11. Creep Behavior of an Epoxy Resin and an Epoxy-Based FRP in Condition of Simultaneous Supply of Radiation and Stress at Cryogenic Temperatures

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ABSTRACT

Creep tests of an epoxy resin and an epoxy-based FRP in bending under irradiation condition have been carried out, to investigate the synergistic effects of radiation and stress on mechanical properties of FRP. Simultaneous supply of stress and irradiation on the epoxy resin and the FRP enhanced creep rates in comparison with that supply of the stress on a post-irradiated one did. ESR spectra measurement was also carried out to study the change of molecule of the resin irradiated. Increase of molecular weight between crosslinks was found out to be enhanced by the synergistic effect of radiation and stress. The mechanism of increased damage of FRP induced by the effects of simultaneous stress and irradiation is discussed.

INTRODUCTION

Materials used to construct a superconducting magnet for a fusion reactor will be subjected to radiation and stress. The mechanical properties of organic materials and organic composite materials (FRP) used as insulators and structural materials are more sensitive to radiation than the other magnet components. To build a successful fusion reactor, the FRP with superior resistance to radiation damage must be developed. There are many reports concerning degradation of the mechanical properties of FRP and polymers due to irradiation[1,2]. Most of the reports, describe test results in which the radiation damage was measured by using the "postirradiated" specimens. In the reactor, however, the resin and the FRP will be stressed during irradiation. To simulated fusion magnet conditions, therefore, the specimen has to be simultaneously subjected to radiation and stress at cryogenic temperature. Studies of the simultaneous effect of stress (or strain) and irradiation on the resin and the FRP are very few[3~10].

Creep tests of nylon fiber in the radiation field were made by Mokulskii et al[3], Regel et al[5], and Stepanov et al[4]. Creep tests of PSF film were conducted by Hill et al[6]. They observed the lifetime to be reduced and the creep rate to be enhanced in such simultaneous condition of stress and radiation. Tensile tests by Dickinson et al[7] were structured to evaluate the mechanical properties of rubber films, and much greater development of crack length was observed.

On bulky specimens of polymer, much greater creep rates during irradiation than before and after were reported by Bell et al[8~10].

Various mechanism on the simultaneous effect of stress and irradiation on the mechanical properties of polymers were proposed. However, the mechanism has not yet been proved, because of the lack of evidence on molecular structure. It is also difficult to apply their results to composites with commercial size.

The degradatiion of macroscopic properties must originate from the radiation induced structural changes at the molecular level. Eda and Iwasaki have investigated the structural change of epoxy resins by means of ESR spectroscopy and found that the cyclohexadienyl-type radical is produced by hydrogene addition to the benzene ring and these reactions result in the radiation resitivity[11].

In the present work, a creep test under irradiation was performed to investigate the effect of simultaneous stress and irradiation on an epoxy resin and an epoxy-based composite.

The purpose of this study was to examine the deformation velocity of materials before, during, and after irradiation, to examine the dependence of the velocity on temperature, and also to examine the radiation induced structural change of epoxy resins by ESR method. The mechanisms of deformation during irradiation are discssed mainly on the basis of their temperature dependence.

EXPERIMENTAL PROCEDURES

Sample and Radiations

The materials were consisted of epoxy resin (Epicote 828-aliphatic amine) and an epoxy-based glass-cloth laminates (FRP from Lamivelle A, Nittoh Electron and Industry Co. Ltd.). Specimens for the test of creep and relaxation were cut to the shape shown in Fig.1 from plates of epoxy resin (5 mm thick) and FRP (2 mm thick); the figure shows the FRP specimens.

These specimens were irradiated with electron beams (20 MeV, 240 mA, 60-120 pps; dose rate of 0.6-2.0 MGy/h) in LINAC at ISIR, Osaka University.

Creep Test

The creep test apparatus and the specimen are shown in Fig. 1. Creep test was performed by measuring the deflection of the specimen which was loaded with a dead weight through lever in the three point bending test with 45 mm span length. Whole of the apparatus was held in the radiation field for the simultaneous effect tests. Creep test for postirradiated specimens was also performed.

