RADIATION PROCESSING FOR PTFE COMPOSITE REINFORCED WITH CARBON FIBER

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1. ABSTRACT

The present work is an attempt to evaluate the performance of crosslinked PTFE as a polymer matrix for carbon fiber-reinforced composite materials. The carbon fiber-reinforced PTFE pre-composite, which is laminated with PTFE fine powder, is crosslinked by electron beam irradiation. Mechanical and frictional properties of the crosslinked PTFE composite obtained are higher than those of PTFE resin. The crosslinked PTFE composite with high mechanical and radiation resistant performance is obtained by radiation crosslinking process.

2. INTRODUCTION

It is well known that polytetrafluoroethylene (PTFE) has the excellent characteristics properties in electric insulation, heat resistance and high frictional properties, compared with those of other hydrocarbon polymers. However, PTFE is so sensitive against irradiation that its mechanical properties degrades with a very low dose either in air or even under vacuum irradiation(1). Therefore, PTFE has been limited use in radiation fields such as in nuclear or space environments.

Recently, in our previous studies on irradiation temperature effects of fluorinated-polymers(2), (3), it was found that the crosslinked PTFE has been attained by irradiation in its molten state just above the melting temperature (600K) under oxygen-free atmosphere(4), (5). The crosslinked PTFE obtained shows remarkable improvements in radiation resistance, mechanical properties, transparency, frictional properties and so on(6), compared with those of PTFE.

On the other hand, a fiber-reinforced PTFE composite has not been developed for high mechanical properties such as flexural strength and flexural modulus, because PTFE is high viscosity (10^{10} ~ 10^{11}P) at 653K in the molten state(7) and insoluble to most chemical solvents(8). Previous PTFE composite materials has been produced by PTFE fine powder mixed with 10 ~ 20wt% of carbon or glass short-fiber. The reinforcement effect in those composite materials is nothing. Therefore, we tried to fabricate PTFE composite with high performance by using radiation crosslinking technique of PTFE.

The present work studied the conditions of impregnation of PTFE with carbon fiber, the fabrication of fiber-reinforced PTFE composite by radiation crosslinking, and the mechanical properties of the composite obtained.

3. EXPERIMENTAL

Materials

Dispersion PTFE (AD1; average diameter of particles: 0.25μm, Mn: 1.4×10^6, Asahi-ICI Fluoropolymers Co. Ltd.) and carbon fiber (T-300; average diameter of fibers: 9μm, filaments: 12,000, TORAY Co. Ltd.) were used in the experiments.

Irradiation

The composite materials based on the dispersion PTFE and the carbon fibers with a size of $200 \times 15 \times 2 mm^3$ were put in an irradiation vessel with a heating device(9). They were heated up to 613K in helium gas atmosphere, and the temperature of the vessel was kept within a range of 613K±5K. And, the composites were irradiated in a range from 100kGy to 2MGy with a dose rate of 0.6kGy/s by the electron accelerator of 2MV installed at JAERI Takasaki.

Radiation resistance of the crosslinked PTFE composites was evaluated by measurements of their mechanical properties after the electron beam (EB) irradiation with a dose rate of 1.2kGy/s under atmosphere.

Measurements

Three points bending test and interlaminar shear strength (ILSS) test were carried out at ambient temperature using an INSTRON machine (type 4302). The crosshead speed in the bending test was 2mm/min with a span length of 32mm. And, the crosshead speed in the ILSS test was 1mm/min with a span length of 14mm. Flexural strength, flexural modulus and ILSS of the test pieces were calculated from the stress–strain curves obtained. Coefficients of friction and abrasion were measured by using thrust type frictional testing machine at ambient temperature. Testing pressure and velocity were $20 kgf/cm^2$ and 10m/min against the standard friction material of S45C (reference ring).

4. RESULTS AND DISCUSSIONS

Impregnation of PTFE to carbon fiber

It is too difficult to fabricate composites used long-fiber and PTFE resin, because PTFE is a high viscosity ($10^{10} \sim 10^{11}$P) at 653K in its molten state and insoluble to most chemical solvents. The condition on impregnation of PTFE resin to carbon fiber was studied. The several impregnation methods are to be considered: (A) impregnation of melting PTFE to the fibers, (B) impregnation of dissolved PTFE and (C) impregnation of dispersion PTFE. Method (A) and (B) could not be applied for the impregnation of PTFE resin to the fibers because of the reason mentioned above. On the other hand, method (C) can be applied for the impregnation process, because dispersion PTFE using for coating is so small that it is impregnated among the carbon fibers. Therefore, in the fabrication of the fiber-reinforced PTFE composite, aqueous dispersion of fine powder PTFE (AD-1) was used for the impregnation to the carbon fibers (T-300). The impregnated PTFE-carbon fiber materials were dried at 323K for 30min in an air oven. And, these were heated up to 623K (sintering temperature of PTFE) which is above the melting point of PTFE resin, compressed up to 15MPa by press, and then cooled down to ambient temperature under the pressure. The sintered composites (preformed PTFE composites) were obtained, and their volume fraction of the fiber (V_f) are 54.3 % and 64.0 %.

