Development of advanced fluoro polymer for nuclear environment

原子力環境用高性能フッ素樹脂の開発

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The irradiation temperature effect on polytetrafluoroethylene (PTFE) was investigated by tensile test and thermal analysis. The behavior of mechanical properties and changes of crystallinity on irradiation indicated the network formation in PTFE molecules by radiation induced crosslinking under oxygen-free atmosphere in the molten state around 613K. The radiation resistance of PTFE was much improved by crosslinking, that is, the irradiation dose at a half value of ultimate elongation was about 1MGy for 500kGy-crosslinked PTFE, while the dose for non-crosslinked PTFE was only 3.5kGy, so it is expected that the crosslinked PTFE can be applied for the nuclear facilities with relatively high radiation environment. Also, the crosslinked PTFE had light transparency due to the decrease of crystallites, and held the electrical insulation and heat resistance. The abrasion factor in frictional test was greatly improved by crosslinking.

Keywords : PTFE, Radiation, Crosslinking, Mechanical properties, Radiation resistance, Light transmittance, Electrical properties, Frictional properties.

I. INTRODUCTION

It is well known that polytetrafluoroethylene (PTFE) so-called Teflon[®] has the excellent properties in electric insulation, high frictional properties, high stability to most chemical solvents and heat resistance in polymer materials. Thus, PTFE is widely used for various purposes under severe conditions. However, PTFE is extremely sensitive to radiation occurring chain scission, to result that the mechanical properties degrade with a small dose of a few kGy either in air or even under vacuum irradiation.¹ Therefore, PTFE with excellent properties has not been applied in radiation fields such as in nuclear or space

environments.

It has been believed past long years that PTFE can't take place crosslinking by any methods as chemical agents and ionizing irradiation. However, in our previous studies on irradiation effects of fluoro-polymers, it was found that PTFE could be induced crosslinking by γ -rays and electron beams (EB) irradiation under a special condition, where the irradiation was carried out at high temperature of the molten state of PTFE under oxygen-free atmosphere.²⁻⁶

In this paper, the processing of PTFE crosslinking by ionizing radiation, and the radiation resistance of crosslinked PTFE and other properties are reported, on the point of

advanced polymer materials for nuclear environment.

II. EXPERIMENTAL

A. Materials and crosslinking

PTFE film with 500 μ m thickness supplied from Asahi Glass Co. Ltd. was used for the experiments. The molecular weight was about 9million, which was determined by Suwa's equation⁷ using a differential scanning calorimetric measurement. PTFE film of 30 $\times$ 9cm² size was put in an EB irradiation vessel with heating device.⁸ The film was heated up to 613K controlled within the range of $\pm$ 3K in argon gas atmosphere, and irradiated up to 10kGy to 3MGy with a dose rate of 0.6kGy/s by an electron accelerator of 2MeV installed at Japan Atomic Energy Research Institute (JAERI). The PTFE specimens with different crosslinking density were prepared by changing irradiation dose. Each crosslinked PTFE was cut to a dumb-bell shape (ASTM D-1822L) specimen for the tensile test.

B. Irradiation for radiation resistant test

The radiation resistance of the crosslinked PTFE was evaluated by the measurements of mechanical and thermal properties after ⁶⁰Co γ -irradiation under vacuum or in air at room temperature (297K). The specimen for vacuum irradiation was sealed in a glass tube after evacuation to 10⁻¹Pa for about 24 hours, then irradiated up to 2kGy - 2.1MGy with a dose rate of 10kGy/h. Also, the specimens were irradiated in air up to 2kGy - 600kGy with the same dose rate.

C. Measurement

The mechanical properties measurement was carried out at room temperature using a tensile test machine (INSTRON type 4302). The stress-strain (S-S) curves of the dumb-bell specimens were observed with a cross head speed of 200mm/min. The ultimate elongation, tensile strength, yield strength and modulus were determined from the S-S curve.

The melting (T_m) and the crystallization (T_c) temperatures, and the heat of crystallization (ΔH) were measured by using a differential scanning calorimeter (DSC; Parkin Elmer, DSC-7) under nitrogen atmosphere. Both the heating and the cooling rates in the DSC measurement were 20K/min. The heat of crystallization was determined from the peak area in the DSC thermogram at crystallization. The melting and the crystallization temperature were determined at the respective peak in the thermograms.

The light transmittance was measured using a spectro-photometer (Beckman, DU-65) at room temperature in air in the range from 200nm to 900nm. The spectrum of each specimen was observed with a scanning speed of 500nm/min.