The test temperature in creep tests was regulated by changing the flow volume of liquid nitrogen with an electromagnetic valve. The maximum fluctuation from the preset temperature value was ±10 K.

ESR Spectra

After irradiation ESR spectra were measured using a Bruker ESP 300(Germany) X-band spectrometer.

The temperature of sample for ESR was raised by lifting the specimen from the suface of liquid nitrogene and was controled by changing the distance lifted.The measurements were made at 77 K(ESR glass tube was dipped in liquid nitrogen).

RESULTS

Creep

Creep results at LNT are shown in Fig. 2 through 7. In the case of the epoxy resin, creep curves under non-irradiated condition reveal almost no increase of deflection except the region just after loading in such loads of 57.9 MPa ando 84.8 MPa (Fig. 2). For 8 MGy irradiated specimens which were irradiated at LNT and raised up to RT before test, as shown in Fig. 3, the creep curves show a similar trend like those of the non-irradiated specimens. When the irradiated specimens at LNT was tested without the warm up to RT, the creep curve shows larger increase in the steady state region than that with warm up does(Fig. 4). In the condition of the creep durig irradiation, creep curves reveal clearly much higher increase of deflection in the steady region than those of the specimens after irradiation(Fig. 5). This deflection increases with loads.

In the case of the FRP, creep curves show almost similar behavior like those in the case of the resin. The creep curves for the specimen during irradiation show higher increase compared with those for the specimen after irradiation, although the increase is smaller than those of epoxy resin(Fig. 6 and 7).

The temperature dependence of creep rates are shown in Fig. 8 and 9. The lines for unirradiated epoxy resin have steeper slopes than the ones obtained during irradiation(Fig. 8). The respective activation energies calculated from these lines are 5.2 kcal/mole and 1.04 kcal/mole. The apparent activation energy of epoxy decreases by about 80% upon introduction into radiation field. Therefore, the mechnism of deformation for epoxy resin must be change involving a decrease in the activation energy.

The temperature dependence of the creep rated for FRP during irradiation is shown in Fig. 9. The rate did not vary with temperature, suggesting that the activation energy is negligible.

From these results, the creep rate under irradiation is confirmed to be accelerated than those for postirradiated specimens.

ESR Spectra

The behavior of ESR spectra with radiation dose is shown in Fig. 10. The intensity of the signal becomes larger with the dose and the shape of the signal does not change. The number of the unpaired electron (radicals) increases almost linearly with the dose (Fig.11).

The spectra behavior induced by raising the temperature of the sample are shown in Fig 12. The spectra become smaller with the temperature and the change of the signal shape is little. The number of the radicals decrease moderately untill 200 K and after that temperature decrease more rapidly (Fig. 13). The radicals are stable at lower temperatures and unstable at higher temperatures. This dependency of the stability on the temperature may be caused by the mobility of polymer segments. The radicals decrease by producing the electron pairs which induce the repairment of the molucule, the unsaturated bonds and the crosslinks. The unsaturated bonds formation among the reactions can make the degradation of polymer (scission of polymer).

DISCUSSION

In the steady state region of creep for the epxy resin after irradiation, the creep rate for the specimen without warm up is higher in comparison with the ones with warm up. This behvior would be understood, assuming that defects in the resin are proportional to the number of radicals, that is, the larger the number of radicals make the larger the nuber of defects. For the epoxy during irradiation, creep rates are much higher than those for the resin after irradiation without warm up. This behavior is not understood from the number of radicals because in situ number of radicals during irradiation must be smaller than those which irradiation is accomplished. Simultaneous effects of stress and radiation on the damage of the resin must be operated.

Stress should affect on the reaction process of scission and crosslink next to the excitation and ionization processes by irradiation. The situation of these processes are similar to the chemical reaction under stress. Three reactions must be considered.

