Reversible Crosslinking in Epoxy Resins. I. Feasibility Studies*

G. C. TESORO and V. SASTRI,[†] *Polytechnic University, Brooklyn, New York 11201*

Synopsis

The objective of the research is to investigate epoxy resins where crosslinks formed in curing reactions can be cleaved and reformed without significant sacrifice in resin properties. In this phase of the investigation, experimental disulfide-containing crosslinking agents have been studied, including dihydrazides of dithiodicarboxylic acids (aliphatic and aromatic) and dithio-aromatic diamines. Conditions for curing reactions and for subsequent cleavage of crosslinks by reduction have been determined in model systems and confirmed for a prototype epoxy resin. A preliminary comparative evaluation of cure kinetics and of crosslink density and thermal and mechanical properties has been carried out for this resin cured with aromatic curing agents (4,4'-dithiodianiline and methylene dianiline) and with aliphatic compounds (3,3'-dithiopropionic acid dihydrazide and hexamethylene diamine). It has been shown that in a resin fully cured with disulfide-containing crosslinking agents, crosslinks could be ruptured by reduction, and reestablished by oxidation under mild conditions.

INTRODUCTION

The recovery of economic value from plastics and polymer composites is becoming increasingly important as interest in minimizing energy consumption continues, and plastics replace other materials in numerous applications. In this context, one element of the Energy Conversion and Utilization Technologies (ECUT) Materials program funded by the U.S. Department of Energy concerns long-range research on approaches designed to yield a new technology base for recovering maximum value from scrap polymeric materials in the future. The recovery—or "recycling" of thermosets—is one challenge of the research program.

In the case of crosslinked polymers- (thermosets), it is necessary to convert cured resin to a processable material that can be subsequently crosslinked anew or chemically modified, to yield products of desirable properties. Depending on the reactions and processing conditions employed, such "recycled" products may exhibit properties that make them suitable for less demanding applications (secondary recycling), or they may approach and even surpass the properties of the parent resin for new applications and recovery of value (tertiary recycling).

The objective of the work reported in this paper has been to investigate a novel concept that would allow recovery, reprocessing, and reuse of epoxy resins, while maintaining, or even improving, the properties of the ultimate products. Crosslinking reactions and properties of a thermoset polymer in

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which crosslinks can be cleaved and reformed have been studied for the reaction of an epoxy resin with experimental crosslinking agents in which epoxy-reactive functional groups are comparable to those known to be effective, *and* a disulfide linkage that can be cleaved by reduction is also present.

Conditions for curing reactions of a prototype epoxy resin with experimental compounds, cleavage and reformation of crosslinks have been determined experimentally and properties have been compared with those of products prepared with known crosslinking agents.

The study of reduction conditions on cured resin demonstrated the importance of crosslink density for attaining complete solubilization. Reoxidation experiments were carried out on solutions of reduced products as a first step in the study of this novel "tertiary recycling" concept. Further investigations of reagents and conditions for reestablishing crosslinks in reduced products by oxidation, and by reaction with polyfunctional reagents are in progress.

The feasibility of the concept has been demonstrated in this first phase of the investigation, and research is continuing on other aspects of this approach to the recovery/reuse of thermosets.

EXPERIMENTAL

Materials

Methylene dianiline (MDA) and 4,4'-dithiodianiline (DTDA) (both Aldrich) were recrystallized from aqueous methanol. 3,3'-Dithiopropionic acid dihydrazide (DTPDH) was synthnesized by the method of Sakamoto et al.[1] and 2,2'-dithiobenzoic acid dihydrazide (DTBDH) by the method of Katz et al.[2]
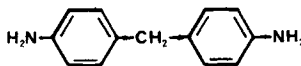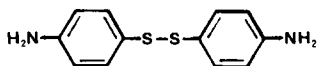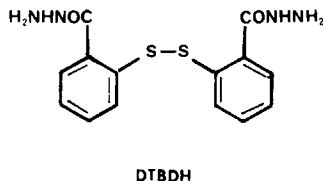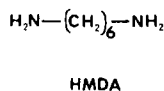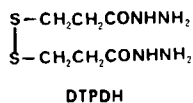

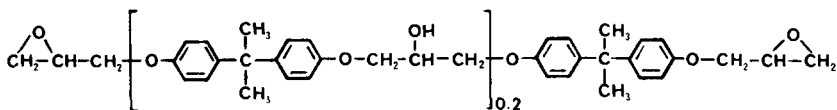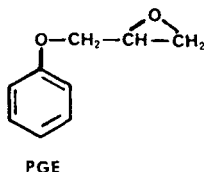
Fig. 1. Structures of curing agents.

