

Molecular Structure and Hydrophobicity of Polymeric Fluorocarbon Films Deposited on PET Substrates

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ABSTRACT: Sputter-coated polymeric fluorocarbon films (PFCF) on poly(ethylene terephthalate) (PET) are prepared under conditions of various power and pressure levels. By analysis of X-ray photoelectron spectroscopy (XPS) and infrared spectroscopy (IR), low fluorine-to-carbon (F/C) ratios, 1.02–0.61, indicate that the deposited films are highly crosslinked-unsaturated and the F/C ratio is found to be remarkably influenced by the power and slightly affected by the pressure due to the change in various structure components in the film molecules. The nonwettability properties of the PFCF are consistent with the results obtained by XPS-IR analysis. The cleavage of the sharp peak assigned to C=O stretch in the FTIR spectra of the PFCF-PET film can be thought to be an evidence related to the newly formed F—C bond on a certain site of ester group next to benzene ring in PET macromolecules. Therefore, the chemical bond at the interface between FCPF and PET can be expected to enhance the joint strength of the interface. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1843–1850, 2002

Key words: molecular structure; fluorocarbon films; characteristic; interface; hydrophobicity

INTRODUCTION

As a popular technology, plasma processing provides a method to modify chemical and physical properties of polymer surfaces without changing bulk properties. Alternatively, sputter technology can also be used for this surface modification because a thin solid film with properties different from substrates can be deposited on various surfaces of substrate materials by sputtering, forming functional films, or functional coatings.

Polymeric fluorocarbon films (PFCF) obtained by sputtering polytetrafluoroethylene (PTFE) exhibit many excellent properties and were fabricated for many applications, including organic

thin film dielectrics,¹ optical layers,² wear-resistant coatings, and solid lubricants.³ To our knowledge, however, only very limited attention has been paid to the application of excellent waterproofness of the films because of the interests in film rather than in coating. To develop new waterproof breathable fabrics, we have recently prepared a series of fluorocarbon polymeric films deposited on poly(ethylene terephthalate) (PET) fabrics or films by ion-beam and radio frequency (RF) magnetron sputtering of PTFE, respectively.^{4,5} We found that the sputter-coated fluorocarbon films exhibit excellent hydrophobicity and moisture-permeability.⁵ Moreover, some of the films consist of numerous nano-sized particles that join each other and construct a special nano-network microstructure, exhibiting properties different from those of large particles of film materials.⁴

There has never previously been a systematic study of the influence of sputter-discharge conditions on both the molecular structure and the

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waterproofness of the fluorocarbon polymer coated on PET substrates, although a lot of studies on fluorocarbon film characteristics were reported.^{6–11} In this study, PET fabric and film were employed as the substrates and each fluorocarbon film was deposited as a coating other than a film, thus the PFCF character, especially the molecular structure at the interface between PFCF and PET, deserved our attention because the characteristic study is necessary to develop the waterproof breathable fabrics.

The purpose of this article is to report the results that we obtained using X-ray photoelectron spectroscopy (XPS) and transmission FTIR for characterizing interfacial molecular structure of the PFCF-PET system, bulk structure of the PFCF, and the relationship between discharge condition and molecular structure of the films, including power-dependence and pressure-dependence of the structure. The influence of the molecular structure on hydrophobicity of the films is also reported.

EXPERIMENTAL

Materials

PET fabric (348 warp, 628 weft, 0.27 mm thick) purchased from Anqiu Textile Ltd. (Shandong, China) and film (1 mm thick) from Hongda Plastics Co. (Shandong, China) were used as substrates.

A PTFE sheet (2 mm thick) obtained from Jinnan Plastics Ltd. (Shandong, China) was used as a target.

