

THE EFFECTS OF ELECTRON AND GAMMA RADIATION
ON EPOXY-BASED MATERIALS

R. E. FORNES, J. D. MEMORY, R. D. GILBERT
NORTH CAROLINA STATE UNIVERSITY
RALEIGH, NORTH CAROLINA

AND

E. R. LONG, JR.
MATERIALS DIVISION
NASA LANGLEY RESEARCH CENTER
HAMPTON, VIRGINIA

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OBJECTIVES AND APPROACH

Radiation effects on epoxy-based materials are being studied at North Carolina State University under a grant (NSG-1562) from the Materials Division of the NASA Langley Research Center. The research is conducted by members of the School of Textiles, Department of Textile Chemistry and Department of Fiber and Polymer Science, and the School of Physical Sciences and Applied Mathematics, Department of Physics and Department of Chemistry. The objectives of this work are to evaluate the effects of radiation on the mechanical properties of epoxy-based structural materials and to measure the fundamental radiation-generated events which cause the changes in mechanical properties. The approach to these objectives is the exposure of specimens of graphite/epoxy composites and epoxy resins to electron and gamma radiation, followed by mechanical property and fundamental measurements. This report will present a portion of the data which has been gathered to date.

OBJECTIVE

EVALUATION OF THE EFFECTS OF RADIATION ON THE MECHANICAL PROPERTIES OF EPOXY-BASED STRUCTURAL MATERIALS.

MEASUREMENT OF THE FUNDAMENTAL, RADIATION-GENERATED EVENTS WHICH CAUSE THE CHANGES IN MECHANICAL PROPERTIES.

APPROACH

EXPOSURE OF SPECIMENS OF GRAPHITE EPOXY COMPOSITE AND EPOXY RESIN TO ELECTRON AND GAMMA RADIATION.

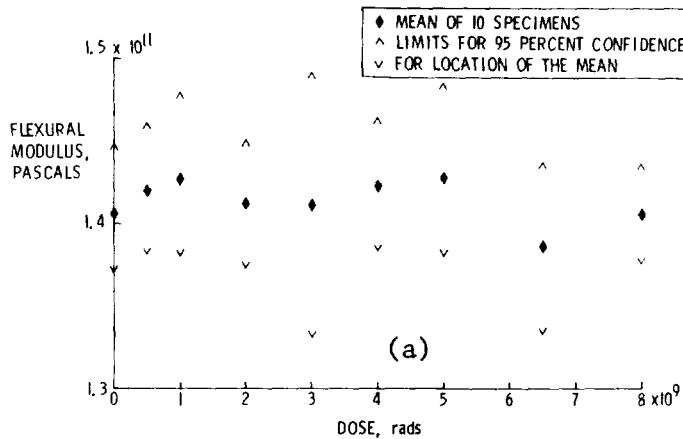
MEASUREMENT OF CHANGES IN THE VALUES OF MECHANICAL AND FUNDAMENTAL PROPERTIES.

Figure 1

RADIATION EFFECTS ON FLEXURAL PROPERTIES OF A GRAPHITE/EPOXY COMPOSITE

The flexural properties of miniature (25 mm x 13 mm x 0.51 mm) unidirectional specimens of T300/5208 composite for electron radiation exposures in vacuum for doses up to and including 8×10^9 rads are shown in figures 2a and 2b. The specimens were fabricated at Langley Research Center from prepreg material. The fiber direction was in the direction of specimen length (longitudinal), so the flexural properties were fiber-dominated. Each datum point is the mean of ten specimens. The 95 percent confidence-of-fit bands for the mean are also shown. The strength appears to slightly increase with dose, approximately four percent at 8×10^9 rads, while the modulus appears unaffected. However, the size of the confidence band is sufficiently large that the location of the mean is uncertain to the extent that larger, perhaps significant, changes in flexural properties with radiation could have occurred. The appreciable uncertainty in the location of the mean does suggest that an additional emphasis on quality control of specimen preparation and/or testing procedures may be necessary.

