Effect of Stoichiometric Concentration of Hardener and Percentage Styrene Oxide Diluent on the Crosslinking and Mechanical Properties of an Epoxy Resin Cured with DEAPA

D. A. WHITING and D. E. KLINE, *Department of Material Sciences, The Pennsylvania State University, University Park, Pennsylvania 16802*

Synopsis

Epoxy resin was cured with diethylaminopropylamine (DEAPA) in amounts ranging from 10% to 50% of stoichiometric amount. The yield strength of resulting thermosets formed by heat curing at 75°C is found to increase with decreasing amount of hardener. This is attributed to a more densely crosslinked structure resulting from increased tertiary amine-initiated epoxide–epoxide chain reaction and decreased primary and secondary amine–epoxide reaction. Infrared analysis and swelling data are also presented. Styrene oxide diluent is found to have a moderate effect on mechanical properties in the range from 10 to 25 parts per hundred (phr).

INTRODUCTION

Although much use is made of reactive diluents in the epoxy resin industry, little work has been done on relating the chemical structure of these diluted resins to their mechanical properties. In addition, epoxy resins cured with tertiary amines have not been studied in great detail, possibly because of the wide usage of polyamines leading to shorter pot lives.

Anderson[1] studied the effect of varying the per cent stoichiometric amount (%SA) of various amine curing agents on the equilibrium swelling and deformation under load of epoxy resin. Diethylaminopropylamine (DEAPA) was included in this study; however, no samples below 25% SA were tested. It appears that no other work using this curing agent has been reported.

Erich[2] has investigated the effect of crosslinking density on the properties of epoxy resin systems by altering the molecular structure of the starting material. These systems are highly idealized and probably do not represent the actual cured products encountered in everyday usage.

May and Nixon[3] studied the effect of various diluents on the bond strength of cured epoxy resins. Helmreich[4] and Voronstov[5] have also studied the effect of diluents on the mechanical properties of epoxy resins. Lee and Neville[6] have included much of these data in their recent handbook.
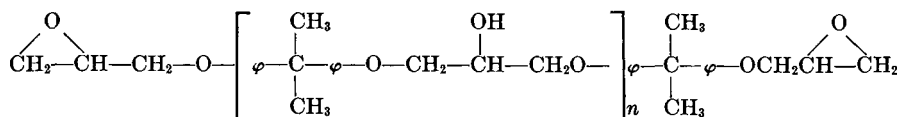
The purpose of the present study is twofold: first, to examine the changes brought about in the structure of the cured resin by varying the %SA of

curing agent added to the mix; second, to determine the effect of styrene oxide diluent on the mechanical properties and crosslinking density of the cured product.

EXPERIMENTAL

Materials

Epon 828 (product of Shell Chemical Co.), a diglycidyl ether of bisphenol A having an average molecular weight of 370–384,[7] was chosen for this study. The molecular structure can be represented as follows (benzene ring indicated by φ):

$$CH_2-CH-CH_2-O-\left[\varphi-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-\varphi-O-CH_2-\overset{\overset{\displaystyle OH}{|}}{CH}-CH_2O-\right]_n \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-\varphi-OCH_2CH-CH_2$$

where $n = 0.2$ for the standard commercial resin.

DEAPA (N,N-diethyl-1,3-propanediamine), termed curing agent A by the manufacturer (Shell Chemical Co.), was chosen as the curing agent. It has a molecular weight of 130, with the following molecular structure:

$$\begin{matrix}(C_2H_5)\\ \qquad\qquad\searrow\\ \qquad\qquad\qquad N-(CH_2)_3-NH_2\\ \qquad\qquad\nearrow\\ (C_2H_5)\end{matrix}$$
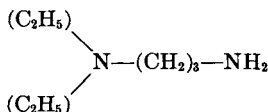
Styrene oxide (1,2-epoxyethylbenzene, Aldrich Chemical Co.), of >97% purity, was chosen as the monofunctional diluent. It has a molecular weight of 120, with the following molecular structure:

$$\varphi-CH-CH_2$$
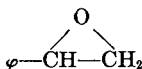
All materials were used as received, with no further purification. Mix proportions were calculated based on equivalent weights of DEAPA, styrene oxide, and Epon 828 (see Appendix).