Preparation of the Films

A series of FCPF were produced by RF diode sputtering of a PTFE target 16 cm in diameter bonded to a water-cooled holder in a chamber with 13.56 MHz power supply fully described elsewhere.¹⁰ The chamber was evacuated to a base pressure of 2×10^{-3} Pa and then pure argon as work gas was introduced and the vacuum was adjusted up to work pressure. Prior to deposition of polymer films, the substrate received a surface treatment in an acetone bath by using an ultrasonic washer for 15 min. During the presputtering operation required for target surface cleaning by ion etching, a shutter was interposed between the substrate holder and the target powered at 0.12 W/cm^2 for 10 min. To examine the effect of the sputtering conditions on the film structure

and thereby on hydrophobicity, the target powered at the values ranging from 200 to 600 W and the total pressure was varied from 1×10^{-1} to 10×10^{-1} Pa.

A VG ESCA LABS5 spectrometer was used for XPS analysis. Magnesium K_{α} X-rays were used as the photoexcitation source at the work voltage of 250 V, 10^{-7} Pa.

A Nicolet 750 FTIR Instrument was used for transmission infrared analysis of RF sputter-coated FPC deposited onto PET films. To examine the difference of structure between the coating and the film, a reference infrared spectrum of FCPF deposited onto pressed potassium bromide (KBr) disk was recorded.

Water contact-angle measurement was carried out by using the sessile-drop technique described elsewhere.¹²

RESULTS AND DISCUSSION

XPS Study

XPS was used to determine the composition and chemical bonding structure of the films. The C1s spectra of each coating displays five prominent peaks and they are resolvable into five regions: $-\text{CF}_3$, $-\text{CF}_2$, $-\text{CF}$, $-\text{C}-\text{CF}$, and $-\text{C}-\text{C}-$, which correspond to the five carbon atom environments in the PFCF and have equal full width at half-maximum (FWHM).⁷ The typical spectra and the data calculated from relative intensities of the deconvoluted peaks in the C1s spectra⁸ are shown in Figures 1 and 2 and listed in Tables I and II.

In Table I, the low F/C ratios, 1.02–0.61, indicate that the deposited films are highly crosslinked and highly unsaturated. The relative contents of the five components vary with increasing power but the change in trend is different: the total of crosslinked-unsaturated components or fluorine-lack components, $-\text{CF}$, $-\text{C}-\text{CF}$, and $-\text{C}-\text{C}-$, increase from 77.44 to 83.80% up to 85.00%, whereas the end components or fluorine-rich components, $-\text{CF}_3$, drop from 6.38 to 4.23% down to 2.37%. Both the components are the major factors affecting the F/C drop. On the other hand, the backbone component $-\text{CF}_2$ may either decrease or increase but the small rise in relative content of $-\text{CF}_2$, 11.87–12.71%, for the specimens obtained at power of 400–600 W has not been enough to restrain the decrease in F/C ratio since it is only the minor factor. Table II shows the pressure dependence of the composition and chemical bond structure of the films. Obviously,

