

# The Effects of Skydrol (a Hydraulic Fluid) on the Curing of Tetraglycidyl 4,4'-Diaminodiphenyl Methane/Diaminodiphenyl Sulfone-Based Resins

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## SYNOPSIS

The effects of Skydrol 500B-4 on the cure characteristics of a diaminodiphenyl sulfone-crosslinked tetraglycidyl 4,4'-diaminodiphenyl methane resin were investigated by the use of calorimetric, rheological, and gravimetric analyses. The chemical system studied was I.C.I.'s Fiberite 934 epoxy resin. The kinetics of cure were determined by the use of differential scanning calorimetry. The results indicated that the hydraulic fluid did not alter the kinetic parameters ( $E_a$ ,  $A$ ,  $k$ ,  $t_{1/2}$ ) of the crosslinking reactions but diminished the overall heat of the reaction. Gelation and vitrification of the growing networks were observed by the use of dynamic mechanical thermal analysis. The results showed that Skydrol had a marked effect on reactions transpiring within the gel. Thermogravimetric analysis (TGA) was used to estimate the extent of Skydrol elimination during cure. TGA curves indicated that a significant degree of interaction occurred between the hydraulic fluid and the component(s) of the resin. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Diaminodiphenyl sulfone (DDS)-cured tetraglycidyl 4,4'-diaminodiphenyl methane (TGDDM) epoxies are presently the most common matrices utilized in high-performance fiber-reinforced composites. Within the aircraft industry, they also find application as adhesives for assembling and repairing these composite structures.

The maintenance environments to which epoxy resins may be subjected is far from ideal. Surface contaminants including hydraulic fluids, degreasing agents, and cured grit resulting from the abrasion of the damaged surface may be present at the adhesive/adherent interface during the repair-bonding process. Hence, possible incorporation of the contaminants within the epoxy adhesive, following absorption during cure, may alter the expected cure characteristics and subsequently the physical and mechanical properties of the final network structure.

The effects of the Ardrox, a degreasing agent, and cured grit have been previously reported.<sup>1</sup>

The scope of this study was to characterize the effects of Skydrol 500B-4 on the kinetics of cure and the network formation of a commercial TGDDM/DDS-based formulation by the use of conventional thermal analyses techniques. The hydraulic fluids used in commercial aviation are fire resistance-based fluids, composed of phosphate esters. Skydrol 500B-4 is a standard fluid, presently used within the aircraft industry, made of alkyl aryl phosphate esters and additives.

Differential scanning calorimetry (DSC) is a valuable technique for investigating the kinetic parameters of the curing reactions of thermosetting polymers.<sup>2</sup> The means of extracting kinetic information from DSC thermograms generated by industrial epoxy formulations is, however, complicated by the appearance of multiple peak exotherms. Such thermograms are characteristic of complex crosslinking reactions characterized by different kinetic parameters and heats of reaction. Dynamic method *B*, which capitalizes on the variation of peak exotherm temperature ( $T_m$ ) with heating rate ( $\beta$ ), was developed for industrial compositions and is the ba-

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sis of the ASTM method E-698-79.<sup>3</sup> However, to relate determined overall kinetic parameters of cure to an actual reaction mechanism necessitates the isolation of single cure reactions transpiring within the resin formulation. DSC must thus be applied to particular conditions of temperature or composition. Because of its high rate constant, primary amine/epoxy addition (PAE) will principally occur in TGDDM/DDS mixtures containing more than an equimolar content of DDS primary amines.<sup>4</sup>

Gelation, the incipient formation of a three-dimensional network, and vitrification, the transformation from a viscous liquid or elastic gel to a glass, are both characteristic events in the cure of thermosetting resins. Concomitant with these changes in structure are very large changes in the rheological properties of the material. Dynamic mechanical thermal analysis (DMTA) has proved a useful tool for monitoring the viscoelastic properties (modulus and damping) of epoxy systems as a function of time and temperature in the liquid, rubbery, and glassy states.<sup>5</sup> Finally, in order to isolate any process of contaminant elimination taking place during cure, a simple thermogravimetric analysis (TGA) was undertaken.

