

The Influence of Extent of Polymerization on the Thermal Behavior of an Epoxy-Based Polyether Resin

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Synopsis

A number of studies have been reported in the literature on the polymerization and thermal decomposition of epoxide resins. Lee¹ and Anderson² have both studied the thermal decomposition of epoxy resins, and they concluded that the characteristic exothermic peak (which can occur anywhere between 300° and 400°C) is caused at least partially by some reaction of the epoxide group. We have been investigating the thermal decomposition of an aromatic polyether resin which is produced by curing the diglycidyl ether of bisphenol A (Epon 825) with the catalytic agent trimethoxyboroxine (Fig. 1). DTA studies of the polyether in an inert atmosphere of N₂ showed exothermic peaks at approximately 390°, 430°, and 470°C, with the major exotherm being the one at 430°C. Our investigation has shown the important role played by low molecular weight epoxides in these exothermic reactions.

EXPERIMENTAL

Materials

The diglycidyl ether of bisphenol A resin used was Epon Resin 825 manufactured by the Shell Chemical Company. This resin was kept at 50°C before use in order to maintain a low enough viscosity to yield good pourability. IR evidence indicates that hydrolysis of the resin does not occur to an appreciable extent due to this method of storage.

The trimethoxyboroxine (TMB) used in our studies was obtained from the Aldrich Chemical Company, Inc., and it was stored in a closed container (at room temperature) prior to use. Again, IR spectra showed that the TMB was stable for many months.

Instrumentation

The IR spectra were recorded on a Perkin-Elmer Model 521 grating infrared spectrophotometer. The infrared spectra of films were taken from NaCl plates while the spectra of solid materials were obtained by using the KBr pellet technique.

The molecular weight studies were carried out with a Waters Model 200 gel permeation chromatograph using three columns to effect the separation. The columns used were 500 Å, 3×10³ Å, and 5×10⁴ Å highly crosslinked poly-

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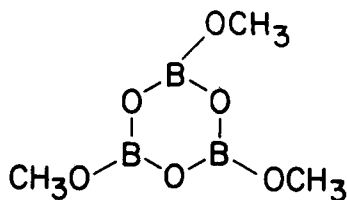


Fig. 1. Trimethoxyboroxine.

styrene gels, and the solvent used was tetrahydrofuran. The tetrahydrofuran (THF) was a Baker Analyzed Reagent. All chromatograms were obtained at room temperature using 1% (approx.) solutions. The flow rate used was 1 cc/min.

The thermal analyses were performed on a du Pont Model 900 thermal analyzer with modular attachments. The differential thermal analysis (DTA) studies were done on a du Pont high-temperature DTA cell (1600°C), and the differential scanning calorimeter (DSC) used was a du Pont DSC cell. The heating rate used throughout our studies was 20°C/min, and all runs were made in ultrapure N₂ gas at a flow rate between 0.1 and 0.2 l./min. This flow rate consistently gave an oxygen concentration of less than 0.5% after 10 min of flow when measured on an oxygen meter.

Formulation and Cure

The aromatic polyether resin which we used in our investigation was prepared by reacting 5 parts of the trimethoxyboroxine catalyst with 100 parts of the Epon 825 resin on a weight basis. This formulation was arrived at in an earlier study where various formulations were tried in order to optimize the mechanical properties of the polyether.³ The above ingredients were mixed thoroughly by hand, and the resin was then degassed at room temperature in a vacuum chamber to about 50 torr until all volatiles had escaped from the viscous solution. The mixture was then poured into a prewarmed metal mold and heated in an oven at 80°C for 3 hr, followed by 3 hr at 135°C, and then 2 1/2 hr at 180°C.

RESULTS AND DISCUSSION

Figure 2 shows the DTA curve of the cured epoxy-based aromatic polyether resin. Based on the results of Lee¹ and Anderson,² it was thought that part of the exotherm observed at about 430°C could be attributed to some reaction(s) of unreacted epoxide rings in the cured resin (the same was thought to be true of the exotherm at about 390°C). In this temperature range, four types of processes

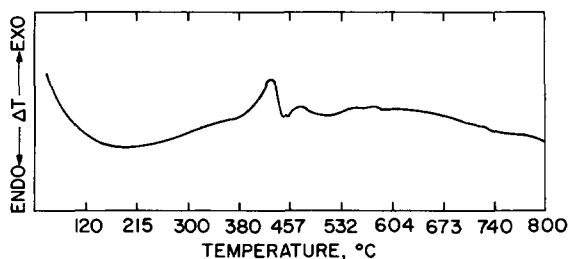


Fig. 2. DTA study of epoxy-based polyether resin.

