# Electron spin resonance study of a cured epoxy resin exposed to high-energy radiation

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Tetraglycidyl-4,4'-diaminodiphenyl methane cured with 4,4'-diaminodiphenyl sulphone was irradiated with varying dosages of 0.5 MeV electrons and 1.17 and 1.33 MeV gamma rays and was studied using electron spin resonance. The radical concentration increases with increasing radiation dose and decays, at ambient temperature, in a way consistent with a model that assumes two simultaneous second-order reactions occurring in different zones.

**Keywords** Epoxy; electron spin resonance; 0.5 MeV electron and $^{60}$Co gamma radiation

## INTRODUCTION

Epoxy resin/graphite fibre composite material is widely used in aerospace applications because of its high strength-to-weight ratio. One proposed application of the material is use in structural members in a device to be kept in geosynchronous orbit for a period of about 30 years. Since the radiation level in geosynchronous orbit is considerably higher than at the Earth's surface[1-4], the question arose as to the effect of radiation on the mechanical properties of the material. Using the facts that radiation damage in polymeric materials is independent to first order of the type of ionizing radiation and dose rate, but principally dependent on total dosage[5], we have simulated the effect of radiation in a 30-year lifetime in geosynchronous orbit by the use of 0.5 MeV electrons and 1.17 and 1.33 MeV gamma rays[6]. Our results have indicated that there is a slight increase in both flexural strength and modulus, as measured by a three-point bending test, for dosages up to 5000 Mrad, which should be greater than the total dosage in geosynchronous orbit in a 30-year lifetime for the structures under consideration. This paper is an extension of that work in which we attempt to determine the nature of the effect of the radiation on the epoxy matrix.

## EXPERIMENTAL PROCEDURE

The epoxy samples were made using Ciba-Geigy MY720 Araldite Epoxy Resin (tetraglycidyl-4,4'-diaminodiphenyl methane; TGDDM) cured with Ciba-Geigy Eporal Hardener (4,4'-diaminodiphenyl sulphone; DDS). The samples were made in the form of cylindrical rods 2.4 mm (3/32 inch) in diameter and had a weight composition of 73% TGDDM and 27% DDS. The radical concentration standard was DPPH (2,2-diphenyl-1-picryl hydrazyl) dispersed in Scotch brand 3M Epoxy Resin and Amide Hardener. The cylindrical samples were irradiated in an oxygen-free environment by 0.5 MeV electrons or by 1.17 and 1.33 MeV gamma rays from a $^{60}$Co source. The electron irradiation took place at room temperature and the gamma irradiation at liquid-nitrogen temperature. In each case, after the desired dosage of radiation, the samples were immersed in a dewar containing liquid nitrogen (−196°C) and stored until electron spin resonance (e.s.r.) measurements were made. Details of the irradiation procedure may be found in ref. 6. E.s.r. measurements were made at liquid-nitrogen temperature in an immersion dewar with a JEOL JES-ME-IX ESR spectrometer. Radical decay was measured by bringing the irradiated sample to room temperature for a period of time and then recording the e.s.r. spectrum at liquid-nitrogen temperature.

## RESULTS AND DISCUSSION

*Figure 1* gives a typical e.s.r. spectrum of gamma-irradiated cured epoxy, and *Figure 2* gives a typical spectrum of electron-irradiated epoxy. *Figure 3* gives an example of a typical e.s.r. spectrum of electron-irradiated epoxy compared with the signal from the DPPH standard.

Typical spectra of samples irradiated either by electrons or gamma rays show a broad, featureless absorption line without resolvable hyperfine structure. The principal difference in the two types of spectra is the presence of the long wings in the spectrum of the gamma-irradiated sample (*Figure 1*) which are not present in the spectrum of

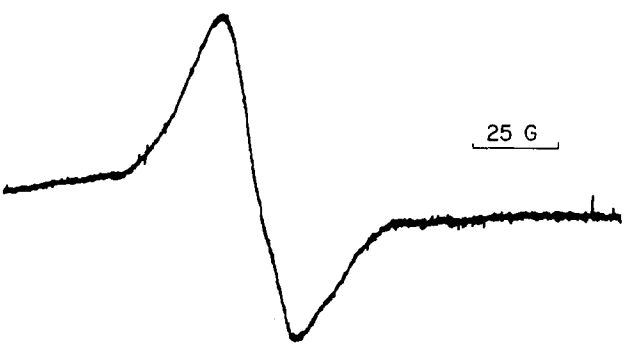


*Figure 1* E.s.r. spectrum of TGDDM/DDS epoxy irradiated at 77K with 53.7 Mrad of $^{60}$Co gamma ($2.4 \times 10^{19}$ radicals/g)