FLEXURAL MODULUS FOR FOUR-PLY, UNIDIRECTIONAL T300/5208 COMPOSITE SPECIMENS. LONGITUDINAL FIBER DIRECTION



FLEXURAL STRENGTHS FOR FOUR-PLY, UNIDIRECTIONAL T300/5208 COMPOSITE SPECIMENS. LONGITUDINAL FIBER DIRECTION.

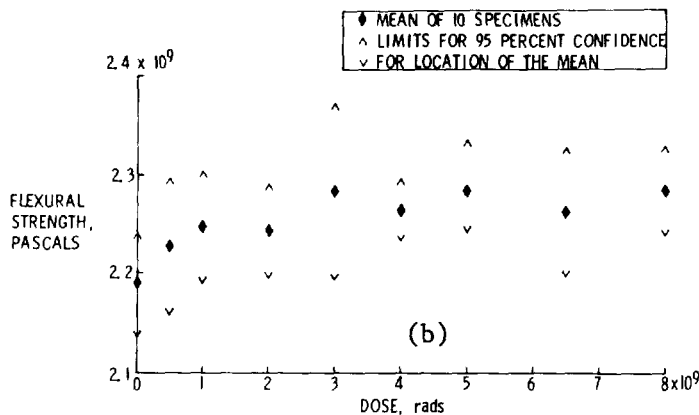
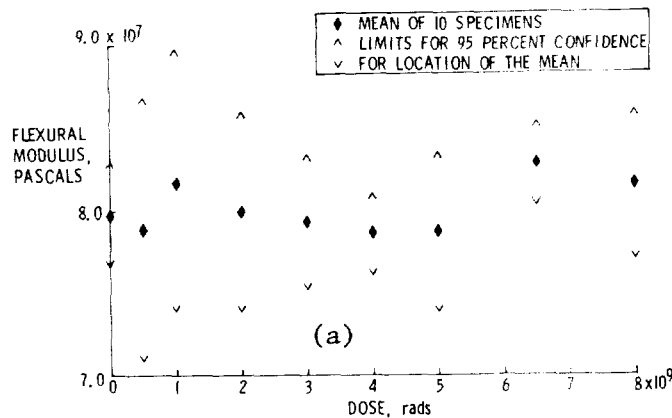


Figure 2

RADIATION EFFECTS ON FLEXURAL PROPERTIES OF A GRAPHITE/POLYIMIDE COMPOSITE

Similar exposures to electron radiation have been made on flexural unidirectional C6000/PMR15 composite specimens, with a longitudinal fiber orientation. The effects on flexural properties were very similar to those just shown for the graphite/epoxy composite material. In figures 3a and 3b, flexural data for specimens of the C6000/PMR15 composite with a transverse fiber orientation are shown for radiation doses also up to and including 8×10^9 rads. The specimens were fabricated at Langley Research Center from neat resin and tows of graphite fiber. For the transverse fiber direction, the means suggest no change in either modulus or strength. But, again the uncertainty in the location of the mean may have masked a more appreciable, perhaps significant, change due to the radiation. Transverse-oriented fiber, unidirectional flexural specimens of the graphite/epoxy composite will be studied in the future. Specimen preparation and testing procedures will be an important consideration while planning and conducting these tests.

FLEXURAL MODULI FOR FOUR-PLY, UNIDIRECTIONAL C6000/PMR15 COMPOSITE SPECIMENS. TRANSVERSE FIBER DIRECTION.