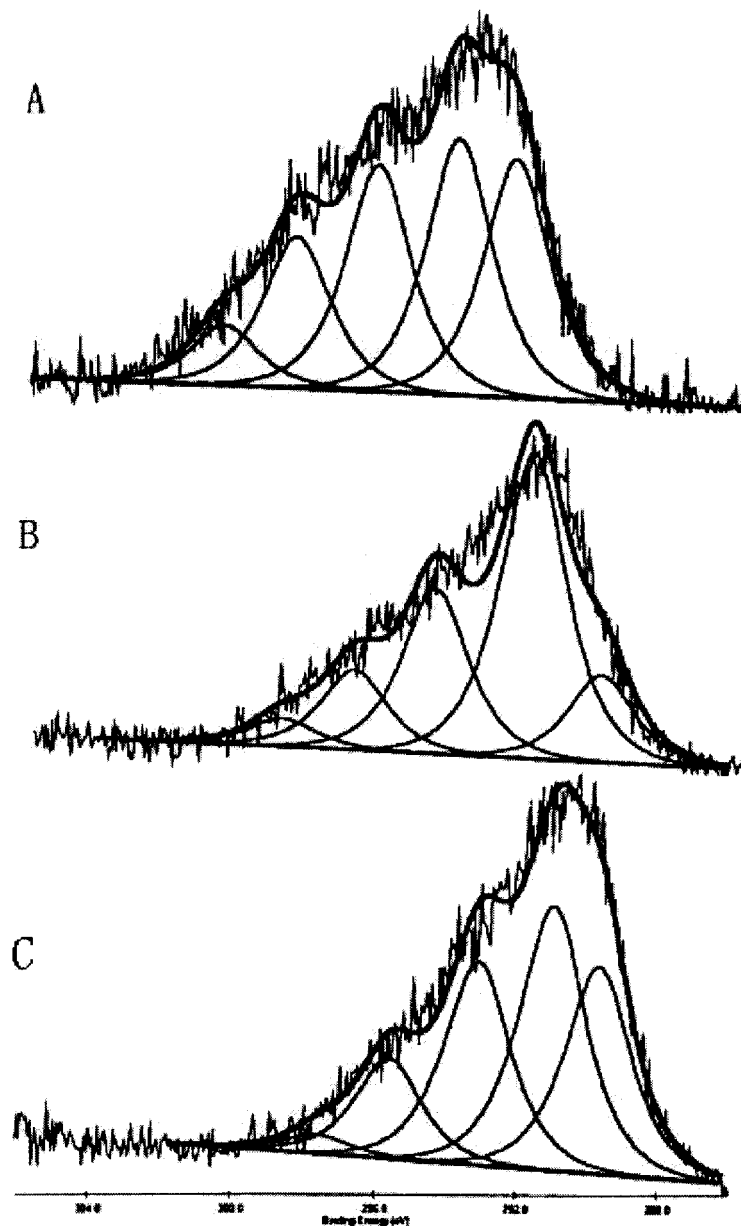


Figure 1 Curve-fit C1s XPS spectra of PFCF obtained at 5×10^{-1} Pa varying with powers: (A) 200 W; (B) 400 W; (C) 600 W.

the F/C ratio increases with pressure, but the effect of pressure on composition is smaller than that of the power, although the changed range of the pressure is greater, 10 times, than that of above given power, 3 times.

The reason for this is probably related to the mechanism of the film growth. Generally, during the sputtering process for this system, polymer fragments are ejected from the target and further molecular dissociation may occur in the plasma. The decomposition of a PTFE target provides low-weight fragments such as CF_4 , C_2F_6 , C_3F_8 , C_3F_6 ,

and C_2F_4 , the last of which is 85 mol % of the total glow discharge.^{9,13} Furthermore, the dissociation of a fluorocarbon gas in a glow discharge supplies free-activated fluorine atoms or fluorine ions.¹⁴ Accordingly, the stoichiometry of $(\text{CF}_x)_n$ polymer films depends on the mass distribution of the molecular fragments arriving at the substrate surface.⁶ In addition, Ryan and coworkers reported that fluorine content drops on moving from helium to neon to argon glow discharge; this appears to be a direct manifestation of momentum transfer phenomena.⁶ Analogously, in this study,

