NOTES

Variation in Radical Decay Rates in Epoxy as a Function of Crosslink Density

INTRODUCTION

Epoxy resins are widely used, especially as a matrix material for high performance composites. Lightweight composites are ideal candidates for space applications that may result in exposure of the materials to large dosages of high energy ionizing radiation. In this paper we have examined the behavior of radicals generated by [60]Co γ-radiation in the epoxy system tetraglycidyl-4,4'-diaminodiphenyl methane (TGDDM) cured with 4,4'-diamino-diphenyl sulfone (DDS). The molar ratio of TGDDM to DDS was varied in the epoxy samples, and they were prepared with the same curing conditions so that extent of crosslinking was varied. In earlier studies,[1-3] we have shown the presence of radicals formed by ionizing radiation that exhibit half-lives at room temperature with two characteristic time constants: one of a few minutes and one of a few days. These two species have been associated with regions of low and high crosslinked density regions, respectively. This study is an independent confirmation of that conclusion.

A number of investigators have reported that epoxy systems vary in crosslink density.[4-9] Brown et al.[4-5] report inhomogeneities in TGDDM cured with N,N'-dimethyl-1,6 diaminohexane characterized by NMR and spin probe and spin label ESR. Kreibich and Schmid[6] observed with a differential scanning calorimeter a splitting of the glass transition temperature after a phase separation of the high and low crosslinked regions achieved through annealing.

Morgan and O'Neal[7,8] and Mijovic and Koutsky[9] using bright field transmission electron microscopy found highly crosslinked nodules 6–10 nm in diameter interconnected by low crosslinked regions in diethylene triamine-cured bisphenol-A-diglycidyl ether epoxies. The size of the nodules was found to vary with the curing agent concentration.

Commercial epoxy resins are reported to exhibit a distribution of crosslink densities in the final network.[10] High crosslinked density regions from 6×10^4 nm to 10^5 nm were observed.

It has also been reported by others[8,10] that at constant curing conditions the extent of crosslinking of the epoxy system TGDDM/DDS increases with increasing DDS concentration up to stoichiometric equivalence.

EXPERIMENTAL

Materials

The structures of the unreacted epoxy resins (TGDDM) and curing agent (DDS) are shown in Figure 1. Rod-shaped samples were prepared by mixing TGDDM and DDS in various reactant ratios at 100–110°C, then pushing Teflon® tubes (0.24 cm i.d., 2.0–2.5 cm in length) into the molten resin and allowing the system to cool to room temperature in vacuum. The filled Teflon® tube sections were broken out of the hardened epoxy system, and the ends were sealed with Teflon® tape in preparation for curing. The samples were then cured in a vacuum desiccator at 137°C for 3 h and 160°C for 5 h. The cured epoxy rods were then pushed out of the Teflon® tubes with a small metal rod.

Cured epoxy samples were prepared in several reactant ratios and three of these are presented in Table I. Samples containing less than 17% DDS by weight were extremely brittle and could not be handled at cryogenic temperatures. It was found that attempting to mix more than 37% DDS (w/w) with TGDDM (stoichiometric equivalence) was extremely difficult since the DDS powder would not readily dissolve. Typical epoxy composite samples containing TGDDM/DDS as a matrix are usually prepared in a weight ratio of 73/27, and this ratio is represented in Table I. Additionally, samples of 100% DDS powder were also investigated. Attempts to examine pure TGDDM failed because the material was too viscous to handle easily.

TETRAGLYCIDYL-4,4'-DIAMINO DIPHENYL METHANE (TGDDM)
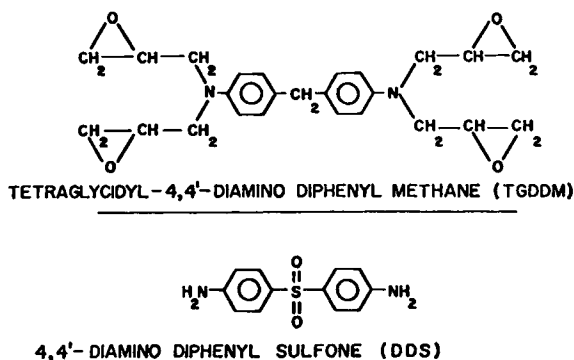

4,4'- DIAMINO DIPHENYL SULFONE (DDS)

Fig. 1. Epoxy resin tetraglycidyl-4,4'-diaminodiphenyl methane (TGDDM) and curing agent 4,4'-diaminodiphenyl sulfone (DDS).

