12.11 Radiation Induced Crosslinking of Polytetrafluoroethylene

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Abstract — The Irradiation temperature effect on polytetrafluoroethylene (PTFE) from room temperature to 380°C was investigated by tensile test and thermal analysis. The behavior of tensile properties and changes of crystallinity on irradiation indicated the formation of a network structure in PTFE by radiation induced crosslinking in inert gas in the molten state just above the melting temperature of PTFE (327°C). The crosslinked PTFE showed a much improved radiation resistance in an atmospheric radiation field.

INTRODUCTION

PTFE has been well recognized as a typical polymer which undergoes chain scission by ionizing irradiation. The mechanical properties decay with a small dose either in air or even under vacuum irradiation(Dole,1973). Therefore, PTFE has limited use as a material in radiation fields such as in a nuclear facility or a space environment.

In recent studies, it was shown that the temperature of irradiation influenced the irradiation effect on polymers. For example, at very low temperature(e.g. 77K) for γ irradiation for PTFE, the probability of chain scission is reduced to 1/5 times, as compared with room temperature irradiation (Kudoh *et al.*,1994).

In the previous studies of irradiation effects on PTFE, some phenomena indicating the possibility of crosslinking were observed. Tutiya (1972) found that abnormal behavior occurred for irradiation around the melting temperature, but concluded it was due to changes in the morphology. Zhang(1988) proposed the possibility of crosslinking of PTFE, and recently the experimental details were disclosed (Sun *et al.*,1994). In Tabata's laboratory at Tokai University, experimental evidence for network formation by radiation crosslinking was observed (Tabata,1992).

In this work, electron beam(EB) irradiation effects on PTFE were investigated for a wide range of irradiation temperatures on the basis of experimental evidence obtained in our laboratory. This paper describes the technique of PTFE crosslinking by EB irradiation, and reports the mechanical and the thermal properties of the crosslinked polymer.

EXPERIMENTAL

Sample; PTFE sheets(Daikin Kogyo Co.Ltd.) with thickness of 0.5mm were used for the

experiments. The molecular weight was about 12 million, which was determined by the heat of crystallization using the differential scanning calorimeter (DSC) measurement technique developed by Suwa *et al.*(1973).

Irradiation; PTFE was set in a vessel with a heating device(Kanazawa *et al.*,1992), and irradiated up to 10kGy-5MGy with a dose rate of 0.5kGy/s using an EB accelerator of 2MeV at various temperatures ranging from room temperature(25°C; RT) to 380°C in an argon gas atmosphere. For assessment of the radiation resistance of the crosslinked PTFE, ^{60}Co-γ irradiation was carried out with a dose rate of 10kGy/h at RT in air.

Measurement; Tensile tests was carried out at RT, and the stress-strain(S-S) relations of the dumbbell (ASTM D-1822L) specimens were obtained with a cross head speed of 200mm/min. The yield strength, tensile strength, elongation at break, and modulus were determined from the S-S relations.

The melting and the crystallization temperatures, and heat of crystallization were measured by DSC under an atmosphere of nitrogen. Both heating and cooling rates in the DSC measurement were 20°C/min.

RESULTS and DISCUSSION

Figure 1 shows the elongation at break and tensile strength against dose for PTFE after EB irradiation to 100kGy at various temperatures in Ar. For the original PTFE, the elongation at break and tensile strength are 400% and 55MPa, respectively. Both elongation at break and tensile strength decreased to a large extent by irradiation at any temperature below the melting point. The both values decrease with increasing temperature until around 325°C, but they change drastically around the melting temperature of 327 °C. The maximum of each peak in Fig.1 was at about 340°C. The elongation at break is rather higher than that of unirradiated PTFE. At temperatures higher than 350°C, both elongation at break and tensile strength decrease sharply, and the mass loss was accelerated with dose, especially, at the surface of the sheets.

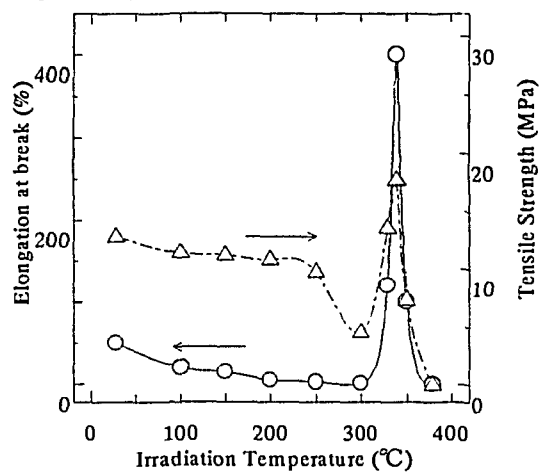

Fig.1 Irradiation temperature vs. mechanical properties for PTFE irradiated by electron beam to 100kGy in Ar gas

The degradation of PTFE is due to chain scission by irradiation, so the experimental results indicate that the probability of chain scission increases with irradiation temperature below the melting temperature. Above 350°C, the chain scission process may be accompanied by thermal depolymerization. At around 340°C, the radiation induced chemical reactions are changed very much, where the chain scission is much reduced or other reactions such as crosslinking may proceed with irradiation.