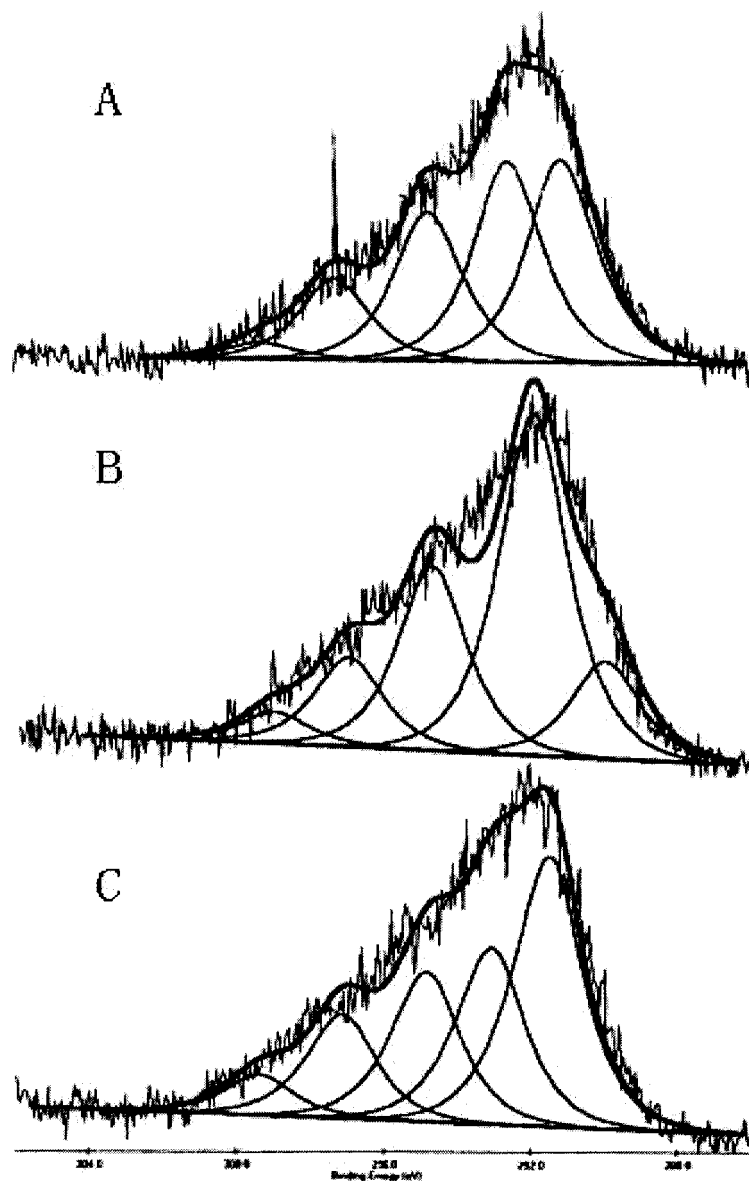


Figure 2 Curve-fit C1s XPS spectra of PFCF obtained at 400W varying with pressure: (A) 1×10^{-1} Pa; (B) 5×10^{-1} Pa; (C) 10×10^{-1} Pa.

Table I Composition of PFCF at Various Supplied Powers^a

Power (W)	—CF ₃	—CF ₂ —	—CF—	—C—CF—	—CF—	C.U.C ^b	F/C
200	6.38	16.18	24.33	27.52	25.59	77.44	1.02
400	4.23	11.89	24.84	45.90	13.06	84.34	0.71
600	2.37	12.71	25.62	33.32	26.06	85.00	0.60

^a Pressure was fitted at 5×10^{-1} Pa.

^b C.U.C.: cross-linked unsaturated carbon.

Table II Composition of PFCF at Various Powers^a

Pressure (Pa)	—CF ₃	—CF ₂ —	—CF—	—C—CF—	—C—	C.U.C.	F/C
1 × 10 ⁻¹	2.51	12.50	22.88	30.85	31.25	84.98	0.71
5 × 10 ⁻¹	4.23	11.89	24.84	45.90	13.06	83.80	0.76
10 × 10 ⁻¹	5.40	13.97	20.33	36.56	23.84	80.73	0.79

^a Power was fitted at 400 W.

the increase in power can lead to the increase in momentum of the particles bombing target material due to increasing mean velocity by power other than particle mass. Moreover, the enhanced effect can also increase the number of activated ejected fragments and the intensity of bombing film surface or the intensity of momentum transfer; thus the relative content of the crosslinked-unsaturated components should be increased because forming these components needs higher momentum transfer. For example, it required simultaneous activation at two special adjacent sites on the fluorocarbon macromolecules.

