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Summary

The effects of electron radiation on Ultem, a polyetherimide manufactured by General Electric Company, were studied for total absorbed doses from 1.0 kGy to 100 MGy at absorbed dose rates from 0.01 to 100 MGy/hr. Tensile property tests and electron paramagnetic resonance (EPR) spectroscopic measurements were conducted on Ultem film. (The EPR spectroscopy provides the density of radicals which are created when molecular bonds are homolytically broken by the radiation.)

There was an effect of total absorbed dose on the tensile properties and the radical densities of Ultem. For a 1.0-kGy total absorbed dose, the elastic modulus, the ultimate tensile strength, and the elongation-to-failure all decreased slightly. These changes in the tensile properties were maintained for all total absorbed doses up to 1.0 MGy. Above 1.0 MGy for the elastic modulus and above 2.5 MGy for the ultimate strength, there were additional changes. For a 100-MGy total absorbed dose, the modulus and the strength were, respectively, 10 percent and 20 percent less than the nonexposed values. A pronounced decrease in elongation-to-failure occurred at approximately 2.5 MGy. Above this total absorbed dose, the elongation-to-failure was 4 percent of the nonexposed value. In contrast to the tensile data, the radical densities increased monotonically with total absorbed dose.

There was no significant absorbed dose rate effect observed for either the tensile properties or radical densities.

A molecular model for the radiation effects has been reported earlier (NASA TP-2663, 1987). The model showed that the radical formation was due to homolytic scissioning of primary bonds within the linear molecular structure and that the radicals were the source of subsequent crosslinking. The chain scissioning and crosslinking cause the changes in the tensile properties. This published model of radiation effects and the radical densities and their rates of change presented in this report are used to explain the effects of total absorbed dose and absorbed dose rate on the tensile properties of Ultem. The onset of changes in the tensile properties at 1.0 to 2.5 MGy occurred because 25 percent or more of the polymer molecules were crosslinked. An absorbed dose rate effect was not found because the rate of radical creation significantly exceeded the rate of radical decay for all the exposures conducted.

Introduction

Polymer resins are useful in space as low density insulations, solar-cell substrates, and composite matrices. Long-term stability in ionizing space radiation environments, as in geosynchronous orbit, is an important consideration for these applications.

Polyetherimides (PEI) are among the high-temperature thermoplastic polymers being considered for future space applications. They maintain desirable mechanical properties at temperatures of 300°C or above. They can be used as foams, films, castings, and matrices for fiber-reinforced composites. However, a recent study, reference 1, has shown that the tensile properties of a PEI are significantly affected by the total absorbed doses anticipated for approximately 30-year service in geosynchronous orbit.

The research reported in references 1 3 used total absorbed doses from 20 to 60 MGy at an absorbed dose rate of 10 MGy/hr exposures to assess the changes in the tensile properties of polyimides for total absorbed doses equivalent to approximately 30-year exposure to the ionizing radiation in geosychronous orbit (GEO). Smaller total absorbed doses were not studied to determine the doses at which changes are first observed nor to determine how the changes vary with total dose. The earlier work used an absorbed dose rate of 10 MGy/hr, for which the specimen temperature was found not to exceed 38°C. An assumption was made that there would not be thermal artifacts at or below this temperature. Additional absorbed dose rates were not studied.

In reference 2, the effects of the ionizing radiation on the molecular structure of the PEI were determined to be both chain scissioning and crosslinking. In brief, the radiation cleaved the main-chain bonds at two sites and dehydrogenated the pendant group as shown in figure 1. These cleavages, or chain scissions, and dehydrogenations were homolytic; therefore, several types of radicals were generated. (Homolytic bond cleavage means that the atoms sharing the bond each retained an electron from the pair shared during bonding; therefore each has an unpaired electron.) The chemical structures of the radicals are shown in figure 2. In all, six different radicals were created. Two of these radicals, the hydrogen and the phenyl, were not observed because they immediately combined with one another. The other four radicals, as shown in figure 3, generated crosslinked structures as shown in figure 4. (The two radicals not observed were known to have initially existed because of the detection of the other four.)

The objectives of this study were (1) to determine the effects of ionizing radiation on the tensile and molecular properties of the polyetherimide for total absorbed doses which are expected in GEO for lengths of time from hours to years,

(2) to determine the effects of absorbed dose rate, and (3) to correlate the radical density and tensile property data to understand total absorbed dose and absorbed dose rate effects. In this report, data are presented and compared for total absorbed doses from 1.0 kGy to 100 MGy and for absorbed dose rates from 0.01 MGy/hr to 100 MGy/hr. The total absorbed doses are equivalent to exposure times from 2.5 hr to 30 years in GEO. The absorbed dose rates are accelerations of the absorbed dose rate in GEO by factors from 26 to 2.6×10^5.

Materials and Specimens

The polyetherimide material was Ultem, a product of General Electric Company. The Ultem was type 1000, the density for which is 1.27 g/cm^3, and was in the form of 0.0075-cm film for both the EPR and the tensile specimens. The tensile specimens were 0.5 ± 0.0025 cm wide and 15 ± 0.25 cm long, with a gage length of 5 cm. The EPR specimens were 0.25 ± 0.0025 cm wide and 0.15 ± 0.0075 cm long. The specimens were fabricated from larger pieces of film, using dual razor blade cutters. Details of the specimen preparation are in reference 2. At least six tensile and four EPR specimens were tested for each exposure condition.

Experimental Procedures

Tensile and EPR specimens in this study were simultaneously exposed to 100-keV electron radiation for total absorbed doses from 1.0 kGy to 100 MGy at absorbed dose rates from 0.01 to 100 MGy/hr. A 1-kGy total absorbed dose is equivalent to a 2.5-hr exposure in GEO. A 100-MGy total absorbed dose is equivalent to the largest absorbed dose estimated for a 30-year exposure in GEO.

Both the tensile and the EPR specimens were placed in liquid nitrogen within 3 min of the completion of an exposure to "freeze" the molecular structural components present at the end of the exposure. For the EPR tests, this meant that all the unpaired electrons (radicals) caused by breaking molecular bonds (except those with half-lives of seconds or less) were trapped and therefore their spectra could be observed. The testing began immediately thereafter.

The tensile specimens were brought to room temperature, one at a time, and tested by using a model 1130 tabletop Instron universal mechanical test machine. The faces of the specimen grips were rubber surfaced. The grip displacement during each test was monitored with a direct displacement transducer (DCDT). The outputs of the DCDT and the load cell were recorded on an X-Y recorder. The crosshead rate was 0.2 in/min. A minimum of six specimens were tested per exposure condition.

For recording spectra, the EPR specimens were placed in quartz glass tubes. The tubes were sealed with rubber caps, and the ends of the tubes containing the specimens were kept in liquid nitrogen until the first EPR scan, during which they were maintained in a thermal environment of −188°C. The EPR spectrometer was a Varian E-Line Century Series Model E-109E. The spectrometer system included a variable temperature accessory for controlling the temperature during the scans, a precision microwave frequency counter, and a gaussmeter. Following the first scan, the sealed tubes were brought to room temperature for 10 min and immediately afterwards stored in the liquid nitrogen. Then, another cycle of EPR scanning was conducted, followed by another 10 min at room temperature. In this manner, the postirradiation radical decay at room temperature was measured for accumulated exposure at room temperature up to 10 hr.

More complete descriptions of the radiation facility, the testing equipment, the specimens, and the manner in which they were prepared and handled are given in reference 2. The methods used for monitoring the dose rate and the specimen temperature and other experimental details are also described in reference 2.

Results and Discussion

Tensile Properties

Load-elongation behavior. With no radiation exposure, Ultem film elongates under tensile loading in a manner shown in figure 5. The load increases with elongation through the elastic region and into the yield or plastic region (region 1 in fig. 5). Further loading causes a local necking in the specimen, during which the load drops because of the sudden additional yielding (region 2). The necking then extends and the load gradually increases (region 3) until the specimen breaks, at which point the load is nearly back to the value it was at the onset of the initial local necking. For specimens exposed to electron radiation, the extent of the local necking is reduced, with increasing total absorbed dose, until there is none; that is, the elongation is uniform along the entire gage length. Further increases of the total absorbed dose reduce the extent of this uniform elongation.

Elastic modulus. In figure 6, the room temperature elastic modulus is plotted as a function of the total absorbed dose. The band shown for each group of data is the envelope for 1σ (one standard deviation) of the data. The tensile modulus decreased

slightly for the smallest total absorbed dose. The average nonirradiated value was 427 ksi, and the average value for a 1-kGy total absorbed dose was 409 ksi, a 4-percent decrease which was within the 1σ of the data. At the largest total absorbed dose, 100 MGy, the average modulus was 384 ksi, a 10-percent decrease from the nonirradiated value.