1) In the case of scission reaction, molecular end groups made by scission are active and have probability of rebonding at the original chain site under no stress or strain. When the stress acts on the scission reaction, the active end groups are separated by the release of strain energy and the probability of rebonding thus decrease and scission of chemical bond is accomplished (diminish of cage effects).

2) In the case of crosslink reaction under stress, specific reaction like decrease of creep deformation may occur.

3) In the case where the reactions of scission and crosslink occur simultaneously under stress, scission releases the stress and the deformation increase and, thereafter, crosslink reaction fixes the deformation. Crosslink density is in this case not estimated to decrease drastically although the deformation increases.

Considering our results, the scission reaction under stress is assumed as the main mechanism of the acceleration of radiation damage.

CONCLUSIONS

Creep tests of an epoxy resin and an epoxy-based FRP during irradiation have been carried out, to investigate the effect of simultaneous stress and irradiation on the mechanical properties of the resin and the FRP. The study resulted in the following conclusions:
(1) The effect of simultaneous stress and irradiation results in more damage on the epoxy resin and the FRP than the effect of stress on a postirradiated one.
(2) ESR spectra is available to detect chemical change of materials at low temperature.
(3) The mechanism of increased deformation of polymers induced by such simultaneous effects has been proposed.
(4) Polymers and FRP in the circumstance of simultaneous existence of stress and irradiation have possibility of large deformation beyond the estimation based on the specimen after irradiation.

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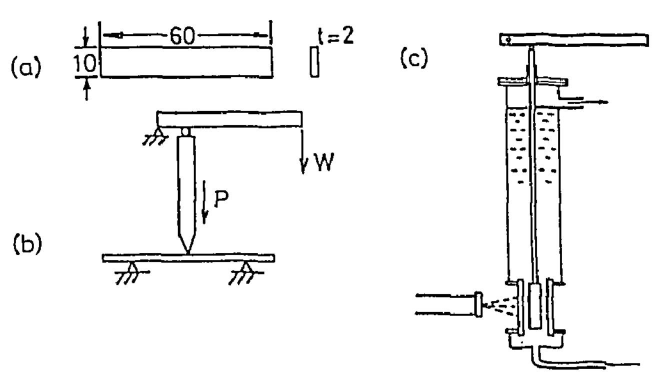

Fig. 1. The creep test specimen(a), the three point bending method(b) and the creep apparatus with e-irradiation source(c).

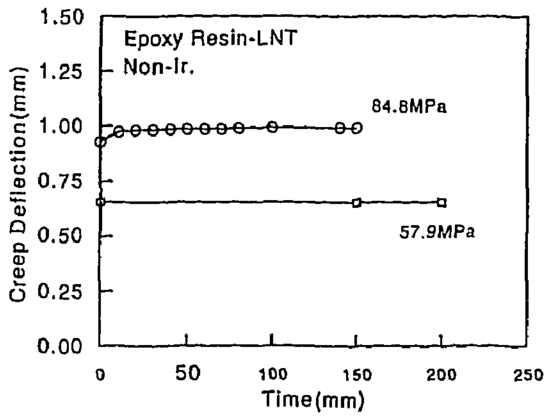

Fig. 2. Creep curves for non-irradiated epoxy-resin at LNT.

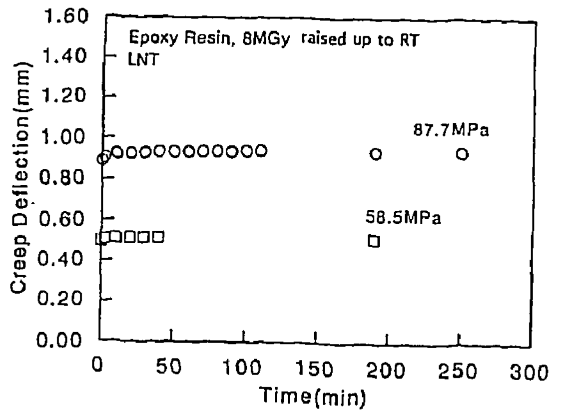

Fig. 3. Creep curves at LNT for irradiated epoxy-resin with raising to RT.