Fig. 2. Structures of epoxides.

Phenyl glycidyl ether (PGE) (Aldrich) was distilled before use and 1,4-dioxane was distilled over Na/benzophenone. Adipic acid dihydrazide (ADH) (Olin), hexamethylene diamine (HMDA), tri-*n*-butyl phosphine (Bu$_3$P), iodine crystals, diglyme (all Aldrich), Epon 828 (Polysciences), and all solvents were used as received. Structures of curing agents and epoxides are given in Figures 1 and 2.

Methods

Differential scanning calorimetry (DSC) was performed on a DuPont 910 instrument under nitrogen at a heating rate of 10°C/min. Thermogravimetric analysis (TGA) was carried out on a DuPont 951 analyzer under nitrogen at a heating rate of 20°C/min. Dynamic mechanical analysis (DMA) was done on a DuPont 982 analyzer at a heating rate of 5°C/min. Thin layer chromatography (TLC) of model compounds was performed on glass plates precoated with silica gel using a 50:50 (v/v) hexane/diethyl ether solvent system as the eluant.

Gel permeation chromatography (GPC) was carried out on a Waters GPC I, Model 590 liquid chromatograph, using the refractive index detector and narrow molecular weight polystyrene standards for the calibration curve. Tetrahydrofuran was the eluant at a flow rate of 0.8 mL/min using Waters μ-styragel columns of 10^4, 10^3, and 500 Å in series.

FT-IR spectra were measured on a Bio-Rad FTS 60 spectrophotometer. Chemical analysis of cure kinetics and epoxide conversion was according to Bell[3] and Lee and Neville.[4] Analysis of thiol groups after reduction (using DMF as the solvent) was by the method of Bald.[5] Elemental analysis was carried out by Microlytics, South Deerfield, MA.

Synthesis and Reduction Reactions of Model Compounds

Reaction temperatures of the experimental curing agents (DTDA, DTPDH, DTBDH) and reference curing agents (MDA, HMDA, ADH) with the mono-

TABLE I
Curing and Reduction of Model Compounds

| Model Compd. no. | Curing agent[a] | DSC cure temps | | Cure temp[b] (°C) | Reduction | | | −SH content (eq/mol) | |
		Onset (°c)	Peak (°C)		Reagents	Conditions[c]	Yield (%)	Theor	Exptl
1	DTDA	161	180	140	Bu₃P, dioxane	100°C, 2 h	96	1.0	0.9887
2	DTPDH	129	151	130	Bu₃P, methanol	60°C, 12 h	94	1.0	0.9907
3	DTBDH	91	96	100	Bu₃P, dioxane	100°C, 24 h	0	1.0	0
4	MDA	100	128	100					
5	HMDA	76	96	80					
6	ADH	159	163	160					

[a] With PGE in a 1 : 4 molar ratio curing agent/PGE.
[b] Cure time for all reactions = 2 h.
[c] Under N_2 atmosphere.

epoxide PGE are shown in Table I. In a typical experiment, 0.01 mol curing agent and 0.04 mol PGE were accurately weighed in a Teflon beaker and mixed well. The mixture was then placed in an oven at the temperature specified in Table I for the corresponding curing agent, for 2 h. The samples were then removed, cooled, and ground to a fine powder for further reactions.

Structures of all model compounds were characterized spectroscopically by FTIR and NMR.

Reduction conditions are given in Table I. A slight molar excess of Bu_3P over the adducts was used in all cases.

Curing of Epon 828 with DTDA and MDA

Stoichiometric amounts (i.e., a 1 : 2 molar ratio diamine/diepoxide) of reagents were accurately weighed into a Teflon beaker and mixed well. The beaker was then placed in an oven at 60°C till the diamine dissolved. The resin was then cured at 80°C for 2 h and 150°C for 2 h for MDA[3] and 100°C for 2 h and 160°C for 2 h for DTDA.

Curing of Epon 828 with DTPDH and HMDA

Stoichiometric amounts of reagents were accurately weighed in a Teflon beaker and mixed well. A cure profile of 110°C for 2 h and 130°C for 2 h was employed for DTPDH and of 60°C for 2 h and 120°C for 2 h for HMDA.[6]

Cure Kinetics of Resin

Stoichiometric ratios of reagents were accurately weighed in a Teflon beaker, mixed well, and isothermally cured at various temperatures. Samples of ∼ 2 g resin were removed at intervals and analyzed for epoxide content[3,4] and their glass transition temperatures (T_g) were measured by DSC.