FLEXURAL STRENGTHS FOR FOUR-PLY, UNIDIRECTIONAL C6000/PMR15 COMPOSITE SPECIMENS. TRANSVERSE FIBER DIRECTION

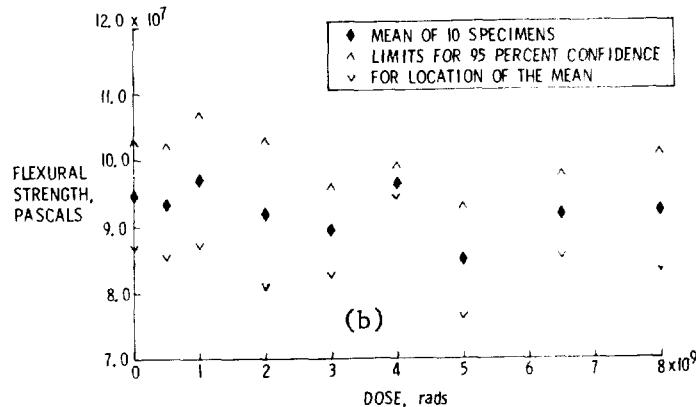
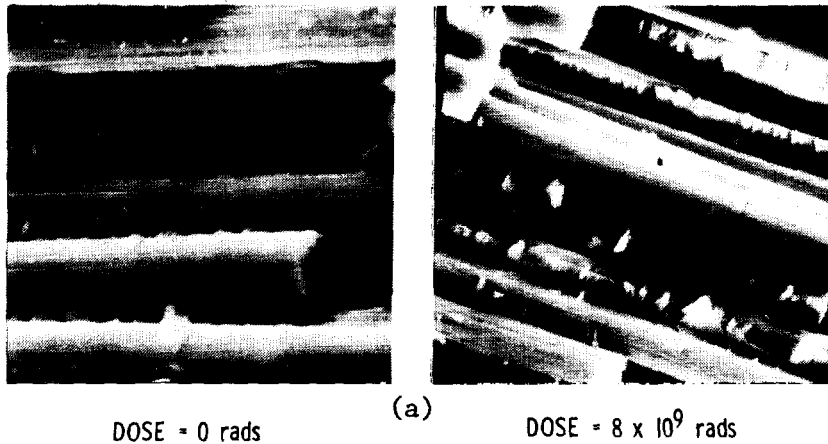


Figure 3

SCANNING ELECTRON MICROSCOPY OF FIBER/RESIN COMPOSITES

Photographs from scanning electron microscopic analysis of the failure edge of a flexural specimen are shown in figure 4a for T300/5208 and in figure 4b for C6000/PMR15. Neither pair of photographs shows a difference in the failure mode at the fiber-resin interface due to radiation exposure. Since the fiber-resin interaction is more mechanical interlocking than chemical interaction, the lack of change in the failure mode had, to a certain extent, been anticipated.