On the bases of the above experiments, the dose dependency at these temperatures was investigated. Elongation at break against dose is shown in Fig.2, for EB irradiated PTFE up to 5MGy in Ar at RT and 340°C. For the irradiation at RT, the elongation at break and tensile

strength decrease sharply with dose within 50kGy, as has been well known. However, for the irradiation at 340°C the elongation at break remains over 150% at 2MGy irradiation. The tensile strength decreases with dose at small dose up to 100kGy, then tends to increase with dose up to 5MGy.

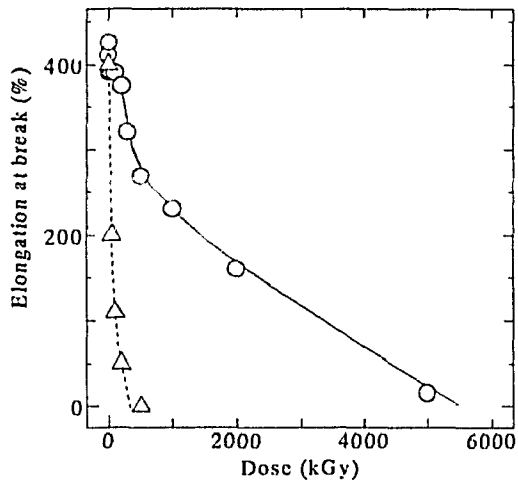

Fig.2 Elongation at break vs. dose for PTFE irradiated by electron beam in Ar gas at 340°C and at RT ; ○: irradiated at 340°C, △:irradiated at RT

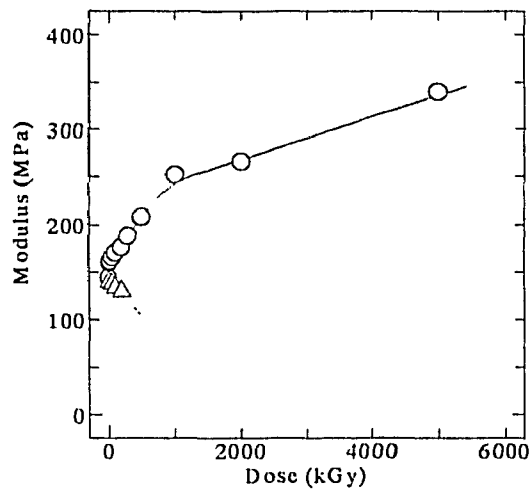

Fig.3 Modulus of PTFE irradiated by electron beam in Ar gas at 340°C and at RT ; ○: irradiated at 340°C, △:irradiated at RT

The yield strength, the stress at the knee point of S-S curve at the strain of about 10%, increases with dose. The modulus, which is determined from the slope of the initial line in the S-S curve increases with dose as shown in Fig.3. These results indicate that the crosslinking takes place preferentially in the molten state and a network structure is formed by the crosslinking.

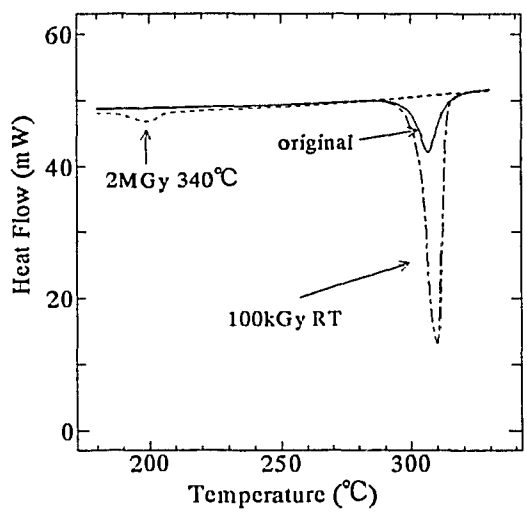

Fig.4 DSC thermograms of crystallization for PTFE irradiated in Ar gas at 340°C and at RT

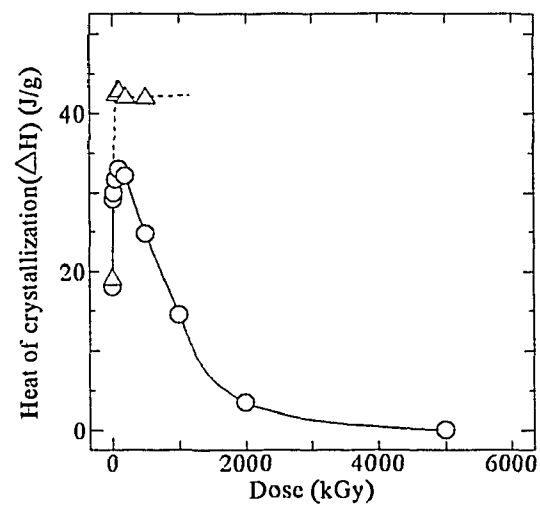

Fig.5 Heat of crystallization(ΔH) for PTFE irradiated in Ar gas at 340°C and at RT ;○: irradiated at 340°C, △:irradiated at RT

