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Endowment with the Wettability on the Surface of Tetrafluoroethylene-Perfluoroalkyl Vinyl Ether Copolymer by Excimer Laser Irradiation

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Tetrafluoroethylene-perfluoroalkyl vinyl ether copolymer (PFA) was endowed with the high wettability by ArF-laser irradiation in water dissolved carbon monoxide. The enhancement of the wettability was closely related to the decrease of the F/C atomic ratio and the increase of the O/C ratio measured by X-ray photoelectron spectroscopy (XPS), suggesting the formation of the polar groups such as ethylene linkage and carbonyl group with the release of fluorine atom.

Perfluoropolymers are well-known for their excellent properties, for example heat resistance and solvent resistance. In addition, PFA has advantages of the molten processing. Therefore, the development of an effective method for the surface modification of PFA which is chemically inactive has become a very important subject for the enlargement of applications such as medical-use. The surface modification, for example endowment with the wettability and improvement of the adhesion, of PFA has been carried out by using an alkaline metallic solution[1] and a plasma discharge,[2] but we could not be satisfied completely with these effects. Therefore, we have attempted to proceed more efficiently the surface modification of PFA by ArF-laser irradiation in water which various gases were dissolved in.

The PFA film (0.1 mm thick) was prepared from the extrusion processing of PFA resin (Teflon PFA-350J Mitsui-Dupont Fluorochemical Co., Ltd.) and was cleaned in ethyl alcohol with a supersonic wave before irradiation. Then the PFA film was irradiated with an ArF laser (Lumonics Hyper EX-460, wavelength: 193 nm, fluence: 12-95.8 mJ cm^{-2} $pulse^{-1}$, frequency: 10-50 Hz, number of pulses: 1870-16000 pulse) in distilled water which various gases were dissolved in. Respective gases were bubbled for 60 min at room temperature to be dissolved up to the saturated concentration (CO: 2.9×10^{-3} wt%, CO_2: 1.7×10^{-1} wt%, N_2: 1.9×10^{-3} wt%, O_2: 4.3×10^{-3} wt% at 20 ℃).[3] The quantity of light was determined by using a calorimeter (Scientech 38-4UV5). The wettability of the PFA film was evaluated from the contact angle towards water at room temperature. The chemical structure of the PFA film was analyzed by XPS (Shimadzu ESCA 850S) measurements.

The contact angle of non-irradiated PFA film was 106 degrees, however, the contact angle decreased remarkably to 34 degrees by ArF-laser irradiation (energy: 208 J cm^{-2}) in water dissolved carbon monoxide. Also by irradiation in water dissolved carbon dioxide or nitrogen, the contact angle considerably decreased to 48 degrees or 70 degrees. On the other hand, no change in contact angle of

the PFA film was observed by irradiation (energy: 208 J cm^{-2}) in water dissolved oxygen. Thus, it was revealed that the endowment with the wettability on the surface of the PFA film is influenced by the dissolved gases in water. We found that carbon monoxide dissolved in water plays an important role in the endowment with the wettability. The endowment with the wettability was hardly observed by KrF-laser (wavelength: 248 nm) irradiation.

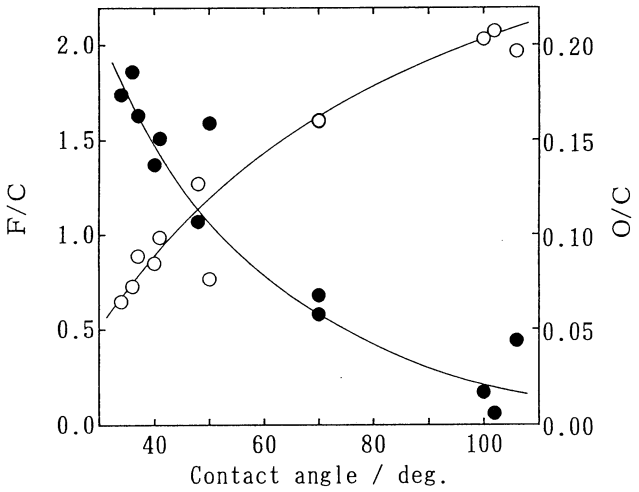

Fig. 1. Relationship between contact angle and ratios of atomic concentrations. ○: F/C,●: O/C.

In the case of ArF-laser irradiation in water dissolved carbon monoxide, C1s XPS spectra of the PFA film showed five peaks, which were newly assigned to -C=C- (285.5 eV), -C=O and -C-O-C- (288 eV), -COO (290 eV), -CF- (292 eV), together with -C-C- (285.5 eV) and $-CF_2-$ (294 eV) observed on non-irradiated PFA. Furthermore, the peak area of the O1s XPS spectra increased, and that of the F1s XPS spectra decreased by ArF-laser irradiation. These results suggest that the release of fluorine atom, the introduction of oxygen atom, and the formation of ethylene linkage occur on the surface of the PFA film by ArF-laser irradiation.

Figure 1 shows a correlation between the atomic ratios (F/C, O/C) and the contact angle on the surface of the PFA film. It is obvious that F/C decreased and O/C increased with the wettability enhanced. In the case of irradiation in water dissolved carbon monoxide, O/C became 4 times and F/C became 1/3 times compared to non-irradiated PFA. Therefore, these results indicate that the enhancement of the wettability, the release of fluorine atom, and the introduction of oxygen atom on the surface of the PFA film were closely related with each other.

It can be considered that the remarkable enhancement of the wettability of the PFA film by ArF-laser irradiation in water dissolved carbon monoxide is mainly attributable to the chemical effect owing to the formation of the polar groups such as ethylene linkage and carbonyl group. Further, the effect of depression of dissolved oxygen gas suggest the possibility of a radical reaction. We are considering that the absorbed energy transfers from carbon monoxide to PFA and water, followed by the chemical reactions such as scission of the C-F bond at the interface between the PFA film and water, because the photon energy of ArF-laser radiation is larger than the binding energy of C-F bond. But details are now investigating.

References

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