SCANNING ELECTRON PHOTOGRAPHS OF THE FAILURE EDGE OF FLEXURAL SPECIMENS OF GRAPHITE/EPOXY COMPOSITE



SCANNING ELECTRON PHOTOGRAPHS OF THE FAILURE EDGE OF FLEXURAL SPECIMENS OF GRAPHITE/POLYIMIDE COMPOSITE

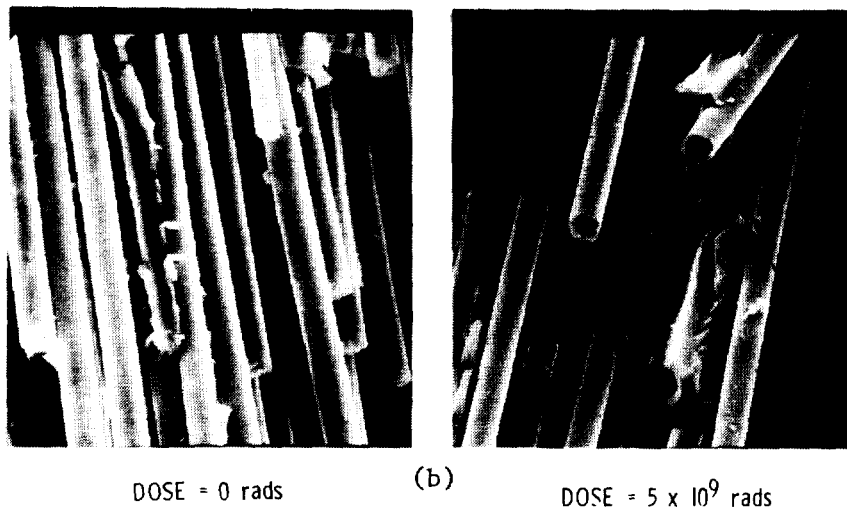
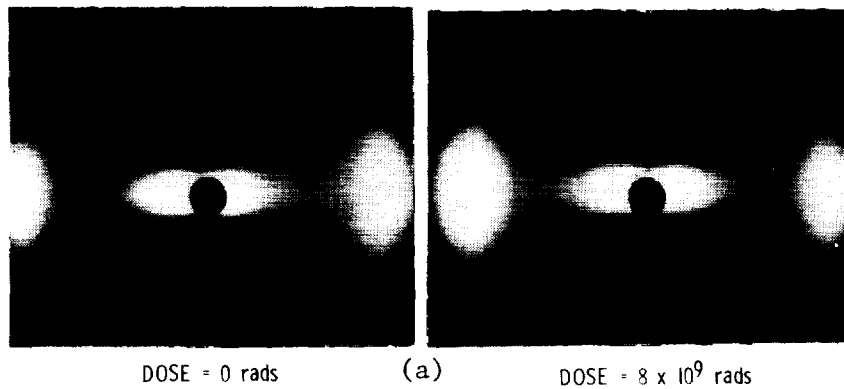


Figure 4

X-RAY DIFFRACTION ANALYSIS OF GRAPHITE/EPOXY COMPOSITE

Figure 5a is a pair of X-ray diffraction photographs of T300/5208 composite with no radiation exposure and with a radiation dose of 8×10^9 rads. There is no change in either the diffuse scatter due to the resin or the broad diffusion peak along the equator due to the graphite fiber. Therefore, the radiation did not affect the crystallinity, either of the amorphous resin or of the graphite fiber which originally consisted of either very small-size crystalline structure or numerous defects. A lack of change in crystallinity confirms that atomic displacement is not one of the effects of electron radiation. Figure 5b is a microdensitometric trace of the photographs. The amplitudes of the traces confirm that no differences exist.

WIDE ANGLE X-RAY PHOTOGRAPHS OF T300/5208 COMPOSITE WITH AND WITHOUT EXPOSURE TO ELECTRON RADIATION.



MICRODENSITOMETER TRACES OF WIDE ANGLE X-RAY PHOTOGRAPHS OF T300/5208

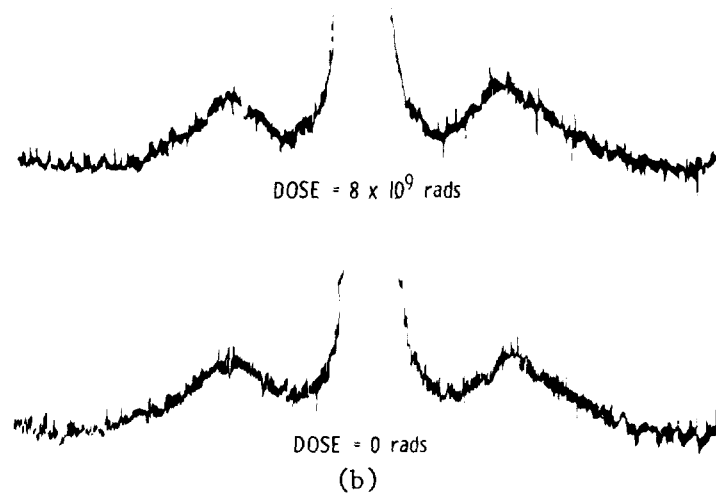
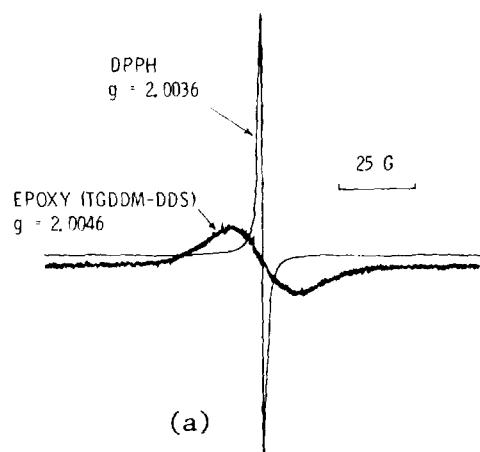


