

Investigations of Water and High Energy Radiation Interactions in an Epoxy

A. N. NETRAVALI, R. E. FORNES, R. D. GILBERT, and J. D. MEMORY,
*Fiber and Polymer Science Program, North Carolina State University,
Raleigh, North Carolina 27650*

Synopsis

Differential scanning calorimetry (DSC) and infrared spectroscopy (IR) have been used to study the crosslinked epoxy system tetraglycidyl-4,4'-diaminodiphenyl methane cured with diaminodiphenyl sulfone. Samples cured at various temperatures were soaked in distilled water for extended periods or irradiated with 0.5 MeV electrons and ^{60}Co gamma. DSC results show that the standard-cured (137°C for 2 h and 160°C for 5 h) dry samples have a T_g around 190°C and a large exothermic reaction at about 260°C. The latter is attributed to further reaction of curing agent with the epoxide rings. The exothermic energy is about 124 cal/g for an uncured specimen, 42 cal/g for standard cured specimen, and 20 cal/g for soaked samples containing 4% H_2O . The exothermic energy is shown to decrease monotonically with the ionizing radiation dosage. IR results show a reduction in the intensity of the epoxide band as the exothermic energy is decreased.

INTRODUCTION

Epoxy matrices have been used extensively in composite materials. Graphite-fiber-reinforced epoxy composites are highly promising for space-structural applications such as solar panel supports, solid fuel rocket motors, etc.^{1,2} Previous studies have suggested that high energy radiation improves some mechanical properties.³ A number of studies have indicated that sorbed moisture and elevated temperature either alone or in combination degrade the mechanical properties of composites.⁴⁻⁶ The degradation of properties with moisture absorption is presumably due largely to matrix plasticization and lowering of the glass transition temperature. The results of a study of the interactions of water and higher energy radiation in an epoxy are reported here.

EXPERIMENTAL

A crosslinked epoxy resin was formed by the reaction of tetraglycidyl-4,4'-diaminodiphenyl methane (TGDDM) and curing agent diaminodiphenyl sulfone (DDS). TGDDM (MY720) and DDS were obtained from Ciba Geigy and used without further purification.

DDS (27 wt %) was dissolved slowly in TGDDM (73 wt %) at 110°C with constant stirring. The mixture (prepolymer mix) was then cooled and solidified, crushed into small pieces, placed in a Ziploc plastic bag, and stored at 5°C until cured. Disc shaped samples were prepared for differential scanning calorimetry (DSC) measurements using silicone rubber molds. The silicone rubber molds containing the prepolymer mix (20–30 mg) were placed in a vacuum desiccator that was heated under partial vacuum in a nitrogen atmosphere at 137°C for 2

h. The temperature was then raised to 160°C and held for 5 h. The desiccator was then allowed to cool to room temperature. The samples were disc-shaped with flat bottoms that fit snugly in DSC-2 sample pans. These samples are termed "standard-cured" samples.

Uncured epoxy samples were prepared also in the same silicone rubber molds to produce disc shaped samples. The prepolymer mix (20–30 mg) was placed in the cavity of the mold and the assembly placed in the vacuum desiccator which was preheated to 137°C. The desiccator was kept under partial vacuum and nitrogen atmosphere at 137°C for 15 min and then allowed to cool. These samples are termed "prepolymer mix" samples.

Dry, standard-cured samples were irradiated with 0.5-MeV electrons or ^{60}Co gamma. The samples for electron irradiation were wrapped in a single Reynolds heavy duty aluminum foil and placed in Ziploc plastic bags. The bags were flattened to squeeze the air out and hung on the electron accelerator (High Voltage Engineering Corp.) conveyor. The samples received 5-Mrad dosages alternately on each side. The total dosage of ≤ 400 Mrads was applied. The samples were scanned on the DSC immediately after irradiation.

The gamma radiation was applied from a Gamma Cell 220 ^{60}Co source with a dose rate of approximately 0.20 Mrad/h. Samples were wrapped in Reynolds heavy duty aluminum foil and mounted on the inside wall of the gamma cell with Scotch tape. To study the effect of radiation at cryogenic temperature, samples wrapped in Reynolds heavy duty aluminum foil were kept in a Dewar filled with liquid nitrogen which was placed in the gamma cell. Samples irradiated both in ambient air and in liquid nitrogen were given a dose of up to 160 Mrads. The samples irradiated at liquid nitrogen temperature were maintained in liquid nitrogen until scanned on the DSC.