Infrared Analysis

Samples were prepared for infrared analysis in the following manner. The cured resins were reduced to a powder by mechanical cutting. This powder was further reduced in mortar and pestle, and then passed through a #200 mesh sieve. The fine powder was the intimately mixed with KBr (Harshaw Chemical Co. I.R. grade) in a 1:20 ratio. Standard-size discs were prepared in a pellet press.

The absorbances of the phenyl ring at 1610 cm^{-1} and of the epoxide ring at 910 cm^{-1} were measured for both cured resin and initial liquid Epon 828. The absorbance of the phenyl ring served as an internal standard, since this group does not participate in any of the chemical reactions. In this manner,

the effects of varying film thickness and resin concentration are eliminated. The per cent epoxide converted is then expressed as follows:

$$\% \text{ converted } = A_{rel} \text{ (initial) } - A_{rel} \text{ (final)}/A_{rel} \text{ (initial) } \times 100$$

where A_{rel} = absorbance at 910 cm^{-1}/absorbance at 1610 cm^{-1}. The relative absorbances of —OH in the region 3600 cm^{-1} — 3100 cm^{-1} and —H$_2$C—O—CH$_2$— in the region of 1170 cm^{-1}–1100 cm^{-1} were also measured. All absorbances were measured by planimetry using baseline techniques, except for those residual epoxide peaks which were too small to be read by planimeter. These were measured by counting squares which had previously been calibrated. Precision of the method is estimated to be within ±3%.

Swelling

The equilibrium swelling of a cured epoxy resin can be used as an indication of the relative density of crosslinking between two similar resins. Experiments were conducted after the method of Dannenberg.[8] Cured resins were finely powdered, placed in small glass vials, and weighed. The vials were then transferred to a desiccator containing approximately 100 ml of chloroform. The desiccator was then evacuated and the samples allowed to come to equilibrium with the chloroform vapor. Samples were removed after 24 hr and reweighed. The swelling valve (%) is expressed as wt CHCl$_3$ imbibed/original wt sample × 100.

Mechanical Testing

Samples were prepared for compression testing by casting liquid resin into $1/_2$ in. in diameter by 1.0 in.-long brass molds coated with a wax–oil mixture. The resin mix was heated prior to casting to 75°C in order to remove entrapped air bubbles and then was cooled to room temperature in an ice bath prior to pouring into the mold. The castings were then allowed to harden at room temperature and then placed in an oven at 75° ± 3°C for 24 hr to complete the cure. The castings were subsequently removed from the molds, and the ends were machined plane to within 0.003 in. in length.

All tests were conducted on a Tinius Olsen Universal Testing Machine with a capacity of 120,000 lb. Tests were run in uniaxial compression, the upper cross head moving at a fixed rate of 0.05 in./min while the bottom platen remained fixed. Load was recorded versus a time base on a Bristol recorder. All samples were run in triplicate. For a given series, yield strength values were within a few per cent, and the mean value was reported.

RESULTS

Infrared analysis indicated that the reaction is essentially completed (>92%) at 75°C when 25–50%SA of DEAPA is used (Table I). In addition, the presence of styrene oxide leads to increased conversion at an equiv-

TABLE I
Degree of Conversion of Epoxy Molecules as a Function of
Stoichiometric Concentration and Percentage Diluent

DEAPA, %SA[a]	Styrene oxide, phr	% Epoxide Converted
10	—	76
25	—	92
50	—	100
10	10	87
25	10	98
50	10	97
10	15	87
25	15	95
50	15	97
10	25	93
25	25	94
50	25	95

