

A Structure-Property Rationalization of Some Poly(carboxyl-Epoxy) Thermosets

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Synopsis

The glass transition temperatures, T_g , and strength properties have been determined for an acrylic-based prepolymer containing 25 mole-% carboxyl functionality crosslinked with five different diepoxides. The T_g values vary from 100° to 200°C, and ultimate elongations of 2% to 7% at 25°C are observed with the different crosslinking agents. These variations are rationalized in terms of the structural elements present in the diepoxides. Thermosets possessing rigid structural units at the crosslink points connected by flexible segments have the best all-around combination of T_g and tensile properties. A decline in these properties was noted when the epoxide/carboxyl ratio exceeded unity owing to the formation of mixed networks and free chain ends.

INTRODUCTION

Structure-property relationships in crosslinked polymers below their glass transition temperature, T_g , are poorly understood.¹ Of particular interest in this work was the influence of the nature of the crosslinking agent on T_g and the stress-strain properties of a crosslinked network. The reactive prepolymer employed was a terpolymer of methacrylic acid, methacrylonitrile, and methyl methacrylate. Crosslinking agents used were commercially available diepoxides containing aromatic, aliphatic, and cycloaliphatic structural units. This particular system was investigated because of the utility of this system, the variety of structural features available in the crosslinking agents, and the expectation that these structural features could be related to the strength characteristics of the cured materials.

It is recognized that many properties of the prepolymer have a profound influence on the final properties of the cured network. However, only preliminary work was done to establish a suitable molecular weight and bulk composition of the prepolymer used in this study, while other parameters such as sequence distribution and tacticity were not used as a part of the experimental study. Only the structural influence of the crosslinking agent on the cured network properties was considered in this work.

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EXPERIMENTAL PROCEDURES AND RESULTS

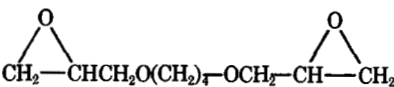
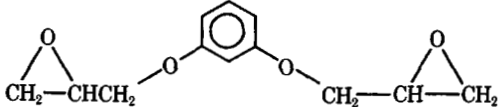
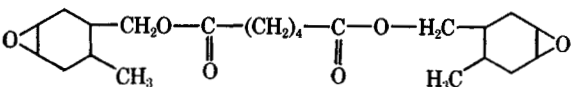
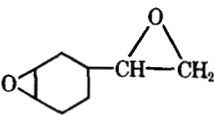
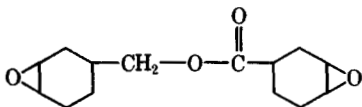
Preparation of Reactive Prepolymer

A mixture of methyl methacrylate (40 mole-%), methacrylic acid (30 mole-%), and methacrylonitrile (30 mole-%) was polymerized in refluxing *p*-dioxane to 60% conversion or more using *tert*-butyl perbenzoate as initiator (nitrogen atmosphere). The product, isolated by coagulation in *n*-hexane, had a number-average molecular weight of 8000 as determined by vapor phase osmometry and an acid value of 1 equivalent per 356 g as determined by titration against 0.100*N* aqueous NaOH using phenolphthalein indicator.

Crosslinking Agents

Commercial-grade diepoxides from Ciba Products Company used to crosslink the above prepolymer are listed in Table I.

TABLE I
Chemical Structure of Crosslinking Agents and Their Effect on Glass
Transition Temperature (T_g) of Cured Polymers

Trade name	Idealized chemical structure	T_g of cured polymer, °C
RD-2		100
ERE-1359		135
CY 178		145
RD-4		160
CY 179		200

Sample Preparation and Molding

To obtain homogeneous molding powders, the prepolymer, diepoxide and *N,N*-dimethylbenzylamine (catalyst, 1% by weight of prepolymer) were dissolved in dioxane and freeze dried. Prepolymer and diepoxide were

combined in the ratio of one epoxide ring per acid group, with the exception that the CY 178-to-acid ratio was varied from 0.4 to 1.8 in increments of 0.2. The molding powder was further dried under vacuum for one day at room temperature and 1 hr at 50°C.