A determination of absorbed dose rate effects on the modulus can be made by plotting a portion of the modulus data as a function of absorbed dose rate. The data at 0.1, 1.0, 10, and 100 MGy in figure 6 (the total absorbed doses for which there was more than one dose rate) are plotted in figure 7 as a function of absorbed dose rate. There is no trend with respect to absorbed dose rate. There is overlap of the 1σ bands, and therefore there is no statistical difference between absorbed dose rates.

Ultimate strength. The ultimate strength data for Ultem film at room temperature are shown as a function of total absorbed dose in figure 8. The ultimate strength was 15.9 ksi for 1-kGy total absorbed dose, a 7-percent decrease from the nonirradiated value of 17.0 ksi. The change was approximately the same for total absorbed doses up to approximately 2.5 MGy, but above this total absorbed dose the ultimate strength decreased further until, at 100 MGy, it was 13.4 ksi, a 21-percent decrease from the nonirradiated value. The onset of additional change at the higher total absorbed doses appears to be a total absorbed dose effect and not an absorbed dose rate effect. Although the ultimate strength data point for 100 MGy/hr suggests an absorbed dose rate effect, it is not interpreted as such because the modulus data and the elongation-to-failure data for that absorbed dose rate do not suggest an absorbed dose rate effect. No explanation can be offered for why the ultimate tensile strength is the value it is for 100 MGy/hr.

The lack of a significant effect of absorbed dose rate on the ultimate strength may be seen by replotting a portion of the ultimate strength data as a function of absorbed dose rate. In figure 9, data for 0.1-, 1-, and 10-MGy total absorbed doses have been plotted as a function of absorbed dose rate. There is no significant change with absorbed dose rate and the 1σ bands overlap each other.

Elongation to failure. Elongation-to-failure (ETF) data are shown as a function of total absorbed dose in figure 10. For total absorbed doses less than 2.5 MGy, the effect was small. At the smallest total absorbed dose, 1 kGy, the ETF was 116 percent, a 9-percent decrease from the nonirradiated value of 126-percent elongation. For total doses of 2.5 MGy or larger, the ETF reduced to 28 percent or less. The ETF was 7.2 percent at 100 MGy, a 94-percent decrease from the nonirradiated value. Clearly there is a total absorbed dose threshold at approximately 2.5 MGy. In earlier studies, references 1–3, the large decreases in ETF at the higher total absorbed doses were shown to be due to crosslinking. The threshold at 2.5 MGy suggests either a sharp transition from little or no crosslinking to extensive crosslinking, or that a threshold amount of crosslinking was required for the large change in ETF. Solubility tests, which have been described in reference 2, were also conducted for these exposures; they indicated that crosslinking occurred for all the total absorbed doses and that the extent of crosslinking increased with the total dose. Hence, the change in ETF at approximately 2.5 MGy is an indication that a threshold amount of crosslinking is responsible, as opposed to a transition from no crosslinking to extensive crosslinking.

Figure 11 is a plot of the portion of ETF data in figure 10 for which there was more than one absorbed dose rate per total dose. The three lines, each of which connect data points for a total absorbed dose, are practically horizontal. Thus different absorbed dose rates did not significantly alter the effect of a given total absorbed dose.

Absorbed Dose Rate Effects

The unpaired electron densities 3 min after completion of the electron exposures are shown in figure 12. (In this study the unpaired electrons were radicals. Each electron has a spin value of 0.5.) As seen from the figure, there is no absorbed dose rate effect. Obviously the electron densities shown result from a combination of both radical creation and decay. The creation and decay rates must be studied separately to understand why there is no absorbed dose rate effect.

The decay of the radiation-generated radical density, starting 3 minutes after the completion of a 2.5-MGy absorbed dose exposure, is shown in figure 13. The decay curve has two parts, an initial portion, defined as the first six data points, and a long-time linear portion, represented by the last six data points.

The long-time portion is a straight line and fits first-order kinetics as discussed in reference 4:

$$-d(R_d)/dt = kR_d$$

The radical density R_d and the rate constant k are determined to be

$$R_d = 7.471 \times (10)^{16} e^{-0.086t}$$

and

$$k = 0.086s^{-1}$$

The rate of decay may be evaluated from this expression for any time; for example, at $t = 5$ hr,

$$d(R_d)/dt = -4.179 \times (10)^{15} \text{ spins/g-hr}$$

The data from the initial portion of the decay curve fit the expression for second-order kinetics

$$-d(R_d)/dt = 2k_1(R_d)^2$$

which integrates to

$$1/R_d - 1/R_{do} = 2k_1 t$$

where R_{do} is the radical density at time $t = 0$, with

$$R_{do} = 1.5 \times (10)^{17} \text{ spins/g}$$

$$d(R_d)/dt = -4.697 \times (10)^{17} \text{ spins/g-hr at } t = 0$$

and

$$k_1 = 5.17 \times (10)^{-18} \text{ (hr-spins/g)}^{-1}$$

In comparison to the decay rates at $t = 0$ hr and $t = 5$ hr, the rate of radical creation for the 2.5-MGy exposure was much higher. The dose was absorbed at a rate of 10 MGy/hr. Therefore, 1.56×10^{22} eV/g were absorbed at a rate of 6.25×10^{22} eV/g-hr. If each ion pair caused by this exposure resulted in a pair of radicals, then approximately 32 eV were required for every two radicals, according to reference 5. Thus, the total number of radicals created during the exposure was 9.7×10^{20} per gram at a rate of 3.9×10^{21} per gram per hour. This rate is four orders of magnitude greater than the decay rate at $t = 0$ hr. Using the same set of assumptions, the lowest absorbed dose rate in this study created radicals at a rate of 3.9×10^{19} per gram per hour, which is two orders of magnitude higher than the initial rate of radical decay. In other words, the rate at which radicals were created by the irradiations exceeded the rate at which these radicals decayed for all the absorbed dose rates investigated and, therefore, there was no absorbed dose rate effect for the tensile properties.

Total Absorbed Dose and Broken Bond Thresholds for Crosslinking

In the preceding discussion of elongation-to-failure data the large change in ETF for total absorbed doses of 2.5 MGy and higher was attributed to a threshold amount of crosslinking where the crosslinking monotonically increases with total absorbed dose. But crosslinking requires that bonds are broken in the original linear molecular structure. Therefore, there should also be a threshold of broken bond density for the large change in ETF to occur. The ETF is plotted as a function of broken bond density (one-half the radical density) in figure 14. Indeed, there appears to be a value for the broken bond density below which there is little or no change and above which there is a very extensive decrease. The threshold value, from figure 14, is approximately 7×10^{16} broken bonds per gram of material.

In the preceding discussion of absorbed dose rate effects, the total number of radicals created per gram of material during the exposure at 10 MGy/hr was estimated to be 9.7×10^{20}, which is twice the total number of broken bonds per gram of material. Not every broken bond will result in a crosslink but, as reference 6 indicates, significant changes in the properties of a polymer will occur if 0.1 percent of the changes, such as crosslinking, are permanent. If 0.1 percent of the broken bonds were to result in crosslinking, then 4.9×10^{17} crosslinks per gram of material would occur. The average molecular weight of Ultem 1000 is 42 000 g/mole (verbal communication with Paul M. Hergenrother, Polymeric Materials Branch, Materials Division, NASA Langley Research Center) so there are 1.48×10^{19} molecules per gram of material. Therefore, at least approximately 3 percent of the polymer molecules must be crosslinked in order for a change in elongation-to-failure to occur. Since hydrogen entrapment occurred, therefore preventing self-healing, the percentage was probably an order of magnitude higher.

Concluding Remarks

The threshold values of total absorbed dose for causing changes in tensile properties of a polyetherimide film and the limitations of the absorbed dose rate for accelerated-exposure evaluation of the effects of electron radiation in geosynchronous orbit have been studied. Total absorbed doses from 1.0 kGy to 100 MGy and absorbed dose rates from 0.01 to 100 MGy/hr were investigated.

Total absorbed doses less than 2.5 MGy did not significantly change the tensile properties of the film, whereas absorbed doses 2.5 MGy or larger significantly reduced the elongation to failure. From electron paramagnetic resonance spectroscopic measurements, at least 3 percent, perhaps as much as an order of magnitude higher, of the molecules of the originally linear polymer were crosslinked by the 2.5-MGy absorbed dose.