## EXPERIMENTAL

### Materials

The resin system chosen for this study was I.C.I.'s Fiberite 934 epoxy resin. The chemical constituents of this formulation are 63.2% by weight of TGDDM (tetrafunctional epoxy), 11.2% of diglycidyl orthophthalate (DGOP, difunctional epoxy), 25.3% of the crosslinking agent DDS, and 0.4% of the boron trifluoride/ethylamine catalyst complex. As an extension of the calorimetric study, a model system based on the two principal components of the 934 resin (TGDDM/DDS) was also investigated. The TGDDM monomer (Ciba Geigy, MY 720) was cured with 1.5 times stoichiometric quantities of DDS. All materials were used as supplied without further purification. The resins were stored at approximately  $-18^{\circ}\text{C}$ , and the DDS hardener was stored in a cool, dry environment. The hydraulic fluid Skydrol 500B-4 (Monsanto) was obtained from TEAM Aer Lingus, with whom it has been used as a standard fluid since 1980.

### Sample Preparation

The commercial 934 resin was heated to  $100^{\circ}\text{C}$  for 10 min before the hydraulic fluid was added at 5.0

and 10.0% by weight of formulation. The resulting formulations were mixed thoroughly and subsequently cooled rapidly in order to prevent further unnecessary thermal aging (changes in the overall heat of reaction,  $\Delta H_{\text{rxn(overall)}}$ , were found to be minimal as a result of this primary treatment).

The additional reactive mixture was prepared by separately dissolving the reactants in a minimum amount of anhydrous acetone, mixing thoroughly, adding the contaminant (percent by weight), and evaporating the solvent under vacuum at room temperature. After this, all of the mixtures were stored at approximately  $-18^{\circ}\text{C}$ .

### Methods

DSC was used to determine the crosslinking kinetics of the commercial and model resin systems and to investigate any possible effects the presence of Skydrol may have on these established parameters of cure. The thermal curves were recorded in a TA 912 dual sample calorimeter (DSDSC) fitted with a thermal analyzer, in accordance with ASTM standard E-698-79. Prior to any quantitative measurements being performed, the instrument was calibrated for both temperature and calorimetry by the use of high-purity indium ( $\Delta H_{\text{rxn}} = 28.4 \text{ J/g}$ ; melting point =  $156.6^{\circ}\text{C}$ ). A sample mass of 10–15 mg was weighed in a hermetic aluminium pan, and dynamic DSC analyses were carried out under air at heating rates of 4, 6, 8, and  $10^{\circ}\text{C min}^{-1}$  over the range 25– $300^{\circ}\text{C}$ . Three scans were performed at each scan rate, thus yielding 12 runs for each formulation.

DMTA was used to monitor the cure reactions and isolate any changes in characteristic events, such as gelation and vitrification, arising from the incorporation of the hydraulic fluid. Dynamic storage moduli ( $E'$ ) and dynamic loss moduli ( $E''$ ) were measured in a Polymer Laboratories Mark II dynamic mechanical thermal analyzer fitted with a torsion head. Scans were performed with a cup and cone assembly on samples held isothermally at  $150^{\circ}\text{C}$  for 120 min. This  $T_{\text{cure}}$  is below the recommended temperature of  $177^{\circ}\text{C}$ . It was used, however, in order to allow observation of the onset of gelation since sufficient time elapsed during the initial thermal ramp up to  $177^{\circ}\text{C}$  to cause the 934 system to gel prior to the commencement of data acquisition. Dynamic scans were run at  $2^{\circ}\text{C min}^{-1}$  from 50 to  $275^{\circ}\text{C}$ , with the same assembly, the selected frequency of measurement in both cases being 1 Hz. DMTA was performed on three samples from each formulation, with the most representative thermal curve being plotted.

**Table I Kinetic Parameters of Cure Determined with Kissinger's Relationship**

| System       | $E_a$ (kJ/mol) | $A$ (l/min)                | $\Delta H_{\text{rxn}}$ (J/g) |
|--------------|----------------|----------------------------|-------------------------------|
| Model        | 68.37          | $5.18 \pm 0.06\text{e}+6$  | $440.1 \pm 6.2$               |
| +5% Skydrol  | 71.69          | $1.15 + 0.01\text{e}+7$    | $426.4 \pm 11.4$              |
| +10% Skydrol | 72.94          | $1.58 \pm 0.01\text{e}+7$  | $389.1 \pm 6.5$               |
| Fiberite 934 | 115.48         | $2.99 \pm 0.06\text{e}+12$ | $447.6 \pm 7.1$               |
| +5% Skydrol  | 120.72         | $1.19 \pm 0.03\text{e}+13$ | $404.0 \pm 6.9$               |
| +10% Skydrol | 116.48         | $3.83 \pm 0.07\text{e}+12$ | $377.9 \pm 12.5$              |

