CONF-841246--15

DE85 006214

NEUTRON AND γ-RAY IRRADIATION EFFECTS IN COMPOSITE ORGANIC INSULATORS*

S. Egusa**, M. A. Kirk, R. C. Birtcher and M. Hagiwara**
Materials Science and Technology Division
Argonne National Laboratory
Argonne, IL 60439

December 1984

Presented at the First International Conference on Fusion Reactor Materials, December 3-6, 1984, Tokyo, Japan.
*Work supported by the U. S. Department of Energy.
**Japan Atomic Energy Research Institute, Takasaki Radiation Chemistry Research Establishment, Takasaki-shi, Gunma 370-12, Japan.

Neutron and γ-Ray Irradiation Effects in Composite Organic Insulators*

S. Egusa,** M. A. Kirk,*** R. C. Birtcher,*** and M. Hagiwara**

**Japan Atomic Energy Research Institute, Takasaki Radiation Chemistry Research Establishment, Takasaki-shi, Gunma 370-12, Japan

***Materials Science and Technology Division, Argonne National Laboratory, Argonne, Illinois 60439, U.S.A.

****
**   **
** FINAL **
**   **
** October 1984 **
**   **
****

To be presented at the First International Conference on Fusion Reactor Materials, December 3-6, 1984, Tokyo, Japan.
*Work supported by the U. S. Department of Energy.

Neutron and γ-Ray Irradiation Effects in Composite Organic Insulators*

S. Egusa,** M. A. Kirk,*** R. C. Birtcher,*** and M. Hagiwara**
**Japan Atomic Energy Research Institute, Takasaki Radiation Chemistry Research Establishment, Takasaki-shi, Gunma 370-12, Japan
***Materials Science and Technology Division, Argonne National Laboratory, Argonne, Illinois 60439, U.S.A.

Abstract

Neutron irradiations with low γ-ray flux in the Intense Pulsed Neutron Source were carried out on four kinds of cloth-filled organic composites (filler: E-glass or carbon fiber; matrix: epoxy or polyimide resin) and a unidirectional alumina fiber/epoxy composite. The mechanical test was performed at room temperature. Following irradiation at room temperature, the glass/epoxy and glass/polyimide composites degrade significantly at a total neutron fluence of 5.0×10^{18} n/cm^2 (1.4×10^{18} n/cm^2 for E > 0.1 MeV), while the other composites do not degrade at this fluence. Comparison of this result with that of ^{60}Co γ-ray irradiations reveals that the $^{10}B(n,\alpha)^7Li$ reaction in E-glass fibers accelerates the degradation of composite materials by increasing the extent of radiation damage at the fiber/matrix interface. Following irradiation at 5 K, the present composites do not degrade up to a total neutron fluence of 1.0×10^{18} n/cm^2 (7.0×10^{17} n/cm^2 for E > 0.1 MeV). The mechanical test performed at 77 K on electron-irradiated composites, on the other hand, shows that the rate of degradation with dose is appreciably greater in the 77 K test than in the room-temperature test.

To be presented at the First International Conference on Fusion Reactor Materials, December 3-6, 1984, Tokyo, Japan.
*Work supported by the U. S. Department of Energy.

1. Introduction

The construction of superconducting magnets for fusion reactors will require large amounts of organic composite materials as mechanical supporters and electrical insulators [1]. The use of organic materials for fusion magnets, however, may be restricted by the radiation sensitivity of these materials. For this reason, several studies have been done recently on the mechanical and electrical properties of composite organic insulaters irradiated at low temperatures [2-6].

In actual fusion magnets the total absorbed dose in organic insulators is deposited by neutrons and concomitant γ-rays, and the ratio of neutron to γ-ray energy deposition depends on the details of the magnet design. Concerning a difference in the type of radiation, it is reported that the degradation efficiency of organic polymers can be several times higher for fast neutrons than for ^{60}Co γ-rays, depending on the kind of polymers [7]. Accordingly, it will be of great importance to study the irradiation effects in organic insulators for neutrons and γ-rays separately. From these points of view, neutron irradiations with low γ-ray flux in the Intense Pulsed Neutron Source (IPNS) were carried out on five kinds of composite organic insulators at room temperature and 5 K. ^{60}Co γ-ray and 2 MeV electron irradiations were also made at room temperature for comparison with neutron irradiations. The present paper mainly describes the neutron irradiation effects in composite organic insulators.