The explanation of the influence of pressure on composition may be the following: at a given power, enhanced pressure tends to increase the

number of particle bombing targets, thereby decreasing the mean energy of the particles. Compared with forming terminal groups, forming crosslinked-unsaturated groups needs higher activation-momentum transfer; therefore, in competition of the two growth factors under the decreased momentum transfer level (mean intensity) and increased momentum transfer frequency, the increase in the rate of CF₃ introduced on the film macromolecules is somewhat high, and thus, the F/C ratio has also slightly increased.

FTIR Analysis

The FTIR transmission absorption spectrum of PFCF deposited on the KBr disk is shown in Figure 3. It presents the spectrum of the FCPF

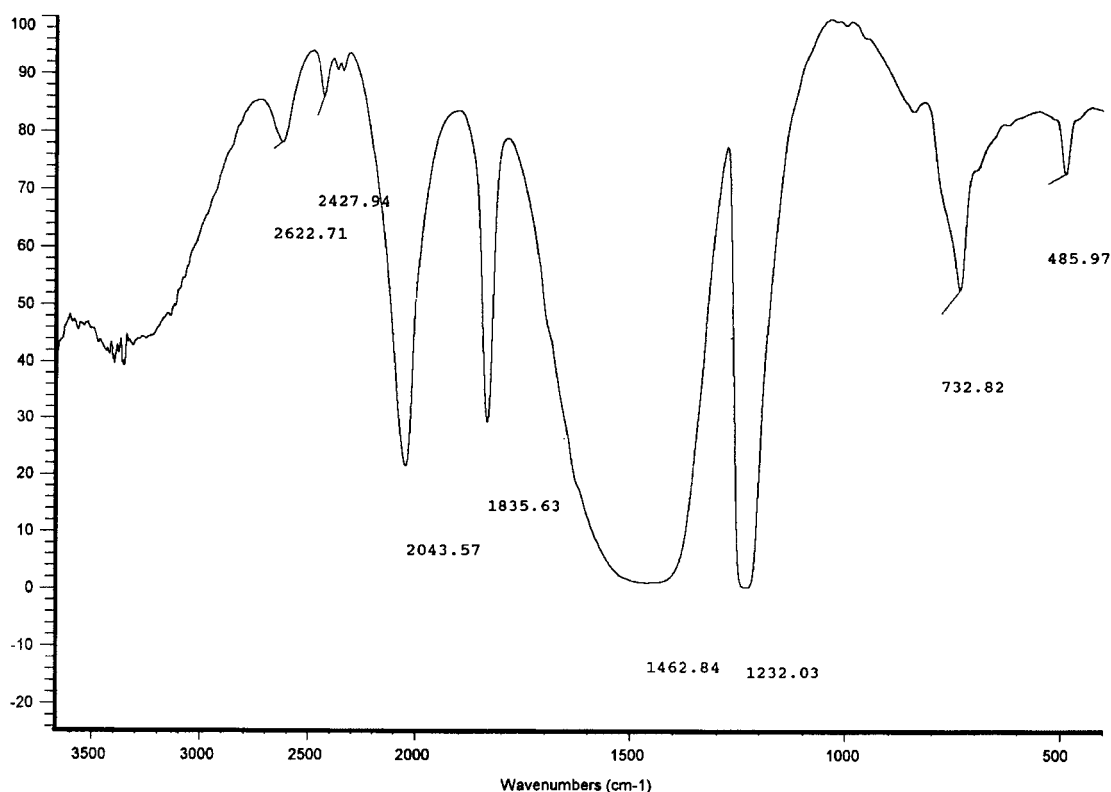


Figure 3 Transition FTIR spectra of PFCF deposited on KBr.