Figure 5

ELECTRON SPIN RESONANCE SPECTROSCOPIC ANALYSIS OF RADIATION EFFECTS

The major effect of radiation upon polymeric materials is the creation of chemical radicals, which are groups with unpaired electrons in molecular orbitals. The presences of these unpaired electrons in a specimen are measured by electron spin resonance (or electron paramagnetic resonance) spectroscopy. The specimen is simultaneously subjected to a fixed frequency signal and a sweeping magnetic field. At a particular combination of signal and field, characteristic of the electron's environment, the unpaired electron's spin is flipped and a net absorption of energy is detected. Usually, the absorption is detected in its first derivative form, as shown in figure 6a for tetraglycidyl diamino diphenyl methane, TGDDM, which has been cured with diamino diphenyl sulphone, DDS. The signal of diphenylpicrylhydrazyl, DPPH, is also shown because it is included with the specimen for calibration purposes. The epoxy's signal shown in figure 6a is due to radiation-generated radicals, the number of which varies with dose. The signal magnitude, position, and structure vary with radiation dose as shown in figure 6b.

ELECTRON SPIN RESONANCE SPECTRA OF ELECTRON-IRRADIATED EPOXY



ELECTRON SPIN RESONANCE OF ELECTRON-IRRADIATED EPOXY (TGDDM-DDS)

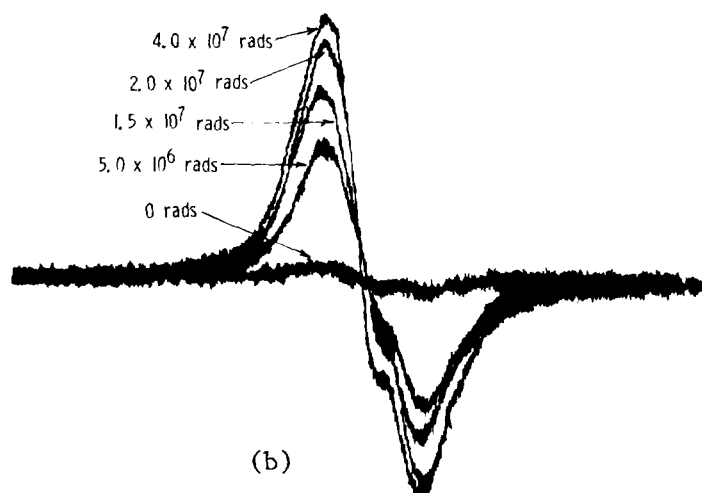
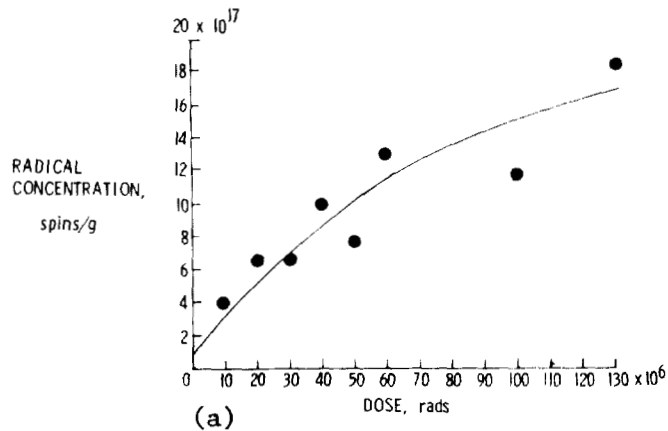