2. Experimental

Four kinds of cloth-filled organic composites were prepared

by Sumitomo Bakelite Co., Ltd., using E-glass fiber cloth (Kanebo KS-1210) or carbon fiber cloth (Torayca #6142) as reinforcing filler, and epoxy (Sumiepoxy ELM-434) or polyimide (Kerimid 601) as matrix resin. A unidirectional alumina fiber/epoxy composite was provided by Sumitomo Kagaku Co., Ltd.

Neutron irradiations were carried out in the IPNS installed at Argonne National Laboratory (ANL) [8]. The in-air room-temperature irradiations were made in the "Rabbit" and "H2" thimbles which were in the Radiation Effects Facility (REF) and in the Neutron Scattering Facility (NSF), respectively. The 5 K irradiations were made in the VT2 thimble in REF. ^{60}Co γ-ray irradiations in air were made at room temperature at a dose rate of 0.046 MGy/h. 2 MeV electron irradiations were made at a dose rate of 21.6 MGy/h at the specimen temperature of ca. 70°C [9].

The mechanical properties were examined by performing three-point bend tests at room temperature or 77 K at a crosshead speed of 0.5 or 0.6 mm/min. The details are described elsewhere [9].

3. Results

3.1. Neutron dose calculations

The total neutron fluence was determined by measuring the radioactivity of nickel wire attached to each specimen or its container. The conversion factors from total neutron fluence to absorbed dose were calculated by Greenwood for elements such as hydrogen, carbon, and oxygen, taking into account almost every nuclear reaction and the exact neutron energy spectra available at IPNS [10,11]. The conversion factors for compounds such as epoxy

and polyimide were evaluated by taking their composition into account. The results are collected in table 1.

Table 1 shows that the conversion factor for each compound does not differ strikingly between the Rabbit and VT2 thimbles. This is because the neutron spectra for these REF thimbles are very similar to each other. The REF neutron spectrum can be characterized as a degraded fission spectrum with a high-energy component [8,11]. The NSF neutron spectrum, on the other hand, is quite different from the REF spectrum, and is characterized by the existence of a large flux of low-energy neutrons [8,11]. As a result, the conversion factor for the H2 thimble in NSF is lower than that for the REF thimbles for every compound except for E-glass. The conversion factor for E-glass is as much as 16-18 times higher than that for epoxy or polyimide resin in the H2 thimble. This is because low-energy neutrons have a large cross section for a $^{10}B(n,\alpha)^{7}Li$ reaction which produces energetic recoil particles within the boron-containing E-glass fibers (1.775 MeV α and 1.015 MeV ^{7}Li). For carbon and alumina, on the other hand, the conversion factor is much lower than that for epoxy or polyimide resin owing to the less efficient energy transfer from neutrons to heavy atoms such as carbon, oxygen, and aluminium.

From these considerations, it follows that the Rabbit or VT2 irradiation results in a major dose to the matrix resin and a lower dose to the fiber. This is also the case for the H2 irradiation of the carbon and alumina fiber composites, but for the E-glass fiber composites the H2 irradiation results in a much greater dose to the fiber compared with the matrix resin.

3.2. Mechanical properties at room temperature

The mechanical properties of neutron and γ-ray irradiated composites were tested at room temperature. The Young's and shear moduli were determined by performing the three-point bend test at various span lengths for each specimen, and by solving the resulting simultaneous equations [9]. The ultimate strength of the composite, σ_{cu}, was calculated from $\sigma_{cu} = 3P_f(\ell/h)/2bh$, where P_f is the applied load at failure, ℓ is the span length, and b and h are the width and depth (thickness) of a rectangular specimen, respectively. The failure test was made at the span length of 12.7 mm three times for each dose.

The Young's modulus of the control specimen increased in the order of the glass/polyimide, glass/epoxy, carbon/polyimide, carbon/epoxy, and alumina/epoxy composites, reflecting differences in the Young's modulus of the constituent materials and in the form of reinforcing fillers [12]. Following irradiation the Young's modulus of these composites remained unchanged up to about 20 MGy regardless of the neutron and γ-ray irradiations at room temperature. This was also the case for the 5 K neutron irradiation up to about 10 MGy.