TABLE II
Properties of Fully Cured Resin (Shell 828)

Resin no.	Curing agent[a]	DSC cure temp			Conditions	Fully cured resin					Elemental cald		Analysis found	
		Onset (°C)	Peak (°C)	Heat of cure (J/g)		T_g^b (°C)	M_c^b Theor	M_c^b Exptl	T_d^c (°C)		S (%)	N (%)	S (%)	N (%)
7	DTDA	140.3	170.8	241	100°C, 2 h; 160°C, 2 h	176	336	370	336.5		6.34	2.77	6.34	2.72
8	DTPDH	136.1	147.8	41.9	110°C, 2 h; 130°C, 2 h	117.5	332	390	302.6		6.41	5.6	6.19	5.48
9	MDA	116.4	146.2	410	80°C, 2 h; 150°C, 2 h; 60°C, 2 h	167	319	357	401		—	—	—	—
10	HMDA	62.6	89.4	475	120°C, 2 h	74	292	301	369.4		—	—	—	—

[a] Molar ratio curing agent/diepoxide = 1:2.
[b] DMA.
[c] TGA.

Reduction and Reoxidation of Resins

Reduction reactions were carried out on finely ground (600-μm-sized particles), fully cured resin. In a typical experiment, 0.5 g resin was weighed in a 50 mL round bottomed flask and 15 mL diglyme, 2 drops dilute HCl (from a stock solution of 15 mL H_2O containing 2 drops concd HCl) and 4 mL Bu_3P were added. The mixture was refluxed under nitrogen with constant stirring for the times specified in Table II, and percent sol and gel were calculated by quantifying the amounts of soluble and insoluble material.

For the reoxidation, 0.5 g of the reduced, soluble polymer was dissolved in 10 mL diglyme and a 10% iodine solution in diglyme was added dropwise with constant stirring. Once a precipitate started to form, the solution was warmed to 60°C and more iodine solution was added until the iodine color persisted. The solution was stirred at 60°C for 15 min, cooled, and the precipitate was filtered, washed with diglyme and methanol, and dried in a vacuum oven.

RESULTS AND DISCUSSION

Reaction temperatures of the dihydrazides and diamines with PGE were determined by DSC in a $1:4$ molar ratio of curing agent to PGE (Table I). DTDA has a higher reaction temperature (onset, 161°C) than MDA (onset, 100°C). Reaction of PGE with the aliphatic dithiodihydrazide DTPDH (onset, 129°C) occurs at a lower temperature so that reaction with ADH (a dihydrazide without the disulfide linkage but with the same number of carbon atoms) (onset, 159°C), but at a higher temperature than either the aromatic dithiodihydrazide DTBDH (onset, 91°C) or the aliphatic diamine HMDA (onset, 71°C). Reaction times of 2 h ensured complete reaction of starting materials as monitored by TLC analysis and by FT-IR (disappearance of the epoxy functionality at 915 cm^{-1}). Figure 3 shows the reaction scheme for the synthesis and reduction reactions of the model compounds.

