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A novel KrF laser-induced graft reaction of poly(acrylic acid) onto tetrafluoroethylene–perfluoroalkyl vinyl ether copolymer film

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The surface of tetrafluoroethylene–perfluoroalkyl vinyl ether copolymer (PFA) film in contact with poly(acrylic acid) (PAA) aqueous solution became wettable by excimer laser irradiation. The water contact angle of the PFA decreased from 106° to 40–60° by irradiation of KrF laser pulses (22.4–67.6 mJ cm^{-2} pulse^{-1}) with total irradiation energy of 100–200 J cm^{-2}. The increase in amount of rhodamine 6G, a basic dye, adsorbed on the irradiated PFA surface showed a good correlation with reduction of the contact angle. Surface analysis by X-ray photoelectron spectroscopy indicated extensive loss of fluorine atoms and increase of oxygen atoms, in addition to a C1s spectrum similar to that of PAA. The present results demonstrate the introduction of a carboxylic group onto the PFA surface through a novel laser-induced graft reaction of PAA. Copyright © 1996 Elsevier Science Ltd.

(Keywords: photochemical graft reaction; poly(acrylic acid); tetrafluoroethylene-perfluoroalkyl vinyl ether copolymer)

Introduction

Since tetrafluoroethylene–perfluoroalkyl vinyl ether copolymer (PFA) has the advantage of molten processing compared with polytetrafluoroethylene (PTFE), PFA has replaced PTFE as a material in many applications. However, it also has difficulties in wettability, adhesiveness and biocompatibility, common to fluoropolymers, owing to extremely low surface energy. Though many methods of surface modification of fluoropolymers for such purposes, e.g. chemical etching, corona discharge, plasma and radiation-induced graft polymerization, have been adopted[1–3], all have problems such as too much sensitivity of the treated surface towards moisture and light, damage in bulk, and overturn of polar groups. Recently, laser-induced surface photoreactions of fluoropolymers have been proposed by several groups including us[4,5]. In the previous papers[6,7], we reported that excimer laser irradiation of PFA in water dissolving various gases or ammonia made the surface wettable. We now report on the surface modification of PFA by KrF laser irradiation with poly(acrylic acid) (PAA) aqueous solution through a novel graft reaction of PAA.

Experimental

A PFA film (0.1 mm thick) prepared by extrusion processing of a virgin resin was washed with ethyl alcohol with supersonication and was air-dried at room temperature before laser irradiation. PAA (Aldrich, $M_w = 2000$ and Wako, $M_w = 150000$) was used as received. PAA was dissolved in distilled water 0.1–5.0 wt%. The solution was purged by a nitrogen stream for 5 min before irradiation. The PFA film placed in contact with the PAA solution was irradiated with KrF laser (Lumonics EX-884, wavelength 248 nm, frequency 40 Hz, fluence 22.4–154.2 mJ cm^{-2} pulse^{-1}, shot number 10–16000 pulses) through the film to excite the film/solution interface. After the irradiation, the film was washed thoroughly with water and ethanol. Surface wettability was estimated by the contact angle of the PFA film with a water droplet. Surface composition of the PFA film was analysed by X-ray photoelectron spectroscopy (X.p.s.) (Shimadzu ESCA-850S) to obtain atomic ratios and C1s spectra. The binding energy of C1s spectra was corrected with that of n-hexatriacontane (n-$C_{36}H_{74}$) as an internal standard (binding energy = 285.0 eV)[8]. Rhodamine 6G (Rh6G) was adsorbed onto the irradiated surface from its aqueous solutions (1×10^{-5} mol dm^{-3}) (ref. 9). Surface morphology was examined by scanning electron microscopy (SEM) (Topcon DS-130S). Adhesive strength was evaluated by measurement of the 180° peel strength of the film adhering to a stainless steel (SUS 304) plate with an epoxy- or cyanoacrylate-type adhesive.