Figure 4 shows the DSC thermograms and the crystallization peaks for specimens irradiated

by EB in Ar at 340°C and at RT. The crystallization of unirradiated PTFE begins at 315°C. However, for the irradiation at RT, the temperature of the peak for crystallization is the same as the original sample but the peak intensity increases with dose. In the case of irradiation at 340°C, with increasing dose the crystallization temperature shifts to lower temperatures, and the peak intensity decreases.

The heat of crystallization(ΔH) determined from the peak area in the DSC thermograms is plotted in Fig.5. The ΔH reflects the amount of the crystalline component in PTFE, so the result indicates that the crystallization is much depressed with increase of dose in the molten state. Above 350°C, the crystallinity also decreased with dose. As the properties of the crystalline component decreased with the increase in the network density, the PTFE sheet became transparent and had a rubber like property.

Figure 6 shows the relative elongation against dose for various crosslinked PTFE samples after γ irradiation up to 600kGy in air at RT. The dose for half decay of ultimate elongation for crosslinked PTFE(500kGy) was about 300kGy, while the dose was only 3kGy for the original PTFE. The radiation resistance at RT increases with the crosslinking density. The crosslinked PTFE showed that the radiation resistance in an atmospheric radiation field was very much improved.

It was found that the changes in the tensile properties and the crystallization behavior of PTFE irradiated at around 340°C in the molten state were completely different from the solid state irradiation. The changes and the behavior in the molten state irradiation strongly suggest that the network is formed by radiation induced crosslinking in PTFE. Especially, the increase in the yield strength and in the modulus indicates an increase in the network density in PTFE. Generally, it is accepted that these values increase with increasing crosslinking density for linear polymers.

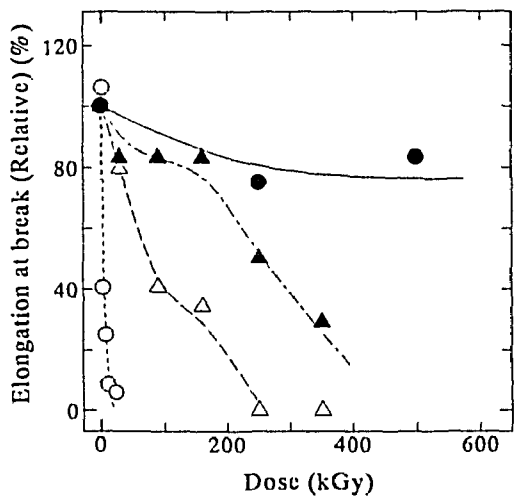

Fig.6 Elongation at break(relative) vs. dose γ-irradiation in air for PTFE crosslinked with various conditions ;○:0kGy at 340°C, △:300kGy at 340°C, ▲:500kGy at 340°C,●: 2MGy at 340°C

The crosslinking between PTFE polymer chains should prevent the crystallization of the chains from the molten state. When the crosslinking density is small, the chains with rather long segments between the crosslinking points may crystallize, but the crystal size becomes smaller with an increase in the crosslinking density. The shift of the crystallization temperature and the decrease in the crystallization enthalpy are well explained by the above model.

Since the PTFE molecule has a helical coil structure in the crystalline state below the melting temperature, the free radicals formed by radiation are restricted in their ability to react with the radicals formed on neighbor molecules by the steric hindrance of the molecular chain. Above the melting temperature molecular mobility would be much improved, and radical could combine more easily with other radicals to form crosslinks.

At temperatures higher than 350°C, the thermal depolymerization of PTFE is accelerated by irradiation, and it may exceed the crosslinking. Then, the mechanical properties decrease greatly

with irradiation dose.

As the radiation resistance of crosslinked PTFE is markedly improved, it is expect to find applications as a material for use in the radiation fields.

CONCLUSION

Main chain scission of PTFE is the predominant reaction on irradiation and tends to increase with irradiation temperature below the melting temperature. On the other hand, network formation proceeds on by irradiation in the molten state just above 340°C. At higher temperature than 350°C, the depolymerization proceeds because of the combined effects of thermal stress and radiation. By network formation through the crosslinking of PTFE, the crystallinity was decreased and the mechanical properties, such as yield strength and modulus, were improved. As the crystalline component decreases with crosslinking density, the crosslinked PTFE will become transparent. The radiation resistance of PTFE is improved significantly by the crosslinking.

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