

Elucidation of Molecular Structure and Adhesion State of Cross-Linked Fluororesin

Kazuaki IKEDA*, Yugo KUBO, and Kentaro OKAMOTO

Fluororesin, represented by polytetrafluoroethylene (PTFE), is an excellent polymer that has the lowest level of friction performance among solids and the highest level of heat resistance, chemical resistance, weather resistance, and electrical properties among resins. In contrast, it has poor wear resistance and hardly adheres to substrates when used as a composite material. Through electron beam irradiation under special conditions, we promoted the cross-linking reaction of fluororesin and developed a new material that features wear resistance improved nearly 1,000 times compared with the conventional material and good adhesion to substrates. This paper investigates the cross-linking state of the new material using solid-state nuclear magnetic resonance, and elucidates its adhesion state to substrates utilizing SPring-8 hard X-rays.

Keywords: cross-linking, fluororesin, electron beam irradiation, wear resistance, adhesion

1. Introduction

Fluororesin, typified by polytetrafluoroethylene (PTFE), is an excellent polymer, having the highest levels of stability in heat resistance, chemical resistance, and weather resistance among commercially available resins due to its structure wherein carbon molecular chains are closely surrounded by fluorine molecules as shown in Fig. 1, in addition to the strongest C-F bond among single bonds (Fig. 2).

Further, fluororesin exhibits excellent non-adhesiveness and sliding performance (due to its coefficient of friction being lower than that of any other solid). The reason is that fluorine atoms with a small van der Waals radius are arranged in the surface, and this reduces the surface free energy—which indicates the magnitude of interaction with substances approaching the surface—to the lowest value among resins.

However, when viewed from another point, the non-adhesiveness and low friction of fluororesin make it difficult for it to adhere to or combine with metals and other materials, thereby preventing its use in industrial products. Such stable characteristics of this resin hinder its chemical modification by a chemical agent, or physical modification by ionizing irradiation.

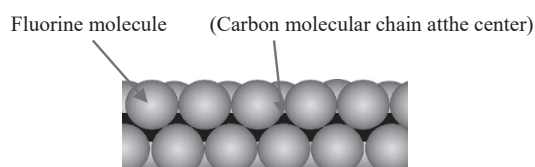


Fig. 1. Schematic illustration of PTFE molecule

Since the fluorine molecules are bonded very weakly to each other in fluororesin, they are easily separated from the surface by an external force as shown in Fig. 2. This

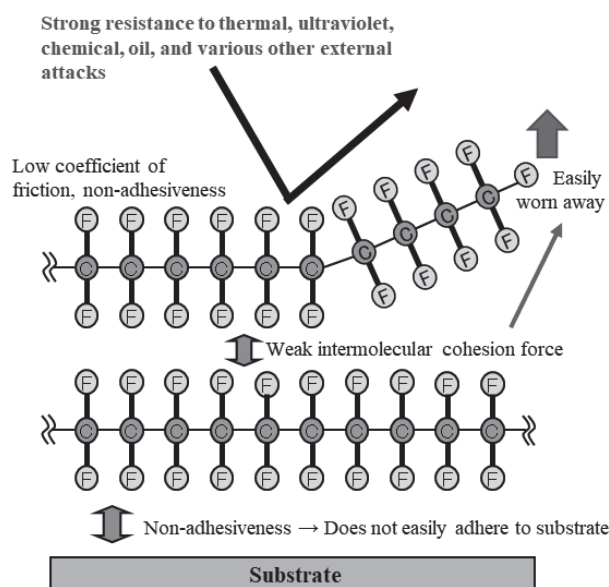


Fig. 2. Molecular structure and feature of PTFE

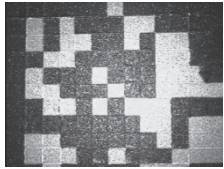
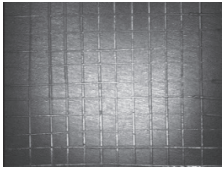
degrades the wear resistance of the resin.

Sumitomo Electric Industries, Ltd. has developed cross-linked fluororesin from which shortcomings are removed by electron beam irradiation under special conditions, and has supplied it under the tradename “FEX” (fluoro ethylene crosslinking (X-linking)).