Figure 6

ELECTRON RADIATION-GENERATED RADICAL CONCENTRATIONS AND DECAYS IN EPOXY RESINS

The variation of radical concentration in the cured epoxy resin TGDDM-DDS with dose after room temperature exposures to electron radiation is shown in figure 7a. For 1.3×10^8 rads, the radical concentration at the end of exposure is approximately 1.9×10^{18} spins/g, or one spin for every 55 molecules. Figure 7b shows the decay in radical concentration at room temperature with time after exposure. Two radical distributions are present, as suggested by the sharp change in the slopes of the curves in figure 7b, one with a half-life on the order of twelve minutes and another with a much longer half-life. Consequently, the total number of spins per gram which occurred over a long exposure period was much larger than the value at the end of exposure and may have amounted to only several molecules per spin. The current literature suggests that each spin would probably, in the end, generate a cross-link or chain scission. In contrast, based upon the mechanical data discussed earlier, the radicals within this epoxy may have decayed in a process of self-healing. But, we must also point out that the EPR data, because of the large radical concentration, can be suggesting a review of the techniques used for the measurements of mechanical properties.

INITIAL RADICAL CONCENTRATIONS IN EPOXY RESIN AFTER ELECTRON IRRADIATION



ROOM-TEMPERATURE DECAY OF ELECTRON-RADIATION-GENERATED RADICALS IN EPOXY RESIN

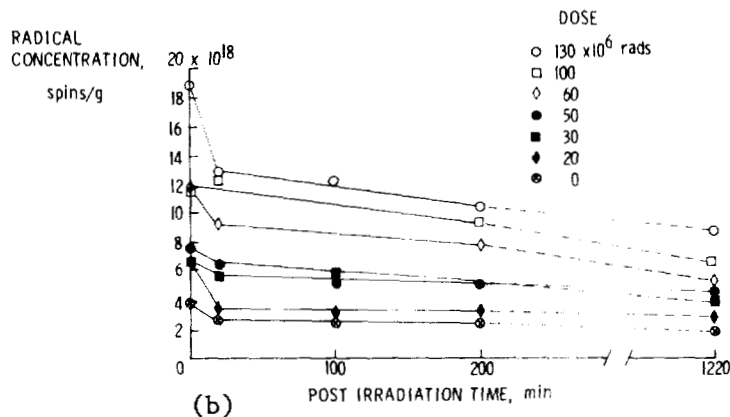
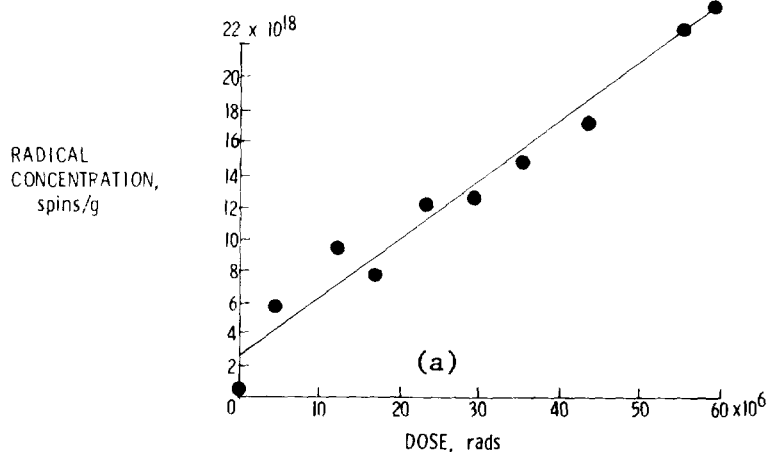


Figure 7

GAMMA RADIATION-GENERATED RADICAL CONCENTRATIONS AND DECAY IN EPOXY RESIN

Radical concentrations in epoxy resin for a range of doses from gamma radiation are shown in figure 8a. The concentrations up to the maximum dose studied, 6×10^7 rads, are approximately twice that for electron radiation. The higher density may be due to the fact that the gamma exposures were conducted at cryogenic temperatures; hence, short-lived species were trapped. This appears, to an extent, to be the case from the decay data shown in figure 8b. Presently, three radical distributions, each with different half-lives, are believed to be within these decay data. The concentration at end of exposure and the decay during exposure suggest, as in the case of the electron radiation, that the total spin formation was sufficient to cause changes in mechanical properties, unless self-healing was the dominant process. Additional studies using EPR for the study of epoxy resin after electron and gamma radiation will be conducted to measure radical densities at higher doses and related to the mechanical data, both for this and other epoxy systems.