The shear modulus and the ultimate strength are shown in figs. 1 and 2 for the glass/epoxy and glass/polyimide composites, respectively. The error bars show the standard deviation, and missing error bars mean that the deviation is too small to be shown. These mechanical properties are plotted as a function of the absorbed dose in matrix, which was calculated by using the conversion factor for epoxy or polyimide resin (table 1),

neglecting an accompanying γ-ray contribution which was estimated to be less than 15% of the total dose [10].

Fig. 1 or 2 demonstrates that not only γ-rays but also neutrons have an incubation dose before these mechanical properties begin to degrade. At high doses above the incubation range, however, the dose dependence is seen to depend on the type of radiation. For the glass/epoxy composite (fig. 1), for instance, the ultimate strength decreases appreciably at 18.5 MGy for neutrons (o), whereas for γ-rays (□) it remains unchanged at 20 MGy. Such a decrease is seen also for the glass/polyimide composite irradiated with neutrons up to 16.5 MGy (o in fig. 2). These decreases in the ultimate strength can be regarded as significant because every data point in figs. 1 and 2 is the average value of three failure tests.

For the carbon/epoxy, carbon/polyimide, and alumina/epoxy composites, on the other hand, neither the ultimate strength nor the shear modulus decreased at all at absorbed doses below 20 MGy, thus giving no difference between the neutron and γ-ray irradiations in the present work.

3.3 Mechanical properties at 77 K

A preliminary experiment of the mechanical test at 77 K was performed on specimens irradiated with 2 MeV electrons at around 70°C. The ultimate strength is plotted in figs. 3 and 4 for the glass/epoxy and glass/polyimide composites, respectively, together with that reported previously for the room-temperature strength [9]. Comparison of the 77 K (o) and room-temperature points (●) reveals that the ultimate strength of the control specimen is

about 1.4 and 1.9 times higher at 77 K for the glass/epoxy and glass/polyimide composites, respectively. In addition, it is seen that the incubation dose observed at room temperature disappears at 77 K for both of these composites. Comparison of the glass/epoxy and glass/polyimide composites, on the other hand, shows that the ultimate strength at 77 K decreases more rapidly with increasing dose for the glass/epoxy composite, reflecting the lower radiation-resistance of the epoxy resin compared with the polyimide resin [2,13,14].

For the carbon/epoxy and carbon/polyimide composites, the ultimate strength of the control specimen at 77 K (552 and 700 MPa) decreased to about 0.8 and 0.95 times that at room temperature (664 and 734 MPa), respectively. Following irradiation, the ultimate strength at 77 K decreased appreciably more rapidly with increasing dose than that at room temperature for both of these carbon fiber composites.

4. Discussion

4.1. Characteristics of neutron irradiations

The Young's modulus of composite materials was found to remain unchanged even when the ultimate strength decreases significantly after the neutron irradiation up to 16.5-18.5 MGy (see figs. 1 and 2). It is therefore speculated that the degradation of neutron-irradiated composites is ascribed to a decrease in the capacity of load transfer at the fiber/matrix interface due to the radiation damage at the interface. This degradation mechanism is exactly the same as that proposed earlier

for electron-irradiated composites [9]. Then it is expected that the degree of degradation of composite materials is virtually determined by the extent of radiation damage at the fiber/matrix interface, no matter what the type of radiation is.

In this connection, it is worth noting that energetic recoil particles are produced by a $^{10}B(n,\alpha)^{7}Li$ reaction in E-glass fibers irradiated with neutrons. Some of such recoil particles will escape from the surface of the fiber into the matrix resin [3], thus increasing the extent of radiation damage significantly in certain localized regions near the fiber/matrix interface. For E-glass fiber composites irradiated with neutrons, therefore, the absorbed dose at interface rather than in matrix should be taken as an exposure parameter. In the present work the absorbed dose at interface, D_i, was tentatively estimated from $D_i = D_s + D_B/2$, where D_s is the absorbed dose due to the direct interaction of silane coupling agents with neutrons, and D_B is the absorbed dose within E-glass fibers due to the ^{10}B reaction. This equation is based on the assumption that at the surface of E-glass fibers, the absorbed dose due to the ^{10}B reaction will be about a half its inside value of D_B.