The effect of adhesiveness improvement by cross-linking was evaluated by a cross-cut tape peeling test (in compliance with JIS-K-5400) by peeling the tape 500 times. Since non-cross-linked fluororesin was easily separated from the substrate and therefore useless for the evaluation, Sumitomo Electric’s SUMIFLON coating, whose adhesiveness was improved to a practical level by etching the metal surface, was used for comparison. After the test, approximately half of the cross-cut SUMIFLON coating was separated (white portions in the picture on the left of

Table 1), while no separation of the cross-linked fluoro-resin FEX coating was observed.

Table 1. Adhesion test result

Product name	SUMIFLON	Cross-linked fluoro-resin FEX
Adhesion method	Etching	Electron beam irradiation
Cross-cut test result		

The wear resistance of cross-linked fluoro-resin FEX was evaluated using a ring-on-disk friction and wear test (in compliance with JISK-7218) (Photos 1 and 2, and Fig. 3).

With the test sample pressed against a S45C (carbon steel) at 10 MPa, the rotation speed of the sample was gradually increased, and the weight loss of the sample was measured. The measurement results are shown in Fig. 4. The cross-linking of the fluoro-resin greatly enhanced its wear resistance to a level far exceeding that of resins commonly used as slide members (poly-ether-ether-ketone (PEEK), polyacetal (POM), and polyphenylene sulfide (PPS)).

This paper reports on the analysis and examination results for the molecular structure of cross-linked fluoro-resin and its adhesion state to a substrate.



Photo 2. Ring-on-disk friction and wear test equipment

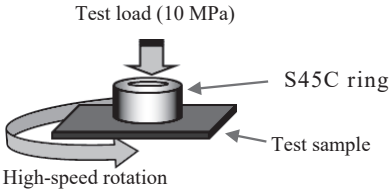


Fig. 3. Wear test method

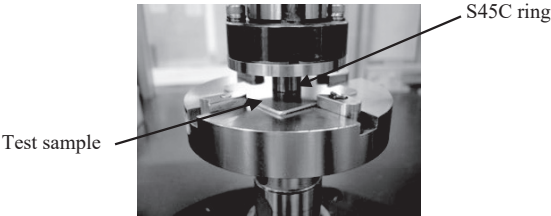


Photo 1. Wear test sample set on the test equipment

2. Analysis of the Molecular Structure of Cross-Linked Fluoro-resin

A change in the molecular structure of PTFE by electron beam irradiation was evaluated by solid-state nuclear magnetic resonance (NMR). Figure 5 shows the solid-state ¹⁹F MAS NMR spectra of PTFE before and after electron beam irradiation. Before the electron beam irradiation, the spectrum of PTFE had only one peak at $\delta = -122$ ppm, but after the irradiation, multiple small peaks were detected.

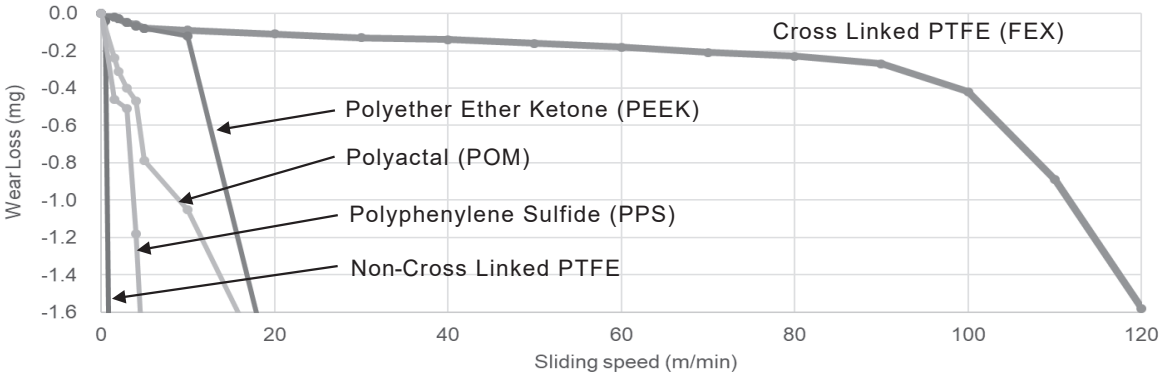


Fig. 4. Ring-on-disk friction and wear test result

The molecular structure assigned to each peak is shown in Fig. 5. It was confirmed that electron beam irradiation not only generates an end group ($\delta = -82$ ppm) by breaking the molecular chains of the tetrafluoroethylene unit, but also produces branched structures ($\delta = -72, -100$ to $-120, -185$ ppm).⁽¹⁾ PTFE usually breaks only molecular chains when irradiated with an electron beam. However, the above results suggest that, under such special irradiation conditions as in this experiment, PTFE not only causes the molecular chain to branch, but also forms a cross-linked structure.