[a] Stoichiometric amount (SA) is 34.9 g per 100 g epoxy resin (Epon 828).
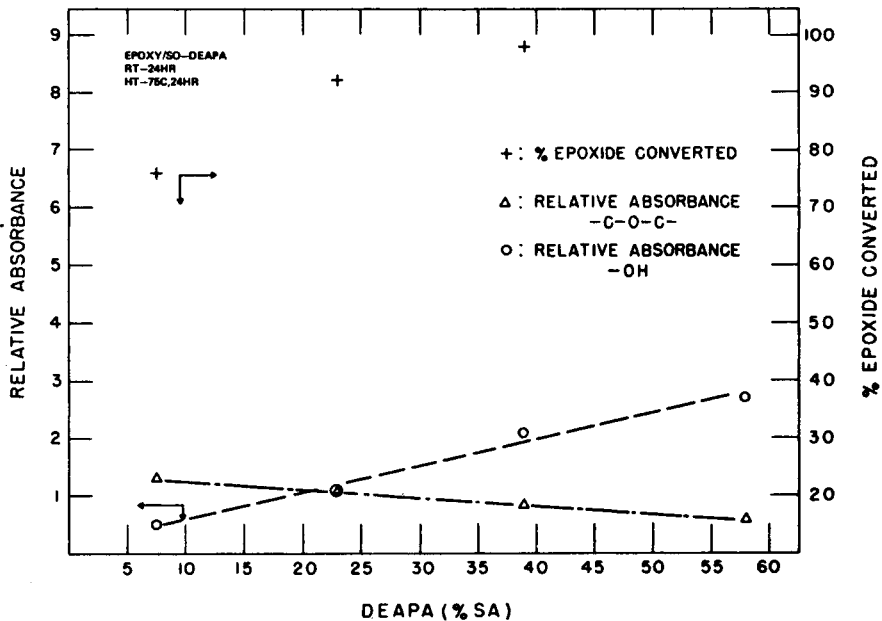
Fig. 1. Infrared relative absorbance and epoxide converted as a function of the percentage stoichiometric concentration of curing agent (DEAPA).

alent amount of curing agent. Analysis of chemical groups indicated that the nature of the reaction changes as the %SA is increased. Below 20%SA, the concentration of alkyl ether groups is somewhat greater than that of hydroxyl groups; but above this value the hydroxyl concentration predominates (Fig. 1).

Swelling versus %SA is presented in Figure 2. One can see that a definite minimum for all curves occurs near 25%SA. This would seem to indicate a

TABLE II
Compressive Yield Strength and Ultimate Strength as a Function
of Stoichiometric Concentration and Percentage Diluent

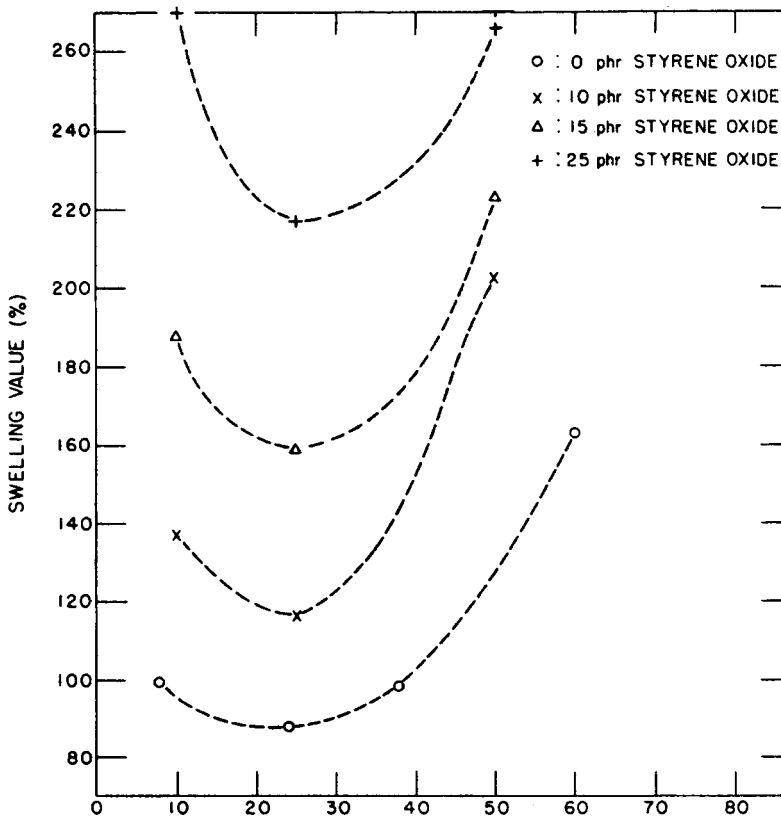| DEAPA %SA	Styrene oxide, phr	Yield strength, psi	Ultimate strength, psi
10	—	15,800	34,200
25	—	13,800	34,800
50	—	11,100	34,800
10	10	14,400	31,800
25	10	13,200	31,300
50	10	12,200	42,900
10	15	12,700	32,700
25	15	12,700	42,100
50	15	11,800	35,600
10	25	9,570	33,500
25	25	12,200	35,100
50	25	11,700	23,900

