A New Development of the Crosslinking Technology for Fluororesin

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Fluoropolymers have excellent properties such as heat resistance, chemical resistance, and low friction. However, their susceptibility to wear has been a significant drawback. The cross-linked fluoropolymer FEX, developed using electron beam crosslinking technology, has significantly enhanced wear resistance and paved the way for its use as a sliding material. In the past, application to general molded products was challenging due to the requirement for electron beam irradiation in a molten state exceeding the resin's melting point, causing to deformation of the molded shape. This paper presents recent insights into the utilization of FEX technology for such molded applications.

Keywords: fluoropolymer, electron beam crosslinking, wear resistance, general molding

1. Introduction

The unique properties of fluoropolymers, including polytetrafluoroethylene (PTFE), as a plastic material, such as high heat resistance, the lowest coefficient of friction, and a non-stick characteristic, are due to their molecular structure, in which fluorine atoms strongly bonded with carbon atoms densely cover carbon backbones (Fig. 1). The atomic radius of fluorine is larger than that of carbon; hence, the PTFE molecule is rigid and is extremely low in mobility.

Meanwhile, in ionizing radiation processing technology, fluoropolymers are generally categorized into a polymeric material that has very low radiation stability, or that cannot be crosslinked by electron beam irradiation. A possible major reason for this is that the material's molecular mobility is inhibited by its molecular stiffness arising from the aforementioned molecular structure, resulting in failure to create additional molecular bonds; in other words, even if radical*1 for crosslinking is generated by irradiation, they cannot meet each other.

For this reason, to enable electron beam crosslinking of a fluoropolymer, it is necessary to melt the polymer by heating it above its melting point so as to expose it to ionizing radiation in a state in which its molecules move freely.(1) However, this limitation that crosslinking is only possible in a molten state has prevented this technology(2) from being widely put to practical use.

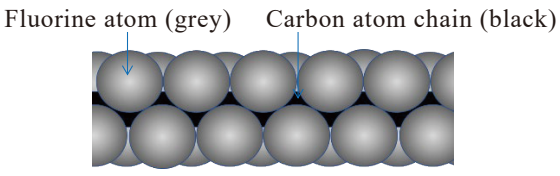


Fig. 1. Rendered image of PTFE molecule

2. Crosslinked Fluoropolymer FEX

Sumitomo Electric is expanding the use of its fluoropolymer product FEX (Fluoro Ethylene crosslinking [X-linking]) to sliding parts, leveraging the material's significant improvement in wear resistance owing to crosslinking of a fluoropolymer coating.(3) In addition, by refining continuous heating and irradiation technology, Sumitomo Electric is promoting the material's application to adhesive tape products.

Figure 2 and Table 1 present a schematic diagram illustrating the mechanism underlying the improved wear resistance of the crosslinked fluoropolymer and critical PV values*2 as an indicator of wear resistance.(4)

Due to their very low surface free energy, fluoropolymer molecules have poor affinity even between the same molecules, let alone other substances. Their molecules easily come off the surface. Use of electron beam crosslinking, however, creates molecular bonds and prevents the molecules from coming off (Fig. 2).

Nonetheless, the reason why plastics are currently in wide general use is that the material can be melted by heat, be molded into the desired shape, and maintain the molded

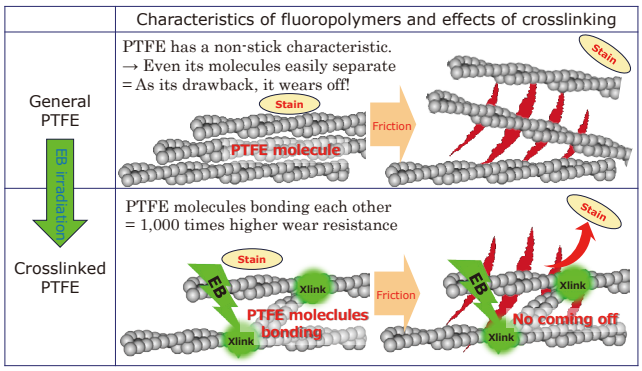


Fig. 2. Conceptual diagram illustrating improved wear resistance of FEX 1 Rendered image of PTFE molecule

shape when it returns to room temperature. Melting a fluoropolymer, for its electron beam crosslinking, results in failure to keep the hot-formed shape. How to make improvements regarding this drawback is a key point for future advances in fluoropolymer crosslinking technology.