The mechanical properties of the sintered PTFE resin (non-crosslinked) and the preformed PTFE composite (non-crosslinked resin, V_f 54.3%) are shown in Table 1. In the preformed PTFE composite, flexural strength and flexural modulus are 42.6MPa and 10.9GPa, respectively, which are higher than those of the PTFE resin. However, the flexural properties of the preformed PTFE composite are poor, compared with those of commercial CFRP (Carbon Fiber-Reinforced Plastics: *e.g.* epoxy resin).

Table.1 Mechanical properties of PTFE resin and preformed PTFE composite (V_f 54.3%).

	Flexural strength (MPa)	Flexural modulus (GPa)
PTFE	17.6	0.59
Preformed PTFE composite	42.6	10.9

PTFE composite by using radiation crosslinking process

The preformed PTFE composite was irradiated by EB in the molten state (613K±5K) of PTFE resin in helium gas atmosphere with dose range from 100kGy to 2MGy to get the final composites (crosslinked PTFE composite) having various degrees of crosslinking.

Figure 1 shows the relationship between the flexural strength of the crosslinked PTFE composites and the crosslinking dose. The flexural strength increases with increasing in the dose until around 1MGy, then tends to decrease with increasing in the dose. Figure 2 shows the flexural modulus of the crosslinked PTFE composites as a function of the crosslinking dose. The flexural modulus increases with increasing in the dose until around 500kGy, then tends to decrease with increasing in the dose. The crosslinked PTFE composite with V_f 54.3% shows higher flexural properties, compared with those with V_f 64.0%.

When the preformed PTFE composite was irradiated by the higher temperatures, the decomposition gases from PTFE resin, such as F_2 or tetrafluoro-ethylene (TFE), are evolved, and the mass of PTFE decreases with increasing in the crosslinking dose with a mass loss rate at 10%/MGy(6). Thus, in the crosslinked PTFE composite with the higher V_f, *i.e.* low content of PTFE, the detachment between PTFE and the fibers would be easily occurred, because micro defects or vacancies are produced by the evolved gases in

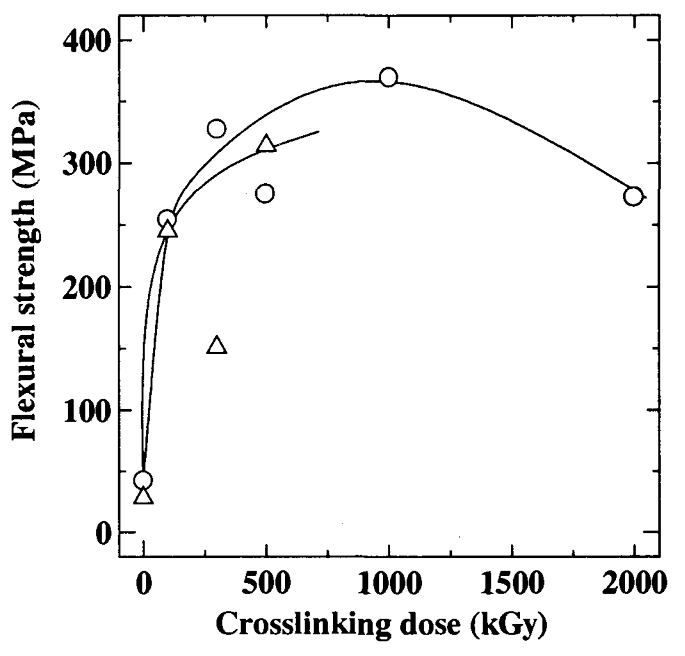

Figure 1 Relationship between flexural strength of crosslinked PTFE composite and crosslinking dose. O:V_f 54.3% and , △: V_f 64.0%.

the matrix resin.