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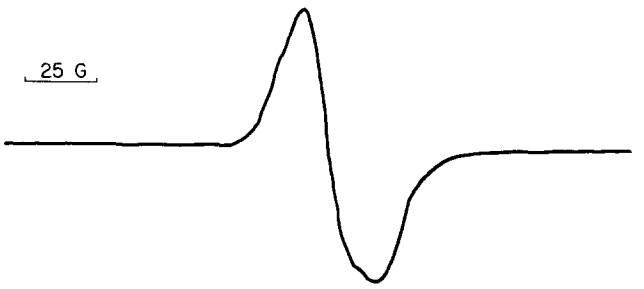


*Figure 2* E.s.r. spectrum of TGDDM/DDS epoxy irradiated at ambient temperature with 60 Mrad of 0.5 MeV electrons. Maintained at 77K following radiation ($1.7 \times 10^{18}$ radicals/g)

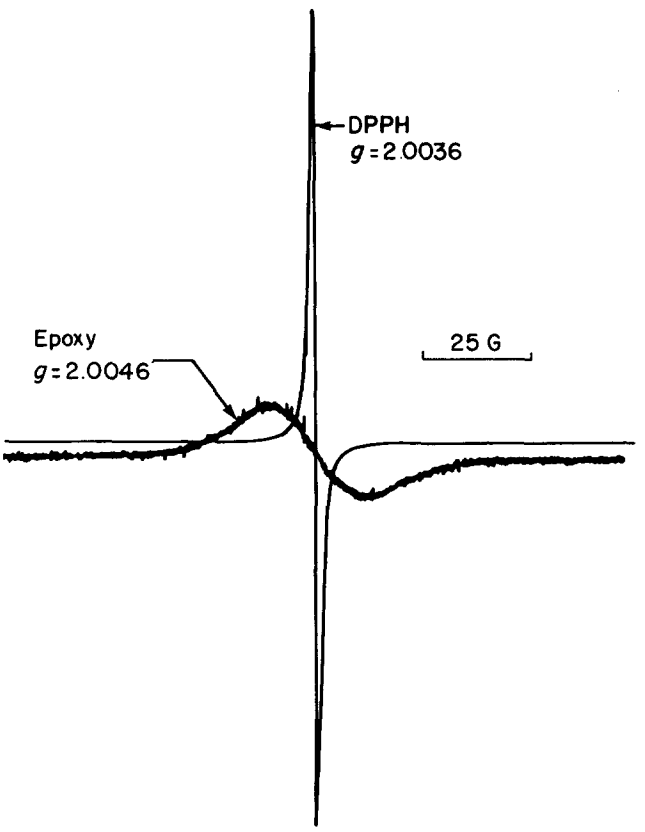


*Figure 3* E.s.r. spectrum of TGDDM/DDS epoxy irradiated with 0.5 MeV electrons with superimposed spectrum of DPPH suspended in epoxy


*Figure 4* E.s.r. spectrum of TGDDM/DDS epoxy after 6 min at ambient temperature following irradiation at 77K with 53.7 Mrad of $^{60}$Co gamma ($1.2 \times 10^{19}$ radicals/g)

the electron-irradiated sample (*Figure 2*). *Figure 4* shows the spectrum of the gamma-irradiated sample after 6 min of decay. Along with a significant decrease in overall intensity of the spectrum, one may note that the decay of the long wings is essentially complete so that the spectrum has the same form as the electron-irradiated sample. This seems to indicate a quickly decaying species trapped in the gamma-irradiated sample because this sample is irradiated at liquid-nitrogen temperature. *Figure 5* shows that the radical concentration versus gamma radiation dose is a linear relationship, as might be expected. A $G$ value (radicals/100 eV) of 0.59 was measured.

*Figure 6* shows the radical concentration versus 0.5 MeV electron radiation dose. It is non-linear since an appreciable fraction decays during the radiation treatment.

*Figures 7* and *8* show the time decay at room temperature of radical concentration for both types of sample. These data fit a model which assumes two simultaneous second-order reactions occurring in different zones: a fast decaying species and a slow decaying species. The equation to which these data fit, referred to as the $Q$ function

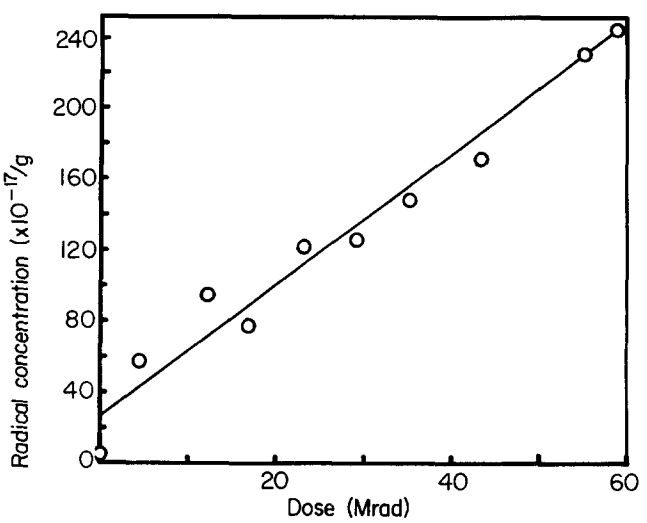


*Figure 5* Radical concentration in TGDDM/DDS epoxy as a function of irradiation dose of $^{60}$Co gamma at 77K