Cured rectangular samples 0.05 in. thick were obtained by compression molding of the dried powder in a press at 375°F and about 1000 psi for 15 min and cooled to room temperature by circulating cold water through the platens.

Infrared Measurements

The state of cure of these materials was assessed by infrared measurements on thin films prepared by grinding and polishing specimens cut from the original moldings. Analysis of the bands at 3.05 μ for the carboxyl group and the 11 to 12 μ region for the epoxy group showed no detectable carboxyl or epoxy groups, indicating a conversion of over 98% for samples having epoxide-to-acid ratios of 1. When the epoxide concentration exceeded the acid concentration, not all the epoxide present was consumed; however, a greater amount than that required to react with the acid was consumed. This indicates the formation of a mixed network of ester linkages (from the carboxyl-epoxy condensation) and ether linkages (from the epoxy-epoxy condensation). Remaining unreacted epoxide groups represent free chain ends.

Torsion Pendulum Measurements

The temperature dependence of the dynamic shear modulus, from 25° to 200°C, of the cured polymers was determined with a torsion pendulum.^{2,3} The T_g of the cured polymers were evaluated to $\pm 5^\circ\text{C}$ from the observed maximum in $\tan \delta$. Results of these measurements are given in Figures 1 and 2 and Table I and show that the T_g varies over a 100°C range for different crosslinking agents.

Tensile Testing

Two types of tensile specimens were machined from the cured polymer sheets:

Type I: Dogbone specimens with a reduced gauge section of 0.25-in. width and parallel gauge length of 1 in. were extended at a rate of 4% per min on an Instron at room temperature using an extensometer clip gauge to measure strain. Data from these specimens were used to compute Young's modulus.

Type II: Dogbone specimens with a reduced gauge section of 0.125-in. width and parallel gauge length of 0.5 in. were extended at a rate of 4% per min on an Instron and were used to compute stress from the observed maximum load based on the original cross-sectional area of the specimens.

By comparing the modulus from type I specimens to the apparent modulus of type II specimens, a correction factor of 2 was calculated and used to

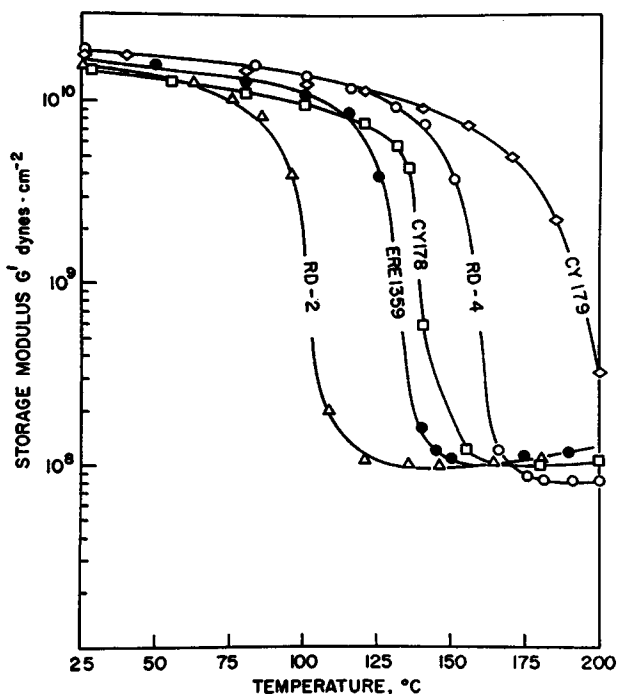


Fig. 1. Plot of shear modulus vs. temperature for prepolymer crosslinked with five

different diepoxide crosslinking agents where $\frac{[\text{C}-\text{C}]}{[\text{COOH}]} = 1$.

compute true strain for type II measurements. Type II specimens were generally employed to conserve material; the extensometer clip gauge was not used with these specimens because the clip gauge knife edges initiated premature fracture. Tensile data are reported in Figure 3 and Table II and show a range of strength characteristics from brittle to ductile (macroscopic yielding) failure. The effect of varying the stoichiometry for the CY 178-cured samples is reported in Table III.