The D_i value thus estimated was found to amount to as high as 168 MGy for the glass/epoxy and glass/polyimide composites irradiated in the H2 thimble up to the absorbed dose in matrix of 16.5-18.5 MGy. This high value of D_i seems to explain, at least partly, why the ultimate strength of these E-glass fiber composites decreases appreciably for neutron irradiation even when the absorbed dose in matrix is below 20 MGy (see figs. 1 and 2). For the Rabbit irradiation, on the other hand, the D_i value was

merely 7.2 MGy for the maximum dose in matrix of 4.2-4.7 MGy, thus causing no appreciable degradation of the E-glass fiber composites in the present work. This will be also the case for the composites irradiated in the VT2 thimble up to the maximum dose in matrix of 7.0-9.2 MGy, giving the absorbed dose at interface of merely 14.1 MGy and, consequently, causing no appreciable degradation.

4.2. Dose dependence of ultimate strength

The ultimate strength of composites tested at room temperature was found to have an incubation dose before beginning to decrease (figs. 1-4). The existence of such an incubation dose may be associated with a network structure of highly-cross-linked polymers in the fiber/matrix interface region. Such a network structure is expected to maintain its initial capacity of load transfer until some accumulation of main-chain scissions of polymer destroys the network structure in certain localized regions. This implies that the initial potential capacity of load transfer is in excess of the capacity needed by the reinforcing fibers. In the reverse case that the fiber strength is beyond the load transfer capacity, therefore, the incubation dose will be absent. These considerations seem to explain, at least partly, why the incubation dose observed at room temperature disappears at 77 K for the glass/epoxy and glass/polyimide composites (see figs. 3 and 4). The strength of E-glass fibers is, in fact, reported to increase with decreasing temperature, reaching a value some 50% higher at 77 K compared with that at room temperature [15].

Taking into consideration these points, we derived the following expression to describe the dose dependence of the ultimate strength of composite materials, σ_{cu}:

$$\sigma_{cu} = \alpha \sigma_{fu} v_f \eta + \sigma_m^* (1 - v_f), \quad (1)$$

$$\eta = (\eta_0 - \eta_\infty)[1 - (1 - e^{-kD})^n] + \eta_\infty, \quad (2)$$

where α is the coefficient dependent on the form of fibers, σ_{fu} is the fiber strength, σ_m^* is the matrix stress at the composite failure, v_f is the volume fraction of fibers, η is the load transfer capacity, k is the radiation-sensitivity parameter, D is the absorbed dose, n is the accumulation parameter, and the subscripts 0 and ∞ refer to the initial and final values, respectively. Further details are described elsewhere [16]. The results of the fitting procedure of these equations to the experimental data are shown by the solid and broken curves in fig. 3 or 4 for the 77 K and room-temperature mechanical tests, respectively. The fit between the calculated and observed plots is seen to be excellent, and accordingly it is expected that eqs. (1) and (2) may be applied to the lifetime analysis of composite organic insulators to be used in fusion magnets.

5. Conclusions

The present work has shown that the $^{10}B(n,\alpha)^7Li$ reaction in E-glass fibers makes a significant contribution to the radiation damage at the fiber/matrix interface, thus accelerating the degradation of E-glass fiber composites. It was also shown that

in the 77 K mechanical test the incubation dose is quite low or practically nil, and the rate of degradation with dose is appreciably greater than in the room-temperature test. Based on these findings, an expression was successfully derived so as to describe the dose dependence of the ultimate strength of organic composites.

Acknowledgements

The authors wish to express their appreciation to Dr. L. R. Greenwood of ANL for neutron dosimetry analysis and his valuable data on neutron dose calculations. Thanks are also due to Dr. C. E. Klabunde of Oak Ridge National Laboratory for his many helpful comments and discussions. The alumina/epoxy composite provided by the Sumitomo Kagaku Co., Ltd. and the electron irradiations performed by Dr. S. Kawanishi of Japan Atomic Energy Research Institute are greatly appreciated. One of the authors (S.E.) is especially grateful to Dr. B. S. Brown of ANL for providing him an opportunity to use the IPNS facilities.

References

[1] B. S. Brown, J. Nucl. Mater. 97 (1981) 1.

[2] R. R. Coltman, Jr. and C. E. Klabunde, J. Nucl. Mater. 103 and 104 (1981) 717; 113 (1983) 268.