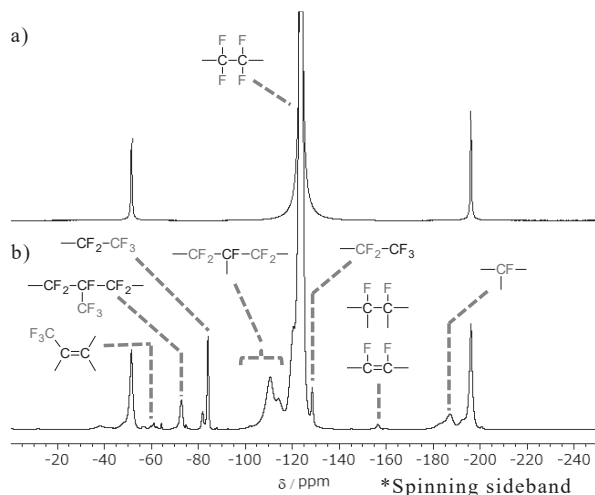


Fig. 5. Solid-state ^{19}F MAS NMR spectra of cross-linked PTFE
a) Before irradiation b) After irradiation

It was found that electron beam irradiation causes both molecular chain breakage and cross-linking reactions, as described above. To stoichiometrically investigate the degree of progress of each reaction, the change in the bonding amount of each bonded structure associated with electron beam irradiation was evaluated based on the area ratio of each assigned peak (which is equivalent to the molar ratio of a molecular structure).

Figure 6 shows the dependence of the change in the chemical bond amount ratio on the irradiation dose. As this figure shows, increasing the irradiation dose increased dramatically branched $-\text{CF} =$ bonds compared to $-\text{CF}_2-\text{CF}_3$ bonds at the end of the molecular chains. The molecular structures at the branched ends were also compared in terms of a short chain that becomes a trifluoromethyl group ($-\text{CF}_3$) and a long chain having two or more carbon atoms. As shown in Fig. 7, electron beam irradiation had a tendency to preferentially recombine long chain molecular structures with the branch points. It was found from these changes that PTFE breaks its molecular chains when exposed to an electron beam (Fig. 8). However under special conditions, the ends of the generated molecular chains are recombined with the original molecular chains, and this promotes the branching of the molecular chains as shown in Fig. 9. The above-described molecular structural change to a cross-linked polymer is considered to increase

the inherently low cohesive force between the molecules of PTFE and to have dramatically improved its wear resistance.