There was no measurable effect of the absorbed dose rate on the tensile properties. The rate at which

radicals were created by the irradiations exceeded the rate at which these radicals decayed, for all the absorbed dose rates investigated.

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June 28, 1989

References

1. Long, Edward R., Jr.; and Long, Sheila Ann T.: *Spectroscopic Comparison of Effects of Electron Radiation on Mechanical Properties of Two Polyimides.* NASA TP-2663, 1987.
2. Long, Edward R., Jr.; and Long, Sheila Ann T.: *Spectroscopic Analysis of Radiation-Generated Changes in Tensile Properties of a Polyetherimide Film.* NASA TP-2429, 1985.
3. Long, Sheila Ann T.; Long, Edward R., Jr.; Ries, Heidi R.; and Harries, Wynford L.: Electron-Radiation Effects on the AC and DC Electrical Properties and Unpaired Electron Densities of Three Aerospace Polymers. *IEEE Trans. Nucl. Sci.*, vol. NS-33, no. 6, Dec. 1986, pp. 1390–1395.
4. Matheson, Max S.; and Dorfman, Leon M.: *Pulse Radiolysis.* M.I.T. Press, c.1969.
5. Bolt, Robert O.; and Carroll, James G., eds.: *Radiation Effects on Organic Materials.* Academic Press, Inc., 1963.
6. Spinks, J. W. T.; and Woods, R. J.: *An Introduction to Radiation Chemistry.* John Wiley & Sons, Inc., c.1964.

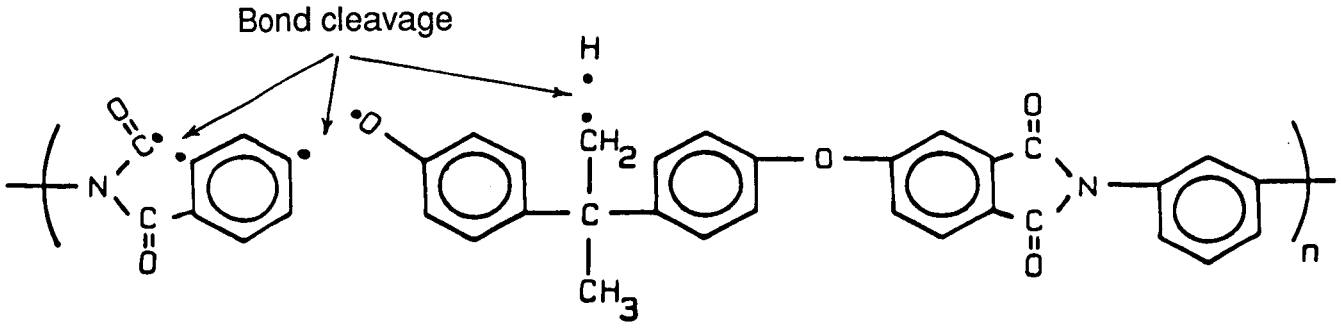


Figure 1. Homolytic bond breakage in polyetherimide caused by electron radiation.

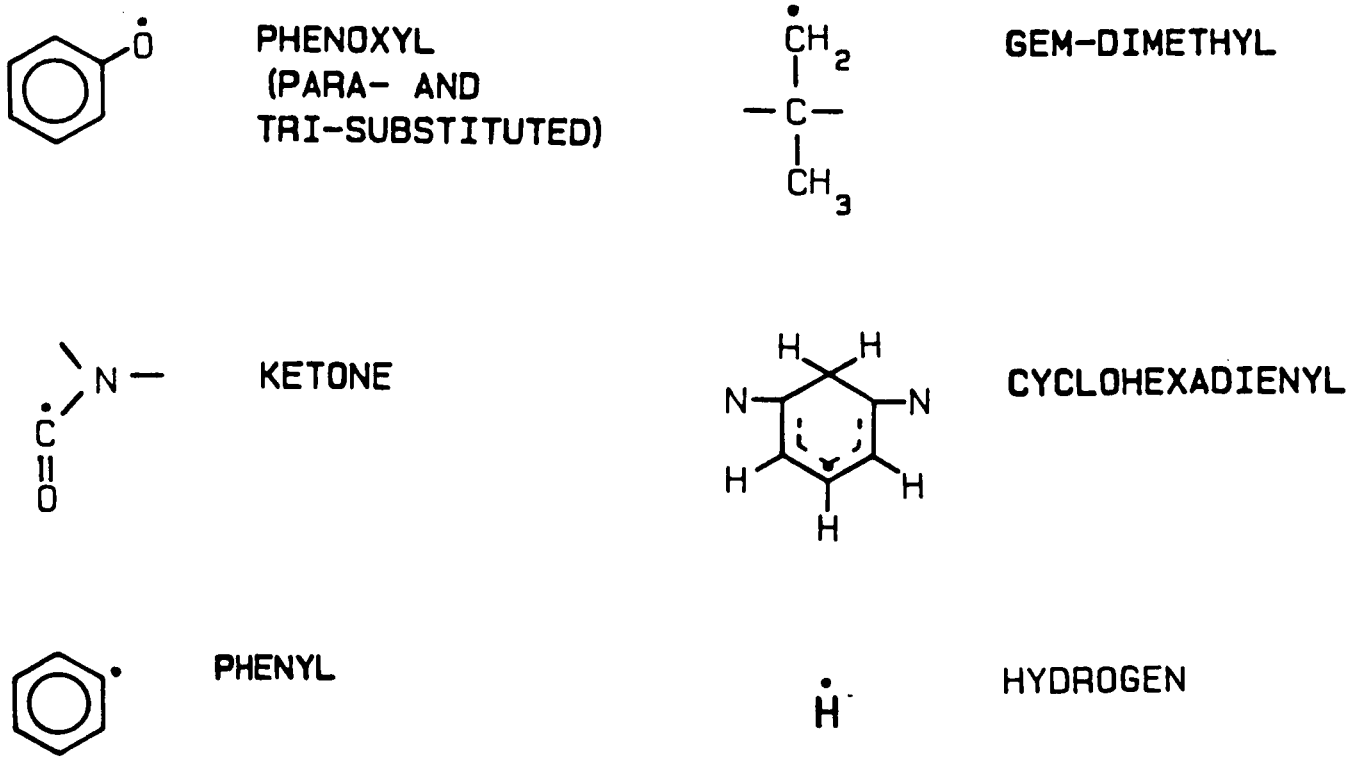


Figure 2. Radical species in polyetherimide generated by electron radiation.

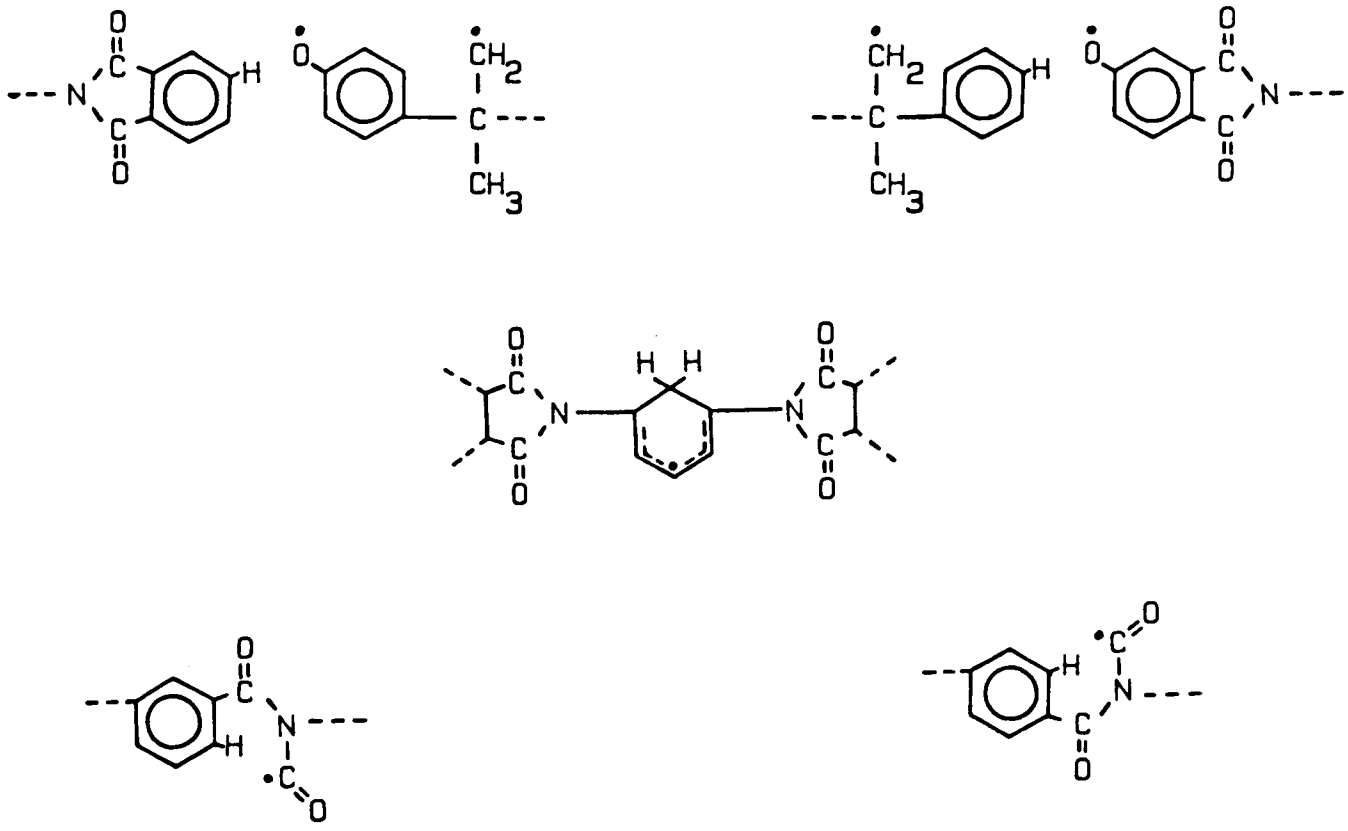
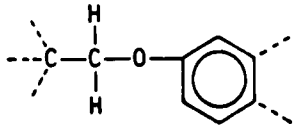
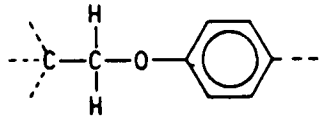