[3] C. E. Klabunde and R. R. Coltman, Jr., J. Nucl. Mater. 117 (1983) 345.

[4] S. Takamura and T. Kato, J. Nucl. Mater. 103 and 104 (1981) 729.

[5] G. F. Hurley, J. D. Fowler, and D. L. Rohr, Cryogenics 23 (1983) 415.

[6] H. W. Weber, E. Kubasta, W. Steiner, H. Benz, and K. Nylund, J. Nucl. Mater. 115 (1983) 11.

[7] S. Egusa, K. Ishigure, and Y. Tabata, Macromolecules 12 (1979) 939; 13 (1980) 171.

[8] R. C. Birtcher, T. H. Blewitt, M. A. Kirk, T. L. Scott, B. S. Brown, and L. R. Greenwood, J. Nucl. Mater. 108 and 109 (1982) 3.

[9] S. Egusa, M. A. Kirk, R. C. Birtcher, M. Hagiwara, and S. Kawanishi, J. Nucl. Mater. 119 (1983) 146; Nucl. Instrum. Methods in Physics Res. B1 (1984) 610.

[10] L. R. Greenwood, Argonne National Laboratory, private communication.

[11] L. R. Greenwood and R. J. Popek, Presented at the ICANS-VI Intl. Collaboration on Advanced Neutron Sources, Argonne National Laboratory (1982) ANL-82-80, p. 605.

[12] S. Egusa, M. A. Kirk, and R. C. Birtcher, J. Nucl. Mater. (in press).

[13] A. Udagawa, S. Kawanishi, S. Egusa, and M. Hagiwara, J. Mater. Sci. Lett. 3 (1984) 68.

[14] J. D. Fowler, Jr. and F. W. Clinard, Jr., in: Sixth Annual Progr. Rep. on Special Purpose Materials for Magnetically Confined Fusion Reactors (U. S. Department of Energy, 1983).

[15] N. M. Cameron, Glass Technol. 9 (1968) 14.

[16] S. Egusa, M. A. Kirk, R. C. Birtcher, and M. Hagiwara, J. Nucl. Mater. (in press).

Table 1
Conversion factors from total neutron fluence to absorbed dose for irradiation thimbles in IPNS

Compound	Conversion factor (10^{-11} Gy/n/cm^2)			Weight fractions (%)
	Rabbit	VT2	H2	
Epoxy	0.885	1.049	0.381	H(6.3), C(66.2), O(14.3), N(8.4), S(4.8)
Polyimide	0.749	0.890	0.326	H(5.1), C(73.4), O(11.5), N(10.1)
E-glass[a]	0.393 [0.317]	0.300 [0.203]	5.857 [5.818]	B(2.3), Ca(13.3), O(48.0), F(0.3), Mg(2.0), Al(7.8), Si(25.7), Na(0.4), Fe(0.2)
Carbon	0.164	0.206	0.067	C(100.0)
Alumina	0.077	0.095	0.040	Al(47.9), O(47.7), Si(4.4)
Silane[b]	1.126	1.327	0.473	H(8.5), C(45.7), O(33.8), Si(11.9)

[a]Values in brackets are contributions due to boron in E-glass. The weight fractions are for Kanebo KS-1210.

[b]γ-glycidoxypropyltrimethoxysilane.