This paper describes studies for improving fluoropolymer crosslinking technology, with the aim of expanding the use of crosslinked fluoropolymers.

Table 1. Critical PV Values of FEX and Other Polymers

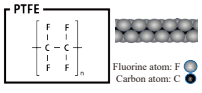
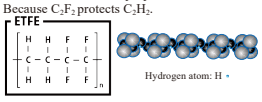
	Velocity (m/min)	Pressure (Mpa)	Critical PV value (Velocity × Pressure)
Crosslinked fluoropolymer FEX	120	10	1,200
Polytetrafluoroethylene (PTFE)	1	1	1
Polyacetal (POM)	10	10	100
Polyetheretherketone (PEEK)	10	10	100
Polyphenylenesulfide (PPS)	5	10	50

3. Development of Crosslinked Fluoropolymer Products

3-1 Crosslinked ETFE products

Ethylene tetrafluoroethylene (ETFE) (Table 2) is the copolymer of ethylene and tetrafluoroethylene. It is the fluoropolymer that exhibits plastic characteristics second most favorable to those of what is called "all-fluoropolymers," including PTFE.

Table 2. Comparison of Structures and Characteristics of PTFE and ETFE

	Polytetrafluoroethylene (PTFE)	Ethylene tetrafluoroethylene copolymer (ETFE)
Structure	Fluorine-14, which is larger than carbon-12, protects carbon chains 	ETFE is a hybrid of PE and PTFE and has a similar level chemical properties to PTFE. Because C_2F_2 protects C_2H_2. 
Melting point	330°C	260°C
Moldability	Fair: The only viable method is cutting of a bulk material	Good: ETFE is compatible with general plastic molding
EB crosslinking situation	Requires a special environment (Oxygen free, Heating over MP)	Good: crosslinked even at room temperature and in the atmosphere

ETFE is a polymer compatible with irradiation-crosslinking and is suitable for electron beam crosslinking using electron beam radiation at room temperature. Moreover, its low melt viscosity makes it possible to apply general plastic molding, such as injection molding, which is difficult to apply to PTFE. Therefore, the material can be molded into previously difficult shapes, such as tubes and complex gears. Unlike FEX, molded pieces of ETFE can be crosslinked by electron beam irradiation with their shape maintained, without heating and melting during irradiation. Consequently, crosslinking can be applied to ETFE products of various shapes (Photo 1).

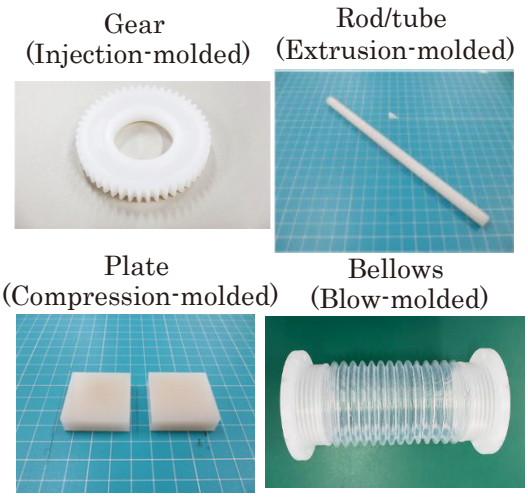


Photo 1. Examples of crosslinked ETFE products

Compared to PTFE, whose coefficient of friction is lowest among plastics, ETFE has twice as much friction resistance as PTFE and is therefore poorer in performance than PTFE as a sliding material. However, the surface of electron-beam-irradiated and crosslinked ETFE exhibits as low friction resistance as that of PTFE (Fig. 3).[5]