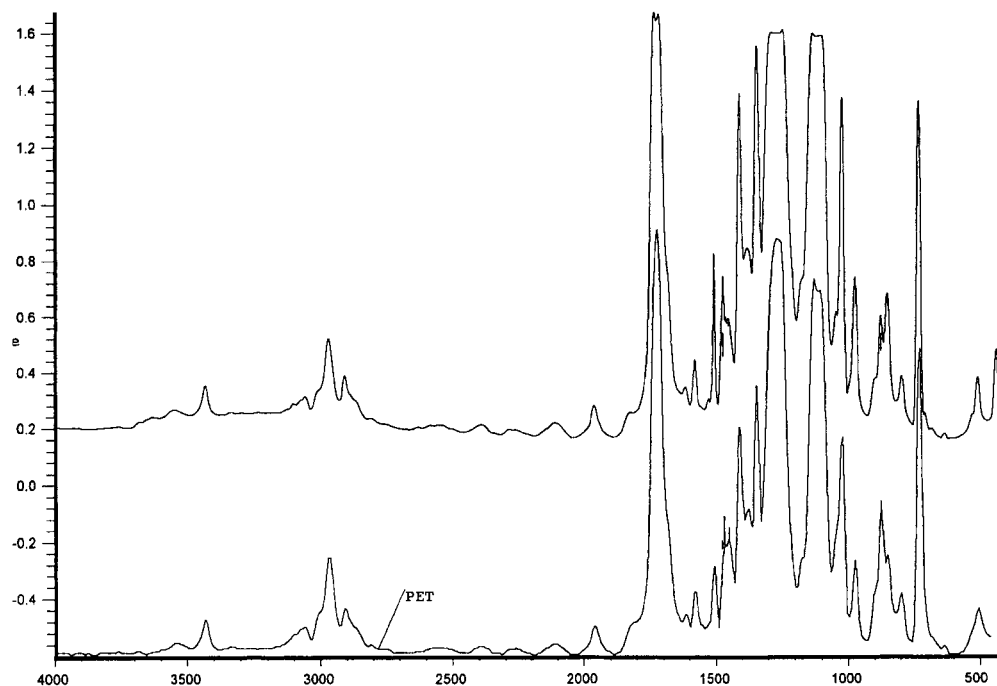


Figure 4 Transition FTIR spectra of PFCF-PET (upper) and PET (lower).

bulk because KBr has no RI absorption and the film is quite thick, about $0.6 \mu\text{m}$. All bands are rather wider; therefore, they are partly overlapping and the assignment is complicated. The typical absorption of the character bands of PTFE has not been found¹⁵: 514 cm^{-1} (CF_2 wagging), 556 cm^{-1} (CF_2 rocking), 640 cm^{-1} (CF_2 rocking), 1152 cm^{-1} (asymmetric C—F stretch), 1208 cm^{-1} (symmetric C—F stretch), which suggests the different structure of FCPF to PTFE.

In Figure 3, the infrared absorption bands in the FCPF were assigned as follows: weak absorptions at $\sim 733 \text{ cm}^{-1}$ (amorphous CF_2 structure¹⁶) and CF_3 stretching deformation,¹⁴ and/or symmetric CF_2 vibration, which becomes active due to the distortion of $(\text{CF}_2)_n$ chains¹⁷; two strong broad bands in the $1050\text{--}1830 \text{ cm}^{-1}$ range, including 1232 cm^{-1} (C—F stretch), 1462 cm^{-1} (F—C=stretch), and probably including 1626 cm^{-1} ($\text{CF}=\text{C}\langle$ stretch in a crosslinked environment¹⁸), 1730 cm^{-1} ($\text{CF}=\text{CF}$ stretch¹⁸); other two stronger bands in the $1830\text{--}2300 \text{ cm}^{-1}$ region (stretch of unsaturated bonds), including 2043 cm^{-1} ($\text{CF}\equiv\text{C}$ — and/or $\text{C}\equiv\text{C}$ — stretch, the latter located at lower wave number), and probably also including 2077 cm^{-1} ($\text{CF}=\text{C}=\text{CF}$ stretching-fluorine substitution caused a shift to higher vibration frequencies away from the usual $2000\text{--}1900 \text{ cm}^{-1}$ region¹⁹). Accordingly, the spectrum of the film