The standard-cured samples were soaked in distilled water at 27°C for 14 days. Two standard-cured samples were soaked at 70°C for 22 days to obtain higher moisture pickup. The surface water on soaked samples was removed before scanning on the DSC.

The prepolymer mix samples, standard-cured samples and the soaked samples were scanned in the DSC from -33°C to 327°C at different scanning rates. All other samples were scanned on the DSC from -33°C to 297°C at $20^\circ\text{C}/\text{min}$ scanning rate after equilibrating the samples at -33°C for 15 min. A Perkin-Elmer Model DSC-2C with a data station was used for this study. All measurements were made in a nitrogen atmosphere.

Standard-cured films for IR investigations were formed by pressing a piece of the prepolymer mix between two smooth Teflon surfaces and curing under a nitrogen atmosphere in a vacuum desiccator as described above. Films thus obtained were about 0.012 mm thick and found suitable for transmission IR study. These films were run on a Perkin-Elmer Model 281-B IR Spectrometer equipped with a data station.

RESULTS AND DISCUSSIONS

Figure 1 shows a typical DSC thermogram of a prepolymer mix sample. Data for several different scanning rates are presented in Table I. The DSC thermogram of the prepolymer mix at $20^\circ\text{C}/\text{min}$ scanning rate showed a distinct glass transition temperature at 39°C and a large exothermic peak at 272°C indicating

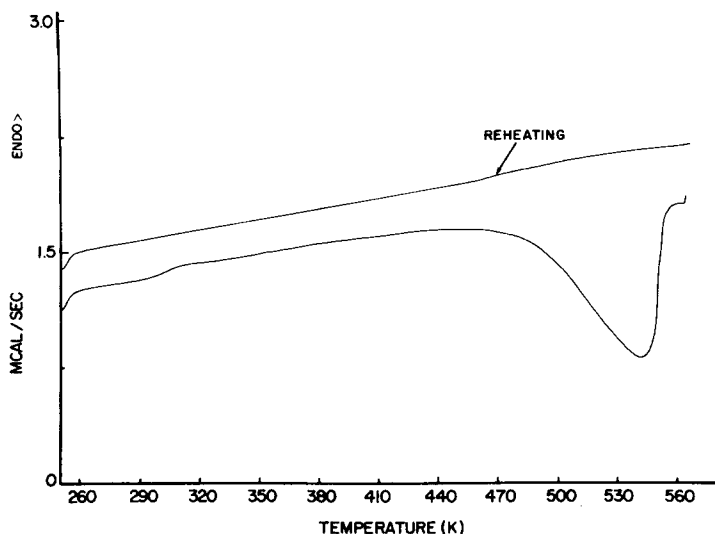


Fig. 1. DSC thermograms of normalized prepolymer mix sample (weight: 15.28 mg; scan rate: 20.0 deg/min) and reheating of the same sample (thermogram of reheated sample shifted upward).

an exothermic curing reaction. On reheating the same sample, the exothermic peak disappeared, implying that curing was complete. The glass transition temperature, curing peak temperature, and the exothermic energy all increased with the scanning rate.

Figure 2 shows a typical DSC thermogram of the standard-cured, dry epoxy sample. The thermogram has an exothermic peak, indicating that a large fraction of the functional groups remain unreacted. The exothermic energy is about 1/3 that of the prepolymer mix. On reheating the same sample, the exothermic peak disappears, indicating no more crosslinking occurs. The cured epoxy has a glass transition temperature ca. 187°C.

Shown in Figure 3 is the DSC thermogram of a standard-cured sample after it had been immersed in water for 14 days at 27°C. The glass transition temperature at 119°C is about 62°C lower than dry, standard-cured epoxy samples presumably due to plasticization. This confirms the results of some of previous studies.^{4,6,7} There was no indication of melting of any clustered, freezable water that would be indicated by an endothermic peak for the melting of ice near 0°C. Samples soaked at 70°C for 22 days with 4.9% weight gain were equilibrated at

TABLE I
DSC Results of Prepolymer Mix Samples^a

Scanning rate (°C/min)	Glass transition temperature (°C)	Curing exothermic energy (cal/g)	Curing peak (°C)
5	32	114.2	236.3
10	38	111.3	252.4
.20	39	124.4	271.8

^a Based on the average of three samples.