The authors have investigated the cause of the reduction in friction resistance. As a result, it is highly likely that an increase in the concentration of fluorine atoms on the surface of the ETFE product is involved in the reduction.[6]

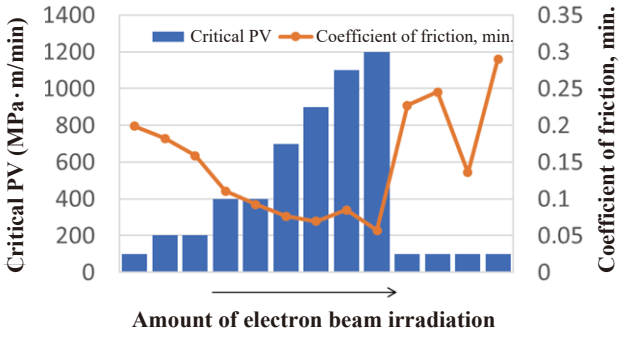


Fig. 3. Effect of electron beam irradiation on ETFE's frictional characteristics

Figure 4 presents the results of measurements of atomic concentrations of surface elements obtained by X-ray photoelectron spectroscopy (XPS: ULVAC PHI Quantes)[7] while digging the surface of crosslinked ETFE in 40 nm increments by means of sputtering. The sputter depth is plotted along the x-axis, while the atomic concentrations of elements are plotted along the y-axis. (In this method, hydrogen was not detected.) This measurement example shows that the atomic concentration of fluorine (F) is higher than that of carbon (C) to a depth of 200 nm from the surface. This *fluorine-rich layer* (indicated with ∗ in Fig. 4) did not exist before electron beam irradiation.

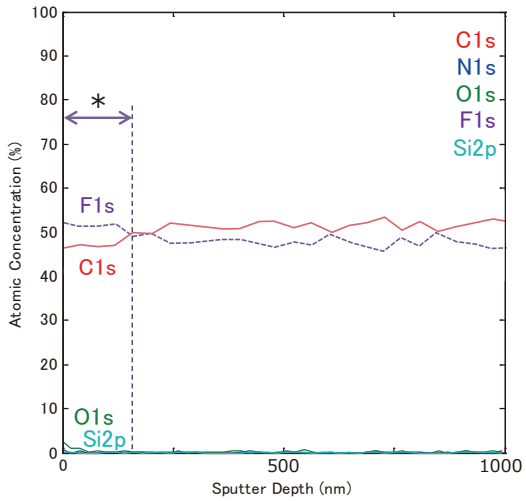


Fig. 4. Fluorine-carbon ratio on electron beam irradiated surface of ETFE

It is known that free fluorine radicals*[1] generated by electron beam irradiation pull out, and replace, atoms of low bonding strength.[8] Therefore, the above-described phenomenon is presumed to be the result of electron beam irradiation, which replaced hydrogen atoms in ETFE molecules in the surface layer with fluorine radicals.

In other words, on the surface of crosslinked ETFE, the concentration of fluorine atoms increased to a depth of a few hundreds of nanometers, probably causing the material's coefficient of friction to decrease to a level close to that of PTFE, with the molecular state being similar to that of PTFE.

3-2 Crosslinked ETFE and surface treatment with fluorine gas

When polyethylene is exposed to fluorine gas in an oxygen-free atmosphere, hydrogen atoms in polyethylene molecules on the surface are replaced with fluorine atoms, similarly to the aforementioned mechanism, contributing to improved chemical resistance of the polyethylene.[9]

It has been known that by combining electron beam crosslinking of ETFE and surface fluorination through fluorine-gas treatment, it is possible to achieve ① a deeper, or thicker, fluorinated layer and ② improved frictional durability.[6]

Thicknesses of fluorine-rich layers of ETFE achieved by fluorine-gas treatment and/or electron beam irradiation were compared by means of the above-described measurement method using XPS. The fluorine-rich layer achieved by electron beam irradiation combined with fluorine-gas treatment was more than twice deeper than that achieved by either electron beam irradiation or fluorine-gas treatment (Table 3).

