Effect of Curing Temperature on the Thermal Degradation of an Epoxide Resin

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A number of investigations of the thermal degradation of epoxide resins have been carried out.[1-4] These studies appear to have been generally made on resins cured at fixed temperatures. In the present work, the effect of varying curing temperature on thermal degradation has been investigated.

Five samples of DER 332 epoxide (diglycidyl ether of bisphenol A), as received from Dow Chemical Co., were cured with m-phenylenediamine stoichiometrically at 75°C for 24 hr. One of the samples was then cured in air at each of the following temperatures for an additional 24 hr: 100°C, 125°C, 150°C, 175°C, 200°C.

A Du Pont 950 Thermogravimetric Analyzer in connection with the 900 Differential Thermal Analyzer recorder was used for both isothermal and dynamic thermogravimetric analysis (TGA). Measurements were made under nitrogen. Powder samples between 400 and 200 mesh were used. The temperature for isothermal degradation measurements was held within ●1°C of the reported constant temperature. The constant heating rates for the dynamic TGA were within ±1% over the range ±150°C from the inflection points on the thermograms.

Primary thermograms of dynamic TGA at several constant heating rates for the five samples cured at different temperatures as well as for uncured DER 332 were normalized, based on the total weight loss as 100%, and corrected for the nonlinearity of the temperature scale. Figure 1 shows

TABLE I
Overall Activation Energy for Thermal Degradation of Cured and Uncured DER 332

Curing temperature, °C	Activation energy (kcal/mole)	
	Isothermal	Dynamic
200	32	32
175	28	30
150	25	26
125	25	26
100	22	20
Uncured	13	14

an example of the thermograms obtained for one curing schedule. Primary thermograms of isothermal degradation were obtained at four constant temperatures between 200° and 350°C for each of the six samples.

The overall energies of activation from both dynamic and isothermal data were determined by the method of Flynn and Wall.[5,6] The results are
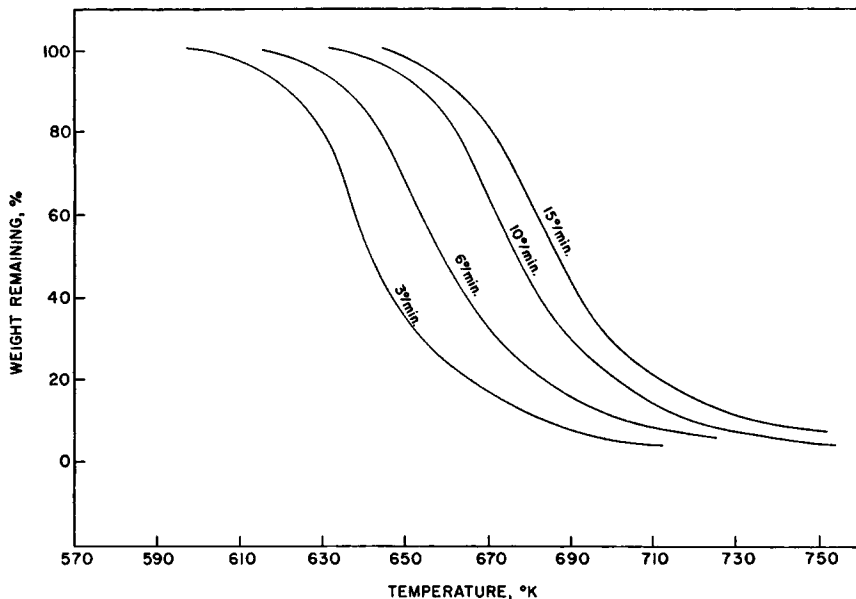
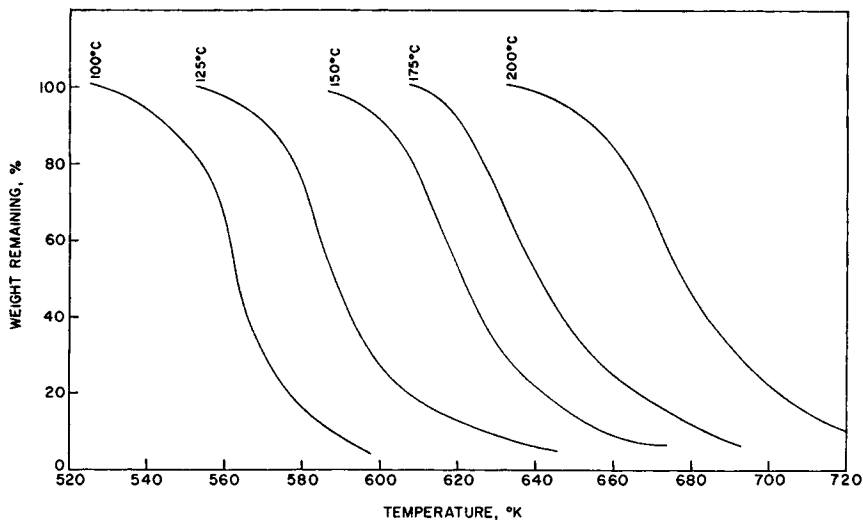

Fig. 1. TGA thermograms of DER 331 cured at 200°C.

Fig. 2. Thermograms at a rate of heating 10°C/min for epoxides cured at the indicated temperature.

shown in Table I. It is noteworthy that higher curing temperatures appear to lead to higher activation energies for degradation. The increased stability for polymers cured at higher temperatures is further illustrated in Figure 2. From this figure it is observed that, at a constant rate of heating, the samples cured at higher temperatures are noticeably more thermally stable. This behavior is consistent with the view that the higher curing temperatures result in a higher degree of crosslinking. More bonds in the chains would have to be broken for release of volatiles in this case.

References

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