The flexural strength and the flexural modulus of the crosslinked PTFE composite irradiated at 1MGy were about 370MPa and 55GPa, respectively. The flexural strength of the crosslinked PTFE composite was 21· times higher than that of the PTFE resin, and 9 times higher than that of the preformed PTFE composite (non-crosslinked). And, the flexural modulus of the crosslinked PTFE composite was about 100 times higher than that of PTFE resin, and 5 times higher than that of the preformed PTFE composite. These show that the composites based on crosslinked PTFE and the carbon fibers are obtained with the high mechanical properties by radiation crosslinking.

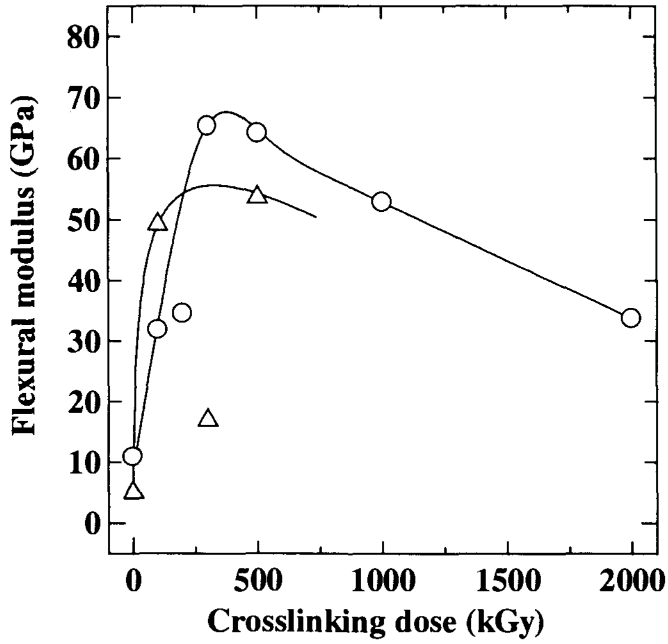

Figure 2 Relationship between flexural modulus of crosslinked PTFE composite and crosslinking dose. O:V_f 54.3% and , △: V_f 64.0%.

The ILSS of the crosslinked PTFE composites as a function of the crosslinking dose is shown in Fig.3. The ILSS of the composite with V_f 54.3% changes sharply with increasing in the crosslinking dose, then increases gradually with increasing in the dose. On the other hand, the flexural strength and the modulus increase with increasing in the dose until around 500-1000kGy, and then decrease with increasing in the dose, as shown in Figs.1 and 2.

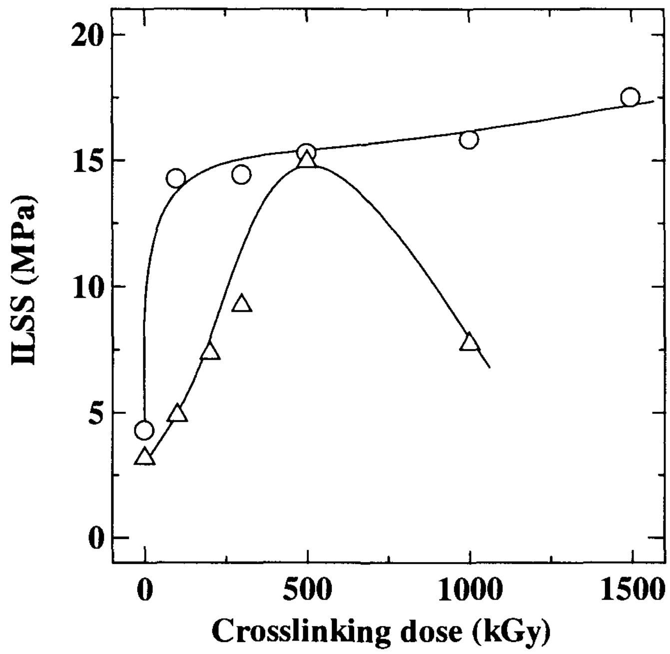

Figure 3 Relationship between the interlaminar shear strength (ILSS) of crosslinked PTFE composite and crosslinking dose. O:V_f 54.3% and , △: V_f 64.0%.

The gradual increase of ILSS in the higher crosslinking doses may be explained by the existence of carbon fibers entwined in the PTFE composites, because the fibers in the composite is not only aligned to one direction, but entwined a little around other direction.

The ILSS value is about 1/3

times lower than that of commercial CFRP (*e.g.* epoxy resin). It is indicated that adhesions between the crosslinked PTFE and the carbon fibers are hardly effective in these PTFE composites.