The electric properties as loss of the dielectricity ($\tan \delta$) and dielectric constant (ϵ) at 60Hz and volume resistance were measured by JIS method at room temperature in air.

Friction coefficient (μ) and abrasion factor by friction were measured using a Matsubara type friction testing machine at room temperature in air. Testing pressure and velocity were 2.5kg/cm² and 0.5m/sec against the friction material of SUS 304.

III. RESULT AND DISCUSSION

A. Radiation induced crosslinking of PTFE

Figure 1 shows the ultimate elongation (strain at break) and tensile strength (stress at break) against irradiation temperature for PTFE after irradiation to 100kGy at various temperatures in inert gas atmosphere. For the virgin (non-irradiated PTFE), the ultimate elongation and tensile strength are about 400% and 55MPa, respectively. Both ultimate elongation and tensile strength decrease with increasing irradiation temperature until around the melting temperature (600K) of PTFE, but they change drastically around 600K, and the sharp peaks in both values are seen at around 613K. At temperatures higher than around 633K, both ultimate elongation and tensile strength have small value, and the mass loss was accelerated with dose, especially, at the

FIG.1. Relationship between mechanical properties and irradiation temperature for PTFE irradiated to 100kGy in inert gas atmosphere. Irradiation was carried out with γ -rays at 77K in liquid nitrogen, and electron beam at the other temperatures in argon gas ; $\circ$: Ultimate elongation, $\triangle$: Tensile strength.

surface of films.

The molecular weight of PTFE calculated from Suwa's equation⁷ decreased with increase of irradiation temperature until 600K. The decrease of molecular weight corresponds to the decay in mechanical properties. The degradation of PTFE by irradiation is due to main chain scission, so the experimental results indicate that the probability of chain scission

increases with irradiation temperature below the melting point. Above 633K, the chain scission occurs, and the process may be accompanied by thermal depolymerization. At around 613K, the radiation induced chemical reactions are changed extremely, where the crosslinking proceeds and the chain scission is much reduced.

On the basis of the above experiments, the dose dependency at 613K was investigated. The ultimate elongation against dose is shown in Fig.2 for irradiated PTFE up to 3MGy in argon gas atmosphere at room temperature and 613K. The ultimate elongation decreased sharply with dose at room temperature irradiation, which was the same as a previous paper.⁹ However, for the irradiation at 613K the ultimate elongation remains over 150% after 2MGy irradiation.

Figure 3 shows the yield strength, which was the stress at the knee point of S-S curve at the strain of about 10%, against dose for irradiated PTFE up to 3MGy in argon gas atmosphere at room temperature and 613K. The yield strength for PTFE irradiated at 613K increases with dose. The modulus, which is determined from the slope of the initial line in the S-S curve increased also with dose. Both increase in the yield strength and in the modulus indicate the increase of network

FIG.2. Ultimate elongation as function of EB dose for PTFE irradiated in argon gas at room temperature and 613K ; $\circ$: 613K, $\triangle$: room temperature.

FIG.3. Yield strength as function of EB dose for PTFE irradiated in argon gas at room temperature and 613K ; $\circ$: 613K, $\triangle$: room temperature.

density in PTFE molecules by crosslinking. Generally, it is accepted that these values increase with increasing crosslinking density for linear polymers. Therefore, these results indicate that the crosslinking takes place preferentially in the molten state and a network structure is formed by radiation induced crosslinking.

The melting(T_m) and the crystallization (T_c) temperatures, and heat of crystallization (ΔH) of PTFE by radiation induced crosslinking was measured by thermal analysis using a DSC. Both T_m and T_c hardly changed by irradiation except the crosslinking condition(613K, oxygen-free atmosphere), but, T_m and T_c shift to lower temperatures by progress of the crosslinking density. Figure 4 shows the ΔH against dose for irradiated PTFE at room temperature and 613K in argon gas atmosphere. The ΔH reflects the amount of the crystalline component in PTFE. PTFE irradiated at room

temperature has high crystallinity due to the crystallization of amorphous region through the main chain scission as reported in previous works.^{10,11} On the other hand, for the molten state irradiation at 613K, the crystallinity decrease greatly with dose except at a small dose. It means that the crystallization is much depressed by the radiation crosslinking at the molten state. As the crystalline region decreased with the progress of crosslinking density, the PTFE films became transparent and had a rubber like property. For the irradiated above 633K, the crystallinity decreased with dose though the mechanical properties degraded where radiation crosslinking proceeds and thermal decomposition would be accompanied.