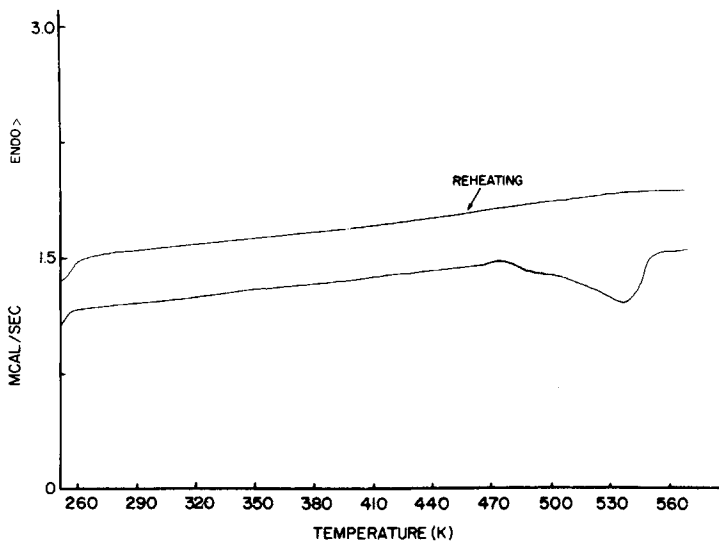


Fig. 2. DSC thermograms of normalized cured epoxy sample (weight: 22.27 mg; scan rate: 20.0 deg/min) and reheating of the same sample (thermogram of reheated sample shifted upward).

-123°C and then scanned on DSC from -123°C to 127°C . Again, no first-order transition associated with the melting of ice was observed. Broadline NMR spectra of a soaked epoxy in earlier studies^{8,9} also failed to show clustered water, although semimobile species were observed.

Kaelble¹⁰ studied Narmco 5208 epoxy. He found that TGDDM/DDS (71/29, w/w), cured for 5 h at 188°C , had a glass transition temperature of 249°C and

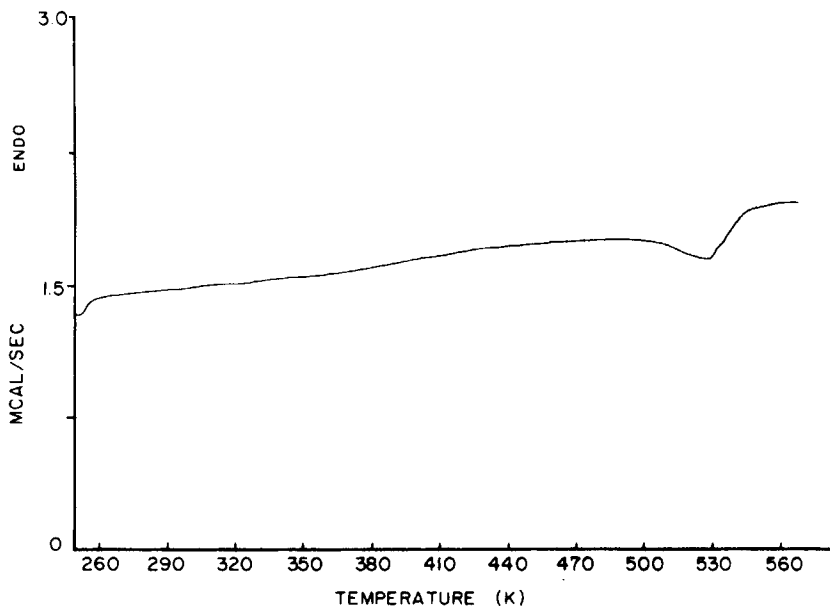


Fig. 3. DSC thermogram of normalized cured and soaked epoxy sample (weight: 25.66 mg; scan rate: 20.0 deg/min).

TABLE II
DSC Results of the Epoxy Samples^a

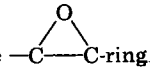
Sample	Glass transition temperature (°C) ^b	Curing exothermic energy (cal/g)	Curing peak temperature (°C)	Moisture content (%)
Prepolymer mix	39	124	272	0.0
Cured epoxy	181	42	267	0.0
Cured, water-soaked epoxy	119	21	255	4.3

^a Scanning rate 20°C/min.