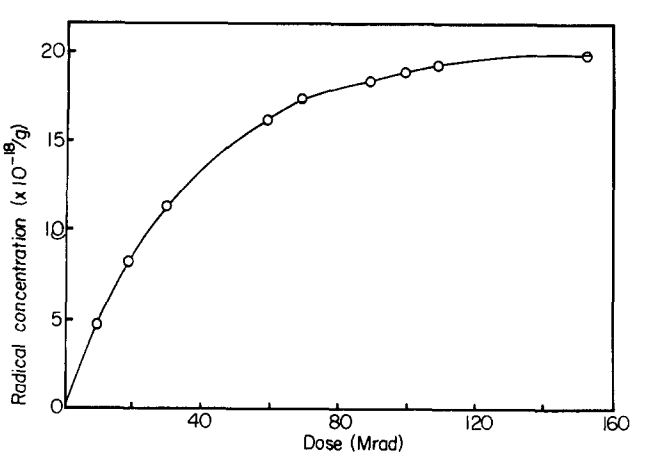


*Figure 6* Radical concentration in TGDDM/DDS epoxy as a function of irradiation dose of 0.5 MeV electrons. Irradiation at ambient temperature, e.s.r. measurements 77K

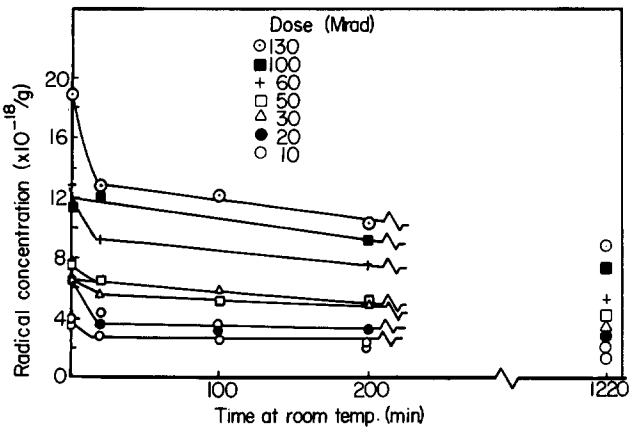


*Figure 7* Radical concentration versus time at ambient temperature following irradiation at ambient temperature with 0.5 MeV electrons

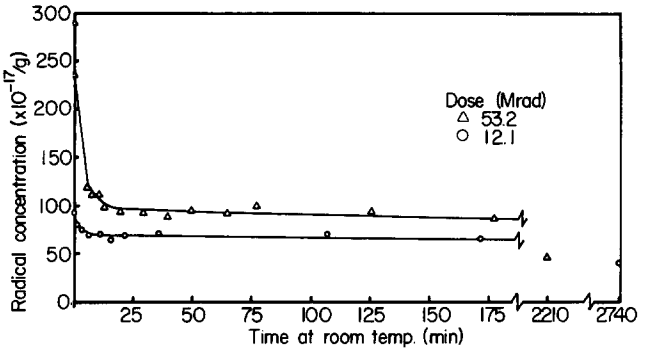


*Figure 8* Radical concentration versus time at ambient temperature following irradiation at 77K with $^{60}$Co gamma

derived by Dole[7], is given below:

$$Q=\frac{t}{1/C-1/C_0}=\frac{1+C_0X_fX_s(k_f+k_s)t}{X_f^2k_f+X_s^2k_s+C_0X_fX_sk_fk_st}$$

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 $t=0$. When the slow decay component undergoes negligible change during measurement, this equation is approximated by a linear function with time. A plot of the $Q$ function for several dose levels resulted in linear functions for times up to 3000 min. In the gamma-irradiated samples, the decay constants for the fast decay were in the range $(1-2)\times10^{-21}$ g min$^{-1}$ spins and for the slow decay $(1-2)\times10^{-23}$ g min$^{-1}$ spins. Since there is evidence from electron microscopy, n.m.r. and e.s.r. spin probe studies that there are inhomogeneous regions of high and low crosslink density in epoxy resins[8-13], we propose that these results arise from the creation of radicals in high and low crosslink density regions in the matrix. The fast decaying species is located in low crosslink density regions where recombination is easier, and the slow decaying species in regions of high crosslink density where recombination is more difficult.

## ACKNOWLEDGEMENTS

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