Figure 3. Radicals in electron-irradiated polyetherimide.

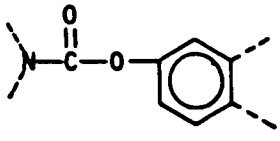
(a) Ethylene.

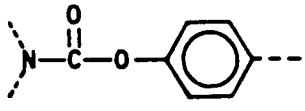
(b) Amide.



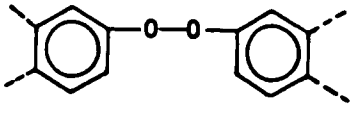


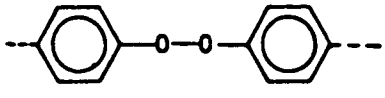
(c) Ether.

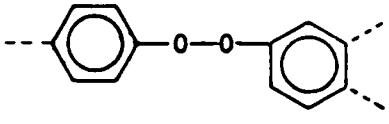




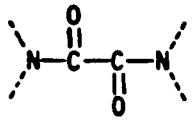
(d) Urethane.







(e) Peroxide.



(f) Ketone-ketone.

Figure 4. Crosslinked structures in electron-irradiated polyetherimide formed by combinations of radicals.

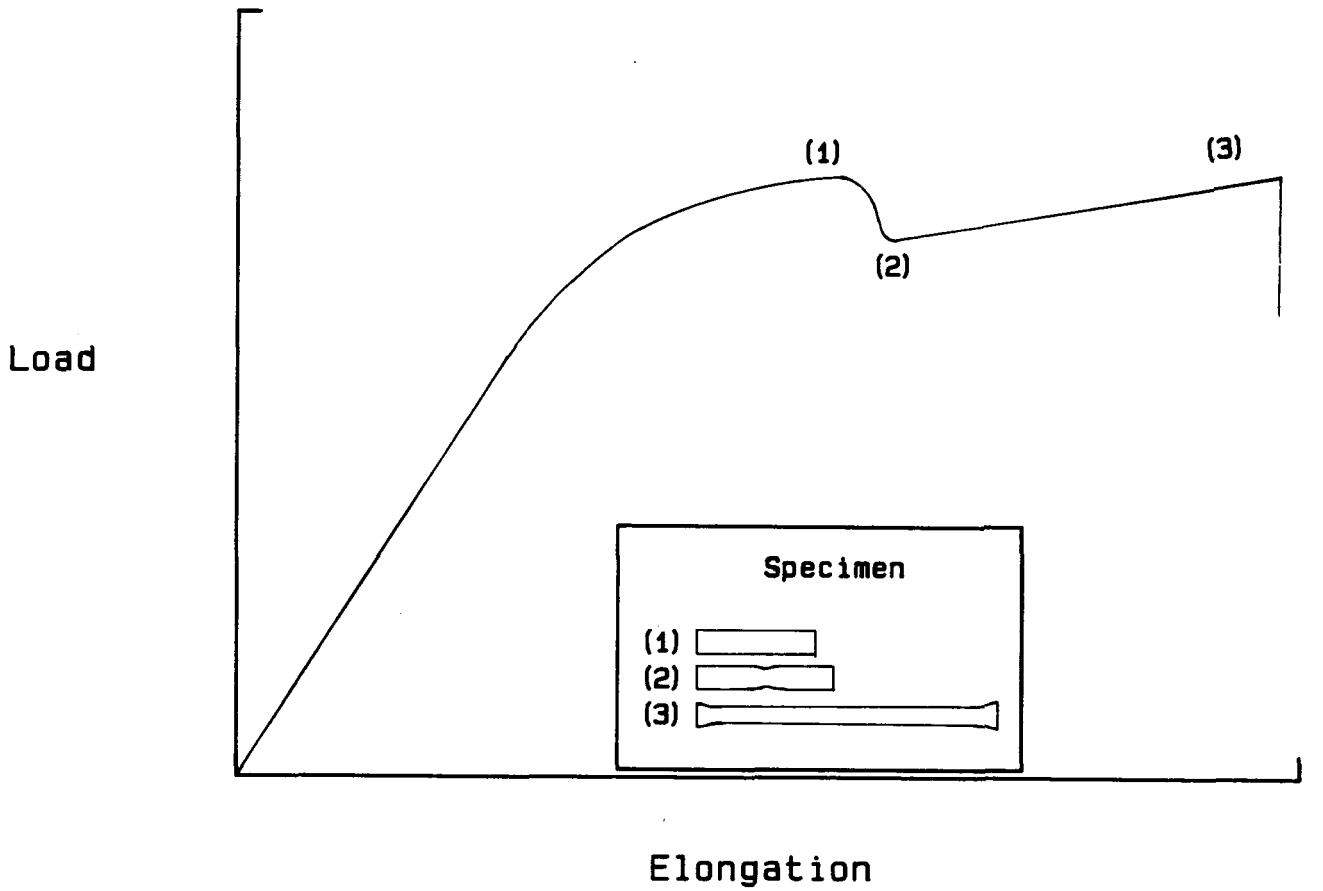


Figure 5. Relationship between load and elongation for nonirradiated polyetherimide. The shape of the gage section of the specimen at three elongations is shown in the insert.