Fig. 2. Swelling value (%) as a function of the percentage stoichiometric concentration of curing agent (DEAPA) for different diluent levels (styrene oxide).

Fig. 3. Swelling value (%) as a function of diluent concentration (styrene oxide) for different percentage stoichiometric amounts of curing agent.
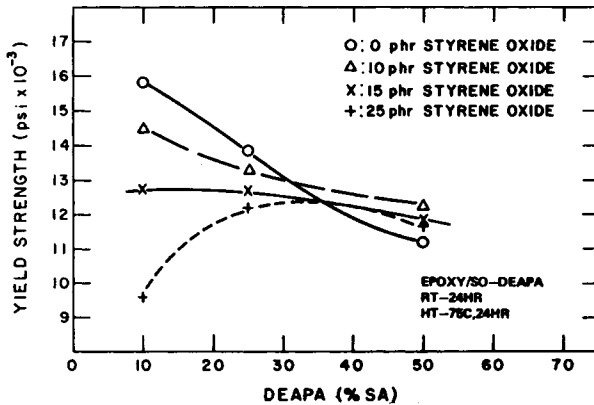
Fig. 4. Yield strength as a function of the percentage stoichiometric concentration of curing agent (DEAPA) for different diluent levels (styrene oxide).

higher degree of crosslinking at this %SA. Figure 3 shows the effect of an increasing amount of styrene oxide on the swelling for resins cured with fixed %SA of DEAPA. As the concentration of diluent increases, the swelling also increases.

Compressive yield strength and ultimate strength data are presented in Table II. Yield strength versus %SA was plotted in Figure 4. As the
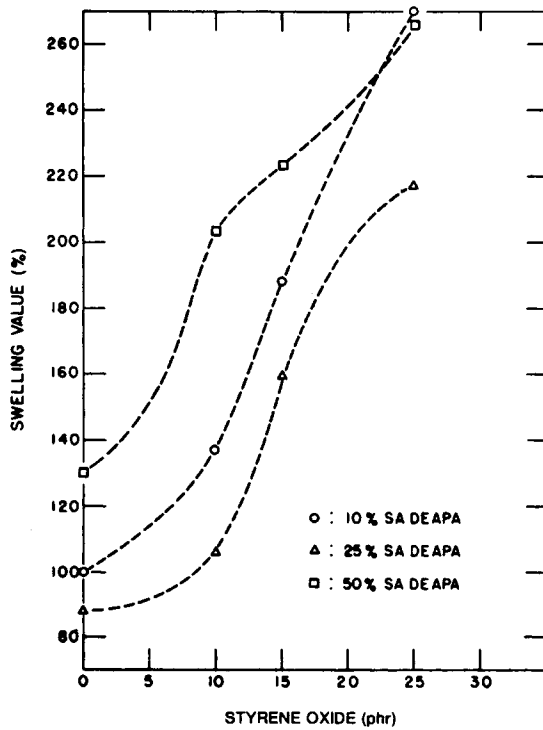
Fig. 5. Yield strength as a function of diluent concentration (styrene oxide) for different percentage stoichiometric amounts of curing agent.
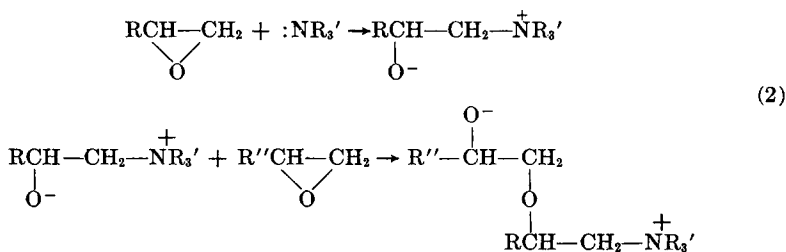
amount of diluent is increased, the shape of the curve changes dramatically for various %SA. Figure 5 shows the same general trend when yield strength is plotted versus phr diluent at fixed %SA. Variations in ultimate strength occur with changes in concentration of curring agent and diluent, as can be observed in Table II.

