CHEMISTRY LETTERS, pp. 2089-2090, 1992.

Surface Modification of Polytetrafluoroethylene 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 strength of polytetrafluoroethylene (PTFE) film was enhanced remarkably by KrF-laser irradiation in air when a small amount of aromatic polyester (APE) was blended with PTFE.

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 in which PTFE is laminated with various materials. Present-day, the surface modification of PTFE has been mainly carried out by the chemical method using a metallic sodium complex,[1] but the adhesive property is not satisfactory. Therefore, we have attempted to proceed more efficiently the surface modification of PTFE by KrF-laser irradiation of PTFE blended APE as an additive which has a strong absorption band in UV region and a high thermostability even at the molding temperature of PTFE.

The PTFE film (0.5 mm thick) was prepared from the blended moldings of PTFE (Fluon G-163, Asahi-ICI Fluoropolymers Co., Ltd.) and APE (Ekonol E-101, Sumitomo Chemical Co., Ltd.) obtained by the sintering at 360 °C for 3 h using a peeling machine and was cleaned in ethanol with the supersonic wave. The PTFE film (30 × 150 mm^2) was irradiated with a KrF laser (Lumonics Hyper EX-460, 248 nm, fluence: 150 mJ $cm^{-2}pulse^{-1}$, frequency: 2-10 Hz) in air at room temperature. The quantity of light was determined by using a calorimeter (Scientech 38-4UV5). The adhesive strength of the PTFE film was evaluated by the measurement of the 180° peel strength of the film adhered on a stainless steel plate (SUS 304) with the epoxy resin adhesive.

Figure 1 shows the peel strength of the PTFE film containing a small amount of APE as a function of the irradiated energy. The peel strength of the PTFE film increased steeply with the irradiated energy up to about 10 J cm^{-2} in 1-20 wt% ranges of APE content and gradually thereafter, and also increased with the APE content. In the case of the PTFE film containing 20 wt% of APE, the peel strength increased remarkably from 0.4 kg cm^{-1} (unirradiated) to 3.9 kg cm^{-1} (at 26 J cm^{-2}). On the other hand, for the PTFE film without APE, the peel strength was less than 0.02 kg cm^{-1} even at irradiation of 150 J cm^{-2}. Thus, it was found that the adhesive strength of the PTFE film containing a small amount of APE was enhanced remarkably by KrF-laser irradiation in air at room temperature. Also, this value was much larger than that (ca. 1.2 kg cm^{-1}) obtained by the chemical method. These results indicate that the laser-irradiation method is favorable for the surface modification of PTFE. Similar

effects were also observed in the PTFE film containing aromatic polymers such as polyetheretherketone (PEEK) and polyimide (PI) having the strong absorption band in UV region and the high thermostability. The peel strength of the PTFE films containing 15 wt% of PEEK and PI increased from 0.4 kg cm^{-1} (unirradiated) to 1.8 and 1.1 kg cm^{-1} at 1.8 J cm^{-2}, respectively.

From the surface analyses of the irradiated PTFE film containing APE by a X-ray photoelectron spectroscopy and a scanning electron microscopy, it was revealed that the release of fluorine atom, the formations of carbonyl group and ethylene linkage, and the carbonization occur on the surface of the film. Such chemical changes were not observed in the case of the PTFE film without APE. These results indicate that the chemical reactions and the laser ablation occur on the surface of the PTFE film containing APE by KrF-laser irradiation. Since the absorption coefficient of PTFE is very small in UV region and APE has a strong absorption band, most of the high intense UV light from the KrF laser would be absorbed in APE. It is therefore considered that the energy transfer from APE to PTFE and the laser ablation occur in the PTFE film containing APE, followed by the chemical reactions described above. It is also considered that a remarkable enhancement in the adhesive strength of the PTFE film containing APE by KrF-laser irradiation is attributable to both the chemical effect owing to the formation of the polar groups such as carbonyl group and ethylene linkage and the physical effect owing to the formation of the fine unevenness by the carbonization.

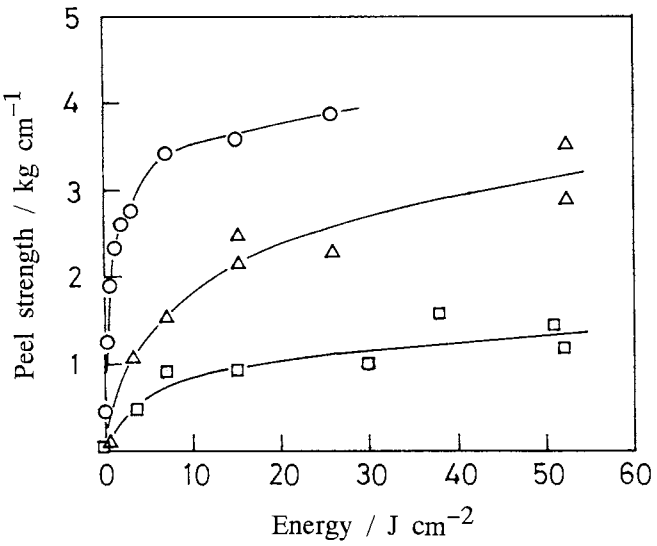

Fig. 1. Peel strength of the PTFE film irradiated by KrF laser.
Fluence : 150 mJ $cm^{-2}pulse^{-1}$,
APE content : □, 1% ; △, 5% ; ○, 20%.

Reference
1) E. R. Nelson, T. J. Kilduff, and A. A. Benderly, Ind. Eng. Chem., 50, 329 (1958).

(Received July 17, 1992)