Standard samples in the identical rod shape as above were prepared by suspending a determined amount of 2,2-diphenyl-1-picryl hydrazyl (DPPH) in Scotch Brand 3M epoxy amide resin and inserting Teflon® tubes prior to curing, which takes place at room temperature. After curing, the tubes were removed, and the rod-shaped standard samples pushed out. The strucutre of DPPH is shown in Figure 2.

Irradiation

Epoxy samples were weighed, wrapped in aluminum foil, labeled, and stored in a vacuum desiccator prior to irradiation. Samples of DDS were placed in tarred, thin-walled NMR tubes, flushed with nitrogen, and placed in the vacuum desiccator also.

Radiation was carried out in a Gammacell 220 by Atomic Energy of Canada, a cobalt-60 source emitting γ-rays (1.33 and 1.17 MeV) at a dose rate of approximately 0.225 Mrad/h. Samples were placed in a dewar containing liquid nitrogen and then into the cavity of the γ cell. Radiation was performed at cryogenic temperature to impede any radical decay which might take place prior to ESR measurement. The liquid nitrogen in the irradiation dewar was replenished as necessary. The samples were irradiated to various doses and, after irradiation, were stored in liquid nitrogen until ESR measurements could be performed.

ESR Spectrometry

The radicals generated by radiation were observed on a Japan Electron Optics Laboratory (JEOL) JES-ME-1X ESR Spectrometer. Measurements were made at liquid nitrogen temperature using a variable temperature adapter.

The first-derivative spectra obtained were double-integrated by the numerical method of Wyard,[11] using

$$A = \frac{1}{2} h^2 \sum_{r=1}^{n} (2n - 2r + 1) Y_r \qquad (1)$$

TABLE I
Reactant Ratios Used in TGDDM/DDS Samples

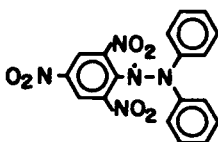| DDS (wt %)	TGDDM (wt %)	Molar ratio DDS/TGDDM
17	83	0.35
27	73	0.63
37	63	1.00
100	0	—

Fig. 2. Radical standard 2,2-diphenyl-1-picryl hydrazyl (DPPH).

where h is the width of the interval into which a spectrum was divided, n is the number of intervals, and Y_r is the height of the rth interval at its center. The intervals are numbered $1-n$, starting at the left side of the spectrum. A is the area of the absorption curve of the spectrum and is proportional to the radical concentration in the sample.

The areas of the DPPH standards with known spin concentration were compared with the areas of the irradiated samples to estimate their radical concentration, using

$$C_u = \frac{A_u}{G_u} \frac{C_D W_D}{A_D/G_D} \frac{1}{W_u} \qquad (2)$$

where subscripts u and D represent the unknown and the standard, respectively, and A is the area of the absorption spectrum. C is the concentration of radicals (spins/g), G is the gain (amplitude) setting, and W is the sample weight.

Radical decay was measured by maintaining the sample at room temperature for a period of time and then recording the ESR spectrum at liquid nitrogen temperature. During decay, the samples were stored in containers flushed with nitrogen to reduce the effects of oxygen on the radical decay.

DISCUSSION

The ESR spectra of a 73/27 TGDDM/DDS sample irradiated with 25 Mrads of ^{60}Co radiation are shown in Figure 3 along with the spectrum of the same sample following a 10-min decay at room temperature. All spectra of irradiated epoxy samples showed the same basic structure regardless
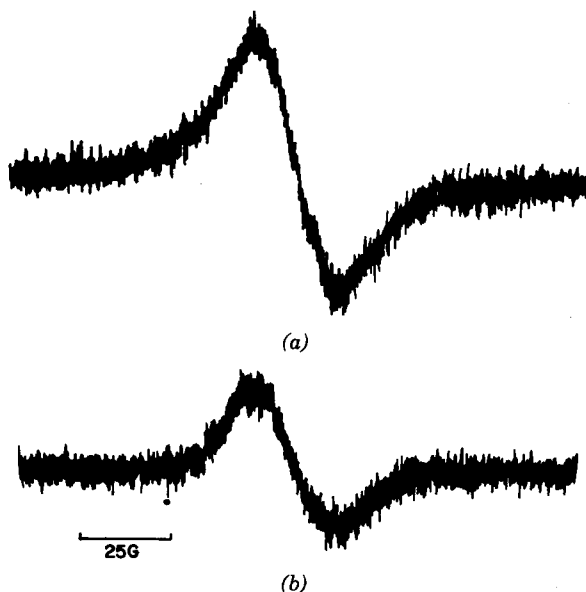