Thermogravimetric analysis (TGA) was used to determine the extent of contaminant evaporation taking place during the crosslinking reaction. A TA 951 thermogravimetric analyzer was used to obtain the TGA curves. Standard hermetic aluminium pans without lids were used as sample holders. Samples were held isothermally at 121°C for 2 h, ramped at 5°C/min to 177°C, and held at 177°C for a further 2 h. A nitrogen flow rate of 50 cm<sup>3</sup>/min was maintained throughout the thermal cycle. Analysis was performed on each of three samples of contaminant, neat 934 epoxy resin, and 934 resin + 10 wt % contaminant, so that for each system three curves, were obtained with the most representative scan being plotted.

## RESULTS AND DISCUSSION

### Kinetic Study

The absolute temperature of the reaction peak maximum ( $T_m$ ,  $K$ ) for each heating rate ( $\beta$ ,  $K/\text{min}$ ) was noted from the characteristic DSC thermograms. The data were fitted to a relationship, based on the work of Kissinger,<sup>6</sup> to obtain the overall activation energy of the crosslinking reaction:

$$E_a = -R \cdot \frac{\Delta \ln(\beta/T_m^2)}{\Delta(1/T_m)} \quad (1)$$

where  $E_a$  = activation energy (J/mol);  $R$  = gas constant, 8.314 J/mol  $K$ ;  $\beta$  = scan rate,  $K/\text{min}$ ; and  $T_m$  = peak exotherm temperature,  $K$ . The preexponential factor ( $A$ ) was subsequently determined by:

$$A = \frac{\beta E_a \exp[E_a/RT_m]}{RT_m^2 [n(1 - \alpha_m)^{n-1}]} \approx \frac{\beta E_a \exp[E_a/RT_m]}{RT_m^2} \quad (2)$$

The activation energy ( $E_a$ ) was previously determined by the use of eq. (1). Baselines under the exotherms were drawn by joining the regions before the

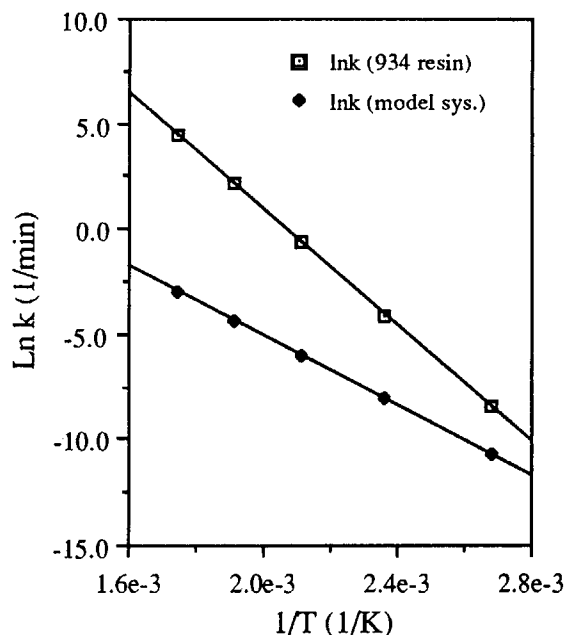
onset and after the completion of the reaction to ascertain the overall heats of reaction ( $\Delta H_{\text{rxn(overall)}}$ ). These values were calculated statistically, thus removing any possible variation in  $\Delta H_{\text{rxn(overall)}}$  arising from changes in scan rate ( $dT/dt$ ). These kinetic parameters are listed in Table I.

The apparent activation energy of the model system is equivalent with previous values determined for the PAE addition reaction.<sup>7,8</sup> The value obtained for the commercial resin is representative of the literature values quoted for DDS-cured TGDDM formulations, although allowance for variations in the exact composition of the system must be allowed.<sup>9,10</sup> The addition of the hydraulic fluid at 5 wt % of formulation had a negligible effect on the values of  $E_a$ . Increasing the level of the addition to 10 wt % similarly produced no pronounced changes, a fact reinforced by the negligible changes in peak exotherm temperatures ( $T_m$ ).