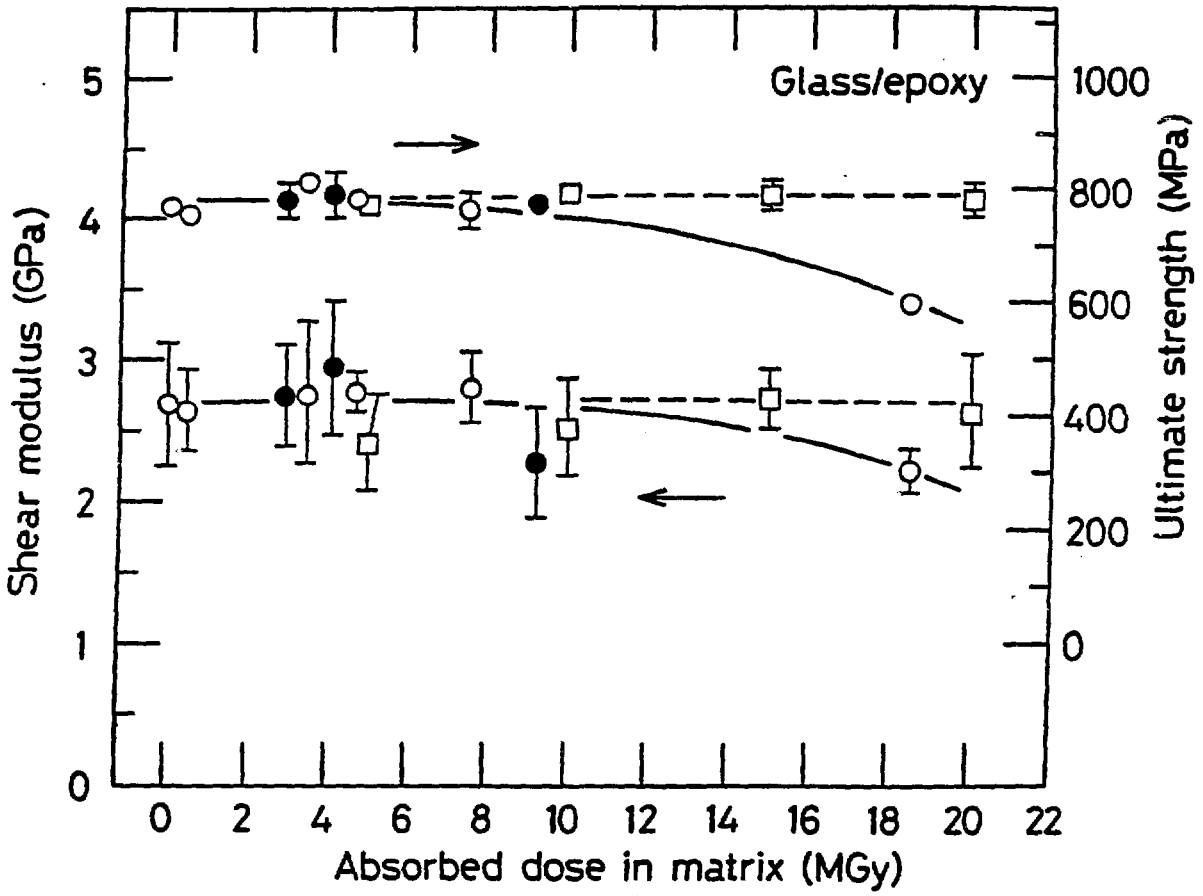

Fig. 1. Plot of the shear modulus and the ultimate strength vs. the absorbed dose in matrix for the glass/epoxy composite tested at room temperature after neutron irradiation at room temperature (o) or at 5 K (●) and after ^{60}Co γ-ray irradiation at room temperature (□).