According to our previous studies on radiation-induced crosslinking of PTFE, the morphology of PTFE is changed from discontinuous stratum of a pile of random crystal phase to continual stratum of visco-elastically amorphous one by radiation crosslinking[6]. Thus, it is thought that the reason for the improvement of the mechanical properties in the crosslinked PTFE composite is caused by morphological change of PTFE from non-crosslinking to crosslinking because there is hardly an adhesion between PTFE and the carbon fibers even in the presence of crosslinking.

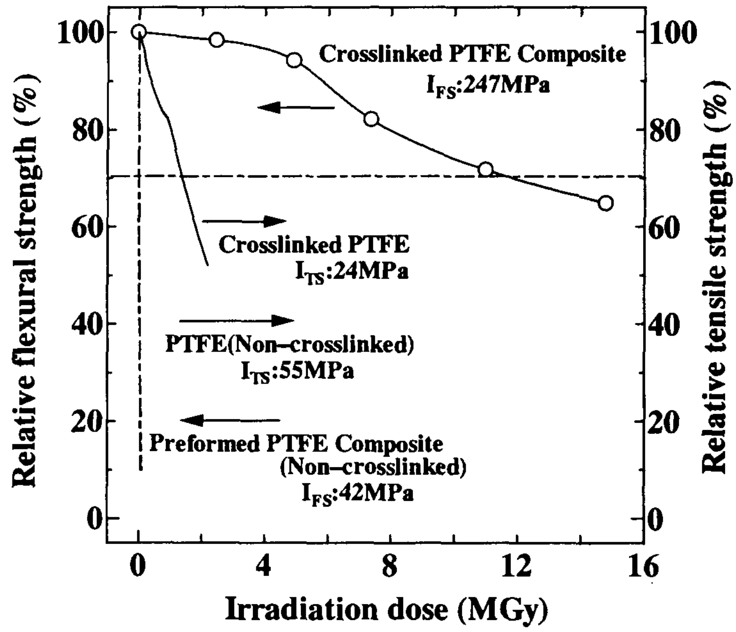

Figure 4 Relative radiation resistance of crosslinked PTFE composite (300kGy for crosslinking) as a function of irradiation dose.
Irradiation: 1.2kGy/s under atmosphere at ambient temperature.

Relative radiation resistances of the PTFE composite materials based on the crosslinked PTFE (300kGy for crosslinking) and the carbon fibers as a function of the dose irradiated under atmosphere are shown in Fig.4. In the preformed PTFE composite, the relative flexural strength decreases with a low dose within a few kGy. On the other hand, the relative strength of the crosslinked PTFE composite decreases slowly with higher doses, and the dose at the relative strength of 70 % is about 11 MGy. This shows that the radiation resistance of the crosslinked PTFE composite is 6 times higher than that of the crosslinked PTFE resin.

The radiation resistance of the crosslinked PTFE composite is much improved by introducing crosslinking of PTFE and by reinforcing with the carbon fibers, so this high radiation resistance could be explained by a radiation resistance of crosslinked PTFE, and a protection effects for radiation, which come from the carbon fibers. It is expected to apply this composite to construction materials in high radiation fields such as in nuclear or space environments.

We also tried to measure frictional properties of the PTFE composites. The frictional properties of the crosslinked PTFE resin (100kGy for crosslinking) and the crosslinked PTFE composite (100kGy) are listed in Table 2. The coefficient of friction for the crosslinked PTFE composite is as same as that of the crosslinked PTFE resin. In contrary, the coefficient of abrasion for the composite is about 4 times smaller than that of the crosslinked PTFE, *i.e.*

the coefficient of abrasion is improved by reinforcing of the carbon fibers. It is expected to use in high frictional properties required, such as bearing.

Table.2 Frictional properties of crosslinked PTFE (100kGy for crosslinking) and crosslinked PTFE composite (100kGy for crosslinking, V_f 54.3%).

	Coefficient of friction	Coefficient of abrasion ($\times 10^{-10} cm^3/kgfm$)
Crosslinked PTFE	0.13	775
Crosslinked PTFE composite	0.10	200

5. CONCLUSION

The crosslinked PTFE-carbon fiber composites are fabricated by using irradiation process. In the three-point bending test, the flexural strength and the flexural modulus of the crosslinked PTFE composite irradiated at 1MGy for crosslinking are about 370MPa and 55GPa, respectively. The frictional properties of the crosslinked PTFE composite are improved by 4 times better than that of the crosslinked PTFE resin. The crosslinked PTFE composite also shows high radiation resistance of 11MGy, compared with PTFE and the crosslinked PTFE.

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