The changes of mechanical and thermal properties of PTFE with various crosslinking are summarized in Table 1.

B. Radiation resistance of crosslinked PTFE

For the virgin PTFE, both of the ultimate elongation and tensile strength degrade greatly with a few kGy by γ -rays irradiation at room temperature under vacuum and in air, which has been the same as a previous paper.⁹ Ultimate elongation for three different radiation crosslinked PTFE(RX-PTFE) are shown in Figs.5-(a) and (b), as a function of γ -irradiation dose at room temperature under vacuum and in air, respectively. The ultimate elongation and the tensile strength for RX-PTFE degraded gradually with dose. For examples, the doses at a half value of the ultimate elongation after irradiation under vacuum are 1.1MGy for RX-

FIG.4. Heat of crystallization(ΔH) as function of EB dose for PTFE irradiated in argon gas at room temperature and 613K ; $\circ$: 613K, $\triangle$: room temperature.

TABLE 1. Mechanical and thermal properties of crosslinked PTFE(RX-PTFE).

Sample code	Dose for EB crosslink (kGy)	Mechanical properties			Thermal properties	
		Eb ^{*1} (%)	Ts ^{*2} (MPa)	Ys ^{*3} (MPa)	Tm ^{*4} (°C)	ΔH ^{*5} (J/g)
Virgin	0	402	55.0	11.3	328	20
RX-50	50	395	21.4	13.0	323	29
RX-100	100	380	22.9	15.2	318	33
RX-500	500	271	25.6	18.7	298	25
RX-1M	1000	235	26.0	21.4	281	16
RX-3M	3000	100	32.5	30.1	178	1.7

*1:Ultimate elongation, *2:Tensile strength, *3:Yield strength, *4:Melting temperature, *5:Heat of crystallization

FIG.5. Ultimate elongation at break as function of γ -dose for crosslinked PTFE; γ irradiation was carried out at room temperature under vacuum(a) and in air(b). $\circ$: 1MGy-crosslinked, $\triangle$: 500kGy-crosslinked, ∇ : 50kGy-crosslinked, ---- (Broken line): virgin(non-crosslinked).

500, and 1.9MGy for RX-1M, and in a case of irradiation in air, the doses are 250kGy and 360kGy, respectively. In contrary, for virgin PTFE, the dose at a half elongation value was only 3.5kGy under vacuum and 2kGy in air. In a case of RX-1M, the radiation resistance, dose at a half of ultimate elongation under vacuum at room temperature, was 540 times higher than the virgin. Doses at the half values for RX-PTFE were compiled in Table 2, as an index of radiation resistance for γ -rays irradiation at room temperature under vacuum and in air. The radiation resistance increases greatly with the increase of crosslinking density either in air or even under vacuum. The radiation resistance under vacuum irradiation is higher by several times than that in atmospheric irradiation as

same as other polymer materials.¹²

The heat of crystallization(ΔH) of virgin and RX-PTFE after γ -rays irradiation at room temperature under vacuum and in air, increases sharply with a small dose for virgin as same work as other researchers,^{10,11} but it is suppressed by increasing in crosslinking density. The changes of ΔH are well related to the mechanical properties in Fig. 5, that is, the crystallinity increase reduces the mechanical properties.

For PTFE, the molecules are aligned in extended chain to form crystals with band structure, and the crystal size(band thickness) is about 0.2-0.5 μm ^{13,14} which is quite different from other polymers such as polyethylene or polypropylene. For the virgin, effective chain scission occurs in disordered, boundary region in the polymer matrices, which makes to proceed further crystallization much easier. As the result, a large number of small crystallites could be formed. The deterioration of non-crosslinked PTFE in mechanical properties would be explained with above model.

As the crosslinking increases, the crystallization temperature decreases. This is indicating that size of the crystallites becomes small, and crystallites with small size are dispersed in the crosslinked polymer matrices. The crosslinked PTFE shows the low crystallinity, because the crosslinking disturbs the alignment of molecular chains as same as other polymers. For the PTFE with a certain crosslinking density, the crystallization of chains could be suppressed to some extent by the network structure. The network structure of RX-PTFE has a high yield strength and a moderate ultimate elongation. The big improvement of the radiation resistance in mechanical properties for crosslinked PTFE can be explained above mechanisms.

TABLE 2. Index of radiation resistance of crosslinked PTFE ; Dose at half value in ultimate elongation(E_b) and tensile strength(T_s).