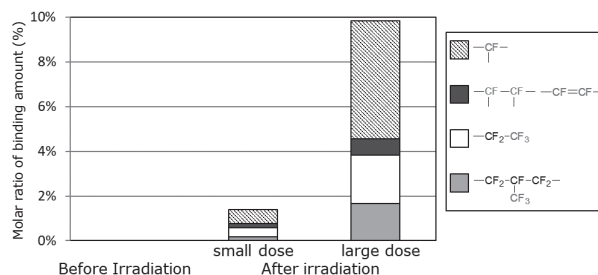


Fig. 6. Change in chemical bond amount due to electron beam irradiation

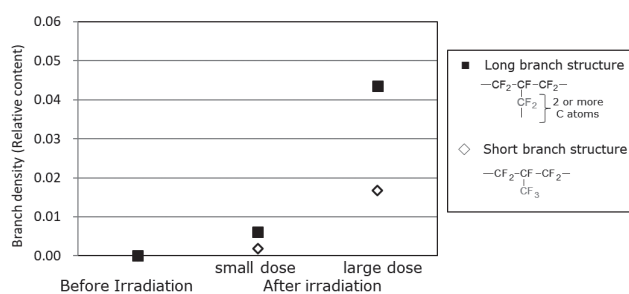


Fig. 7. Change in bond structure due to electron beam irradiation

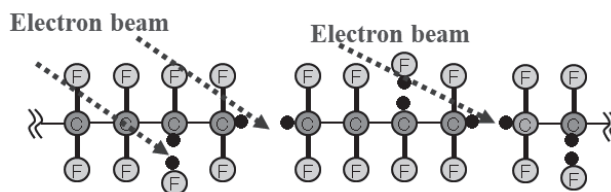


Fig. 8. Breaking of molecule by electron beam

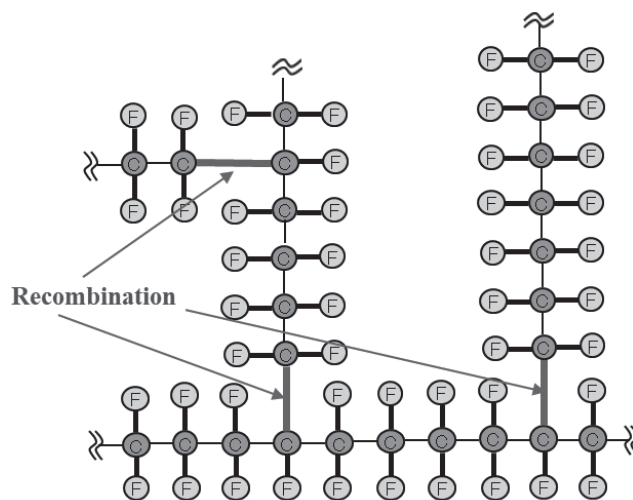


Fig. 9. Molecular structure of cross-linked fluororesin

3. Elucidation of the State of Adhesion between Cross-Linked Fluororesin and a Substrate

A hard X-ray photoelectron spectroscopic (HAXPES) analysis was carried out to elucidate the mechanism of improving the adhesiveness of cross-linked fluororesin to a metal substrate by electron beam irradiation (Table 1). Since the maximum analyzable depth of HAXPES is several tens of nanometers, the depth of the interface to be analyzed was required to lie within the above limit. We developed a method for fabricating an analytical sample that can be used to simulate the actual process (resin coating on a metal substrate) while satisfying the above requirement for analysis depth. An outline of the sample fabrication and analysis methods is shown in Fig. 10. Fe and fluororesin layers were sequentially laminated on a thin SiO₂ film layer formed on a smooth-surfaced GaAs substrate, and only the GaAs substrate and the SiO₂ film layer were removed from the sample after it was irradiated with electron beams under special conditions.⁽²⁾

The morphology of the cross section of the sample was observed with a transmission electron microscope (TEM). The results revealed that a thin Fe film layer about 20 nanometers thick had been formed on the fluororesin, which was several tens of micrometers thick, verifying that the sample had the expected structure (Fig. 11).

The chemical state of the Fe/resin interface in this sample was analyzed using the HAXPES installed in the SPring-8, a large synchrotron radiation facility. In the analysis, an X-ray with an incident X-ray energy of about 8 keV was delivered to the top surface of the thin Fe film to detect the photoelectron signal of the interface. In this process, electrostatic charge was neutralized with an electron gun to

prevent the shifting of photoelectron peaks due to charging.

Figure 12 shows the HAXPES analysis results (C1s spectrum) for two types of samples with and without electron beam irradiation.

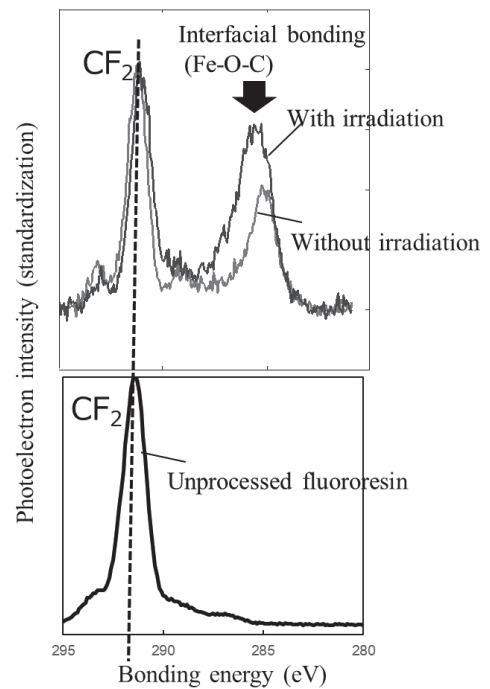


Fig. 12. HAXPES analysis result for Fe/fluororesin sample (The figure on the bottom shows analysis results for fluororesin alone (C 1s spectrum))