Table 3. Depth of fluorine-rich layer on the surface of differently treated ETFE

	Depth of fluorine-rich layer (nm)
Untreated ETFE	0
EB crosslinking only	200
Fluorine-gas only	720
Crosslinking + Fluorine gas	1440

The fluorine-rich layer grew significantly thicker due to the combination of electron beam crosslinking and surface treatment with fluorine gas probably because of different sources of fluorine radicals—from the surface of ETFE in the case of gas treatment and from within ETFE itself in the case of electron beam irradiation liberating fluorine.

Next, the friction resistance of an electron beam crosslinked ETFE tube having undergone fluorine-gas treatment was measured. The tube was secured in the shape of the letter S, a nylon-coated stainless steel wire was inserted through the tube, the upper end of the wire was attached to a load cell, a 1 kgf weight was suspended from the lower end of the wire, and the load cell moved up and down a total of 100 cycles. The apparatus is illustrated in Photo 2. The test conditions are listed below.

- Measurement apparatus: Imada Seisakusho SDT-503NB
- Measurement procedure: Moving by +12 mm from home position, then returning to home position
- Moving rate: 10 mm/min both ways, 20 s at rest when changing direction
- Number of cycles: 100 (consecutive)

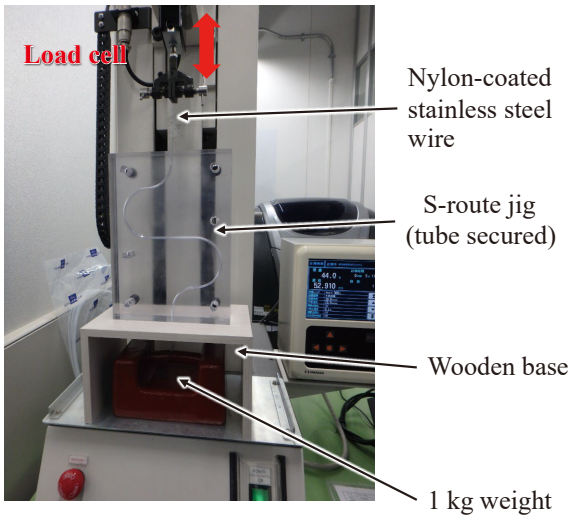


Photo 2. Exterior of measurement apparatus for friction resistance of tube inner surface

Figure 5 illustrates a measurement example, which plots load-stroke curves of the first and 100th cycles. The arrows with a dashed line indicate the order in which the data was measured. The data represents the results obtained with an untreated ETFE tube used as a control sample, whose friction resistance increased by approximately 50% by the 100th cycle as compared to the first cycle.

Figure 6 presents graphs representing changes in friction resistance as a result of repeated abrasion, in other words, durability. The number of cycles is plotted along the x-axis, and the maximum friction resistance in each cycle is plotted along the y-axis.

The resistance value of the aforementioned uncrosslinked ETFE quickly doubled, while that of samples having