The preexponential factor, the interpretation of which is still in question, was computed for each heating rate, and agreement was within  $\pm 3\%$  of the mean, as suggested by Duswalt.<sup>11</sup> The values did not vary significantly at 5 or 10 wt % addition and were considered unchanged.

The hydraulic fluid had a visible effect on the overall heats of reaction, these values having been corrected for the contaminant content. In both resin systems, the presence of Skydrol reduced the overall heats of reaction relative to the neat systems.

The overall rate constants were determined on the basis of the assumption that the reactions may be described as Arrhenius type temperature dependent. The excellent linearity of the  $\ln k$  versus  $1/T$  plots for the neat resin systems (Fig. 1 – regression analysis = 0.999) confirmed this assumption. Furthermore, thermal aging of the 934 resin at 150°C for 42 min, the apparent half-life of the system determined with the corresponding value of  $k$  at 150°C, reduced the overall heat of reaction by 56%, as predicted. No significant changes in the reaction rate constants or half-life times resulting from the in-



**Figure 1** Arrhenius plots of values determined by the use of Kissinger's method for the neat 934 and model resin systems.

corporation of Skydrol were observed over the temperature range of 100–300°C.

**Rheological Study**

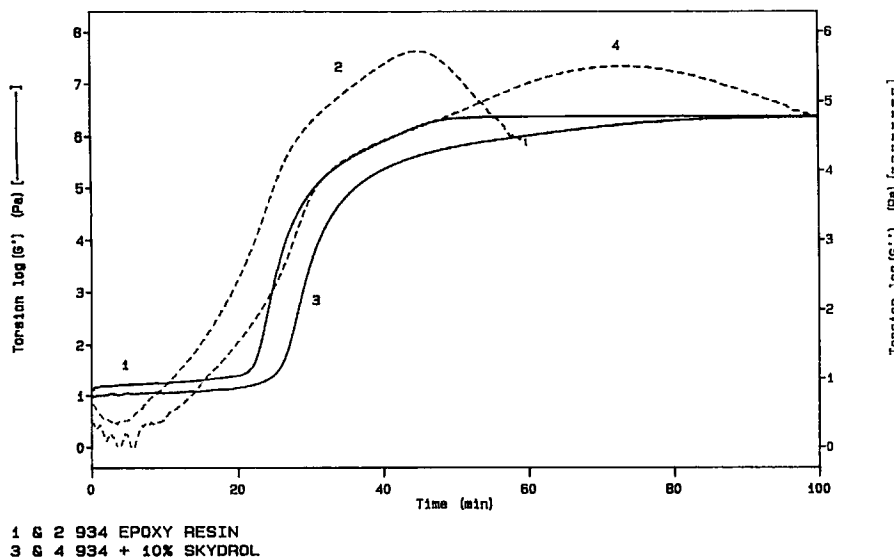
Shown in Figure 2 are isothermal DMTA thermograms of the cure reactions of the neat 934 resin and the same system contaminated with 10 wt %

Skydrol. These traces compare well with those previously obtained for commercial epoxy resins.<sup>12,13</sup> Linear polymerization and branching of the growing chains are observed in both scans as the gentle increase in the storage modulus ( $E'$ ) values occurring during the initial 20 min of the cure cycle. The incipient formation of a three-dimensional network is identified as the sharp change in slope of the same storage modulus curve, which for the neat 934 resin system occurred at 22 min. The significant increase in storage modulus after gelation corresponds to the rapid increase in crosslink density as cure proceeds. The curves indicate that the presence of Skydrol within the curing system did not significantly alter the time required to reach this critical event.

Vitrification occurs when the continuously increasing  $T_g$  of the growing network reaches  $T_{cure}$  or, more precisely, when the elastic gel changes to a glass. By the use of the loss modulus curve ( $E''$ ) to view this event, because loss modulus curves are most sensitive to molecular motions, it is apparent that the presence of Skydrol had a marked effect on this fundamental transition in the cure process. Dynamic DMTA curves were also obtained, and these confirmed, as shown in Figure 3, the notable effect of the hydraulic fluid on vitrification.

**Thermogravimetric Analysis**

Outlined in Table II are the weight losses that occurred during the cure cycle of the neat 934 resin, 934 resin + 10 wt % Skydrol, and the Skydrol alone.



**Figure 2** Changes in the dynamic mechanical properties of I.C.I's 934 resin and the same system contaminated with 10 wt % Skydrol during isothermal cure at 150°C.