Results and discussion

The PFA films in 1.0 wt% solutions of high and low molecular weight PAA were irradiated with 10000 pulses at a fluence of 22 mJ cm^{-2} pulse^{-1}. The surfaces of the films became hydrophilic as judged by changes in the contact angle from 106 to 40–60° before and after the irradiation, respectively. With PAA solutions whose concentrations were greater than 3 wt%, however, considerable gelation occurred in the liquid phase, but the surface was less wettable. The gel formation was

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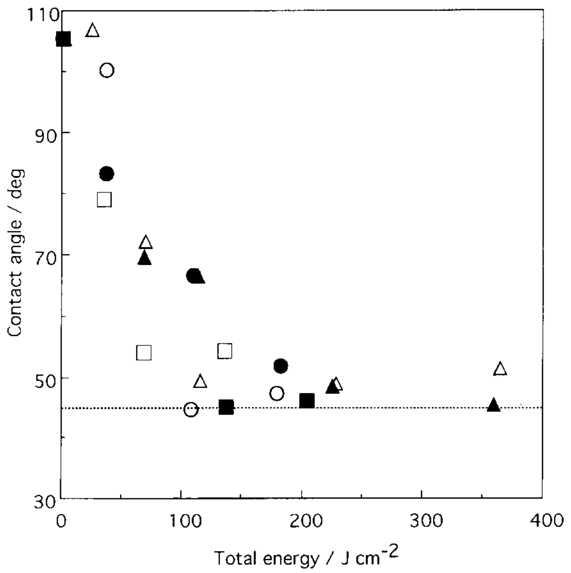


Figure 1 Plot of contact angle on the PFA films irradiated with 1.0 wt% PAA solutions at 248 nm vs. total laser energy with several laser fluences and molecular weights: (▲) 22.4 mJ cm^{-2} pulse^{-1}, M_w = 150 000; (●) 36.3 mJ cm^{-2} pulse^{-1}, M_w = 150 000; (■) 67.6 mJ cm^{-2} pulse^{-1}, M_w = 150 000; (△) 22.6 mJ cm^{-2} pulse^{-1}, M_w = 2000; (○) 35.6 mJ cm^{-2} pulse^{-1}, M_w = 2000; (□) 67.4 mJ cm^{-2} pulse^{-1}, M_w = 2000

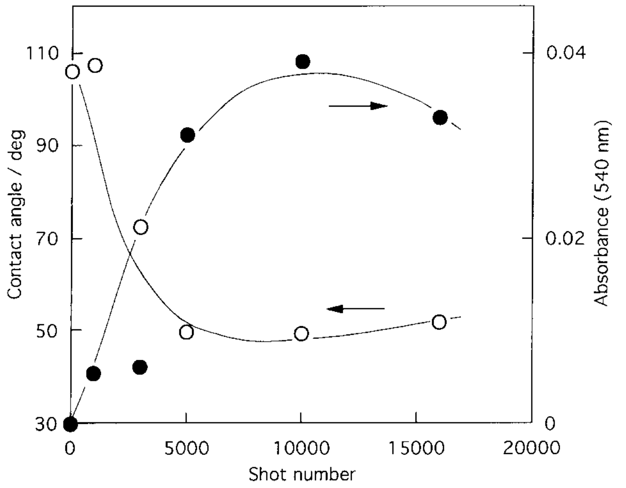


Figure 2 Plot of the contact angle of the irradiated PFA films with water droplet (○) and absorption at 540 nm based on the adsorption of rhodamine 6G (●) vs. shot number of KrF laser pulse (22.6 mJ cm^{-2} pulse^{-1})

considerably suppressed by the use of PAA with low molecular weight (M_w = 2000) as compared to that with high molecular weight (M_w = 150 000). The use of the low molecular weight PAA gave a noticeably more wettable surface of the irradiated film than use of the high molecular weight PAA, because intramolecular cross-linking, which competes with the reaction with PFA surface, will be favourable for the high molecular weight of PAA. On the other hand, the irradiation with solutions whose concentrations were smaller than 0.5 wt% was less effective than that with solution of 1.0 wt% throughout the present study. *Figure 1* shows changes in the contact angles of the PFA film as a function of the irradiation energy with various laser fluences. Though the decrease of contact angle with total energy was observed for each fluence, the contact angle levelled off at 45–50° in the range of irradiation energy >100 J cm^{-2}. With the laser pulses of >150 mJ cm^{-2} pulse^{-1}, ablation of PFA or its reacted layer took place to result in damage of the surface. There seems to be little fluence dependence in the wettability, which is governed more by the total energy than by the fluence.