Fig. 3. ESR spectra of a 73/27 (w/w) TGDDM/DDS samples (a) irradiated with 25 Mrads of cobalt-60 γ-radiation and (b) irradiated with 25 Mrads of γ-radiation after a 10-min decay at room temperature.
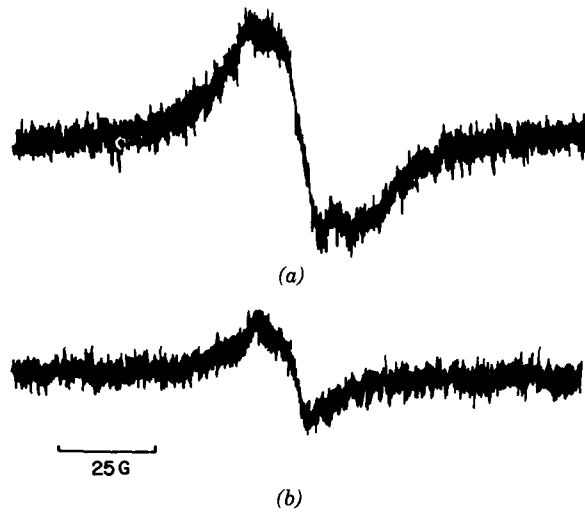
Fig. 4. ESR spectra of 100% DDS (a) irradiated with 30 Mrads of γ-radiation and (b) irradiated with 30 Mrads of γ-radiation after a 10-min decay at room temperature.

of percentage of hardener present. No fine structure is exhibited, although there is an asymmetry present.

The radicals formed in irradiated DDS create a more asymmetric spectrum than the TGDDM/DDS samples, although the line widths are about the same and hyperfine structure is still not seen. The ESR spectra of 100% DDS irradiated with 30 Mrads of γ-radiation and after a 10-min decay at room temperature is shown in Figure 4.

For the TGDDM/DDS-cured epoxy resin samples, radical concentration for a given dose was found to exhibit an approximate G (radical) value of 0.59 radicals/100 eV. Irradiated DDS was found to have a G (radical) value of 0.42 radicals/100 eV, the difference probably being due to a higher concentration of stable radiation-resistant aromatic rings in the DDS samples. Unirradiated control samples of TGDDM/DDS were found to have radical concentrations ca. 3×10^{17} spins per gram compared to ca. 2×10^{18} after 5 Mrads of γ-radiation. Control DDS samples had a radical concentration of approximately 10^{16} spins/g compared to 1.3×10^{18} after 5 Mrads.

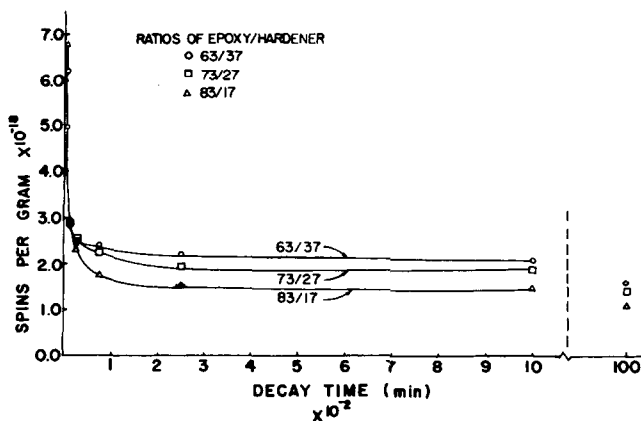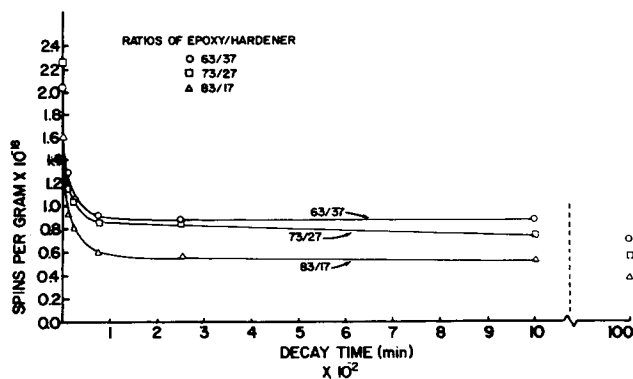Figures 5 and 6 show radical concentration versus time at room temperature for TGDDM/DDS

Fig. 5. Radical concentration vs. time at room temperature for TGDDM/DDS samples varying in epoxy/harderner (w/w) ratio irradiated with 5 Mrads of γ-radiation: (O) 63/37; ($\square$) 73/27; ($\triangle$) 83/17.