It should be noted that these figures refer to the specific geometry of the sample pans used. Any change in volume/surface area could clearly modify the data. The most striking feature of these results is the substantial reduction in Skydrol evaporation after incorporation within the resin.

### Extent of Reactions in the Gelled State

The rheological study indicated that the presence of Skydrol within the gel interfered in some fashion with the cure process, hence delaying the onset of the vitreous state. Monitoring the degree of conversion of chemical reactions occurring after the onset of gelation became, therefore, a necessity and was performed by the use of DSC.

The extent of reaction or fractional conversion,  $\alpha$ , was determined from the following expression:

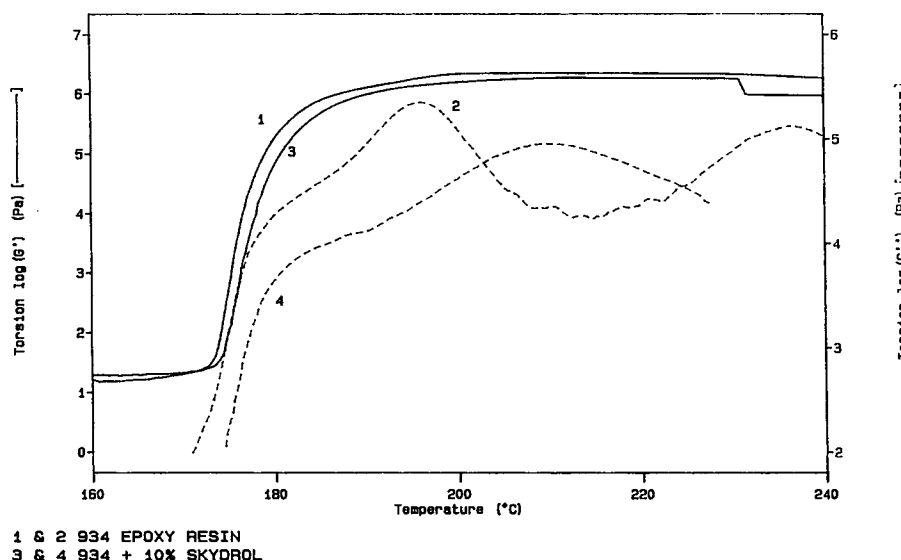
$$\alpha = \frac{\Delta H_{\text{rxn}} - \Delta H_r}{\Delta H_{\text{rxn}}} \quad (3)$$

where  $\Delta H_{\text{rxn}}$  = the overall heat of reaction ( $J/g$  of reaction mixture) and  $\Delta H_r$  = the residual heat of reaction ( $J/g$  of reaction mixture). In this particular instance,  $\Delta H_{\text{rxn}}$  represents the overall heat evolved from the point of gelation to reaction completion. Because the extent of reaction up to gelation is a constant for any particular epoxy resin formulation,<sup>14</sup> and because the neat 934- and Skydrol-con-

**Table II** Percent Weight Loss of Pure Resin, Skydrol, and Skydrol-Contaminated 934 Resin after the Recommended Cure Cycle of the 934 Epoxy Resin

| System                | Weight Loss (%) |
|-----------------------|-----------------|
| 934 neat resin        | 2.0             |
| 934 + 10 wt % Skydrol | 2.5             |
| Skydrol               | 88.0            |

taminated systems gelled after the same time interval after isothermal cure at 150°C, conversion versus time plots from this point onward could be constructed and compared. However, the value of  $\Delta H_{\text{rxn}}$  is specific to each resin formulation because the overall degree of cure varied with the percentage weight Skydrol incorporated within the 934 resin [see reduced  $\Delta H_{\text{rxn(overall)}}$  values for complete reactions in Table I]. For the neat system, this value was determined by curing a sample isothermally for 22 min at 150°C and subsequently performing a dynamic scan from ambient to 300°C at a heating rate of 10 K/min. The area beneath the residual cure exotherm represented  $\Delta H_{\text{rxn}}$ . This procedure allowed the facile determination of the heat of reaction up to gelation,  $\Delta H_{\text{rxn(gel)}}$ . Because the extent of reaction up to this event in the cure cycle is constant,  $\Delta H_{\text{rxn}}$  for the Skydrol-contaminated mixtures was obtained by subtracting  $\Delta H_{\text{rxn(gel)}}$  from  $\Delta H_{\text{rxn(overall)}}$  for that specific mixture.