Reduction of the DTDA/PGE adduct (1) proceeded very smoothly. Reduction times were decreased by half using a reflux temperature instead of 60°C.[7] TLC analysis of the reduced product showed complete disappearance of starting materials and its FT-IR spectrum exhibited thiol absorbance at 2550 cm^{-1}. Thiol content (Table I) was very close to the theoretical value of 1.0 eq/mol. The reduction of the DTPDH/PGE adduct (2) with tributyl phosphine was carried out at neutral pH in refluxing aqueous methanol.[1] Reduction was complete in 7 h. Difference FT-IR spectra of reduced product and starting material showed a strong thiol absorption band at 2555 cm^{-1}. Similar results were obtained when Bu_3P was used at acidic pH in refluxing dioxane and, under these conditions, the reaction time was 2 h. Reduction of (1) was also feasible with triphenyl phosphine, but this reagent gave unwanted side reactions in the reduction of (2). Overman[7,8] described the reaction of various aromatic disulfides with triphenyl phosphine. The efficiency of the reaction was dependent upon both the substituents on the aromatic rings as well as the substitution pattern of the disulfides. Electron withdrawing groups enhanced the reactions rates and para-substituted disulfides were much more reactive than their ortho-substituted counterparts. Dimethyl-2,2'-dithiobenzoate—the prescursor in the synthesis of DTBDH—was reduced at 40°C in 1 h with triphenyl phosphine. Reduction of the DTBDH/PGE adduct (3) was, how-
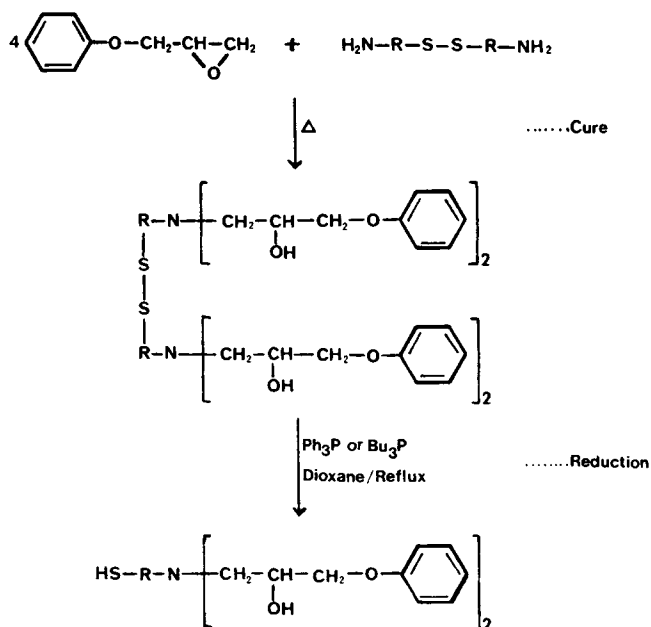
Fig. 3.   Schematic reactions of model compounds.

ever, unsuccessful (Table I). Reaction at 60°C for 12 h and at reflux for 24 h with Ph$_3$P or Bu$_3$P in dioxane, produced no change in the TLC of the starting materials. Thiol content was negligible and the FT-IR spectrum matched that of the starting material.[3] Detailed reoxidation reactions of the model compounds were not investigated. However, a preliminary solution reoxidation of the reduced product of (1) with an iodine solution in diglyme gave a product with the same TLC elution profile as (1), whose spectral characteristics (IR and NMR) were practically identical to those of (1). The main thrust of the model compound studies was, however, to identify appropriate reducing agents and reduction conditions for subsequent reactions on the fully cured epoxy resin.

Based on the results of the reduction experiments on the model compounds, DTDA and DTPDH were chosen as the preferred curing agents for the study of the reduction of disulfide linkages in a prototype fully cured epoxy resin. Two reference compounds, namely, methylene dianiline (MDA) and hexamethyle diamine (HMDA), were used for comparison with the experimental curing agents DTDA and DTPDH, respectively. Epon 828 (epoxide equivalent weight = 190) was the epoxy resin used in this first phase of the investigation.

DSC scans of DTDA and MDA with Epon 828 in stoichiometric ratios (i.e., 1 : 2 molar ratio diamine/diepoxide) are shown in Figure 4 and Table II. The lower reactivity of DTDA, as compared to MDA (onset, 116°C) is reflected in the higher onset of cure (140°C). Due to this lower reactivity, the two-stage cure profile established for MDA/Epon 828 (80°C, 2 h; 150°C) was not deemed appropriate for DTDA. Epoxide conversion with time was analyzed at various isothermal cure temperatures[3] for both DTDA/Epon 828 (7) and MDA/Epon 828 (9) in order to establish an appropriate temperature for the
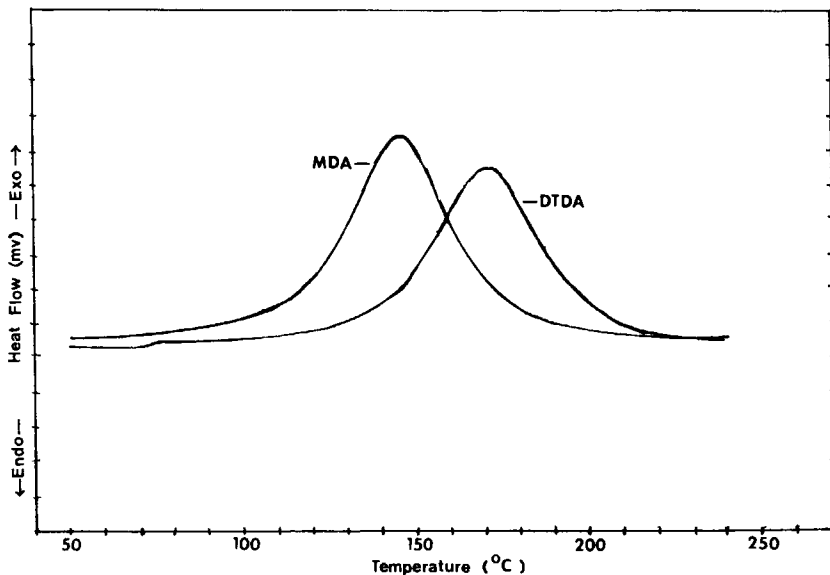
Fig. 4.   DSC cure profiles of (7) and (9).