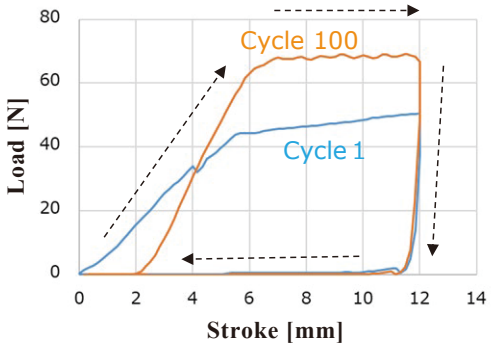


Fig. 5. Example of measuring friction resistance of tube inner surface

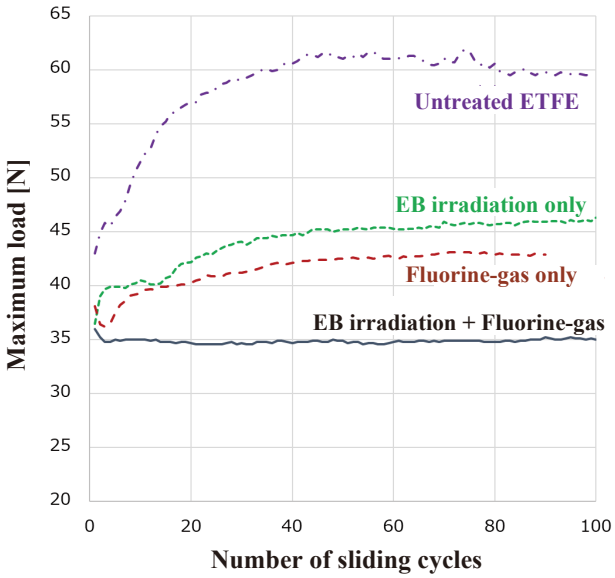


Fig. 6. Change in friction resistance during repeated abrasion

undergone either fluorine-gas treatment or electron beam crosslinking gradually increased. In contrast, the sample having undergone the combination of fluorine-gas treatment and electron beam crosslinking exhibited no change in resistance even at the 100th cycle of sliding abrasion.

After the 100th cycle was completed, plastic dust resulting from wear of the stainless wire surface was evident with the uncrosslinked ETFE and was scarcely observed with electron beam crosslinked ETFE. The effect of crosslinking in improving wear resistance was also observed with the tube shape.

Thus, as a sliding material, crosslinked ETFE has excellent characteristics comparable to crosslinked PTFE. The material is promising as a material for various low-friction and wear-resistant parts in that it can be molded into shapes such as tubes.

3-3 Surface crosslinking

To apply FEX technology to molded parts, methods of maintaining the molded shape even through electron beam crosslinking of FEX, which necessitates heating and melting, are under study, including the irradiation method of surface crosslinking (surface FEX). Figure 7 illustrates the concept of the method.

First, the entire sample is heated close to the melting point of the polymer; then, the sample is irradiated with electron beams accelerated at a relatively low voltage such that the electron beam will only reach the surface layer of the sample.

Normally, irradiation conditions of electron beam density and radiation time are set to avoid increases in the temperature of the irradiated object. However, in the case of surface crosslinking, the sample is heated so that its surface temperature rises above its melting point due to electron beam radiation. The surface of the sample where electron beams reach is melted and crosslinked, while the central part of the sample, deeper than the surface layer, will not melt although it is not crosslinked, thus avoiding any significant deformation of the sample shape.

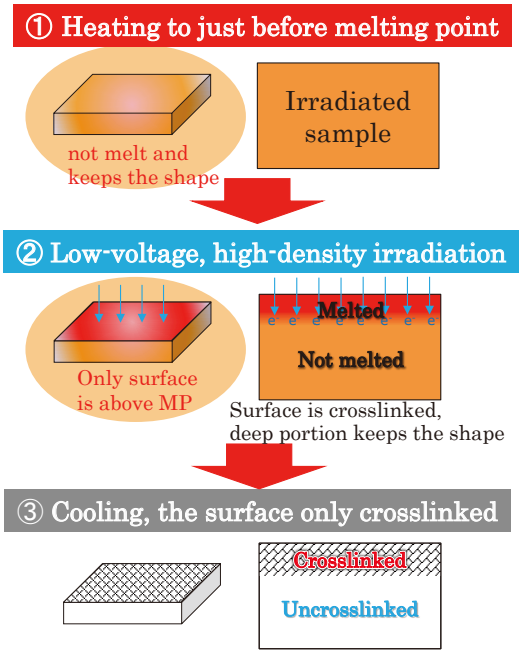


Fig. 7. Rendered image of surface crosslinking (surface FEX)

We conducted a demonstration experiment of surface FEX using perfluoroalkoxy alkane (PFA), which has a low melt viscosity and is easy to be deformed by heating above its melting point. PFA is a polymer that has improved formability by branching in the molecule and lowering the crystallinity. It is a fluoropolymer with superb plastic characteristics similar to those of PTFE.