**Figure 3** Changes in the dynamic mechanical properties of I.C.I.'s 934 resin and the same system contaminated with 10 wt % Skydrol during dynamic cure (portions of dynamic runs from 50 to 250°C at 2°C min<sup>-1</sup>).

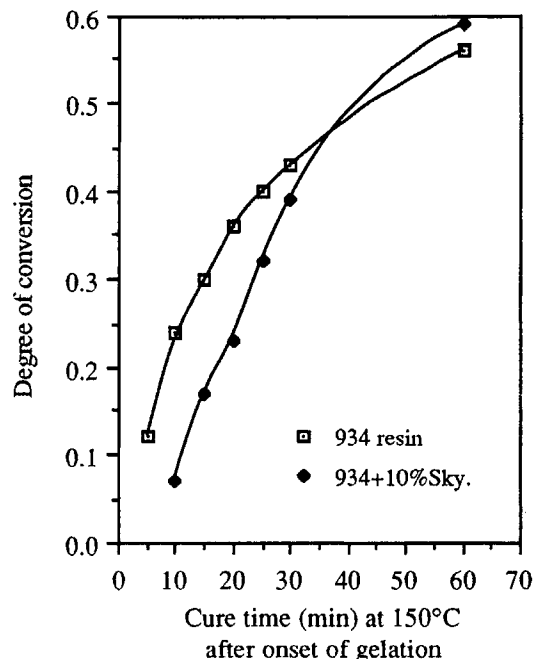
Hence, isothermally curing resin formulations for various time intervals at 150°C after gelation and subsequently determining the residual heat of reaction permitted plots such as those in Figure 4 to be generated by the use of eq. (3). As before, all values were corrected for Skydrol content.

These curves complement the rheological data and confirm that the presence of Skydrol, within the three-dimensional network, had interfered with events occurring during the latter stages of the cure process. The intersection of the curves is a consequence of their relative nature and the selected  $T_{\text{cure}}$ , 22°C below the recommended value.

## DISCUSSION

The rate expressions used in determining the kinetic parameters of cure are derived on the basis of the assumption that the reactions under consideration are kinetically driven and, in the case of single reactions, that they may further be described as Arrhenius type temperature dependent. The overall kinetic parameters of cure determined with Kissinger's relations are derived from two components—the programmed heating rate ( $\beta$ ) and the temperature of the reaction exotherm maximum ( $T_m$ ).<sup>6</sup> The latter represents a peak in the reaction rate, a manifestation of chemical control. Hence, the negligible effect of Skydrol on the kinetic parameters ( $E_a$ ,  $A$ ,  $k$ ,  $t_{1/2}$ ) suggests that it should have no effect on gelation either, because the reactions involved before the formation of a three-dimensional network are kinetically governed.<sup>15</sup> The excellent linearity of the  $\ln k$  versus  $1/T$  plots, shown in Figure I, portray this "kinetically driven" condition.

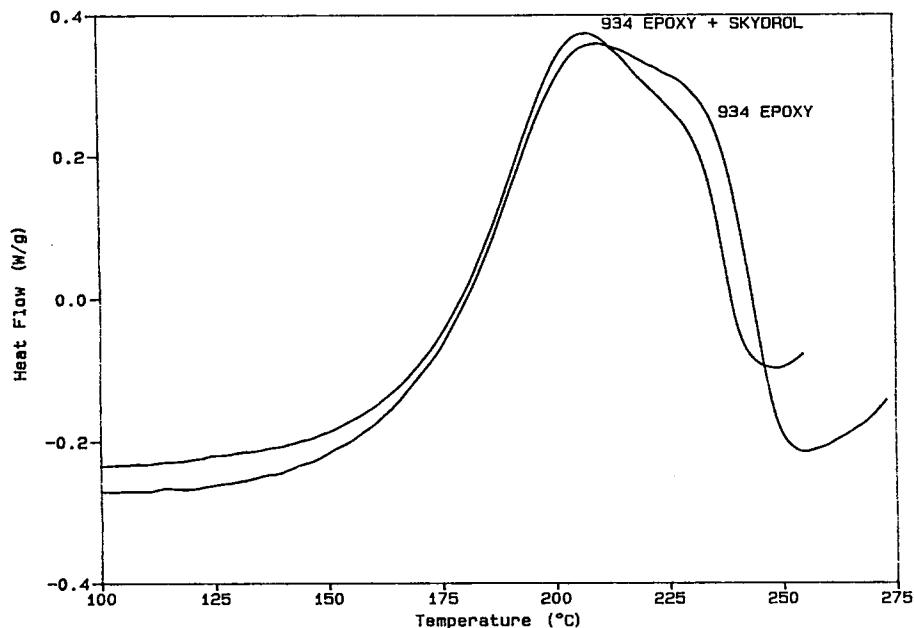
The diminished overall heats of reaction, observed for both resin mixtures after the incorporation of Skydrol, indicate a reduction in the extent of primary chemical reactions occurring within these reactive formulations. Because the extent of reaction up to the point of gelation is constant for any particular resin system, and because this event was essentially unaffected by the presence of the hydraulic fluid, it is the abatement of reactions transpiring within the gel which must give rise to this phenomenon. Thermogravimetric analysis confirmed the presence of Skydrol throughout the entire cure cycle. The retention of the hydraulic fluid within the curing epoxy suggests that chemical bonding must be occurring between the contaminant and component(s) of the 934 system. Any such intermolecular forces of attraction should play a dominant role in the gel