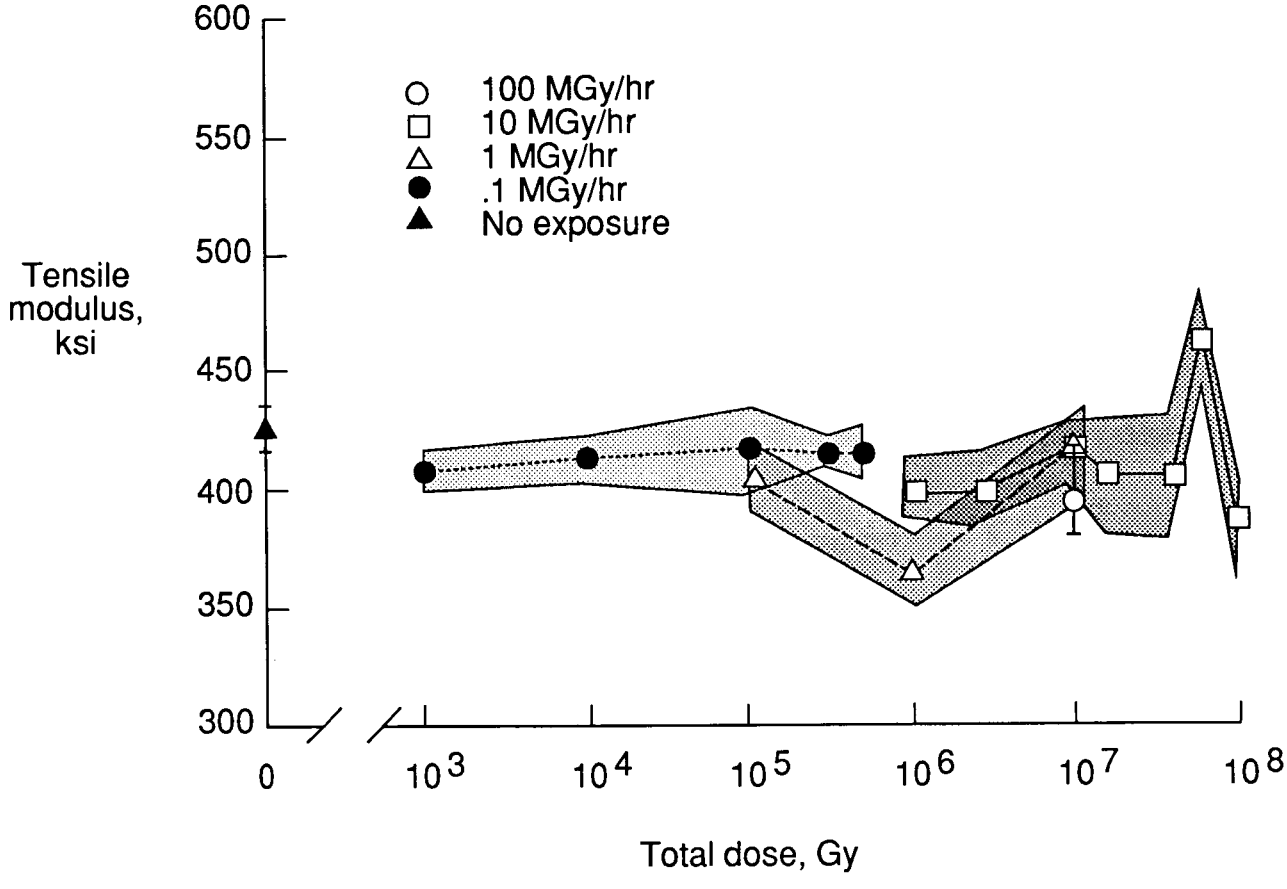


Figure 6. Elastic tensile modulus of electron-irradiated polyetherimide for four dose rates.

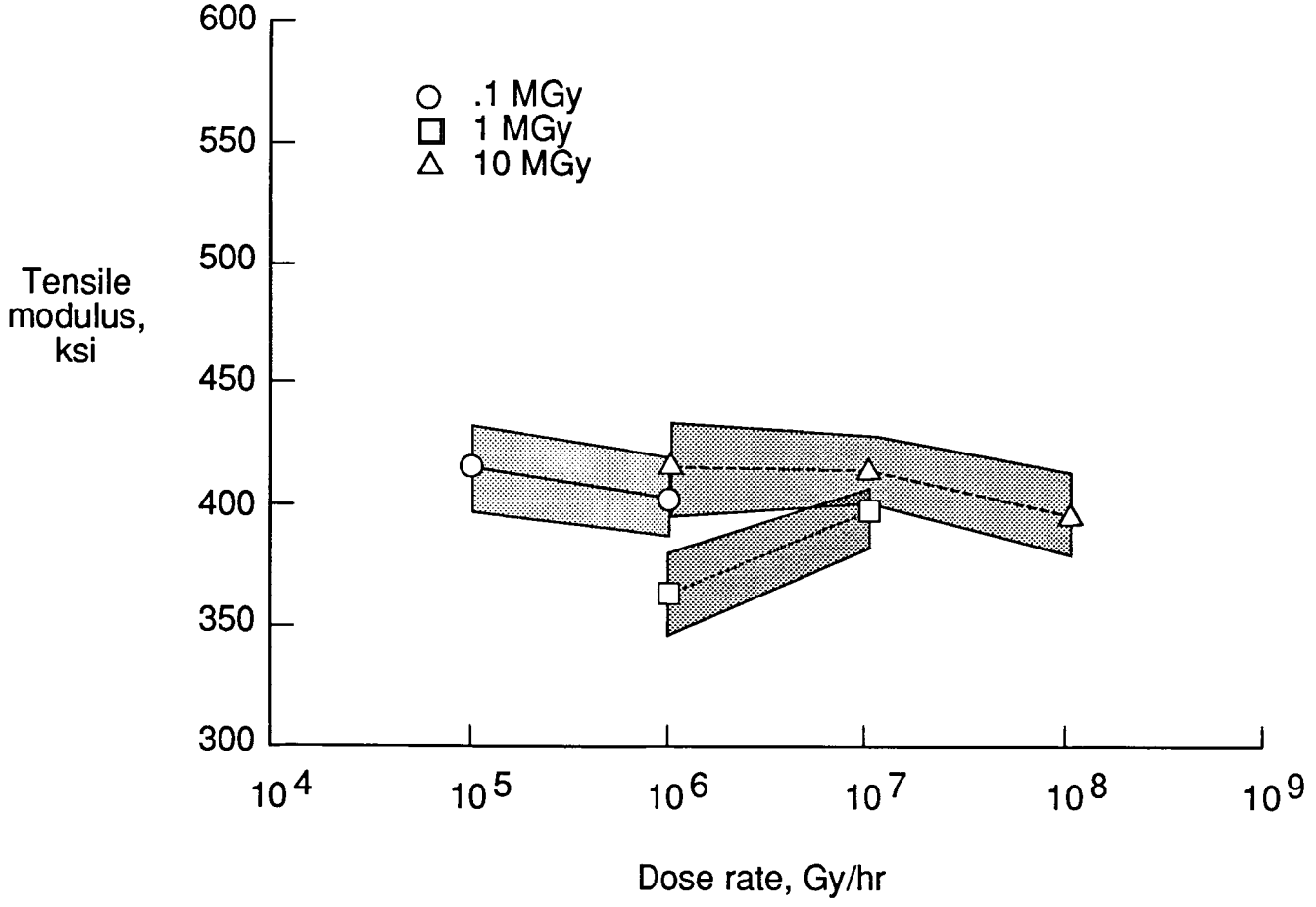


Figure 7. Elastic tensile modulus of electron-irradiated polyetherimide for three total absorbed doses.