first stage of the cure profile of (7). Figure 5 shows the percent conversion of epoxy groups for these two systems at 80 and 100°C. At 80°C, 50% epoxide conversion for (9) occurs in 62 min and this value is in excellent agreement with the time of 60 min reported by Bell.[3] In contrast, 50% of the epoxide is consumed for (7) in 200 min at 80°C and in 80 min at 100°C. A cure temperature of 100°C was thus selected as the first stage of the cure profile, followed by 160°C as the second stage for (7). Some properties of the fully cured resins are summarized in Table II.
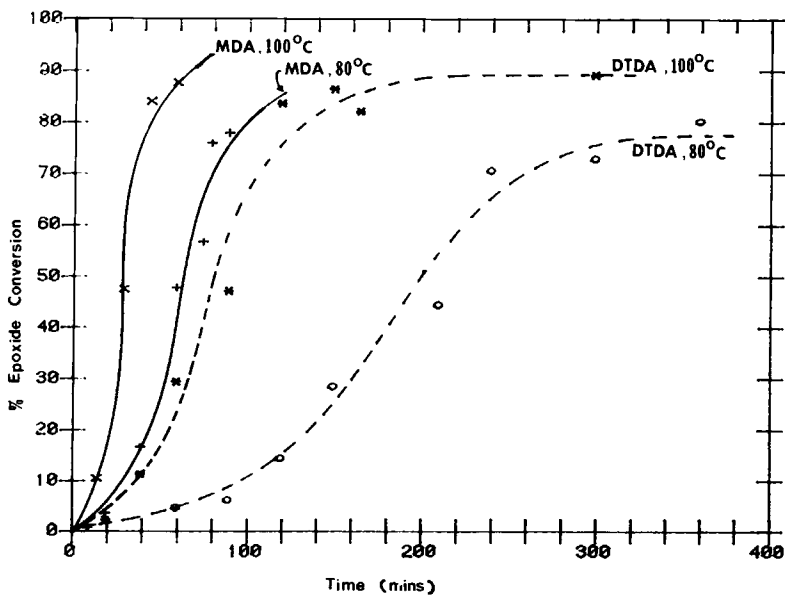

Fig. 5.   Epoxide conversion with time for (7) and (9), at cure temperatures of 80 and 100°C.
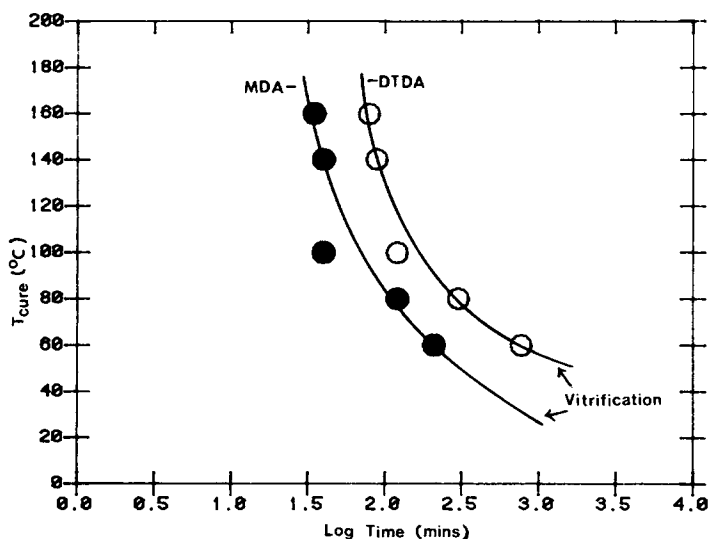
Fig. 6.   TTT isothermal cure diagram for (7) and (9).

