

# Graft Polymerization of Fluorinated Monomer onto Corona-treated PVA and Cellulose Films

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## SYNOPSIS

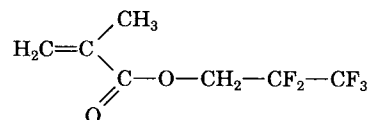
Surface graft polymerization of a hydrophobic monomer, 2,2,3,3,3-pentafluoropropyl methacrylate (5FMA), onto hydrophilic poly(vinyl alcohol) (PVA) and cellulose films was studied after corona discharge of the films. It was found that grafting strongly depended on the reaction medium; especially, addition of alcohol to the monomer greatly accelerated graft polymerization. For instance, when an ethanol/water/5FMA mixture (65/25/10, by volume) was used as the polymerization medium, the PVA and cellulose films corona-discharged for a few minutes exhibited a high contact angle up to 100° after 30 min polymerization, the graft density being approximately 170  $\mu\text{g}/\text{cm}^2$  for cellulose and 80  $\mu\text{g}/\text{cm}^2$  for PVA. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Low-temperature plasmas have been extensively used to modify surface properties of various kinds of polymers, either by plasma polymerization, in which polymerization proceeds *in situ* under plasma conditions, or by plasma-induced polymerization, in which polymerization takes place after the plasma treatment of substrate materials.<sup>1,2</sup> To render hydrophilic substrate polymers hydrophobic, plasma polymerization has been most widely applied to deposit silicon- or fluorine-containing compounds on these surfaces.

The conventional corona-discharge treatment, which applies a nonpolymer-forming plasma at atmospheric pressure, can provide a substrate surface with active species capable of initiating radical polymerization. The corona-discharge treatment has been used mainly to change the surface properties of hydrophobic materials,<sup>3-6</sup> but also to initiate graft polymerization onto cellulose.<sup>7</sup> This method, however, has not yet been used to render a hydrophilic surface hydrophobic, so far as we know. The present work describes the surface grafting of corona-treated poly(vinyl alcohol) (PVA) and cellulose films using

a very hydrophobic monomer, 2,2,3,3,3-pentafluoropropyl methacrylate (5FMA), with the following chemical structure:



## EXPERIMENTAL

### Materials

Commercially available PVA and cellulose films were used as substrate material for the graft polymerization. The PVA film of 50–60  $\mu\text{m}$  thickness was annealed for 30 min at 120°C. Both the PVA and the cellulose film (10–15  $\mu\text{m}$  thickness and no annealing) were purified by Soxhlet extraction with methanol for 20 h and stored in a desiccator. The 5FMA monomer was kindly supplied by Daikin Industries, Osaka, Japan, and used as obtained. Other solvents were all guaranteed reagents and used as obtained.

### Graft Polymerization

The corona treatment of PVA and cellulose films was performed in dry air at room temperature and

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atmospheric pressure. The corona discharger was fabricated referring to that of Blythe et al.<sup>8</sup> It was equipped with two circular parallel-plate electrodes of 75 mm in diameter. The gap between the plates was 2 mm and 15 kV was applied as peak voltage. Each film was exposed to corona discharge twice with different sides up.

To effect graft polymerization, the films exposed to corona discharge were put into glass ampules immediately after the corona treatment and the reaction medium containing the monomer was added. After vigorous degassing, the ampules were sealed and kept at an elevated temperature for a predetermined period of time. After reaction, the films were washed with acetone, a good solvent of the 5FMA polymer, under overnight stirring to remove the 5FMA homopolymer formed and the 5FMA monomer.

### Characterization of Grafted Films

Static contact angles of water on the films were measured at 25°C and 65% relative humidity with the sessile drop method. Double-distilled, deionized water was used for this measurement and 10 readings were averaged.

A spectrometer ESCA 750 manufactured by Shimadzu Corp., Kyoto, Japan, was employed to carry out the X-ray photoelectron spectroscopy (XPS) measurements of the grafted films using a MgK $\alpha$  X-ray source. The XPS data were processed with an ESCA PAC 760 analyzer.

The graft density on the substrate films was quantified using a Shimadzu FTIR 8100 spectrophotometer. A calibration curve was constructed by mixing certain amounts of 5FMA homopolymer with KBr. The absorbance of the carbonyl peak appearing at 1750 cm<sup>-1</sup> was measured.