Fig. 6. Radical concentration vs. time at room temperature for TGDDM/DDS samples varying in epoxy/hardener (w/w) ratio irradiated with 25 Mrads of γ-radiation: (O) 63/37; ($\square$) 73/27; ($\triangle$) 83/17.

samples irradiated to 5 Mrads and 25 Mrads, respectively. The epoxy samples exhibit an initial fast decay of radicals followed by a much slower decay, indicating that relatively fast and slow reacting species are present. Our hypotheses are that the fast-reacting species occur in the less crosslinked regions of the epoxy resin where chain mobility facilitates rapid recombination and that the slow-reacting species occur in the more highly crosslinked regions where immobile chains restrict recombination of the radicals.

At the same cure conditions, the extent of crosslinking of the epoxy system increases with increasing hardener concentration up to stoichiometric equivalence. Figures 5 and 6 show that the relative fraction of slow- to fast-decaying radicals increases with increasing hardener concentration, suggesting that the size and number of more highly crosslinked regions must be increasing.

The effect seen in Figures 5 and 6 indicates a difference in extent of crosslinking and not just a difference in amount of DDS present. Irradiated DDS was found to exhibit a much lower relative fraction of slow to fast decaying radicals than any of the TGDDM/DDS samples. Figure 7 shows radical concentration vs. time for DDS irradiated to 5 and 30 Mrads.

Radicals formed in the unreacted DDS molecules may be contributing slightly to the relative fractions of the fast- and slow-decaying species in the TGDDM/DDS samples. Since the amount of unreacted DDS is small and increases as the molar ratio TGDDM/DDS decreases and since irradiated pure DDS contains about 8 times as many fast decaying radicals as slow decaying radicals, the effect seen in Figures 5 and 6 must be due predominantly to a difference in extent of crosslinking.
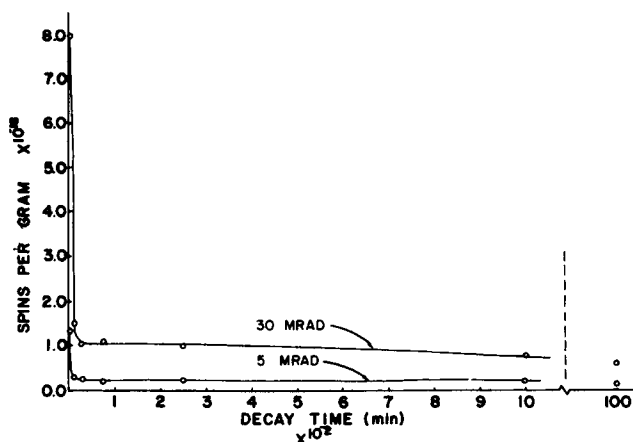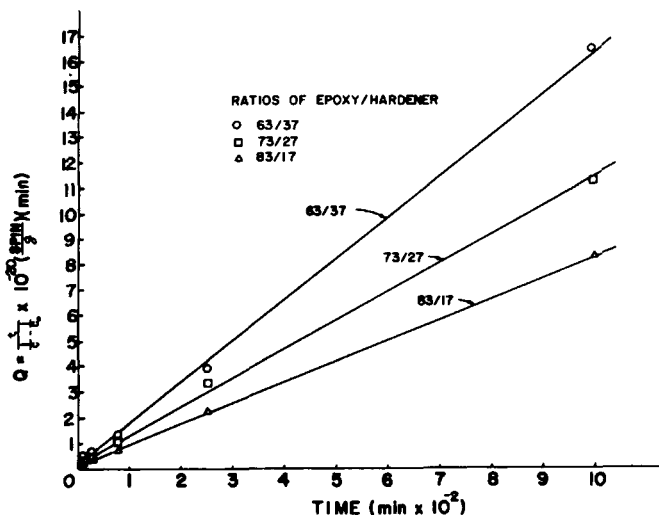

Fig. 7. Radical concentration vs. time at room temperature for 100% DDS irradiated with various dosages of γ-radiation.

Fig. 8. Q vs. time for the radical decay data of Figure 5.