TABLE II
Effect of Diepoxide Structure on Tensile Properties of Cured Polymers at 25°C^a

Diepoxide	Ultimate elongation, %	Maximum stress, psi	Young's modulus, psi $\times 10^{-5}$
RD-2	6	9900	4.6
ERE 1359	3	13200	6.8
CY 178	7	13200	5.4
RD-4	2	10600	6.8
CY 179	2	9700	6.6

^a Epoxide/carboxyl ratio equals unity in these preparations.

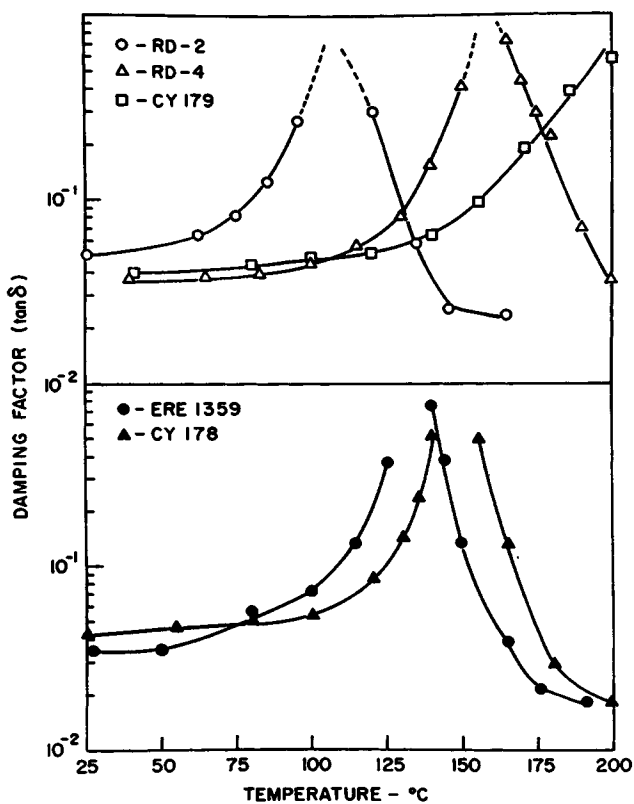


Fig. 2. Plot of $\tan \delta$ vs. temperature for prepolymer crosslinked with five different di-

epoxide crosslinking agents where $\frac{[\text{C}-\text{C}]}{[\text{COOH}]} = 1$.

TABLE III

Effect of $\frac{[\text{C}-\text{C}]}{[\text{COOH}]}$ Ratio on Mechanical Properties at 25°C

CY 178 concn., % of stoichiometry	T_g , °C	Ultimate elongation, %	Maximum stress, psi	Young's modulus, psi $\times 10^{-5}$
40	122	5	11200	4.4
60	141	6	12600	4.4
80	150	6	13000	4.4
100	145	7	13200	5.4
120	145	4	10000	4.4
140	135	4	11400	4.4
160	127	4	10600	4.2
180	120	4	11100	4.2

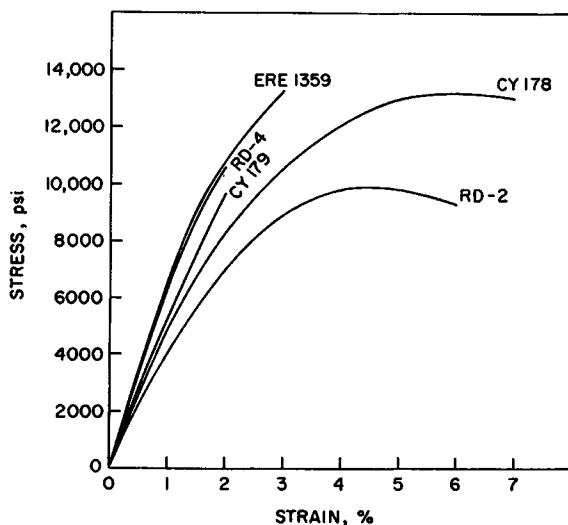


Fig. 3. Stress-strain curves for prepolymer crosslinked with five different diepoxide

crosslinking agents where $\frac{[\text{C}-\text{C}]}{[\text{COOH}]} = 1$.