Gillham[9,10] has reported a generalized model for the formation and properties of thermosetting systems called a time–temperature–transformation (TTT) isothermal cure diagram. The model can be used to understand and compare the cure and physical properties of thermosetting systems depending upon the specific events measured. In the present study, times to vitrification at different isothermal temperatures of cure were measured. Vitrification occurs when the glass transition temperature of the resin rises to the isothermal temperature of cure. Figure 6 shows the curves for the resins (7) and (9). MDA, the more reactive diamine, vitrifies at shorter times than does DTDA for the same isothermal cure temperature. Figure 7 is a more detailed TTT diagram for the DTDA/Epon 828 system (7), and includes the gelation curve. The gelation curve is obtained by recording the time at which the gel point is reached (measured using diglyme as the solvent) for the respective cure temperatures. T_{g0} is the glass transition temperature of the uncured resin mixture, $T_{g\infty}$ that of the fully cured resin, and $T_{g\,gel}$ is the glass transition of the gel.

The T_g of (7) is somewhat higher than that of (9) (Table II), but the onset of decomposition T_D is 64.5°C lower than that of (9) due to the presence of thermally labile disulfide bond.

Fully cured resins were cooled and cut into samples with dimensions of $3 \times 1 \times 0.1$ cm for DMA. Young's modulus (for M_c) and $\tan^\delta_{max}$ (for T_g) were measured.

The molecular weight between crosslinks (M_c) of the polymer can be calculated by the formula

$$M_c = 3\rho RT/E' \tag{1}$$

where ρ = density of the polymer, R = gas constant, T = absolute temperature at $T_g + 40°C$, and E' = Young's modulus at $T_g + 40°C$. For a 1:2 molar ratio diamine/diepoxide, the M_c can be calculated from eq. 2,[3] assuming
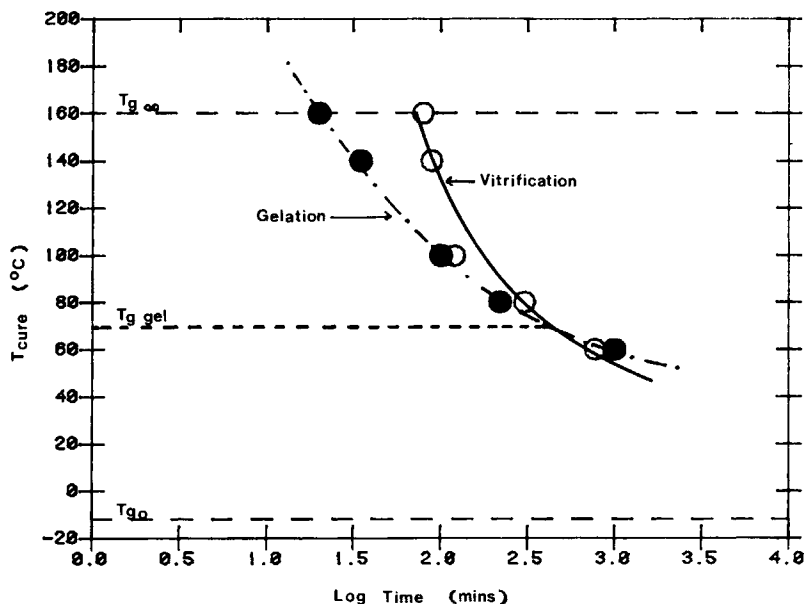
Fig. 7.   Detailed TTT isothermal cure diagram for (7). T_{g0} = glass transition temperature of the uncured resin mixture; $T_{g\infty}$ = glass transition temperature of the fully cured resin; T_g gel = glass transition temperature of the gel.

complete consumption of all reactive groups:

$$M_c = (M_a + 2M_b)/3 \tag{2}$$

where M_a = molecular weight of diamine and M_b = molecular weight of diepoxide.

For resin (9), a value of $M_c = 357$ was obtained by DMA from the Young's modulus (assuming a density of unity for the resin). This is in good agreement with Bell[11] and Manson[12] and with the value calculated ($M_c = 319$) from eq. (2). The glass transition temperature was 167°C (compared to 168.7°C by Bell and Murayama[11] for a 2.4% excess epoxy resin). The T_g of (7) is 176°C and the value of $M_c = 370$ as obtained from the rubbery region compared to the theoretical value of 336 obtained from eq. (2). Results are shown in Table II.