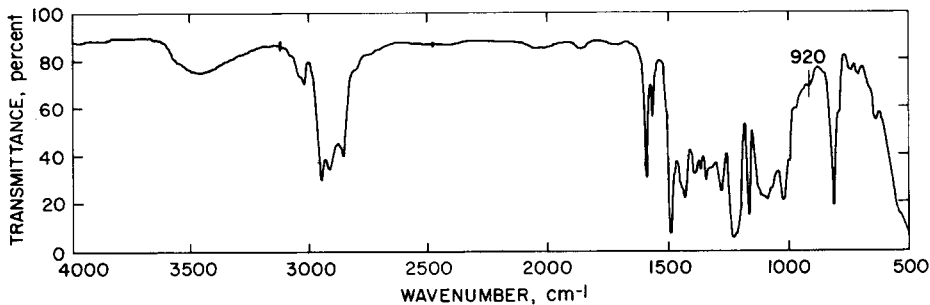


Fig. 3. Infrared absorption spectrum of epoxy-based polyether resin.

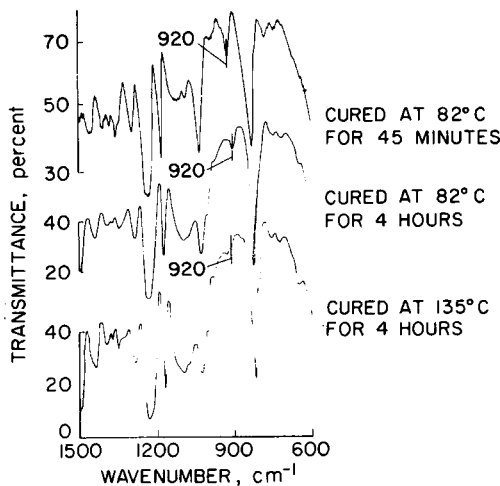


Fig. 4. IR spectrum of polyether as a function of cure.

seem likely for unreacted epoxide groups: (i) isomerization of unreacted epoxide groups to carbonyl groups; (ii) thermal polymerization; (iii) decomposition; and (iv) volatilization. The first two processes are known to be highly exothermic, and thus they could contribute to the observed exothermal behavior.

This hypothesis is supported by the results of infrared studies on the cured resin and by other DTA studies carried out on the diglycidyl ether of bisphenol A. Lee¹ has shown that under an inert atmosphere of N_2 , the diglycidyl ether of bisphenol A displays a small exotherm in the neighborhood of $420^\circ C$. Figure 3 shows the infrared absorption spectrum of the cured resin in the wavelength range of 4000 to 500 cm^{-1} . The epoxide group is known to have a moderately intense absorption band at about 920 cm^{-1} ($10.95\ \mu$) in Epon 825 resin.⁴ Since this resin is the monomer unit for our polyether, we would expect to observe any unreacted epoxy groups at approximately 920 cm^{-1} . As Figure 3 shows, there is still an appreciable epoxide absorption in our cured polyether.

That unreacted epoxide groups contribute to the exotherm at $430^\circ C$ in the cured polyether resin is also borne out by studying the polymerization reaction via infrared spectroscopy and differential thermal analysis. Early in the cure cycle, when a lot of the epoxide rings are unreacted, we observe a strong absorption at 920 cm^{-1} in the IR spectrum and also a large exotherm (at about $430^\circ C$) in the DTA curve. As the cure proceeds, the epoxide ring is opened to give an ether linkage, and the absorption band at 920 cm^{-1} decreases in intensity (Fig. 4).

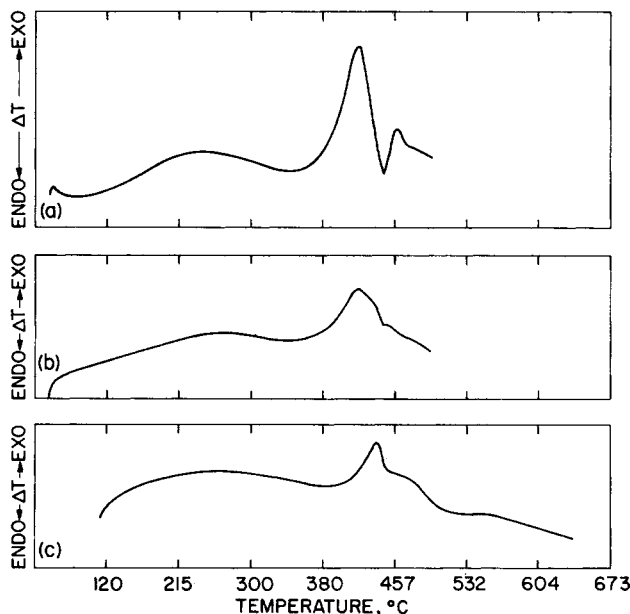


Fig. 5. DTA of polyether as a function of cure.