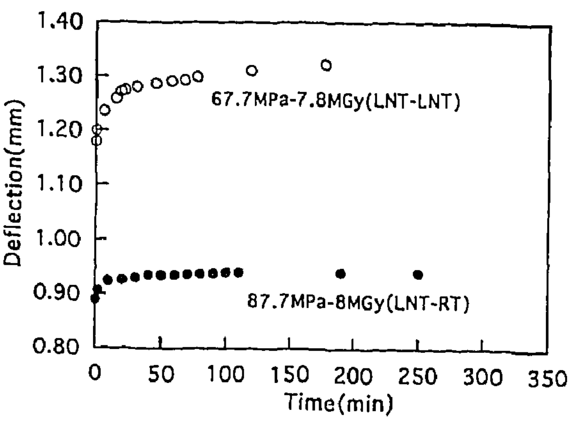

Fig. 4. Comparison of creep curves at LNT for irradiated epoxy resin between with and without raising to RT.

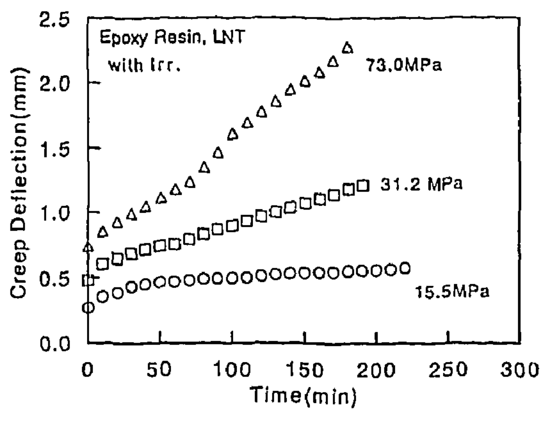

Fig. 5. Creep curves for epoxy-resin at LNT during irradiation.

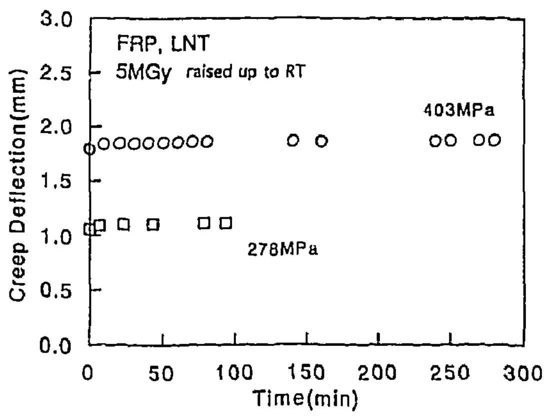

Fig. 6. Creep curves at LNT for irradiated FRP with rasing to RT.

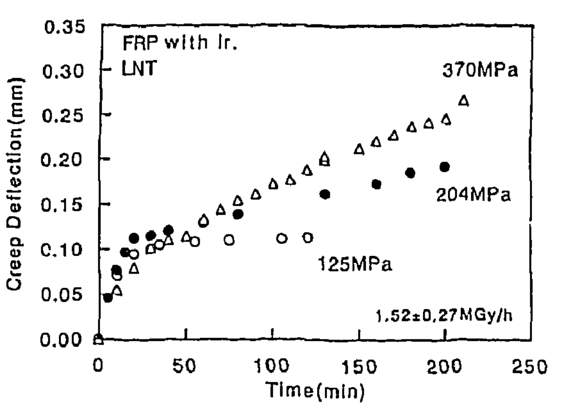

Fig. 7. Creep curves for FRP at LNT during irradiation.