The contact angle was not changed by irradiation with water which did not contain PAA[6]. The wettability was not affected by washing with 0.5 N NaOH followed by 0.5 N HCl and water to rule out simple adsorption of PAA. No morphological change in the irradiated PFA surface was observed with SEM (×10 000). The surface was smooth, which rules out contribution of surface roughness induced by laser ablation on the wettability. Therefore, the surface wettability was attributed to a photochemical reaction between PFA and PAA. Whereas an adhesive strength of <0.1 kgf cm^{-1} (kgf cm^{-1} = 980.7 N m^{-1}) was shown for raw PFA film, the values for the irradiated PFA films (KrF laser: 64.8 mJ cm^{-2} pulse^{-1}, 1000–2000 pulses, 0.1 wt% low molecular weight PAA solution) were 0.8 and 1.1 kgf cm^{-1} with cyanoacrylate- and epoxy-type adhesives, respectively, which also suggests the presence of some polar functionalities. The surface was well stained with a basic dye such as rhodamine 6G (Rh6G) and not with acidic dyes such as sulforhodamine. The absorbance (A) at 540 nm based on Rh6G adsorbed on the surface increased with shot number as shown in *Figure 2*. These results suggested the introduction of a carboxylic group which was induced by a photochemical reaction between PAA and the PFA surface. The quantity of carboxylic group at the surface coverage of the dye (S) $S = A/1000\epsilon$, assuming 1 : 1 adsorption of Rh6G to carboxylic group and a molar extinction coefficient (ϵ) for adsorbed Rh6G at 540 mm of 1×10^5 mol^{-1} dm^3 cm^{-1}, the same as that in water. For 10 000 pulses, $A = 0.039$ in *Figure 2*, the surface coverage was calculated to be 3.9×10^{-10} mol cm^{-2} (2.3 molecule nm^{-2}).

Figure 3 shows C1s X.p.s. spectra of the PFA film before and after the irradiation together with that of PAA. A large peak of the PFA film before irradiation