INITIAL RADICAL CONCENTRATIONS IN EPOXY RESIN AFTER GAMMA IRRADIATION



ROOM-TEMPERATURE DECAY OF GAMMA-RADIATION-GENERATED RADICALS IN EPOXY RESIN

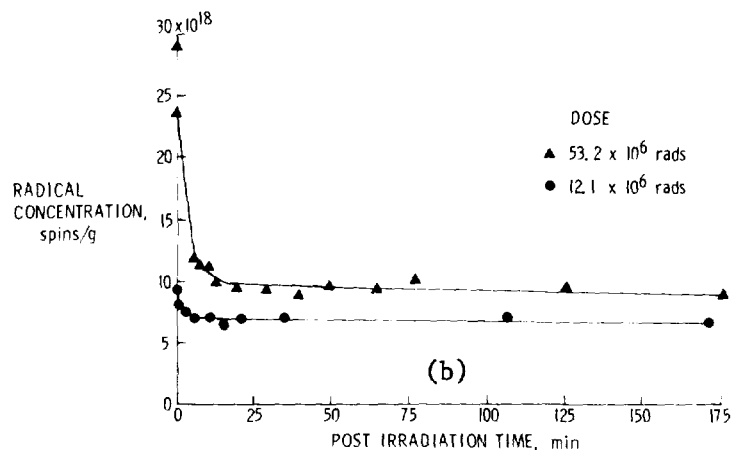


Figure 8

SUMMARY

The study at North Carolina State University has, to date, shown little or no change in flexural properties of miniature specimens of a graphite/epoxy composite due to exposure to electron and to gamma radiation. (A study of just the flexural properties of specimens of a graphite/polyimide composite also showed little or no change due to exposure to radiation.) In addition, no change in failure mode at the fiber-resin interface and in the crystallinity of the fiber and the resin has been found. The absence of changes at the fiber-resin interface and in the crystallinities was expected. However, the observation of only a small change in flexural properties was a pleasant surprise. Some doubt in the observation of stable flexural properties is cast, though, by electron paramagnetic resonance spectra of a relatively large number of radiation-generated radicals. The latter generally lead to a change in cross-linking and in chain-scissioning which should alter mechanical properties. Consequently, the measurements of flexural properties will continue, both for the epoxy discussed in this report and for simpler epoxy systems. Also, fundamental analysis will be conducted for the higher doses used in the mechanical property studies. EPR and other fundamental methods will be used to better understand the chemical changes and mechanisms caused by the radiation.

SUMMARY

RESULTS

1. - NO MAJOR CHANGES IN FLEXURAL PROPERTIES OF SPECIMENS OF A GRAPHITE EPOXY COMPOSITE FOR RADIATION DOSES UP TO 5×10^9 rads.
2. - NO CHANGES IN THE FAILURE MODE AT THE FIBER-RESIN INTERFACE OR IN THE CRYSTALLINITY OF THE FIBER OR THE RESIN FOR RADIATION DOSES UP TO 5×10^9 rads.
3. - A HIGH CONCENTRATION OF RADIATION-GENERATED RADICALS WITH MULTIPLE DECAY CONSTANTS FOR DOSES UP TO 130 Mrads.

FUTURE WORK

1. - CONTINUED STUDY OF FLEXURAL PROPERTIES OF EPOXY-BASED MATERIALS FOR SEVERAL EPOXY SYSTEMS.
2. - FUNDAMENTAL ANALYSIS FOR CHARACTERIZATION OF RADIATION EFFECTS ON THE CHEMICAL STRUCTURE OF EPOXY RESINS

Figure 9