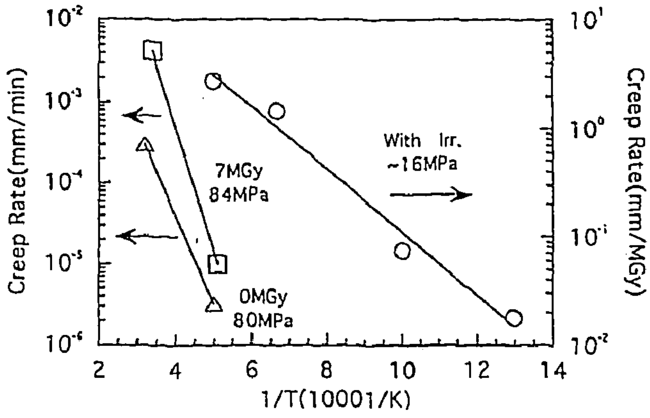

Fig. 8. The dependency of the creep rates of epoxy-resin on temperatures.

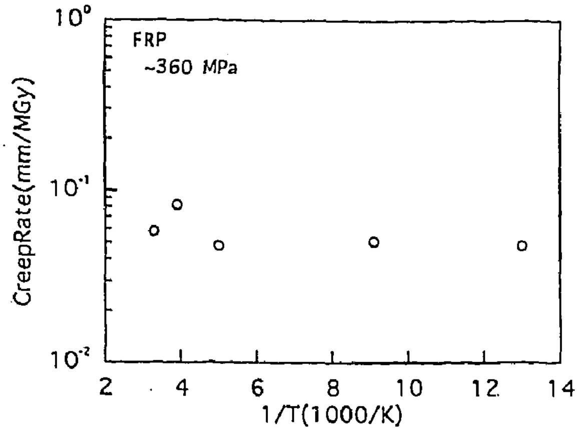

Fig. 9. The dependency of the creep rates of FRP on temperatures.

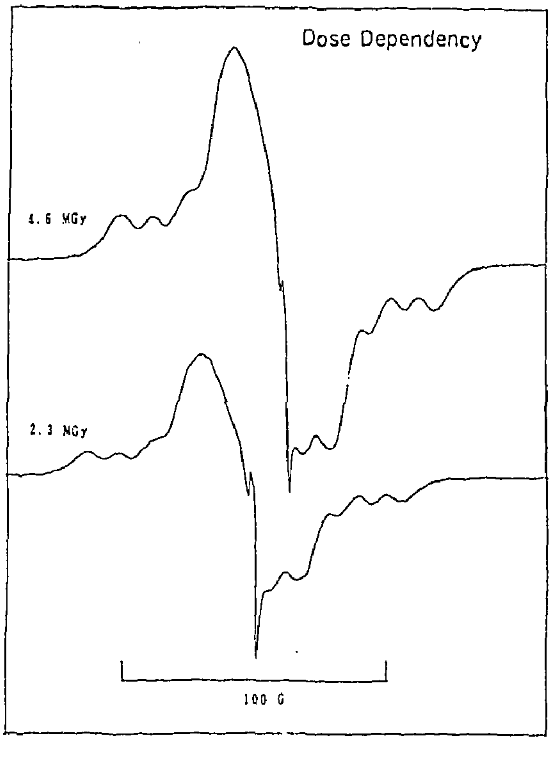

Fig. 10. Change of ESR signals with radiation dose.

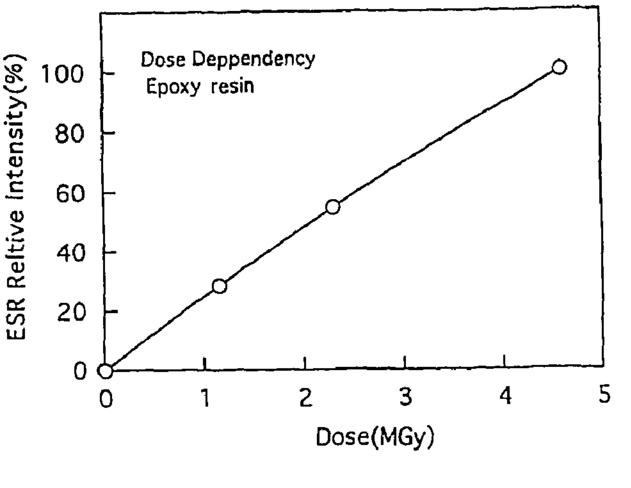

Fig. 11. The dependency of the number of radicals (ESR intensity) on radiation dose.