**Figure 4** Fractional conversion as a function of time curves for the 934 and 934 + 10 wt % Skydrol systems as determined from the isothermal and residual heats of reaction.

where diminished molecular motions enhance possible interactions.

In TGDDM/DDS (25 wt % DDS) (0.4 wt %  $\text{BF}_3$  :  $\text{NH}_2\text{C}_2\text{H}_5$ ) mixtures cured at 177°C, previous investigations agreed with the conclusion that three reactions dominate the cure behavior, namely, epoxy-primary amine addition (E-P. A.), epoxy etherification with the hydroxyls (E-OH), and the epoxy-secondary amine addition (E-S. A.).<sup>4,7,16</sup> It was also observed that the E-S. A. addition reactions play a minor role, whereas the kinetically distinct E-P. A. addition and etherification reactions govern the cure, the former dominating the early stages up to the point of gelation and the latter principally occurring once all of the primary amines are exhausted. It would appear, therefore, that the presence of Skydrol has little or no effect on the E-P. A. addition reactions which govern gelation and that it hinders the crosslinking reactions occurring through the E—OH groups subsequent to this event in the cure cycle. Indeed, DSC thermal curves of the residual heats of reaction of the 934 and 934 + 10 wt % Skydrol, shown in Figure 5, indicate a notable narrowing of the trace on the high temperature side of the curve for the contaminated system. This is the temperature region where etherification reactions should be most prominent.



**Figure 5** DSC thermograms of the residual heats of reaction for the 934 and the same system contaminated with 10 wt % Skydrol after isothermal runs at 150°C for 22 min.

At the more advanced stages of cure, intramolecular reactions between epoxy groups and other reactive sites on the same molecule or in neighboring domains become dominant. The rate of segmental reorientation subsequently dominates the cure process.<sup>15</sup> The notable effect of Skydrol on vitrification and fractional conversions within the gel may thus arise from a simple increase in steric restrictions caused by the encapsulation of the contaminant within the growing network. The kinetic parameters of cure of neat TGDDM, which characterizes the etherification reaction, were unaltered by the presence of the hydraulic fluid. It would appear thus that the change in phase is fundamental to Skydrol hindering chemical crosslinking reactions. Hence, diminished molecular mobility arising from the confinement of the contaminant within the expanding network appears the most plausible cause for the noted effects of Skydrol on the cure characteristics investigated.

Changes in the variables contributing to the crosslink density of the network ( $1/M_c$ ) and modification of the constituent components of the resin which promote secondary bonding with the hydraulic fluid should be the fundamental parameters contributing to the extent of the observed effects. Finally, examination of the physical and mechanical properties of the final three-dimensional network,

the focus of part II, should elucidate the nature of the role played by Skydrol in affecting the growing network.

## CONCLUSIONS

The cure characteristics of I.C.I.'s 934 epoxy resin are susceptible to the presence of Skydrol. The incorporation of the hydraulic fluid within the crosslinking resin diminishes the overall heat of reaction and delays the onset of vitrification. Diminished molecular mobility within the gel, caused from the presence of Skydrol, is advanced as a plausible mechanism.

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Received January 5, 1996

Accepted June 30, 1996