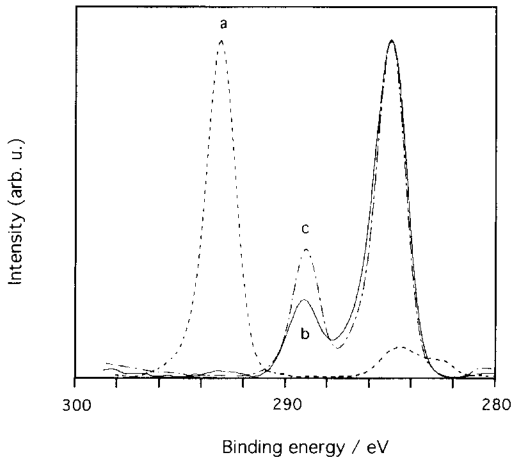
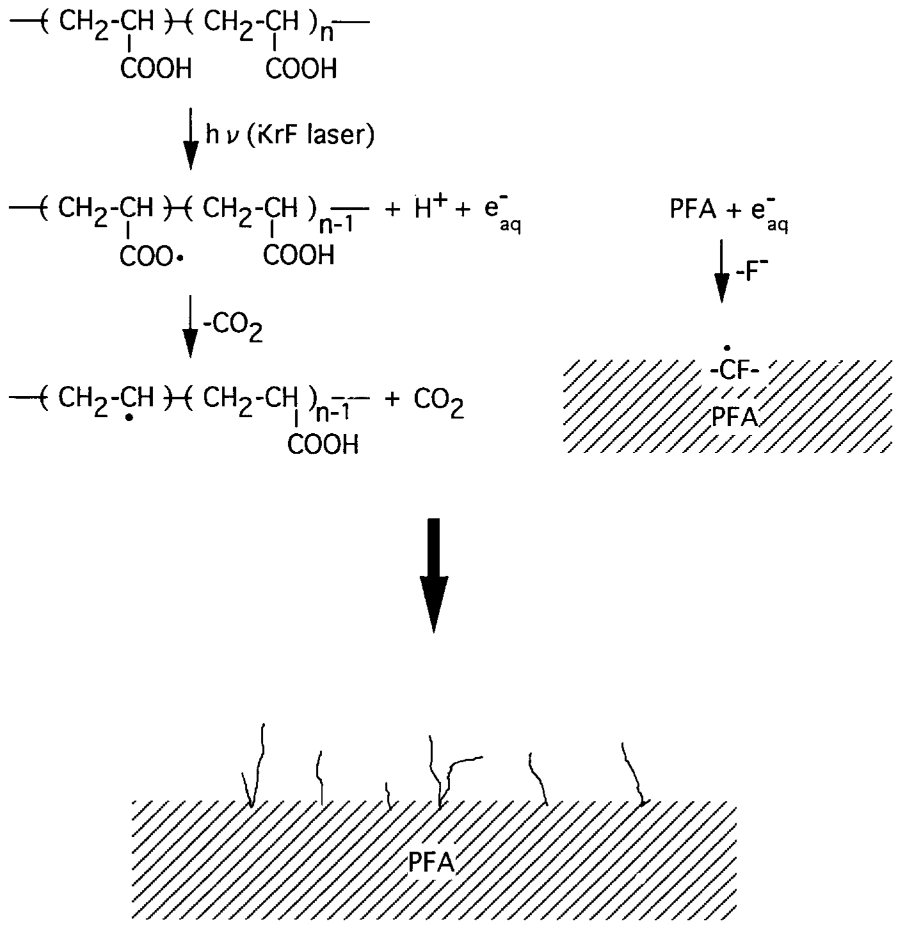


Figure 3 Normalized X.p.s. C1s spectra of PFA film (a) before and (b) after irradiation (KrF laser: 22.6 mJ cm^{-2} pulse^{-1}, 16 000 pulses) in contact with a 1.0 wt% low molecular weight PAA solution, and (c) that of PAA cast film



Scheme 1

assigned to $-CF_2-$ (293.0 eV) decreased after irradiation, and growth of two new peaks was observed at 285.0 and 289.2 eV which can be assigned to methylene or methine and carboxylic groups, respectively. Since the spectrum after irradiation resembled that of PAA, the origin of the carboxylic group at the surface was attributable to photochemical grafting of the PAA chain onto the PFA surface in the form of a thin layer or sparse cluster. The results for contact angle and dye adsorption also seemed to be in accordance with thin or sparse coverage. Elemental analysis of the surface by X.p.s. indicated considerable loss of fluorine (F/C ratio from 2.18 to 0.07) and increase of oxygen (O/C ratio from 0.004 to 0.384) by irradiation (KrF laser: 22.6 mJ cm^{-2} pulse^{-1}, 16 000 pulses, 1.0 wt% low molecular weight PAA solution).

The mechanism of the present graft reaction of PAA onto the PFA surface must be based on photoionization of the carboxylic group giving a hydrated electron and a radical centre on the PAA chain via decarboxylation, which is followed by electron capture by fluoropolymer giving a radical centre at the PFA surface via elimination of fluoride ion (*Scheme 1*)[10]. The low O/C ratio also supports the decarboxylation of PAA.

The present reaction is a new approach for grafting PAA without the use of acrylic acid monomer and will modify the surface without damage in bulk. Various functional groups can be introduced onto the surface through the present reaction of copolymers of acrylic acid to enhance affinity to various organic chemicals such as inks or adhesives. Detailed work with simple carboxylic acids concerning mechanistic features is now in progress[10].

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