^b Based on average of three samples.

an equilibrium water uptake (immersion at 100°C) of about 6.0%. The curing exothermic energy was 140 cal/g for the uncured epoxy which compares to 124 cal/g for uncured epoxy (73/27, w/w) found in the present study. In Table II, the data for a prepolymer mix, standard-cured epoxy, and cured epoxy soaked in distilled water are presented.

The water soaked samples had an exothermic peak energy about half that of dry cured samples. Probably two factors are responsible for this: first, the moisture diffuses out from the sample during heating, reducing the net exothermic reaction; second, water reacts with some of the epoxide rings. This has been confirmed by the IR spectrum of a soaked epoxy film that showed a smaller

absorption intensity at 904 cm^{-1} corresponding to the -ring absorption. The presence of the absorption peak at 904 cm^{-1} in the cured epoxy film also confirms the DSC result that a fraction of functional groups remain unreacted after the standard cure.

The IR spectrum of a water-soaked epoxy does not differ much from the dry epoxy spectrum except that the intensity of the OH and/or stretching NH peak increases (Fig. 4). The water absorbed by the resin is involved in an exchange between the hydrogens of water and the hydrogens on the hydroxyl and amine groups of the epoxy. The IR spectrum of epoxy film soaked in D₂O (Fig. 5) shows a new peak at 2500–2600 cm^{-1} corresponding to OD and/or ND stretching accompanied by a decrease in intensity of OH and/or NH stretching peak, dem-

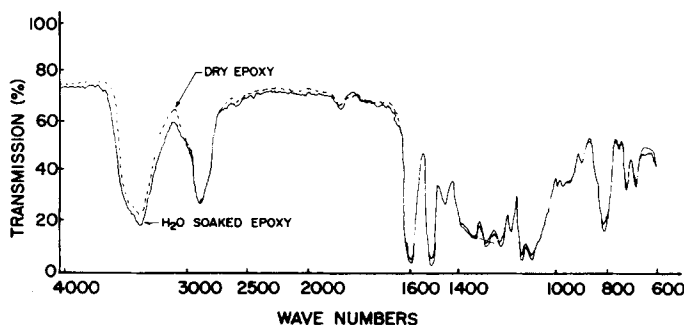


Fig. 4. IR spectra of dry and water soaked epoxy samples.

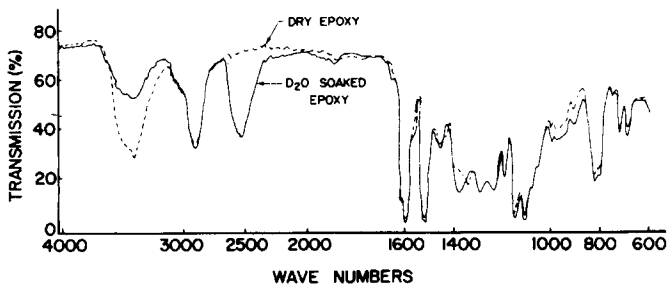


Fig. 5. IR spectra of dry and D₂O soaked epoxy samples.

onstrating that the deuterons from D₂O exchange with protons on the epoxy. This confirmed the earlier work by Fuller et al.¹¹

The results of DSC scans of cured epoxy samples irradiated with 0.5-MeV electrons are in Table III. Figure 6 shows thermogram of the dry, irradiated epoxy sample. The curing exothermic energy is presented as a ratio (percent) of curing energy of the irradiated to the nonirradiated samples (Table III). The curing peak temperatures decrease monotonically and the exothermic energy decreases with increase in radiation dose. For a 400-Mrad dose, the decrease in the curing exothermic energy is about 22%. Apparently, the radiation has further crosslinked the epoxy. Also the glass transition was not observed in the thermograms of the irradiated samples. The glass transition apparently shifts to a higher temperature and is hidden by the curing peak. The IR spectra show that the absorption associated with the epoxide ring at 904 cm⁻¹ is reduced in intensity after irradiation. Both observations suggest additional crosslinking.

The IR spectra of the irradiated samples also show a small absorption at 1720 cm⁻¹ indicating existence of carbonyl groups. The samples were irradiated in air, and hence some oxidation is likely to have occurred.