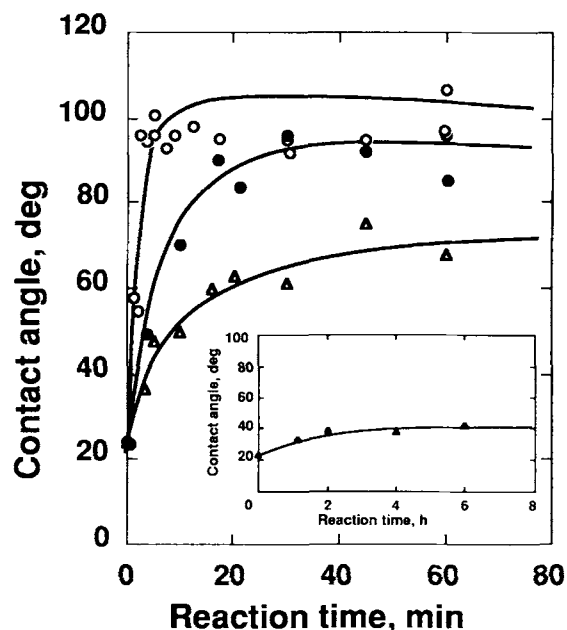
The tensile strength of corona-treated and grafted dumbbell-shaped samples was measured using Autograph S-100 WZ manufactured by Shimadzu Corp. The measurements were done at 25°C and 65% relative humidity. A crosshead speed of 40 mm/min was applied.

## RESULTS AND DISCUSSION

Graft polymerization did not take place and the contact angle of the films remained almost unvaried, when polymerization was carried out in the absence of any solvent, i.e., in the pure monomer. On the contrary, polymerization medium became turbid, indicating that precipitation of the formed homo-

polymer and the contact angle significantly increased upon graft polymerization when alcohol was added to the monomer. However, no measurable weight increase was observed even on the films whose surface drastically changed from water-wettable to water-repellent. Figure 1 shows the change of water contact angle for the PVA film by graft polymerization of 5FMA conducted in different solvents.

It seems likely that the site of graft polymerization is confined in the surface region of the PVA film, because the active species responsible for the polymerization initiation such as polymeric free radicals and peroxides will be generated by corona discharge only in the surface region of the substrate film. Unfortunately, the dyeing technique<sup>9</sup> that we have usually employed to demonstrate the occurrence of surface graft polymerization of hydrophilic monomers onto hydrophobic substrates could not be applied in the present case, because any dye for the hydrophobic surface was not available. As is apparent from Figure 1, the contact angle change is greatly dependent on the nature of the solvent used for the graft polymerization. Generally, the surface graft polymerization takes place not only onto the outermost surface of the substrate polymer but also into the surface region to some extent. To effect the



**Figure 1** Increase in contact angle with the reaction time at 70°C for PVA films in different reaction media: (O) ethanol/water/5FMA (65/25/10 by vol); (Δ) ethanol/5FMA (90/10 by vol); (●) methanol/5FMA (90/10 by vol); (▲) 5FMA (inset).

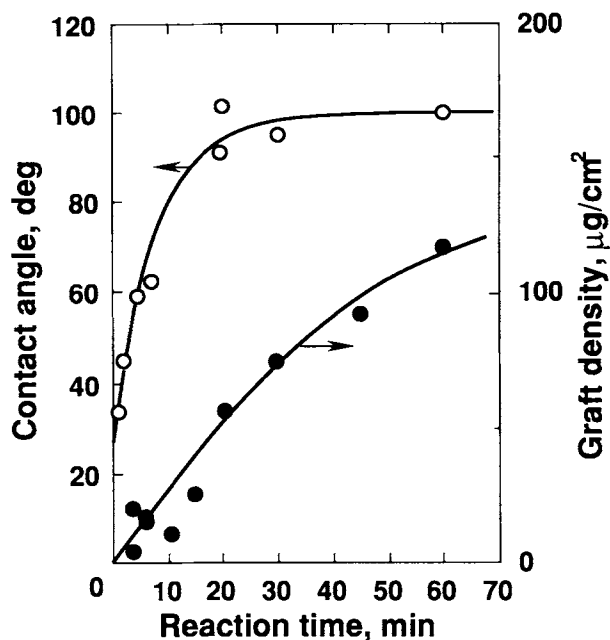
**Table I Degree of Swelling of PVA and Cellulose Films in Alcohol-Monomer Mixtures**

Solvent	Ratio	Degree of Swelling <sup>a</sup> (%)	
		PVA	Cellulose
Ethanol/water/5FMA	65/25/10	38.8	3.0
Ethanol/5FMA	90/10	0.0	2.0
Methanol/5FMA	90/10	6.9	1.2
5FMA	—	0.0	3.2

<sup>a</sup> Weight increase of films was measured after immersion in solvents at 60°C for 30 min.

graft polymerization also inside the film, the monomer molecules have to penetrate into the substrate bulk from the outermost surface. However, the 5FMA monomer was found not to be diffusable into the PVA film, probably because it is too hydrophobic to go into the matrix of hydrophilic PVA.