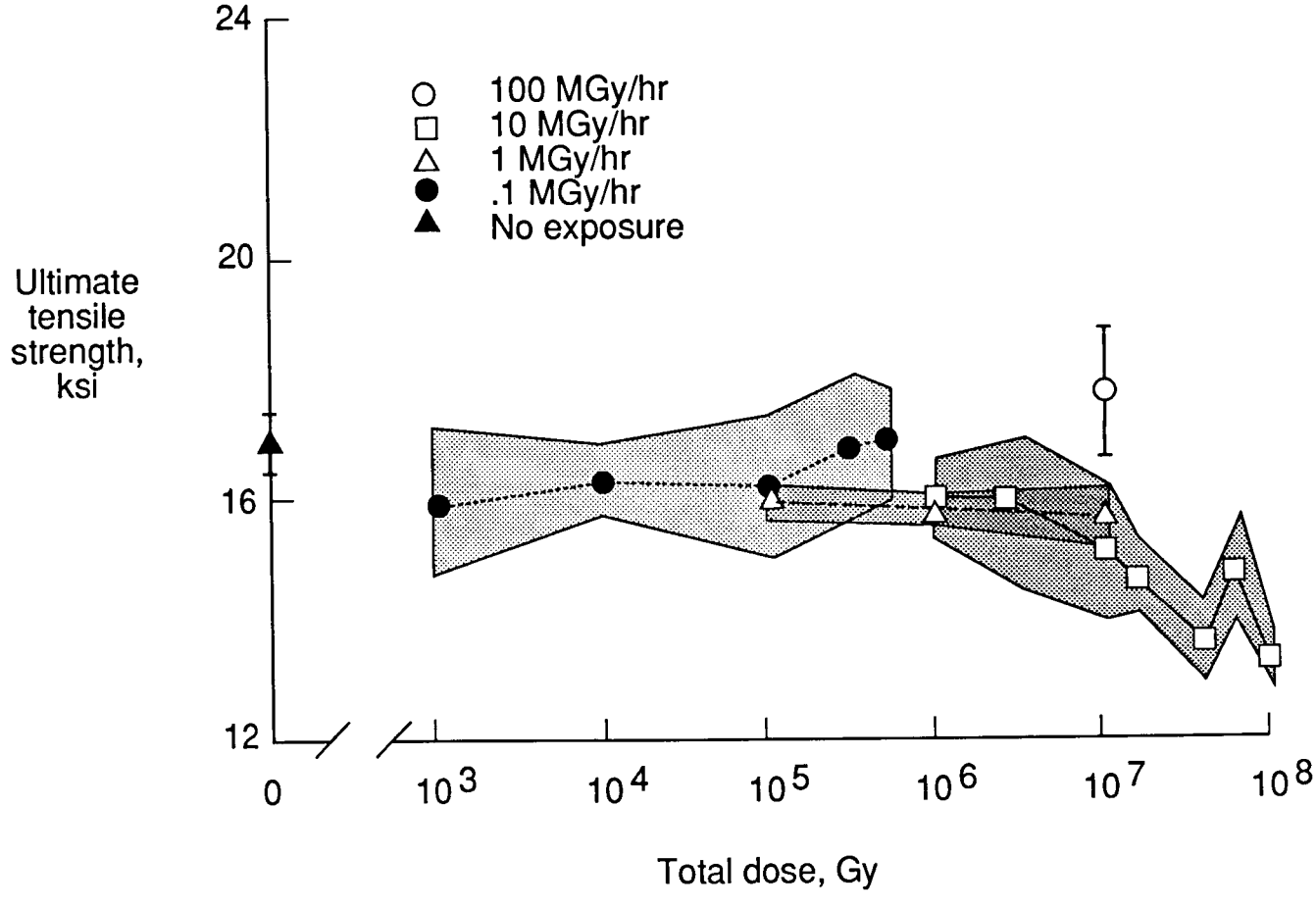


Figure 8. Ultimate tensile strength of electron-irradiated polyetherimide for four dose rates.

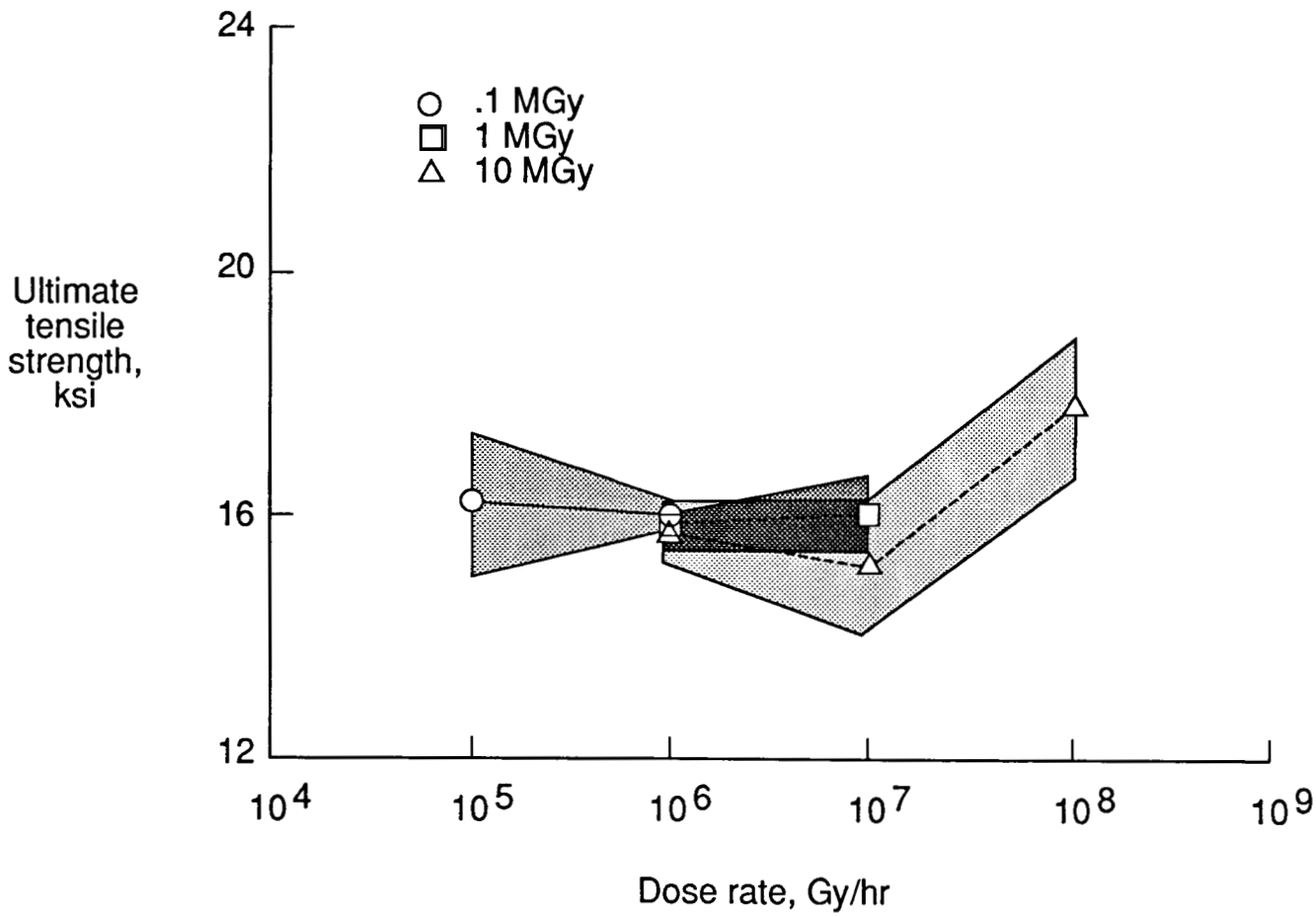


Figure 9. Ultimate tensile strength of electron-irradiated polyetherimide for three total absorbed doses.

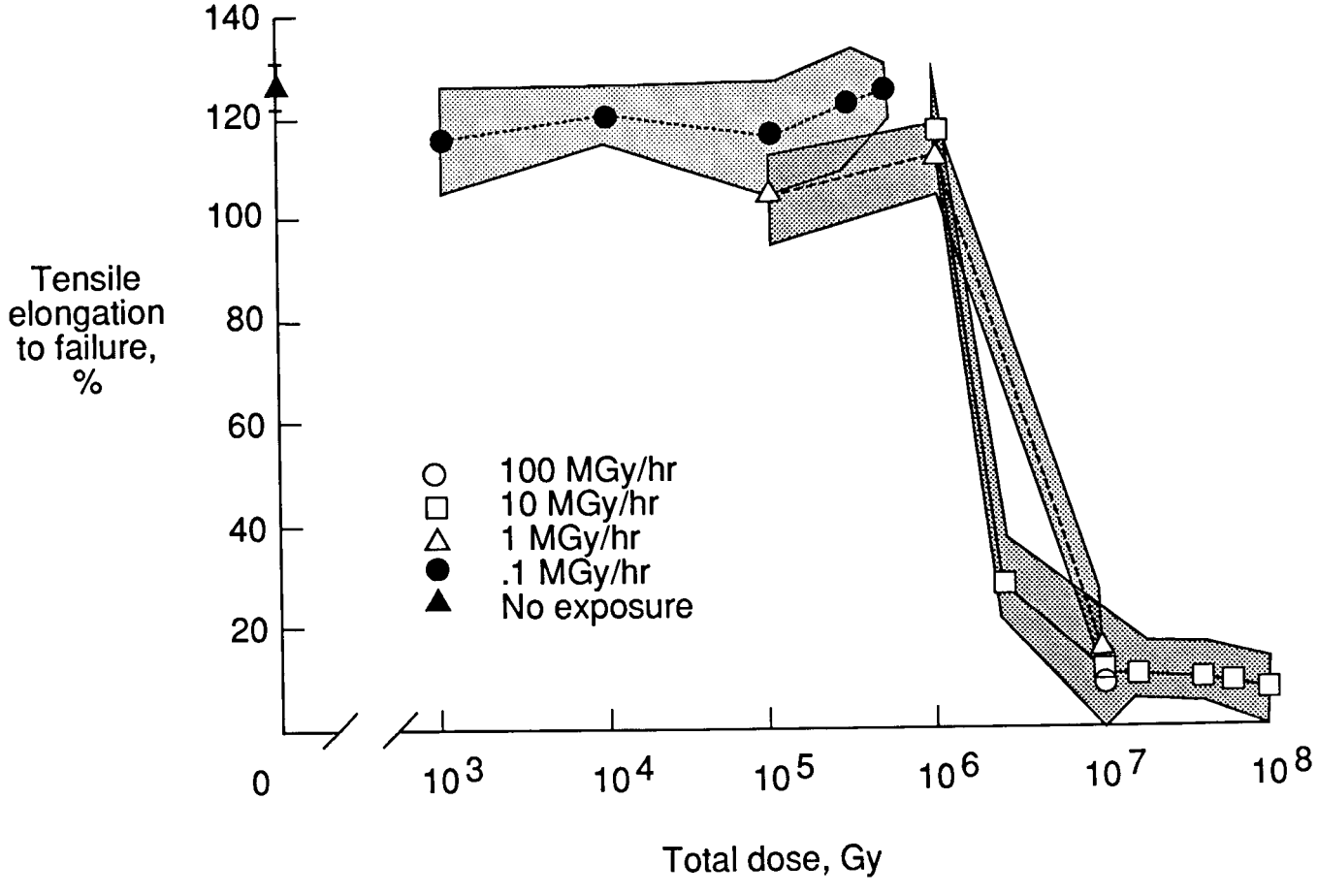


Figure 10. Elongation-to-failure of electron-irradiated polyetherimide for four dose rates.