DISCUSSION

Infrared analysis of the cured resins indicated the coexistence of two separate chemical reactions, one resulting in the formation of hydroxyl groups and the other resulting in the formation of alkyl ether linkages. The first of these, initiated by primary and secondary amines, can be assumed to follow the mechanism first proposed by Schechter et al.[9] and further elucidated by Smith,[10] Horie et al.,[11] and Acitelli et al.[12] A simplified mechanism is outlined in reaction scheme (1):

$$RCH\text{---}CH_2 + HX \rightleftharpoons R\text{---}CH\text{---}CH_2$$

$$\text{(1)}$$

The catalyst HX can be any species capable of donating a hydrogen bond to the epoxide oxygen. Indeed, Gough[13] has found that species capable of hydrogen bond donation can greatly accelerate amine–epoxide reactions. In the present case, the catalytic effect is assumed due to the hydroxyl group present initially on the epoxy molecule, as well as any hydroxyl groups present as impurities in the mix, perhaps due to absorbed water vapor.

The second reaction which could occur in the system under investigation is trans etherification through ring-opening polymerization of epoxide initiated by tertiary amine. Narracott[14] has proposed the following mechanism for this reaction:

$$RCH\!-\!CH_2 + :NR_3' \rightarrow RCH\!-\!CH_2\!-\!\overset{+}{N}R_3'$$
$$\underset{O}{\diagdown\!\diagup} \qquad\qquad \underset{O^-}{|}$$

(2)

$$RCH\!-\!CH_2\!-\!\overset{+}{N}R_3' + R''CH\!-\!CH_2 \rightarrow R''\!-\!\overset{O^-}{\underset{|}{CH}}\!-\!CH_2$$
$$\underset{O^-}{|} \qquad\qquad \underset{O}{\diagdown\!\diagup} \qquad\qquad \underset{O}{|}$$
$$RCH\!-\!CH_2\!-\!\overset{+}{N}R_3'$$

Thus, additional epoxide groups can add on to the end of the growing chain until all epoxide has been consumed. Termination of the growing chain can occur with regeneration of the tertiary amine and formation of unsaturated endgroups.[15]

Since the reactants DGEBA and DEAPA are bifunctional with respect to reaction (1), only linear macromolecules could be formed as a result of this reaction. Thus, as one increases %SA of DEAPA in the resin mix, the product becomes increasingly linear in nature. This is verified by IR analysis (Fig. 1), which shows that the relative concentration of hydroxyl groups increases sixfold as one increases the %SA from 10% to 50%.

In reaction (2), the epoxy molecule is rendered effectively tetrafunctional, since both epoxide groups can participate in acceptance of the alkoxide ion and propagation of the chain through another epoxide ring. Thus, a crosslinked network consisting mainly of ether linkages could be formed. This is verified by IR analysis, which shows a greater relative concentration of ether bonds as the %SA is decreased. At these low amounts of curing agent, there are less active hydrogens to participate in reaction (1), and thus reaction (2) predominates.