For the reduction of (7), finely ground resin (600-μm-sized particles) was employed in order to provide maximum surface area for the reaction. Nevertheless, reduction to the point of complete dissolution was exceedingly slow under the conditions evaluated (Table III). It was postulated that a resin with a lower crosslink density (higher M_c) would be more susceptible to reduction

TABLE III
Reduction of Resins (7) and (8)

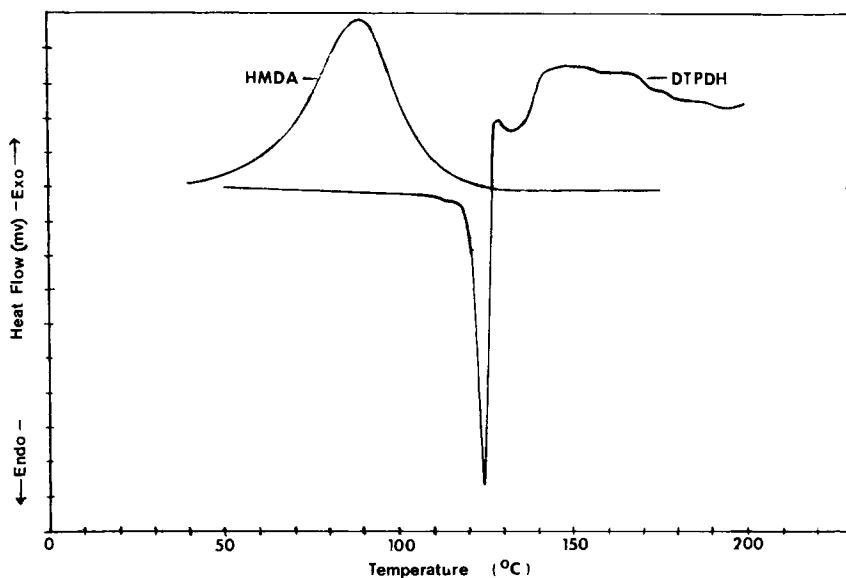| Resin	Conditions	Solubles (%)	— SH content (meq/g)	Molecular weight
7	Bu$_3$P, diglyme, 160°C, 10 days	65	—	—
8	Bu$_3$P, diglyme, 160°C, 6 days	100	1.31	$\overline{M}_n = 1400$, $\overline{M}_w = 1600$

Fig. 8.   DSC cure profiles of (8) and (10).

to a completely soluble material. Details of such a system (for DTDA and Epon 828), and for resins from DTDA and higher molecular weight epoxy resins will be discussed in a subsequent paper.

The fully cured resin from Epon 828 and the aliphatic dithiodihydrazide DTPDH (8) with its long alkyl chain would be expected to be more easily reduced than the aromatic disulfide resin (7) at comparable crosslink densities. DSC scans of the DTPDH/Epon 828 (8) and HMDA/Epon 828 (10) resins are shown in Figure 8 and Table II. DTPDH first melts and is then cured while dissolving into the epoxy resin. The onset of cure is 73°C higher than for HMDA. Cure kinetics (Fig. 9) further shows the significant difference in reactivity between DTPDH and HMDA with Epon 828. The dihydrazide does not cure uniformly, as evidenced by the scatter of experimental points at cure temperatures of 130 and 150°C. The dihydrazide reacts as soon as it melts into the epoxy resin and as a result produces localized areas of unmelted (i.e., unreacted) curing agent and other domains of melted, reacted resin which soon gels. This poses a problem in the preparation of uniformly cured samples. An isothermal cure temperature of 110°C was also examined for epoxide conversion in the case of (8) and the reaction was more uniform, though slower. This temperature was therefore selected as the first stage of the cure profile, and 130°C as the second stage (Table II).

Properties of the fully cured resins are shown in Table II. Resin (8) has a higher T_g (117°C) than (10) ($T_g = 74°C$), but the onset of decomposition temperature (T_D) is 66°C lower for resin (8) than for (10), due to the presence of thermally labile S—S bonds. Molecular weight between crosslinks (M_c) from DMA measurements was in good agreement with theoretically calculated values for both resins.