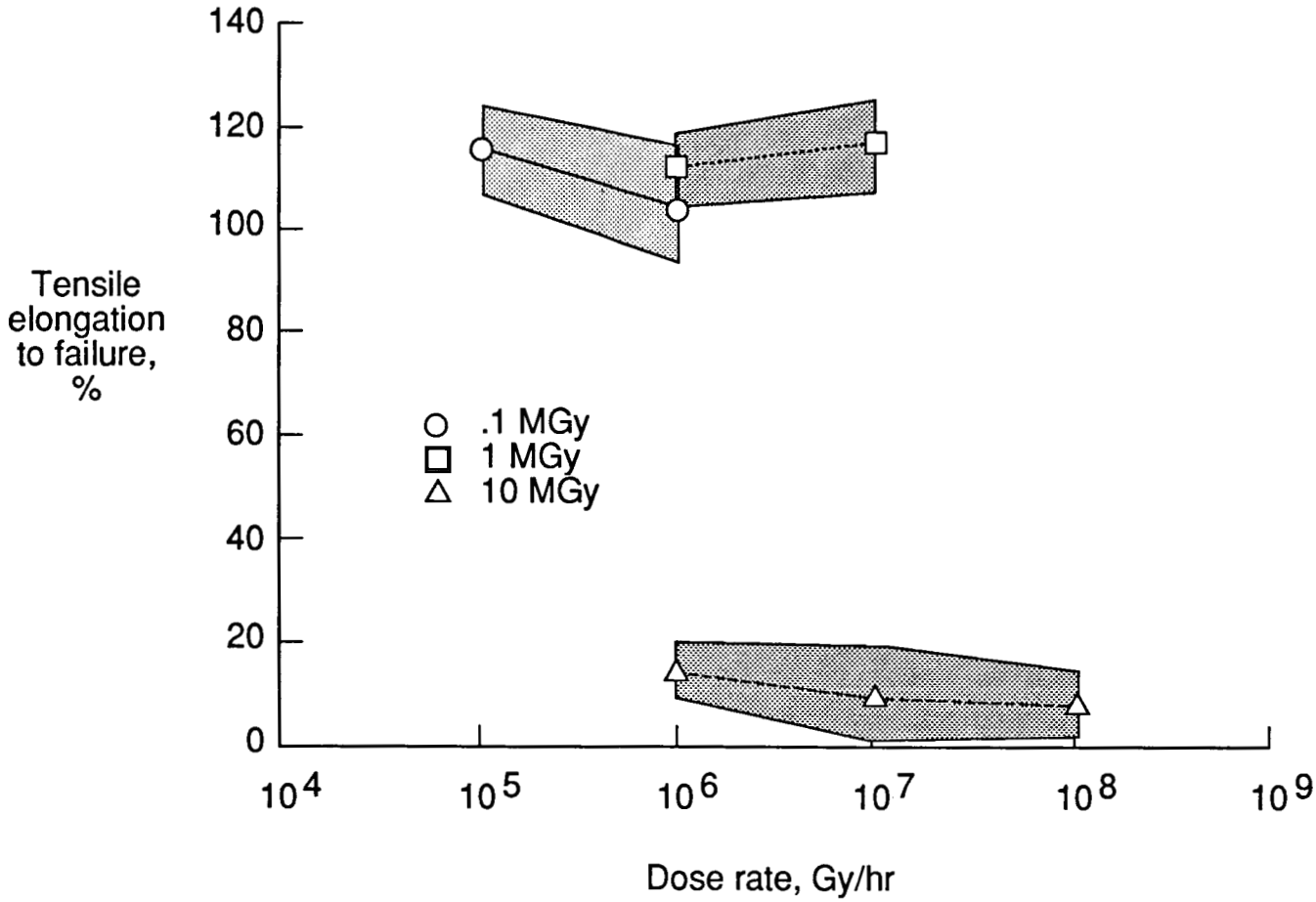


Figure 11. Elongation-to-failure of electron-irradiated polyetherimide for three total absorbed doses.

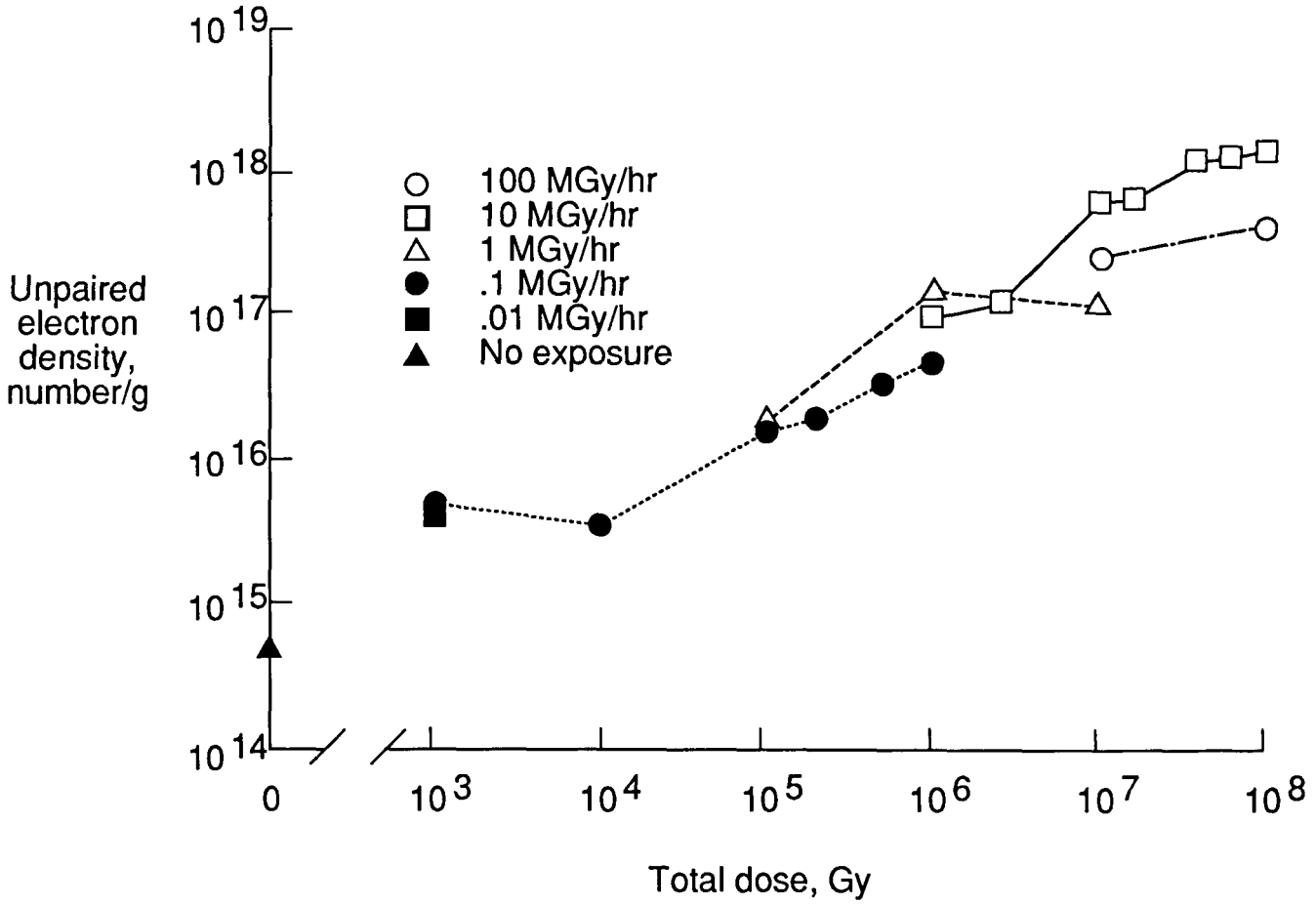


Figure 12. Unpaired electron density of electron-irradiated polyetherimide for five dose rates.