Another interesting point brought out in the IR analysis is that for low concentrations of DEAPA, the per cent of epoxide converted tended to increase as the amount of diluent added to the mix was increased. This is apparent in comparing the mix containing 10%SA of DEAPA. This may be associated with the increased mobility imparted to the system, styrene oxide being capable of lowering the viscosity to approximately 300 cps from an initial viscosity of 15,000 cps when 25 phr of diluent is used.[6]

An examination of the yield strength data at 0 phr diluent indicates that as the %SA of DEAPA is increased, the yield strength falls continuously. A linear polymer, where the chains are held together only by secondary forces, would be expected to yield at lower stress levels than a cross linked one, where primary forces contribute to the mechanical stability. Thus, as the %SA of curing agent in the present case is increased, the structure becomes more linear, the density of crosslinking decreases, and the activation energy required for yielding probably decreases.

The effect of styrene oxide on yield stress varies with the %SA of DEAPA added to the mix. For the mixes containing 10%SA, the yield stress falls continuously as the amount of diluent is increased (Fig. 5). This effect becomes less noticeable as the %SA is increased. For the mix containing 50%SA, the yield stress varies only slightly as the amount of diluent is increased. This behavior may be explained in the following manner: At low %SA, the resin is highly crosslinked, since the epoxy molecules have a functionality of 4. Addition of styrene oxide with a functionality of 2 effectively lowers the average functionality of the system and thus lowers the crosslinking density and decreases the stress needed to initiate yielding. At higher %SA, reaction (2) predominates, the average functionality is lower leading to less crosslinking, and the addition of diluent is relatively ineffective.

While yield strength decreases continuously as the %SA of DEAPA is increased, swelling goes through a minimum at approximately 25%SA. A theoretical relationship between swelling of a polymer and the molecular weight between crosslinks (M_c) was first derived by Flory[16] and later modified by Hermans.[17] Other workers[18-20] have applied these equations to cured epoxy systems with limited success. However, if one is not interested in absolute values of M_c but rather in relative degree of crosslinking, then swelling measurements can be an extremely useful tool.

From the data presented in Figure 2 it is evident that the swelling reaches a minimum value at 25%SA of DEAPA, irrespective of the amount of diluent added to the mix. This may be explained as follows: Above 25%SA reaction (1) predominates, and the molecules are more linear and hence swell more in a given solvent. Below 25%SA, the resin is not completely converted, hence the unconverted material likewise leads to increased swelling. In the vicinity of 25%SA, a balance is achieved between per cent conversion and linearity, hence the swelling reaches a minimum value at this point.

CONCLUSIONS

1. The nature of the chemical reaction between Epon 828 and DEAPA changes as the %SA of DEAPA is increased.

2. Increasing the amount of diluent added to the mix increases the conversion of epoxide groups.

3. The mechanical yield strength of the cured resin is a function of both the %SA of curing agent and the amount of diluent added to the mix, the former being the predominant factor.

Appendix

Stoichiometric Calculations

Stoichiometric calculations were based on the reaction of one equivalent weight (GMW/2) of DEAPA with one average equivalent weight (GMW/2) of Epon 828 or one equivalent weight (GMW) of styrene oxide. The average equivalent weight of

TABLE III
Batch Mix Quantities[a] for Varying %SA of DEAPA and phr of Styrene Oxide

Styrene oxide, phr	DEAPA/%SA, g		
	10%SA	25%SA	50%SA
0	3.5	8.7	17.9
10	4.0	10.1	20.1
15	4.3	10.8	21.5
25	4.8	12.1	24.1

[a] 100 g Epon 828 used for all batches.

Epon 828 was taken as 186, the equivalent weight of DEAPA as 65, and the equivalent weight of styrene oxide as 120. Thus, to calculate the amount of DEAPA necessary, one can set up the following relationships:

$$(65/186) = (x_1/100); \quad (65/120) = (x_2/100)$$

where x_1 is the 100% stoichiometric amount (SA) of DEAPA needed to react with 100 g Epon 828, and x_2 is the 100%SA of DEAPA needed to react with 100 g styrene oxide. Since lower %SA were used in this study, the amounts were reduced proportionally (see Table III).

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