Table I gives the swelling degree of PVA and cellulose films when immersed in the alcohol-monomer mixtures at 60°C for 0.5 h. It is obvious that the mixture that can make the hydrophilic films to swell to a higher degree leads to production of grafted films with higher contact angles. This finding supports the above assumption that the solvent penetration into the substrate is required for the surface graft polymerization. Even if monomer cannot penetrate into the substrate film, graft polymerization should take place at least onto the outermost surface, because there is substantial contact between the monomer molecules and the film at the interface. Indeed, evidence for the surface graft polymerization was provided by an XPS study. The result of XPS on the PVA film subjected to graft polymerization in the pure monomer is given in Table II. It is seen that the F/C ratio of the grafted film measured at the XPS angle of 15° is practically equal to that of



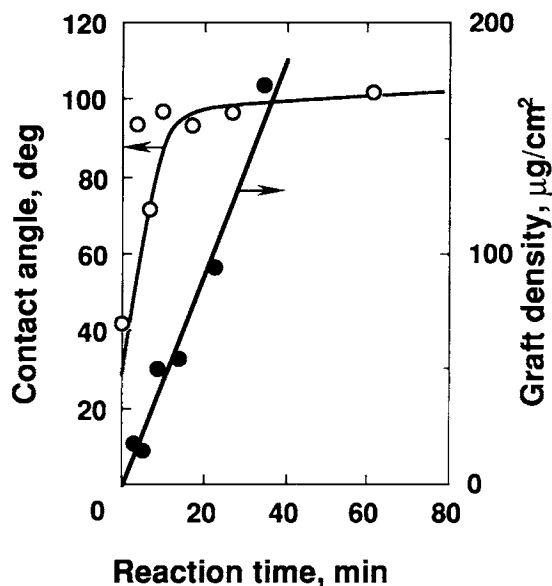
**Figure 2** Increase in contact angle and graft density with the reaction time for the PVA film (2 min corona discharge and 70°C).

the 5FMA homopolymer. It is interesting to note that the contact angle is rather low at 36°, although the film surface appears to be entirely covered with the 5FMA polymer. This may be because the water droplet can interact with the PVA chains existing just beneath the thin 5FMA polymer layer.

The progression of graft polymerization from the outermost surface to the inside of film is evidenced further by the results shown in Figures 2 and 3, where the graft density, together with the contact angle, is given as a function of the polymerization time for the PVA and the cellulose film, respectively. In both the cases, graft polymerization was carried out in the ethanol/water/5FMA mixture with a fixed volume ratio of 65/25/10 after corona dis-

**Table II F/C Stoichiometries of the PVA Films Grafted in Pure Monomer**

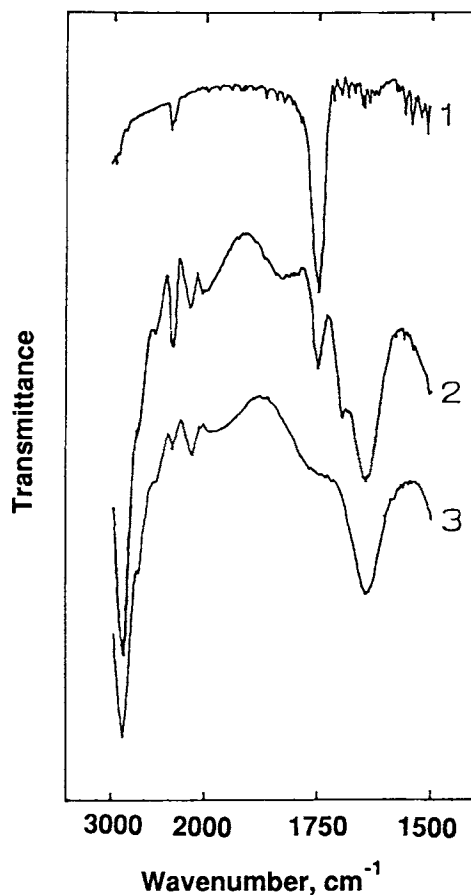
Sample	Corona Discharge Time (min)	Reaction Time (h)	Contact Angle (deg)	XPS Angle (deg)	F/C
P5FMA			100	90	0.79
Virgin PVA	2	0	25	90	0.00
PVA-graft	2	20	36	90	0.19
PVA-graft	2	20	36	60	0.48
PVA-graft	2	20	36	45	0.70
PVA-graft	2	20	36	15	0.76