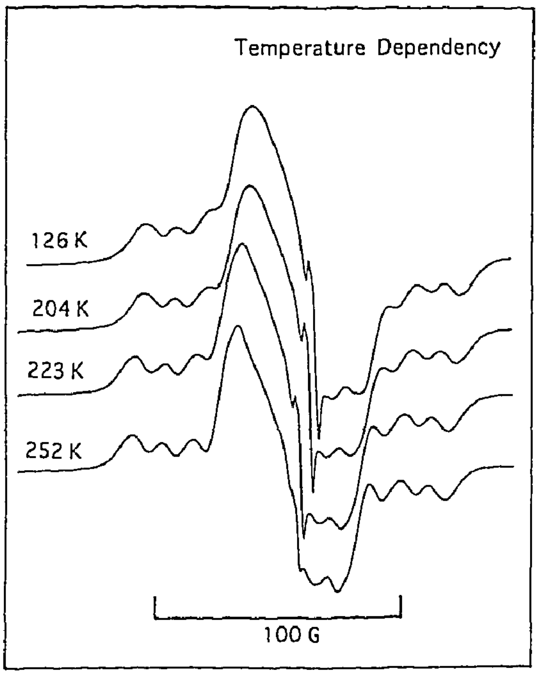

Fig. 12. Change of ESR signals with temperature.

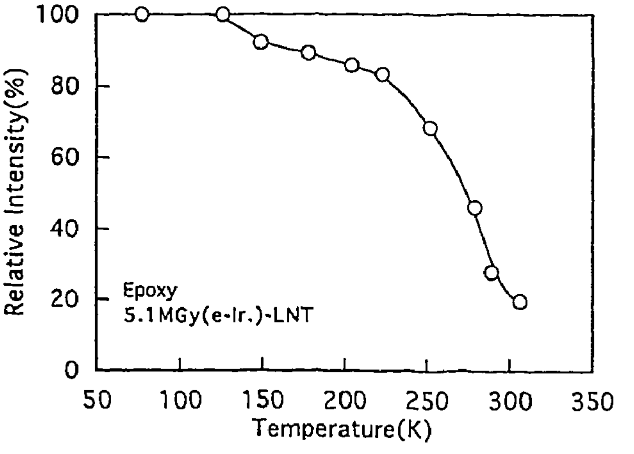

Fig. 13. The dependency of the number of radicals (ESR intensity) on temperatures.

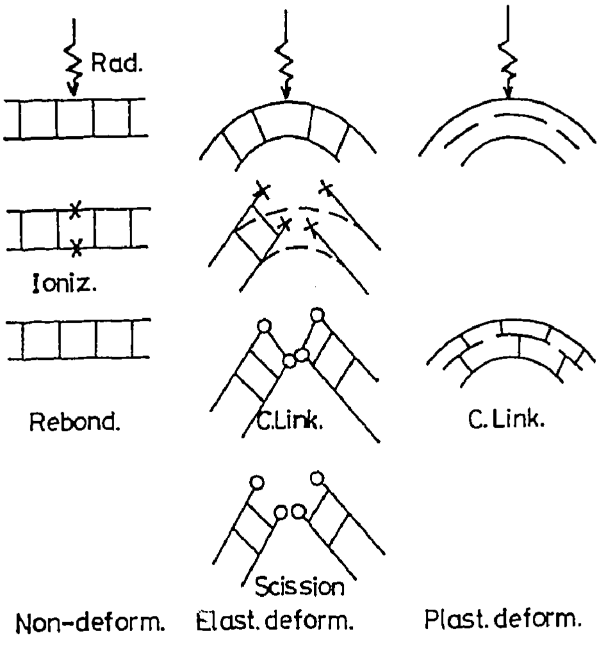

Fig. 14. Effects of stress on the deformation of the resin during irradiation.