Sample code	Dose at 1/2 E_b (kGy)		Dose at 1/2 T_s (kGy)	
	vacuum	air	vacuum	air
Virgin	3.5	2.0	3.5	1.5
RX-50	510	70	> 900	100
RX-500	1050	250	>2100	450
RX-1M	1900	360	>2100	>600

Concerning the improvement of radiation resistance, energy or charge transfer to the crosslinking sites also may play an important role.¹⁵

The radiation degradation of crosslinked PTFE is more accelerated in air than under vacuum, as same as that for other chain scission type polymers. In air irradiation, the oxidation takes place to accelerate the chain scission, and the mechanism of radiation induced oxidation for PTFE was studied by electron spin resonance(ESR) technique.¹⁶ Generally, radiation induced oxidation in polymer sheet depends on the dose rate and the sheet thickness due to the oxygen diffusion control into the sheet. For PTFE, the oxygen permeability is rather large, the oxidation proceeds well throughout the PTFE film of 500 μ m thickness when the γ -rays dose rate is high as 10kGy/h or so.

The radiation resistance increases greatly with the crosslinking density both under vacuum and in air, so it is expected that the crosslinked PTFE can be used for the nuclear facilities with relatively high radiation environment. The improvement by crosslinking is very much pronounced compared with other polymers, which indicates that the change of morphology in PTFE by crosslinking would much contribute to radiation resistance.

C. Other properties of crosslinked PTFE

Light transmission for various crosslinked PTFE films(500 μ m) as a function of the wavelength was measured as shown in Fig.6. The virgin PTFE was a very poor transparency at wide range from near infrared to near ultra violet. However, the transmission increases much in the infrared range with progress of the crosslinking density. For near ultra violet range of 320nm, the 90% transmission can be achieved after 3MGy irradiation in crosslinking condition(RX-3M). The light transmission would be disturbed by light scattering of PTFE crystals. With increase of crosslinking density, the size of crystallites become small and the quantity decreases, so the light transmission was improved by decreasing the light scattering

FIG.6. Light transmittance as function of wavelength for crosslinked PTFE.

with the crosslinking.

The change of electric properties by crosslinking was listed in Table 3. The loss of dielectricity($\tan \delta$) increased slightly and dielectric constant(ϵ) tended to decrease by the progress of crosslinking density. The volume resistance was hardly changed by highly crosslinking PTFE as RX-1M. Thus, it is confirmed that the electrical insulation are held for crosslinked PTFE.

Friction coefficient(μ) and abrasion factor for virgin and crosslinked PTFE were listed in Table 4. The μ of virgin is very low and decreased at small crosslinking density but

TABLE 3. Electrical properties of crosslinked PTFE ; Volume resistance(V.R.), loss of the dielectricity($\tan \delta$) and dielectric constant(ϵ) at 60Hz.

Sample code	Electrical properties		
	V.R. (Ω cm)	$\tan \delta$ (% , 60Hz)	ϵ (60Hz)
Virgin	$>1.0 \times 10^{18}$	0.004	2.05
RX-100	$>1.0 \times 10^{18}$	0.004	1.98
RX-500	$>1.0 \times 10^{18}$	0.005	1.97
RX-1M	$>1.0 \times 10^{18}$	0.005	1.90

TABLE 4. Frictional properties of crosslinked PTFE ; Friction coefficient(μ) and abrasion factor(A).

Sample code	Frictional properties	
	μ	A($\text{cm}^2 \cdot \text{s} / \text{kgf} \cdot \text{m} \cdot \text{h}$)
Virgin	0.35	2.0×10^{-2}
RX-100	0.31	4.6×10^{-6}
RX-500	0.41	1.9×10^{-5}
RX-1M	0.44	2.8×10^{-5}

tends to increase. The abrasion factor decreases drastically by crosslinking, that is, the value decreases by more than 3 order after 100kGy-crosslinking(RX-100).

IV. 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, the crosslinking proceeds well by irradiation in the molten state at around 613K in the oxygen-free atmosphere. At higher temperature than 633K, the depolymerization proceeds because of the combined effects of thermal stress and radiation.

The crosslinked PTFE showed an excellent radiation resistance, which is the same grade of polyethylene or polyvinylchloride(PVC), so it is expected to apply for the nuclear environment such as nuclear facilities. Also, the crosslinked PTFE became transparency due to the decrease of crystallites. The radiation resistance and abrasion factor of PTFE were greatly improved by crosslinking. The crosslinked PTFE holds electrical insulation and heat resistance like as virgin.

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