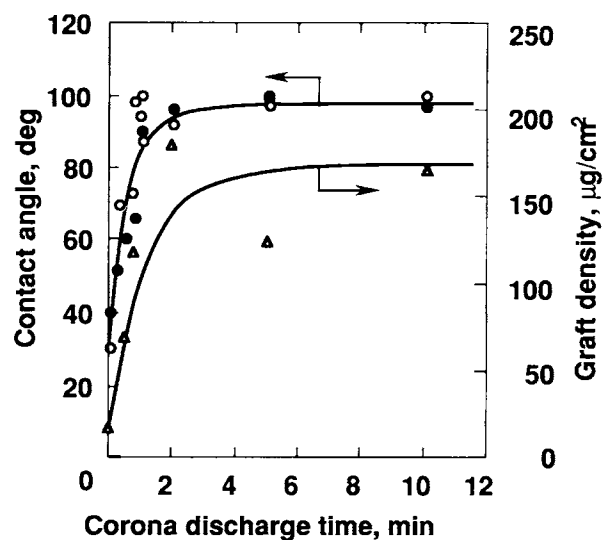
**Figure 3** Increase in contact angle and graft density with the reaction time for the cellulose film (2 min corona discharge and 50°C).

charge for 2 min. It is seen in both cases that the contact angle leveled off to 90–100° after polymerization for 10–20 min, whereas the graft density increased almost linearly still after 20 min. This implies that the grafted 5FMA polymer chains would cover the film surface after polymerization for 10–20 min so completely that the water droplet could not interact with the hydrophilic PVA chains present inside the film. After that, the grafted 5FMA chains might be formed in the film. This was supported also by IR spectra, which is given in Figure 4. Clearly, the spectrum due to the 5FMA polymer can be seen in the IR spectrum of the grafted film. This peak at 1750  $\text{cm}^{-1}$  was not observed when only the outermost surface would be grafted with the 5FMA polymer. The IR spectrum of the starting cellulose film had no significant absorbance over the wavelength from 1500 to 2800  $\text{cm}^{-1}$ .

Figure 5 shows the effect of corona discharge time on the graft polymerization of 5FMA carried out in a medium of ethanol/water/5FMA (65/25/10). As can be seen, a few minutes is sufficient for the corona discharge treatment to obtain the saturated graft polymerization both for the PVA and the cellulose film if polymerization is allowed to proceed for 30 min at an elevated temperature around 50–70°C. When graft polymerization was performed at room temperature, a high contact angle such as 100° could



**Figure 4** (1) Typical IR spectra of the 5FMA homopolymer; (2) the grafted cellulose film with the graft density of 68  $\mu\text{g}/\text{cm}^2$ ; (3) the corona-treated cellulose film.



**Figure 5** Increase in contact angle and graft density with the corona discharge time: (○, △) cellulose film (30 min reaction time, 50°C); (●) PVA film (30 min reaction time, 70°C).

be realized after 4 h polymerization. This indicates that the active species of graft polymerization is not only peroxides but also trapped free radicals, as was found for cellulose. It is interesting to point out that the dried film of PVA and cellulose has a markedly low oxygen permeability compared with the conventional polymers. With 2 min corona discharge, the cellulose film of 33  $\mu\text{m}$  thickness as well as the PVA film of 60  $\mu\text{m}$  thickness did not undergo detectable deterioration in mechanical properties. However, corona discharge for 2 min reduced the strength of the cellulose film to about half of its starting value when the thickness was 12  $\mu\text{m}$  and the subsequent graft polymerization slightly lowered the strength of PVA film of 60  $\mu\text{m}$  thickness. It follows that the bulk structure of the PVA film is slightly destroyed by graft polymerization, probably because of invasion of the grafted chains into the PVA matrix since the film was subjected to the graft polymerization in a state swollen with the monomer mixture.

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