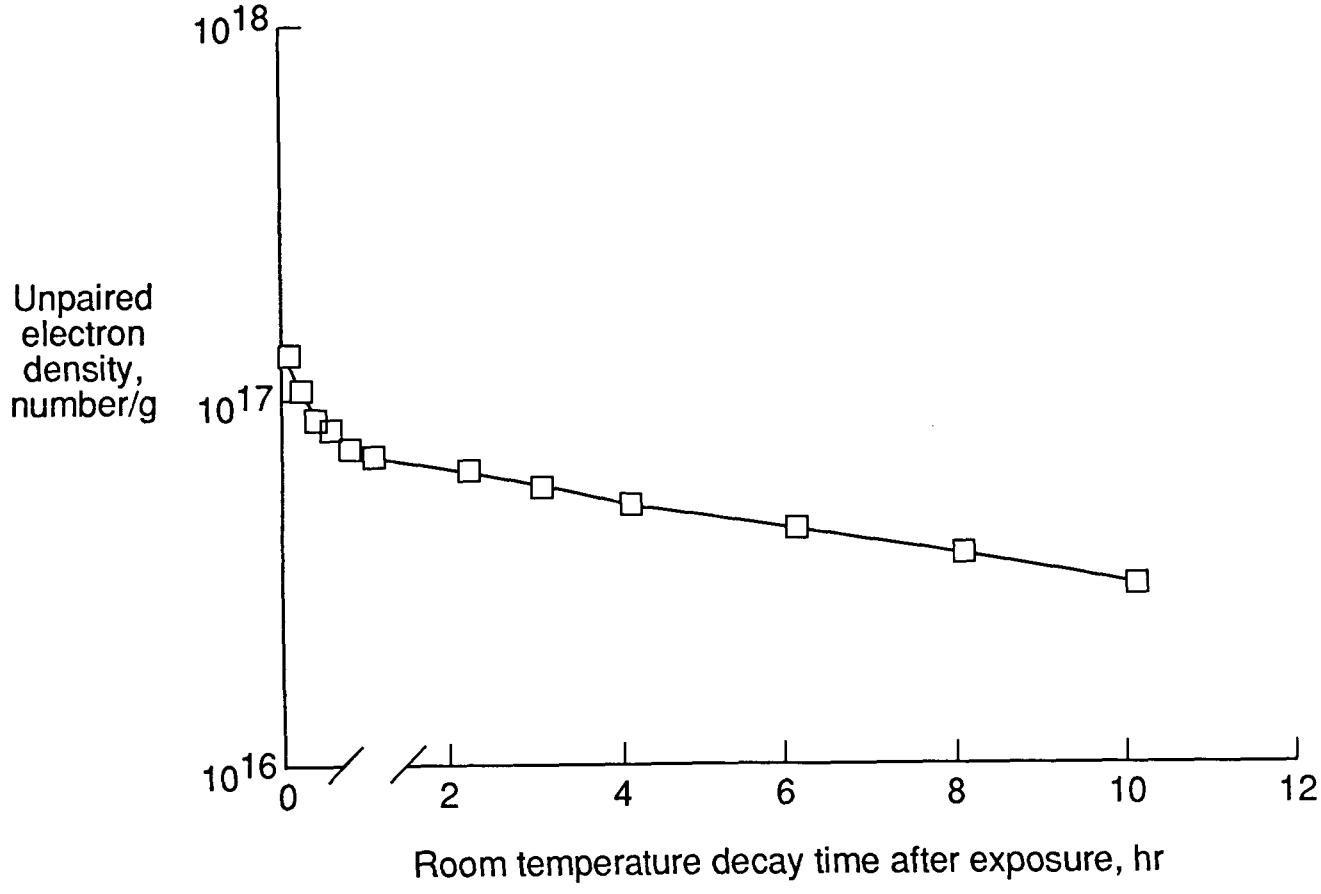


Figure 13. Room temperature decay of unpaired electron density of electron-irradiated polyetherimide for 2.5-MGy total absorbed dose at a dose rate of 10 MGy/hr.

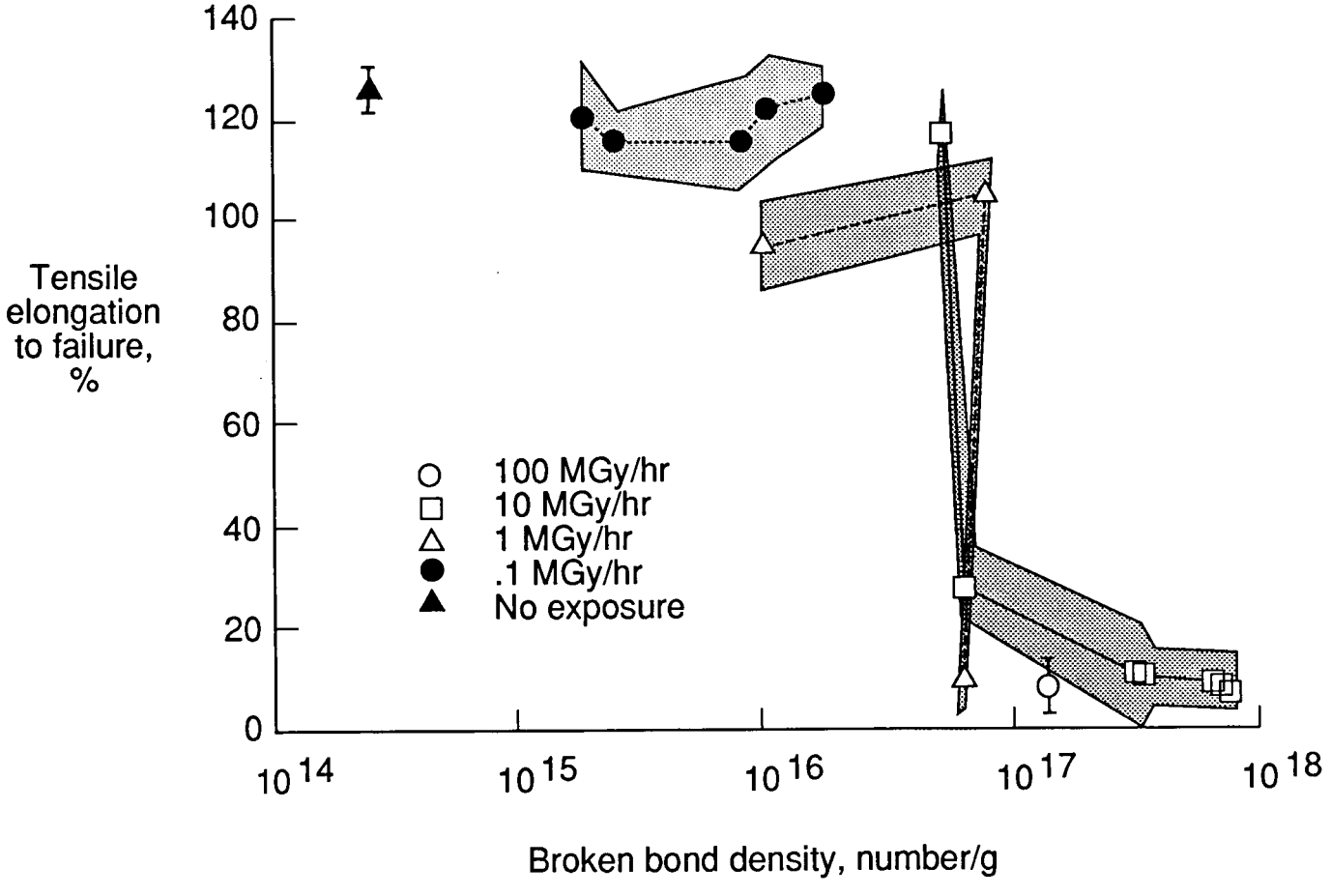


Figure 14. Relationship of elongation-to-failure with broken bond density for electron-irradiated polyetherimide.

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16. Abstract

The threshold values of total absorbed dose for causing changes in tensile properties of a polyetherimide film and the limitations of the absorbed dose rate for accelerated-exposure evaluation of the effects of electron radiation in geosynchronous orbit have been studied. Total absorbed doses from 1.0 kGy to 100 MGy and absorbed dose rates from 0.01 to 100 MGy/hr were investigated, where 1 Gy equals 100 rads. Total doses less than 2.5 MGy did not significantly change the tensile properties of the film, whereas doses higher than 2.5 MGy significantly reduced elongation-to-failure. There was no measurable effect of the dose rate on the tensile properties for accelerated electron exposures.

17. Key Words (Suggested by Authors(s))

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