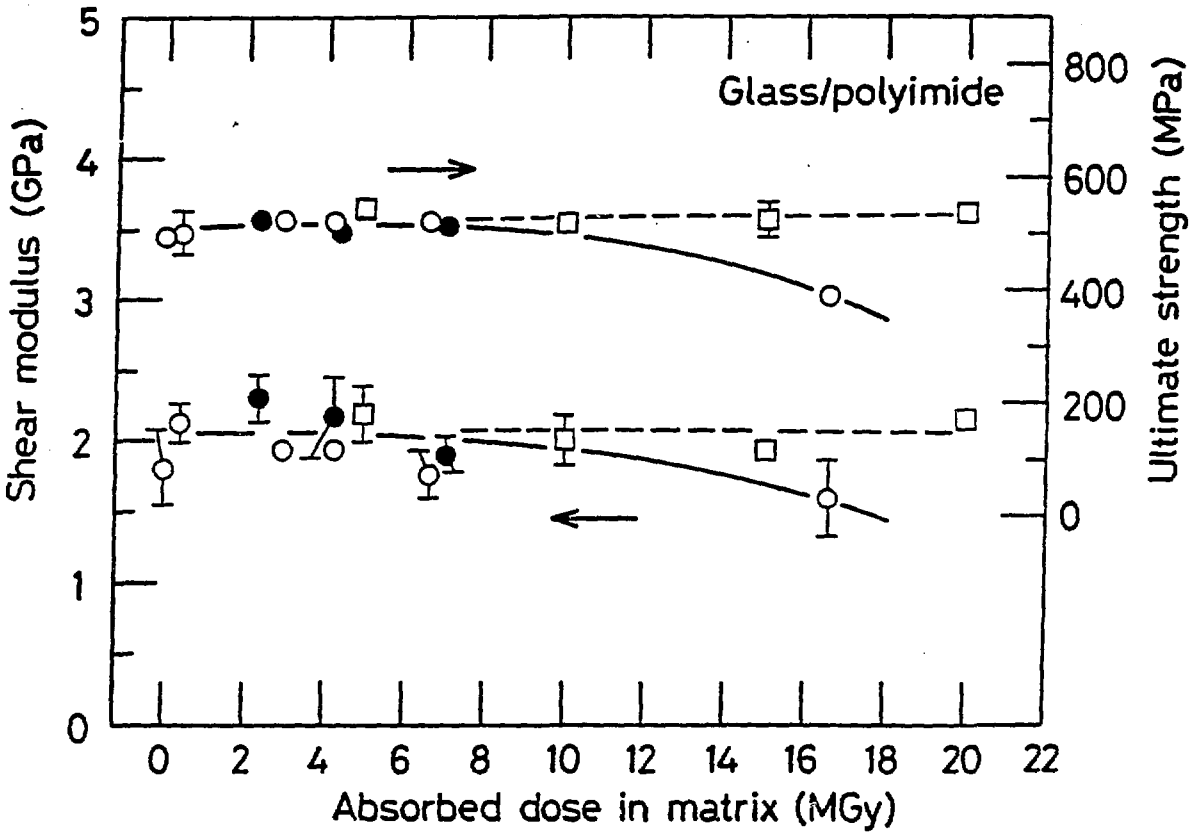

Fig. 2. Plot of the shear modulus and the ultimate strength vs. the absorbed dose in matrix for the glass/polyimide composite tested at room temperature after neutron irradiation at room temperature (o) or at 5 K (●) and after ^{60}Co γ-ray irradiation at room temperature (□).