The overall kinetics of the TGDDM/DDS system can be fitted to a model assuming two simultaneous reactions occurring in different regions, one crosslinked more highly than the other. Figures 8 and 9 show plots of the Q function derived by Dole[12] vs. time for TGDDM/DDS samples irradiated with 5 and 25 Mrads of γ-radiation, respectively. The equation that defines the line is

$$Q = \frac{t}{1/C - 1/C_0} = \frac{1 + C_0 X_f X_s (k_f k_s) t}{X_f^2 k_f + X_s^2 k_s + C_0 X_f X_s k_f k_s t} \tag{3}$$

where C is the total radical concentration at time t, C_0 is the concentration at $t = 0$, k_f and k_s are the second-order reaction rate constants for the fast- and slow-decaying regions, respectively, and X_f and X_s are the mole fractions of the fast- and slow-decaying regions at $t = 0$. This equation is a simplification of the general case where the slow decay component is assumed to undergo negligible change during measurement. The linearity of the plots indicates that a model with two characteristic decay rates is consistent with the data and may be attributed to reactions occurring in different regions, one being much faster than the other.
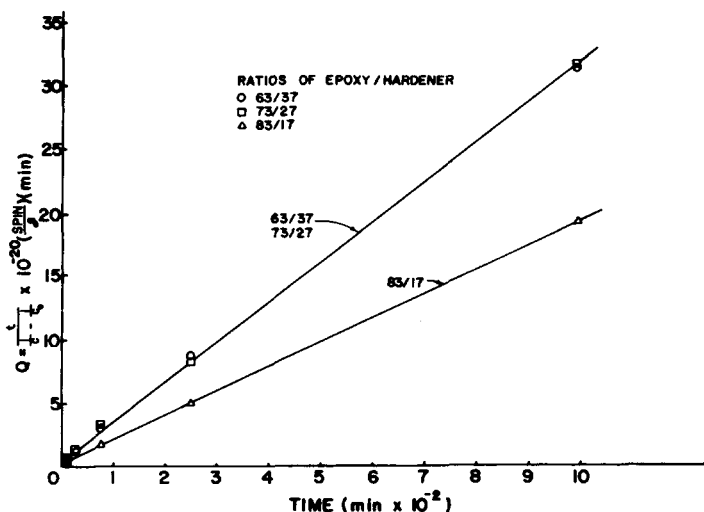
Fig. 9. Q vs. time for the radical decay data of Figure 6.

The increase in the slope of the Q function with percentage of hardener present occurs because the overall radical concentration C decreases at a slower rate in samples containing a higher mole fraction of highly crosslinked regions.

In conclusion, this work suggests that the rate of decay of radicals is related to inhomogeneities in the resin. For example, those in the more highly crosslinked regions would have relatively long decay rates. While ESR is a possible tool for monitoring the inhomogeneities in epoxies, it does not explain why they exist. The inhomogeneities could be due to statistical variation associated with the complex crosslinking reactions or, as Bell[13] has suggested, they could be due to difficulties in mixing the reactants.

References

1. K. Schaffer, "Characterization of a Cured Epoxy Resin Exposed to High Energy Radiation with Electron Spin Resonance," M.S. thesis, North Carolina State University, 1981.

2. K. Schaffer, R. D. Gilbert, J. D. Memory, and R. E. Fornes, *Bull. Am. Phys. Soc.*, **26**, 432 (1981).

3. K. Schaffer, R. E. Fornes, R. D. Gilbert and J. D. Memory, *Polymer*, to appear.

4. I. M. Brown, A. C. Lind, and T. C. Sandreczki, *Department of the Navy Contract Report* MDC 00721, 1980.

5. I. M. Brown, A. C. Lind, and T. C. Sandreczki, *Department of the Navy Contract Report* MDC 00673, 1979.

6. Ursula T. Kreibich and Rolf Schmid, *J. Polym. Sci., Symp.* **53**, 177 (1975).

7. Roger J. Morgan and James E. O'Neal, *J. Maters. Sci.*, **12**, 1966 (1977).

8. R. J. Morgan and J. E. O'Neal, *Am. Chem. Soc., Div. Org. Coatings Plast. Chem.*, **38**, 485 (1977).

9. Jovan Mijovic and J. A. Koutsky, *Polymer*, **20**, 1095 (1979).

10. R. J. Morgan, *Am. Chem. Soc., Div. Org. Coatings Plast. Chem.*, **40**, 678 (1980).

11. S. J. Wyard, *J. Sci. Instrum.*, **2**, 769 (1965).

12. M. Dole, C. Hso, V. M. Patel, and G. N. Patel, *J. Phys. Chem.*, **19**, 2473 (1975).

13. James P. Bell, *J. Appl. Polym. Sci.*, **27**, 3503 (1982).

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