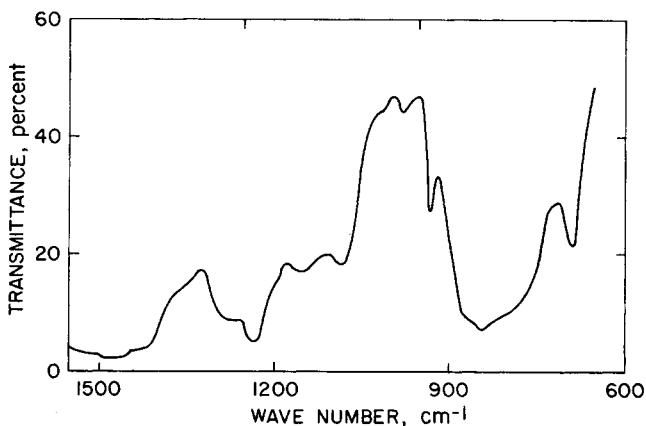


Fig. 6. IR spectrum of sol fraction of polyether.

Simultaneously, we see a diminishing in the size of the exotherm observed at 430°C in the DTA curve (Fig. 5). Both of these findings are consistent with our hypothesis that unreacted epoxide groups do in fact contribute to the exotherm at 430°C in the cured resin.

In an attempt to be somewhat more quantitative in determining how much unreacted epoxy remains in the cured polyether resin, we undertook a sol fraction study. Filings were taken from a bulk sample of the cured resin and refluxed in a Soxhlet apparatus for 24 hr using tetrahydrofuran as solvent. At the end of this extraction procedure, the residue, i.e., the insoluble fraction of the cured resin, was vacuum dried to constant weight at room temperature. The polyether lost 24.8 mg out of a starting weight of 1.0901 g (2.3% weight loss). An IR spectrum of the sol fraction is shown in Figure 6; note the substituted phenyl absorption

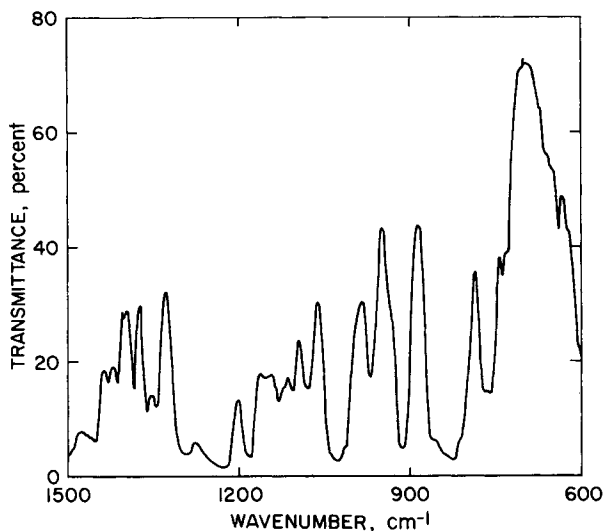


Fig. 7. IR spectrum of Epon 825.

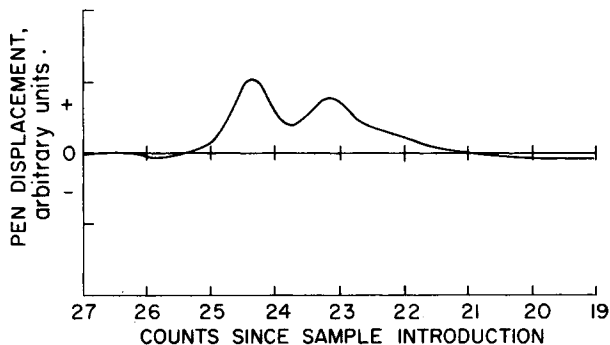


Fig. 8. Gel permeation chromatogram of sol fraction of epoxy-based polyether resin.

centered at 860 cm^{-1} , the epoxide absorption at about 930 cm^{-1} , and the aromatic ether band at approximately 1230 cm^{-1} . While this spectrum is somewhat distorted due to sample preparation, it is still similar to the spectrum of Epon 825 shown in Figure 7. We then did a gel permeation chromatograph of the sol fraction, and the results are displayed in Figure 8. Three positive peaks are observed in the chromatogram: the shoulder at an elution count of 22.29 corresponds to a weight-average molecular weight of 1910 g, the larger peak at a count of 23.13 corresponds to a weight of 1220 g, while the largest peak is of molecular weight 620. Although the lowest molecular weight is approximately twice the value expected for a monomer of Epon 825, this is undoubtedly caused by the different retention times due to the differences in the chemical constitution of the epoxide and the calibration standards (we used polystyrene compounds to calibrate the high molecular weights and polyethylene glycols were used for the low molecular weights). The important point is that these molecular weights are in the ratio 1:1.97:3.08, i.e., monomer:dimer:trimer.