Preliminary reduction reactions on 600-μm particles of (8) showed that diglyme was preferable to dioxane as a solvent because it was a better swelling agent for the cured resin, making it more accessible to the reducing agent
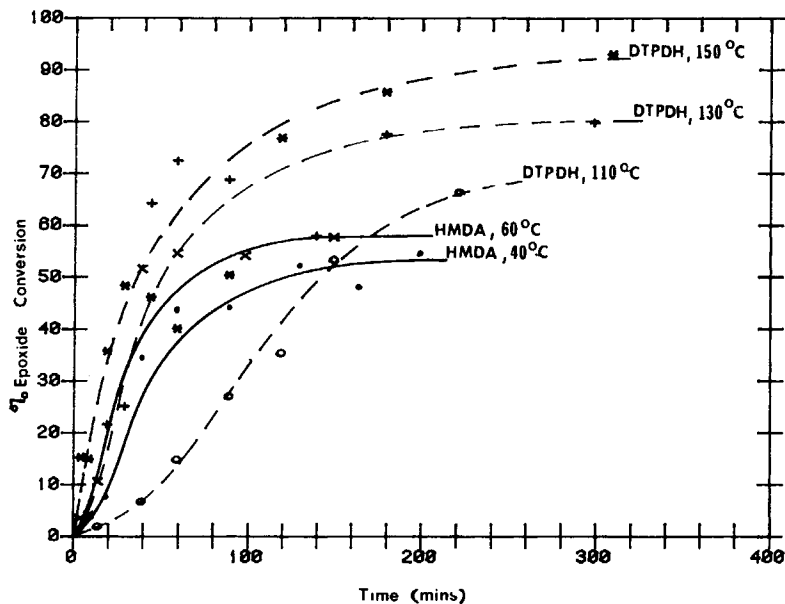
Fig. 9. Epoxide conversion with time for (8) at cure temperatures of 110, 130, and 150°C, and for (10) at cure temperatures of 40 and 60°C.

(Bu $_3$P) and therefore more susceptible to cleavage. In addition, a higher reflux temperature (160°C) could be used with diglyme as compared to dioxane (100°C). Reduction of individual samples was carried out for various times in diglyme and the reaction mixtures were analyzed for soluble and insoluble resin. Percent sol and gel were calculated and plotted versus time (Fig. 10). The resin was reduced to complete dissolution after 6 days. The thiol content and molecular weight of reduced polymer are shown in Table III. In prelimi-
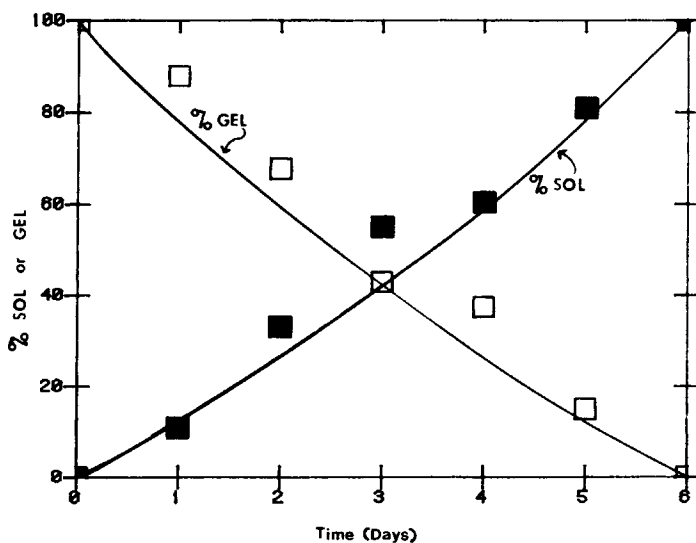

Fig. 10. Percent sol and gel vs. time in the reduction of (8) to the point of complete dissolution.

nary experiments, solution reoxidation of this reduced polymer with iodine produced a material with an onset of decomposition (T_D) of 226°C. The conditions for reoxidation to obtain materials of improved thermal and mechanical properties will be studied further in future work.

SUMMARY AND CONCLUSIONS

The results of a preliminary study of reversible crosslinking in epoxy resins for a prototype epoxy (Shell Epon 828) cured with a disulfide-containing aromatic diamine (DTDA) have shown that cleavage and reformation of crosslinks in epoxy resins cured with disulfide-containing crosslinking agents is feasible.

At stoichiometric ratios (2/1) of epoxy to crosslinking agent, cure kinetics, gelation behavior, crosslink density, and glass transition temperatures of cured resin are essentially comparable for resins cured with DTDA and with MDA. However, under the conditions explored, reduction of disulfide bonds in the DTDA cured resin is difficult because of slow penetration of reducing agent into the tightly crosslinked network. At lower crosslink density (1.75/1 ratio), reduction to soluble polymer and reoxidation (recrosslinking) have been obtained.

At comparable crosslink density, the onset of decomposition temperature (TGA) for resin cured with DTDA is lower than for resin cured with MDA (but higher than observed for resins cured with aliphatic crosslinking agents).

On the basis of results obtained to date, it is postulated that viable products and processes can be developed by this approach. However, further work is required to determine the compositions, reaction conditions and modifications that can provide optimum results and additional studies of recurring reactions are essential.

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