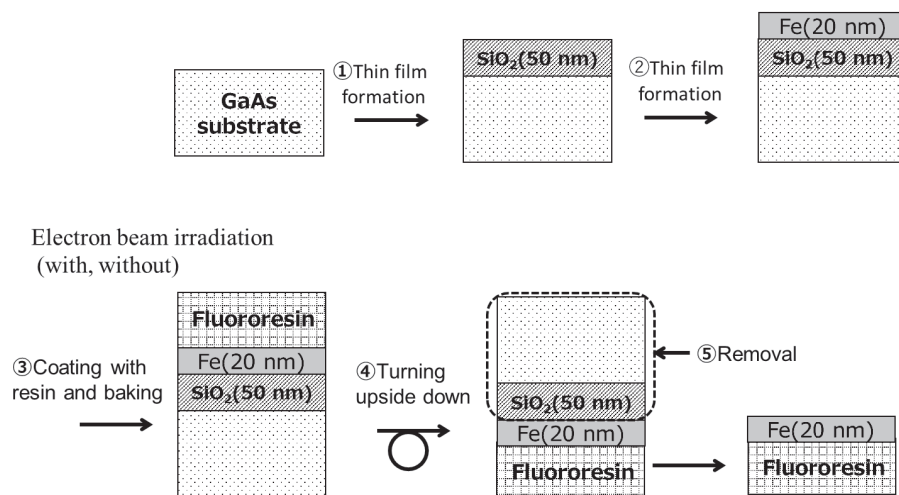


Fig. 10. Outline of sample fabrication and analysis methods

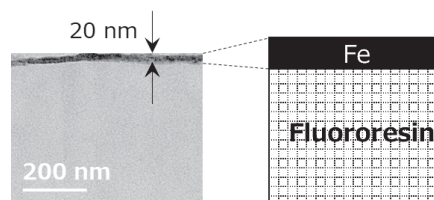


Fig. 11. TEM observation result for a cross section of Fe/fluororesin sample and schematic illustration of sample layer structure

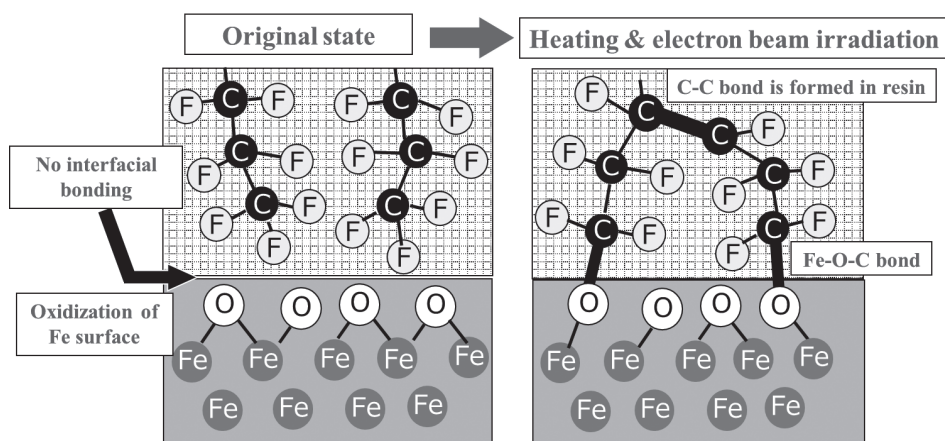


Fig. 13. Estimation of mechanism for improving adhesiveness of Fe/resin interface by electron beam irradiation

One of the two peaks observed, the peak near 291 eV, was also found in the spectrum of fluororesin alone (bottom figure of Fig. 12), suggesting that this peak was derived from C of -CF₂-.

However, the peak near 285 eV is not observed in the case of fluororesin alone. Furthermore, since the height of this peak increased as the X-ray take-off angle decreased, this suggests that this peak was attributable to a bond being present near the interface between the Fe and the fluororesin. This peak also suggests the presence of a chemical bond (Fe-O-C) at the interface between the Fe and the resin.