Because a differential thermal analyzer measures temperature differences between sample and reference instead of heat differences, it is relatively difficult

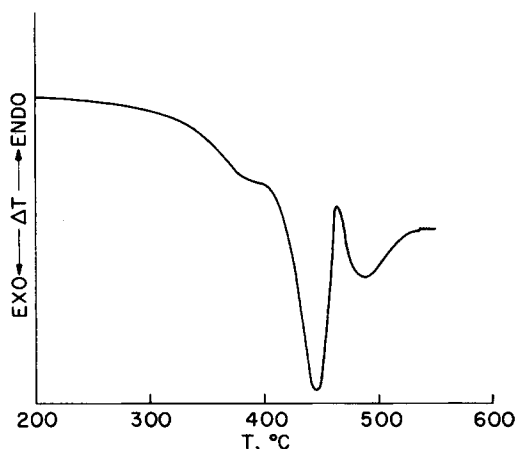


Fig. 9. DSC study of epoxy-based polyether resin.

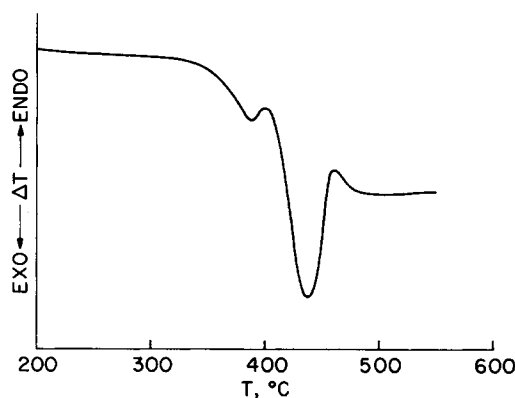


Fig. 10. DSC study of polyether Soxhlet extraction residue.

to obtain quantitative estimates of heats of reaction using DTA. For this reason, we used a differential scanning calorimeter to estimate the difference in heat evolved by the cured polyether resin and by the residue left after Soxhlet extraction of the cured material. Figure 9 shows the DSC curve obtained for the cured polyether, while Figure 10 displays the DSC curve of the Soxhlet extraction residue. (Note that an exothermic reaction corresponds to a negative pen displacement for the DSC cell, whereas a similar reaction gives a positive displacement in the DTA unit.) The definite exotherm observed at 380°C in the DSC curve of the Soxhlet extraction residue does not represent an increase brought about by the extraction procedure—the magnitude of this exotherm varied from sample to sample of the cured materials.

It is possible to estimate the heat evolved in the exothermic reaction observed at 430°C by using eq. (1):

$$\Delta H \text{ (mcal/mg)} = E \frac{A \Delta T_s T_s}{M a} \quad (1)$$

where E = calibration coefficient, mc cal/°C min; A = peak area, in.²; ΔT_s = y-axis sensitivity setting, °C/in.; T_s = x-axis sensitivity setting, °C/in.; M =

sample mass, mg; and α = heating rate, °C/min. The calibration coefficient E in eq. (1) is calculated for the particular instrument used by relating peak areas to known heats of fusion of standards. Using a calibration coefficient of 187 mc cal/°C min for our instrument, we calculate a heat of reaction of 17.36 mc cal/mg for the heat liberated at 430°C by the cured polyether resin and a heat of reaction of 14.36 mc cal/mg for the heat liberated (at the same temperature) by the Soxhlet extraction residue.

The difference in the heat of reaction at 430°C of the cured polyether and of the Soxhlet extraction residue is thus seen to be 3.0 mc cal/mg, with less heat being evolved per gram of extraction residue than is evolved per gram of virgin material. This difference in heat of reaction is due to the sol fraction of the cured resin which is removed by the Soxhlet extraction. The sol accounts for only 2.3% by weight of the virgin polymer, yet its contribution to the heat evolved at 430°C (3.0 mc cal/mg) is 17.3%.

It is possible to estimate the heat expected from polymerization of the unreacted epoxide groups present in the sol fraction. We have observed that 2.3% by weight of the cured resin is low molecular weight sol fraction. Assuming that the entire mass of sol is monomer with a molecular weight of 340 g/mole, there are 0.669×10^{-4} moles of monomer per gram of polymer. Lee and Neville⁵ quote a value of 22 kcal/mole of epoxide as the heat of polymerization of the diglycidyl ether of bisphenol A when catalytically polymerized. Using this value for the heat of polymerization of Epon 825, we calculate a heat of 2.94 calories per gram of cured resin as a result of polymerization. Thus, we obtain good agreement between the heat expected from polymerization of unreacted epoxide groups in the sol fraction of the cured resin (2.94 cal/g) and the actual heat observed experimentally as being due to the sol fraction (3.0 cal/g of cured resin). This result supports our hypothesis that unreacted epoxide groups present in the cured polyether resin play a very important role in determining the thermal properties of the cured resin.

References

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