DISCUSSION

Torsion Pendulum Data for $\frac{[\text{C}-\text{C}]}{[\text{COOH}]} = 1$

These data were used primarily to determine the T_g of the cured materials obtained with different crosslinking agents. Qualitatively, the differences in T_g can be rationalized by considering the relative rotational freedom of the diepoxides and the effect of cycloaliphatic versus linear epoxy groups. The RD-2 diepoxide may be used as a basis of comparison: note that it has two linear aliphatic epoxy groups connected by four methylene units. When the four methylene groups are replaced by a rigid benzene ring, i.e., ERE 1359, the T_g increases 35°C. The effect of changing from linear aliphatic epoxy groups to cycloaliphatic epoxy can be seen by comparing CY 178 to RD-2; here, T_g increases 45°C. The combined effect of using one cycloaliphatic group and eliminating six methylene and two ether linkages, when comparing RD-2 and RD-4, may be seen by noting the 60°C increase in T_g . In the case of CY 179, where there are two cycloaliphatic groups with a short connecting linear aliphatic group, the structural "opposite" of RD-2, the T_g increases 100°C.


Tensile Properties for $\frac{[\text{C}-\text{C}]}{[\text{COOH}]} = 1$

The modulus, maximum stress, and ultimate elongation of these cross-linked polymers show that these materials vary considerably in their re-

sponse to tensile loading. The room-temperature Young's moduli for the RD-2 and CY 178 samples are lower than those of the other polymers. Also compare the shear moduli of CY 178, RD-4, and CY 179 at 125°C below their respective T_g values; they are not equivalent, with CY 178 being the lowest. These comparisons are made to point out that (a) similar polymers do not all have the same glassy modulus and (b) the glassy modulus is not solely a function of T_g .

A rationalization for the above results may be found in the structural differences among the diepoxides. Note that both RD-2 and CY 178 have long flexible linear aliphatic chains, the other diepoxides do not. The flexible linear aliphatic chain appears to be necessary for high elongation to break. Thus, ductile or brittle response at room temperature does not depend on solely T_g , and the optimum combination of tensile properties and T_g are obtained when the crosslinked polymers contain rigid structural units at the crosslink points connected by flexible segments.


Effects of [C—C]/[COOH] Ratio on Mechanical Properties



The effect of varying the [C—C]/[COOH] ratio on the mechanical properties of the CY 178-cured polymer may be seen in Table III, which shows that optimum values are obtained when this ratio is 0.8 to 1. As this ratio increases from 0.4 to 1, the number of network chains that are load bearing increases while the number of free chain ends decreases. The observed increase in T_g and the gradually improving tensile properties are consistent with these structural variations.

When the epoxy-to-carboxy ratio exceeds 1, T_g and the tensile properties decrease. Under these conditions, infrared studies indicate the formation of a mixed network and free chain ends. The latter accounts for a decrease in T_g and both account for the loss in tensile properties.

SUMMARY AND CONCLUSIONS

This investigation demonstrates that the glass transition temperature of a carboxyl-containing prepolymer crosslinked with diepoxides depends on the flexibility of the crosslinking agent and whether the epoxide group is aliphatic or cycloaliphatic. Also, the strength properties of these materials at room temperature are dependent on chemical structure and T_g . The materials that show a combination of good strength properties and high T_g possess a network structure of rigid structural units at the crosslink points connected by flexible segments.

The mechanical properties of the thermosets are dependent on the ratio of crosslinking agent to crosslink sites on the prepolymer. Optimum properties are obtained when this ratio has a value between 0.8 and 1. It is con-

cluded that the presence of a mixed network and free chain ends decreases both the strength properties and the T_g of a crosslinked glass.

References

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