For a combination of various metals and resins, many papers report the bonding mechanism between the metal elements and the carbon in the resin at the metal/resin interface via oxygen in the metal oxide.⁽³⁾

When the HAXPES analysis results are taken into account in conjunction with the conclusions of these papers, fluororesin is considered to adhere to a metal via the oxide film on the metal surface (Fig. 13).

4. Conclusion

The characteristics of the fluororesin (PTFE) and cross-linked fluororesin (FEX) are shown in Table 2. The fluororesin is excellent in stability and electrical properties, but has a disadvantage in terms of wear resistance and adhesiveness to substrates. The cross-linked fluororesin FEX has eliminated the disadvantage of PTFE and expanded its application range in various industries by taking advantages of the intrinsic excellent characteristics of fluororesin.

FEX is commercially available in the forms of cross-linked fluororesin sheets and tapes processed from the sheets (Photo 3), aluminum and steel substrates coated with cross-linked fluororesin, and products made by stamping these substrates. In practice, slide bearings (Photo 4), oil pumps (Photo 5), sliding packing, nip plates for office automation (OA) equipment, and various types of molds and jigs are coated with FEX.

Table 2. Summary of characteristics of PTFE and FEX

	PTFE	FEX
Wear resistance (limit PV-value MPa·m/min)	About 1	1,000–1,200
Adhesion to substrate	Difficult (essential to use primer or other suitable coat)	Possible to adhere
Coefficient of kinetic friction	Lowest level among solids (0.08)	Same as on the left
Heat resistance	260 °C	Same as on the left
Chemical resistance	Inactive (except with hot aqua regia)	Same as on the left
Flame resistance (limiting oxygen index)	95% min.	Same as on the left
Weather resistance	Can be used outdoors for a long period	Same as on the left
Dielectric constant (10 ³ – 10 ⁶ Hz) D150	Lowest level among solids (2.1)	Same as on the left
Dielectric dissipation factor (10 ⁶ Hz) D150	Lowest level among solids (2 × 10 ⁻³)	Same as on the left
Pencil hardness	HB	Same as on the left

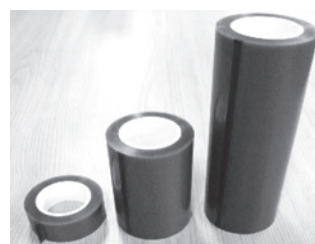


Photo 3. Cross-linked fluororesin tapes



Photo 4. Slide bearing



Photo 5. Oil pump

Sumitomo Electric Fine Polymer, Inc. has introduced various fluororesin products into the market. These products include fuser rollers for OA equipment, porous membranes (POREFLON), and rice cooker pots (SUMIFLON), as well as heat-shrinkable tubing made using an electron beam irradiation technique (SUMITUBE).

Cross-linked fluororesin, FEX, is a new product developed by combining two core technologies of the company: fluorine processing and electron beam irradiation.

We will work to cultivate the application of this product and spread it, thereby developing it as a new pillar of our business subsequent to the current pillars.

5. Acknowledgments

Part of the sample fabrication was supported by the Nanotechnology Platform Project launched by the Ministry of Education, Culture, Sports, Science and Technology (Kyoto University Microfabrication Platform). The HAXPES experiments were carried out using BL16XU and 46XU installed in SPring-8 (Research task numbers: 2015B5030, 2015B1870, 2016A5031, 2016B5030).

• FEX, SUMIFLON, POREFLON, and SUMITUBE are trademarks or registered trademarks of Sumitomo Electric Industries, Ltd.

References

- (1) Radiation Physics and Chemistry 54 (1999) 165-171
- (2) Y. Kubo, H. Tanaka, Y. Saito, A. Mizoguchi, ACS Appl. Mater. Interfaces 2018, 10, 51, 44589-44602
- (3) S. Maeda, J. Jpn. Soc. Colour Mater, 2005, 78, 3, 131-140

Contributors

The lead author is indicated by an asterisk (*).

K. IKEDA*

• Assistant General Manager, Advanced Automotive Systems R&D Center



Y. KUBO

• Ph.D.
Assistant General Manager, Analysis Technology Research Center



K. OKAMOTO

• Ph.D.
Assistant Manager, Analysis Technology Research Center

