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Surface Modification of Polytetrafluoroethylene Containing Carbonaceous Materials by KrF-Laser Irradiation

Masanobu NISHII,* Shun'ichi SUGIMOTO, Yuichi SHIMIZU, Nobutake SUZUKI, Tomohiro NAGASE,† Masao ENDO,† and Yosuke EGUCHI†
Osaka Laboratory for Radiation Chemistry, Japan Atomic Energy Research Institute, 25-1 Mii-minami, Neyagawa, Osaka 572
†Technical Research Laboratory, Kurabo Industries, Ltd., 14-5 Shimokida, Neyagawa, Osaka 572

The adhesive property of polytetrafluoroethylene (PTFE) film containing a small amount of carbonaceous materials such as carbon black and graphite was improved remarkably by KrF-laser irradiation in air. The adhesive strength increased with the irradiated energy and the fluence of laser.

The development of an effective method for the surface modification of PTFE which is chemically inactive is very important from a viewpoint of the enlargement of applications owing to the lamination with various materials. In the previous paper,[1] we reported that the adhesive strength of the PTFE film containing a small amount of the light-absorbable and heat-resistant polymers such as aromatic polyester was enhanced remarkably by KrF-laser irradiation in air. On the basis of this finding, we have attempted to develop more useful method for the surface modification of PTFE by KrF-laser irradiation of PTFE blended with carbonaceous materials such as carbon black and graphite which are expected to give antistatic property and abrasion resistance.

The procedure of KrF-laser irradiation of the PTFE film was the same as that used in the previous paper.[1] The PTFE film (0.5 mm thick) was prepared using a peeling machine from the moldings of PTFE (Fluon G-163, Asahi-ICI Fluoropolymers Co.,Ltd.) blended with carbon black (FD-0721, Dainichi Seika Colour & Chemicals Mfg.) or graphite (ACP, Nippon Kokuen Kogyo Co. Ltd.) which were obtained by the sintering at 360° C for 3 h. The film was cleaned in ethanol with the supersonic wave before irradiation. The adhesive strength of the irradiated PTFE film was evaluated by the measurement of the 180° peel strength of the film adhered at room temperature on a stainless steel plate (SUS 304) with the epoxy resin adhesive. The surface analyses of the irradiated PTFE film were carried out with a X-ray photoelectron

spectroscopy (XPS, Shimadzu ESCA 850S, MgKα X-ray source) and a scanning electron microscopy (SEM, Hitachi S-2400).

Figure 1 shows the peel strength of the PTFE films containing 5 wt% of carbon black or graphite as a function of the irradiation energy. The peel strength of the PTFE film containing carbon black increased with the irradiation energy and became 1.8 kg cm^{-1} at 7.1 J cm^{-2}. Similarly, the peel strength of the PTFE film containing graphite increased with the irradiation energy and became 1.3 kg cm^{-1} at 7.1 J cm^{-2}. The peel strength was much larger for the PTFE film containing carbon black than for the film containing graphite. On the other hand, in the case of the PTFE film without carbon black or graphite, the peel strength was less than 0.02 kg cm^{-1} even at irradiation of 30 J cm^{-2}. These results indicate that the adhesive strength of the PTFE films containing a small amount of carbon black or graphite was enhanced remarkably by KrF-laser irradiation in air at room temperature.

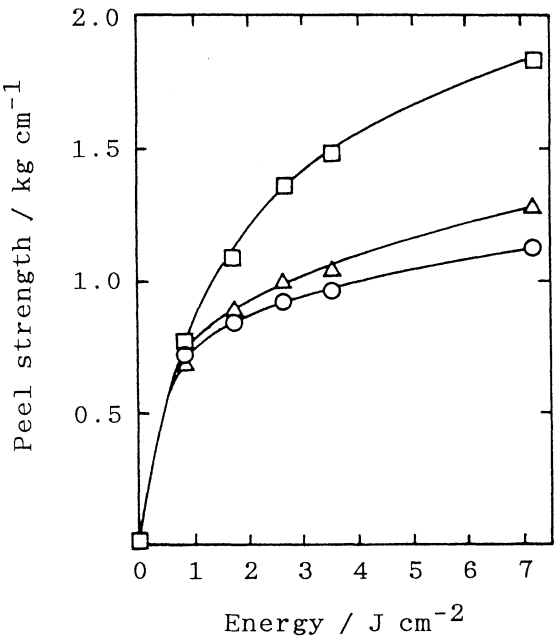

Fig. 1. Peel strength of irradiated PTFE films containing carbonaceous materials. Fluence : 300 mJ cm^{-2} pulse^{-1}. Content of carbonaceous materials : 5 wt%.
□: carbon black; △: graphite(AT-20); ○: graphite(AT-10).