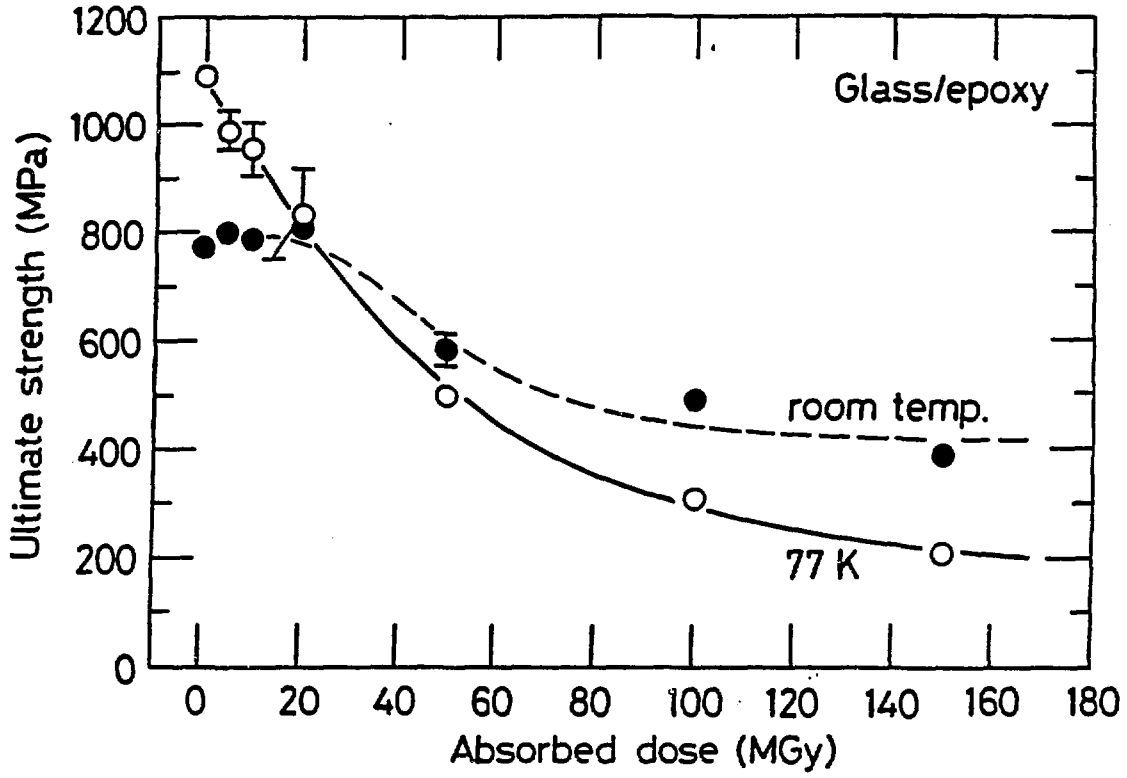

Fig. 3. Plot of the the ultimate strength vs. the absorbed dose in matrix for the glass/epoxy composite tested at 77 K (o) and at room temperature (●) after 2 MeV electron irradiation at around 70°C. The solid and broken curves are the results of fitting procedure made by using eqs. (1) and (2) with $n = 1.17$, $k = 0.0218\ MGy^{-1}$ for solid curve and $n = 5.97$, $k = 0.0447\ MGy^{-1}$ for broken curve (see text).

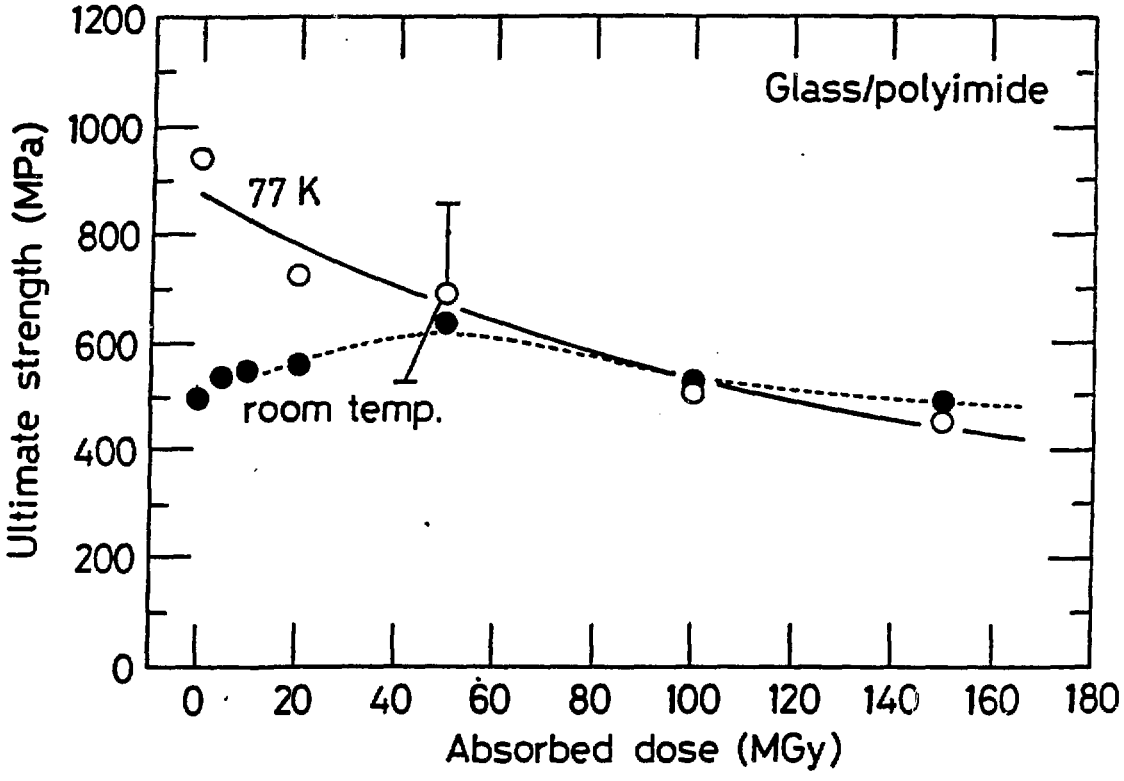

Fig. 4. Plot of the the ultimate strength vs. the absorbed dose in matrix for the glass/polyimide composite tested at 77 K (o) and at room temperature (•) after 2 MeV electron irradiation at around 70°C. The solid curve is the result of fitting procedure made by using eqs. (1) and (2) with n = 1.0 and k = 0.00749 MGy^{-1} (see text).