Prior to electron beam irradiation, a 2 mm thick PFA plate (with a melting point of 304°C) was placed in a gastight enclosure, the ambient oxygen concentration in the enclosure was reduced to 10 ppm or less by replacement with nitrogen gas, and the plate was heated to the pre-irradiation temperature shown in Table 4. This was followed by electron beam radiation to a total of 100 kGy at a net acceleration voltage of 80 keV. Meanwhile, increases in the temperature of the sample's surface irradiated in advance at the same electron beam density and radiation time were 20°C at the maximum. The results are presented in Table 4.

When the increase in the critical PV value observed in ring-on-disc wear testing is used as an indicator of crosslinking, crosslinking occurred under conditions 2 to 4 among conditions 1 to 4, and the shape was maintained under conditions 1 and 2. Consequently, under no conditions but condition 2, electron beam irradiation initiated in a state below the melting point achieved surface crosslinking.

Meanwhile, the depth to which 80% of electrons reach at a net acceleration voltage*3 of 80 keV is estimated at about 30 μm. Because the reaching depth of electron beams depends on the electron acceleration voltage, it is necessary to change conditions according to the depth of the sample to be irradiated.

Table 4. Surface FEX Experimental Results for PFA

	Condition 1	Condition 2	Condition 3	Condition 4	Control
Pre-irradiation temperature	270℃	285℃	300℃	320℃	Untreated
Temperature expected to be reached during irradiation	290℃	305℃	320℃	340℃	
Deformation of plate shape	None	Almost none	Terible,bubbled		
Critical PV value	100	800	800	Unmeasurable	10

In the above-described surface crosslinking, to maximally maintain the shape present before electron beam irradiation, it is necessary to implement very strict temperature distribution control and limit the surface crosslinking layer to the minimum required thickness. However, as illustrated by this example experiment, electron beam crosslinking, even on the surface, is effective for improving chemical resistance in addition to improvement in wear resistance.(10) Consequently, it is a more effective means especially for materials made of such PTFE that has high melt viscosity and is resistant to deformation even over the melting point.

4. Conclusion

We have continuously conducted various studies aiming at popularization and expanded use of electron beam crosslinking technology for fluoropolymers. In recent years, we have continuously focused on technological studies regarding avoidance of the use of fluoropolymers with inferior properties and methods enabling crosslinking of portions other than the surface layer.

We hope that electron beam processing technology will advance further and that the technology will be applied to an expanded range of products.

Technical Terms

∗1 Radical, Fluorine radical: Fluorine atoms whose bonds with carbon atoms are cleaved and liberated from molecules due to electron beams or other high-energy beams enter a reactive, activated state. This state is called a “radical”, and the fluorine atoms in this state are known as “fluorine radicals.”

∗2 Critical PV value: In the ring-on-disc abrasion test (JIS K-7218 compliant), the steel material is rotated while a cylindrical steel material is pressed against the flat sample surface. Critical PV value is the value of the product PV of the pressure P pressing against the steel material and the rotation speed V just before the sample surface begins to be scraped, and the higher the value, the higher the wear resistance.

∗3 Net acceleration voltage: Electron beams used in electron beam irradiation have different energy levels depending on the acceleration voltage, and the depth they reach with the capability of rendering crosslinking and other irradiation effects in a material changes.(11) Compared to the acceleration voltage applied by the electron beam accelerator, electron beams are attenuated due to passage through the thin titanium membrane used to provide gas tightness and through the air before they reach the surface of the material. The term “net acceleration voltage” refers to the acceleration voltage that corresponds to the energy possessed by the electron beams that actually reach the material.

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