In the case of the PTFE film containing graphite, the peel strength was larger for the film (1.3 kg cm^{-1} at 7.1 J cm^{-2}) containing graphite (AT-20) with 8 μm of particle size than for the film (1.1 kg cm^{-1} at 7.1 J cm^{-2}) containing graphite (AT-10) with 18 μm of particle size. This suggests that an enhancement in the peel strength by KrF-laser irradiation is affected by the particle size of materials blended in PTFE. It is therefore assumed that a remarkable increase in the peel strength for the PTFE film containing carbon black (particle size : 0.03 μm) compared with the case of the film containing graphite may be attributed to the promotion of the laser-induced reaction on the surface of the PTFE film by effective light-absorption owing to more fine particle size of carbon black. Also, as shown in Table 1, in the case of the PTFE film containing carbon black, the peel strength increased with the content of carbon black and the fluence of the laser beam. Thus, it was found that the adhesive property of the PTFE films containing a small amount of carbon black and graphite which have the light-absorbable and heat-

Table 1. Effects of the content of carbon black and the fluence on peel strength of PTFE film

Content of carbon black wt%	Fluence mJ cm^{-2} $pulse^{-1}$	Peel strength[a] kg cm^{-1}
1	150	0.44
	225	0.88
	300	0.96
5	150	0.88
	225	1.24
	300	1.36

Irradiation energy : 2.7 J cm^{-2}.
a)Peel strength of unirradiated film was less than 0.02 kg cm^{-1}.

resistant properties was improved remarkably by KrF-laser irradiation in air at room temperature. It is also expected that the addition of carbonaceous materials in the PTFE film improves not only the adhesive property by KrF-laser irradiation but also other characteristics such as abrasion resistance, antistatic property, and low frictional property, because carbon black and graphite are excellent in mechanical hardness and electrical conductive property.

The changes in the chemical structure and the morphology on the surface of the PTFE films containing carbon black and graphite by KrF-laser irradiation were examined with XPS and SEM. Figure 2 shows the C1s XPS spectra on the surface of the PTFE film containing 5 wt% of carbon black irradiated with the KrF laser in air. The intensity of the peak (binding energy : 294.5 eV) assigned to carbon of $-CF_2-$ group decreased remarkably by KrF-laser irradiation, and at the same time, a peak (binding energy :

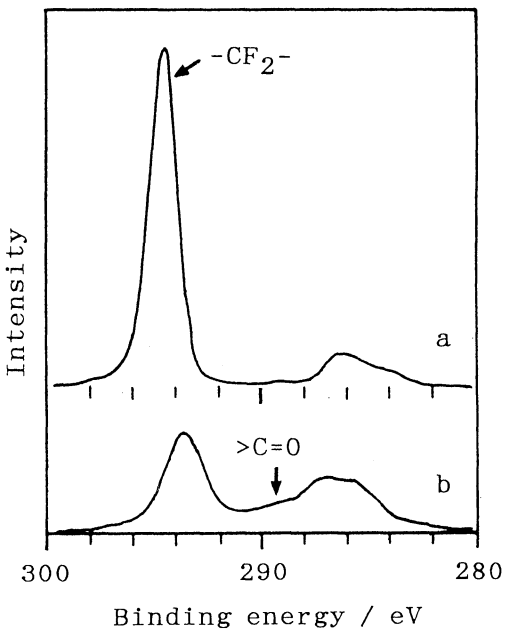

Fig. 2. C1s XPS spectra of irradiated (a) and unirradiated(b) PTFE films containing 5 wt% of carbon black. Irradiation energy : 2.7 J cm^{-2}. Fluence : 300 mJ cm^{-2} $pulse^{-1}$.

289 eV) assigned to carbon of carbonyl group appeared newly.[2-4] Also, the atomic ratio, F/C, obtained from the peak areas of the C1s and F1s XPS spectra, decreased remarkably from 2.1 (unirradiated) to 1.1 at irradiation of 2.7 J cm^{-2}, and on the contrary, the O/C ratio obtained from the C1s and O1s XPS spectra increased from 0.01 (unirradiated) to 0.06 at irradiation of 2.7 J cm^{-2}. Similar changes in the chemical structure were observed in the case of the PTFE film containing graphite. Such chemical changes were not observed in the case of the PTFE film without carbon black and graphite. It was revealed from these results that the release of F atom in $-CF_2-$ group and the formation of carbonyl group occurred on the surface of the PTFE film containing carbon black and graphite by KrF-laser irradiation in air. From the surface observation of the irradiated PTFE film containing carbon black by SEM, it was also revealed that fine unevenness with about 1 μm in diameter was formed on the surface of the film. These results indicate that the chemical reaction and the laser ablation occur on the surface of the PTFE films containing carbon black and graphite by KrF-laser irradiation in air.

Since the absorption coefficient of PTFE is very small in UV region and carbon black and graphite have a strong absorption band, most of the energy of highly intense UV beam from the KrF laser would be absorbed in carbon black or graphite. It is therefore considered that when the PTFE film containing carbon black or graphite is irradiated with the KrF laser in air, the energy transfer from carbon black or graphite to PTFE and the laser ablation occur on the surface of the films, followed by the chemical reactions and the formation of fine unevenness described above, and as the result, the adhesive strength is improved. It is also considered that a remarkable enhancement in the adhesive strength of the PTFE films containing carbon black and graphite by KrF-laser irradiation is attributed to both the chemical effect owing to the formation of the polar groups such as carbonyl group and the physical effect owing to the formation of the fine unevenness.

References

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