Table IV shows the DSC data of epoxy samples irradiated at room temperature with ⁶⁰Co gamma radiation to a maximum dosage of 160 Mrads. Unlike the case of the electron beam radiation, the glass transition temperature did not change significantly. The curing exothermic energy decreased by 16% after 160-Mrad dosage. Gamma radiation also further crosslinks the epoxy. The curing peak

TABLE III
DSC Results of Standard Cured, Dry, Irradiated (0.5-MeV Electrons) Epoxy

0.5-MeV electron radiation dose (Mrads)	Glass transition temperature (°C)	Ratio of curing exothermic energy to control (0 Mrad) (%)	Curing peak temperature (°C)
0	193	100	264
100	N.S. ^a	93	260
200	N.S.	85	258
300	N.S.	83	257
400	N.S.	78	256

^a Not seen = N.S.

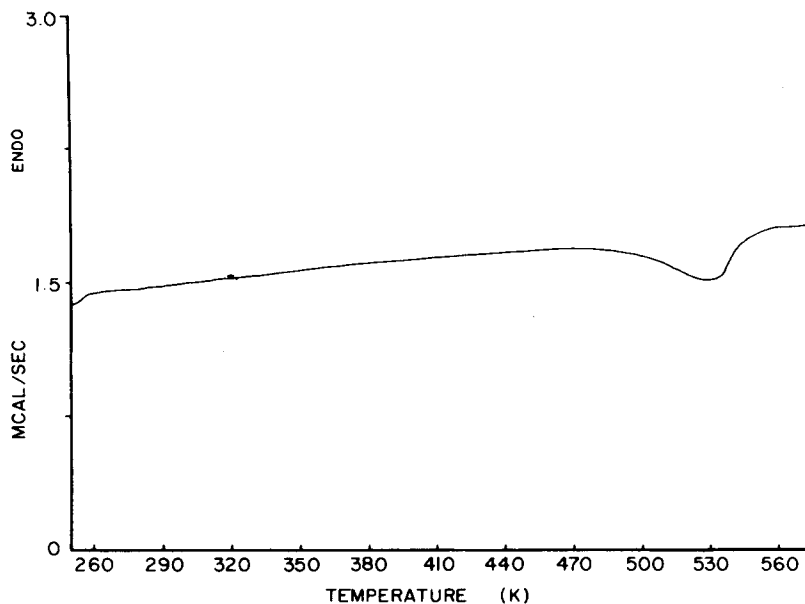


Fig. 6. DSC thermogram of irradiated normalized cured epoxy sample (400 Mrad; weight: 21.47 mg; scan rate: 20.0 deg/min).

temperature decreased steadily from 264.3°C to 260.5°C with increasing dosage.

DSC results of epoxy samples standard-cured and irradiated in liquid nitrogen with ⁶⁰Co gamma are reported in Table V. The results are very similar to those obtained for samples irradiated at ambient conditions, although the observed changes are smaller. The glass transition does not change. The curing energy decreased only 6% compared to 16% after irradiation under ambient conditions. At liquid N₂ temperatures, molecular motion is greatly decreased, generated radicals are relatively immobile, and little crosslinking can occur until the sample is heated.

CONCLUSIONS

Sorbed moisture plasticizes the TGDDM/DDS epoxy system and lowers the *T_g*, and part of the sorbed water reacts with and opens the epoxide rings. No

TABLE IV
DSC Results of Standard Cured, Dry, Gamma Irradiated (in Air) Epoxy

Gamma radiation dose (Mrads)	Glass transition temperature (°C)	Curing exothermic energy (%)	Curing peak temperature (°C)
0	170	100	264.3
40	174	93	262.9
80	168	90	262.4
120	169	87	261.6
160	167	84	260.5

TABLE V
DSC Results of Standard Cured, Dry, Gamma Irradiated (Liquid N₂) Epoxy

Gamma radiation dose (Mrads)	Glass transition temperature (°C)	Curing exothermic energy (%)	Curing peak temperature (°C)
0	170	100	264.3
40	174	97	264.4
80	171	96	265.3
120	173	93	264.2
160	171	94	263.7

freezable water can be detected with DSC. The hydrogens in water exchange with the hydrogens on the hydroxyl and amine groups in the epoxy. DSC analysis and IR spectroscopy indicate that both electron beam and cobalt ⁶⁰Co gamma radiation further crosslink the epoxy.

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