	G' (GPa) 40°C	120°C	150°C	220°C	*RS**
Epon 828/DTDA 2:1	0.41	0.33	0.28	—	0.01
Epon 828/MDA 2:1	0.35	0.27	0.23	—	0.01
Epon 828/DTDA 1.75:1	0.40	0.33	0.27	—	0.008
Epon 828/MDA 1.75:1	0.33	0.28	0.24	—	0.008
Epon 836/DTDA 2:1	0.38	0.31	0.10	—	0.007
Epon 836 MDA 2:1	0.32	0.27	0.07	—	0.007
Epon 1071/DTDA 1:1	0.55	0.51	0.40	0.31	0.01
Epon 1071/MDA 1:1	0.49	0.50	0.41	0.31	0.009

* *RS*—Rubbery state (about 20°C above T_g for each system).

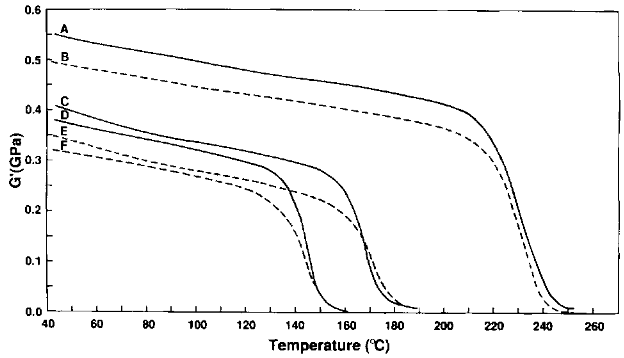


Fig. 2. DMA plots of shear storage modulus, G', as a function of temperature for the epoxy resins cured with DTDA (———) and MDA (– – – –). A: Epon HPT 1071/DTDA, B: Epon HPT 1071/MDA, C: Epon 828/DTDA, D: Epon 836/DTDA, E: Epon 828/MDA, F: Epon 836/MDA.

Shear Storage Modulus (G')

Figure 2 is a DMA plot of G' as a function of temperature for the epoxy resins cured with the conventional crosslinking agent MDA and with the disulfide-containing crosslinking agent DTDA. *Table 5* shows the values of G' at five temperatures (40, 120, 150, and 220°C), and in the rubbery state (the shear storage modulus in the rubbery state ($G'r$) was measured at about 20°C above T_g for each system), as measured by DMA. As expected, at low temperature (40°C) the value of G' for a particular system is about one-third of the Young's modulus, *E*, (*Table 2*) measured by the Instron tester for the same system. Until 120°C, all systems maintain high G' values, but when the temperature is raised to 150°C the values of G' for the systems Epon 836/MDA and Epon 836/DTDA drop drastically (0.07 to 0.10 GPa), due to the lower T_g (154°C) of those two systems. When the temperature exceeds 160°C, the G' values of the systems based on Epon 828 also drop rapidly although the values of G' for systems based on the multifunctional epoxy, Epon HPT 1071, remain relatively high (0.31 GPa) up to 220°C. In the rubbery state the cured polymer chains are able to slide passed each other reversibly when deformed and the shear modulus for all the systems is very low (0.007 to 0.01 GPa). As can be seen from *Fig. 2* and *Table 5*, the values of G', at all temperatures for each type of epoxy resin cured with DTDA are equal to, or higher than the values of G' for the equivalent epoxy resin cured with MDA. These results suggest that epoxy resins cured with DTDA could be used in the same temperature range as epoxy resins cured with MDA.

Loss tangent (tanδ)

Tan δ is the ratio between the shear loss modulus (G'') and the shear storage modulus (G'). Tan δ is related to the damping characteristics of the material. The height of its peak expresses the ability of the material to dissipate energy as heat during a cycle of deformation. *Figure 3* is a DMA plot of tan δ as a function of temperature for the three epoxy resins

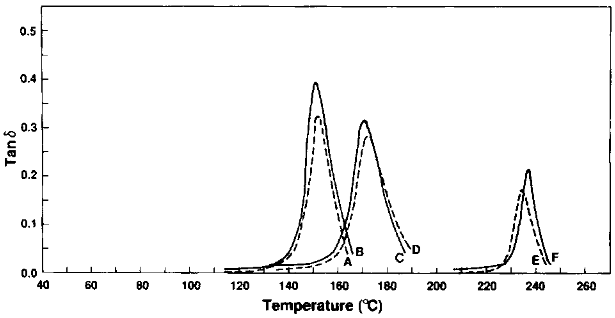


Fig. 3. DMA plots of loss tangent, Tan δ, as a function of temperature for the epoxy resins cured with DTDA (———) and MDA (----). A: Epon 836/MDA, B: Epon 836/DTDA, C: Epon 828/DTDA, D: Epon 828/MDA, E: Epon HPT 1071/MDA, F: Epon HPT 1071/DTDA.

cured with MDA and DTDA. As can be seen from the *figure*, the resins cured with DTDA have slightly higher loss peaks than those cured with MDA. This can perhaps be attributed to the flexibility of the disulfide bond in the systems crosslinked by DTDA. As expected, the Epon 836 resins show the highest tan δ peak, due to their relatively low crosslink density. On the other hand, the cured tetrafunctional epoxy resin, Epon HPT 1071 has a rigid structure and hence the loss peak is lowest. The significant shift of tan δ peak towards higher temperature in the systems Epon HPT 1071/MDA and Epon HPT 1071/DTDA shows the clear advantage of Epon HPT 1071 for applications in hot environments.

CONCLUSIONS

4.4-Dithiodianiline (DTDA) is a satisfactory crosslinking agent for the epoxide resins that have been studied (Epon 828, Epon 836, and Epon HPT 1071). For all properties evaluated for the epoxy/DTDA systems, tensile properties, T_g measurements and dynamic mechanical responses, results are equal to (or even better than) those obtained for the same epoxy resins cured with the well-known crosslinking agent methylene dianiline (MDA).

The system Epon 828/DTDA can be cured at the ratio 1.75 Epon 828 to 1.0 DTDA, without significant loss of T_g and mechanical properties as compared to Epon 828 cured with DTDA at stoichiometric ratio (2:1). This conclusion is important for reprocessing and reuse because the system Epon 828/DTDA (1.75:1) can be reduced to the point of complete solubility under mild conditions (1).

The glass transition temperature of the cured tetrafunctional epoxy resin Epon HPT 1071 (235°C) is high compared to that of cured difunctional epoxy resins like Epon 828 (T_g – 175°C), but the product is too brittle for use without plasticizer.

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