exhibits weak absorption of CF_3 and the strong absorption of unsaturated groups such as $\text{CF}=\text{C}=\text{CF}$, $\text{CF}=\text{C}\langle$, $\text{CF}\equiv\text{C}$ —, and $\text{C}\equiv\text{C}$ —, which are consistent with the above XPS results.

To study the molecular structure at the interface between FCPF and PET, we prepared a series of FCPF-PET thin film specimens by means of a special scraping method for transmission IR experiment. As is well known, such investigations are complicated by the fact that the interface is buried between two relatively thick phases: the substrate and deposited film. To make the PET phase very thin to characterize the interface, we carefully scraped each backside without deposits of the coated PET substrates by PFCF and made the residual PET surface as thin as possible to reveal the information of the interface structure by FTIR. On the other hand, the deposited fluorocarbon films on the PET also require very thin phases and we achieved the aim by decreasing deposit time. Figure 4 compares typical transmission FTIR spectra of the scraped FCPF-PET film (the upper one) and PET film (the nether one). We have observed some important differences between them, although both spectra are similar. In the typical spectrum of the scraped FCPF-PET, the band at 1130 cm^{-1} (C—O—C symmetric stretch) and the band at 1270 cm^{-1} (C—O—C asymmetric stretch) are somewhat broader

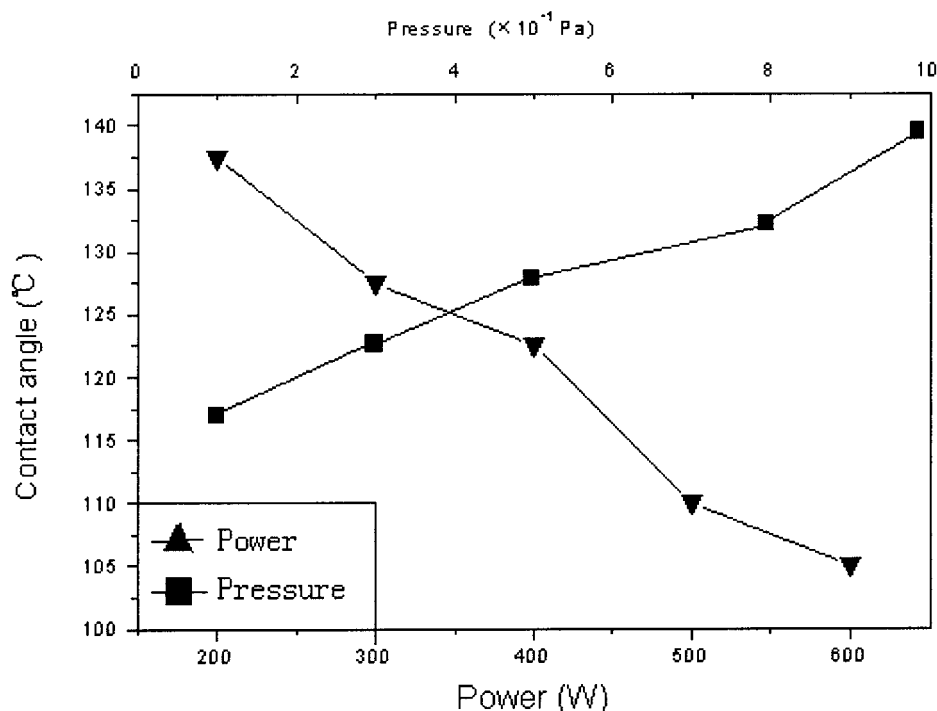
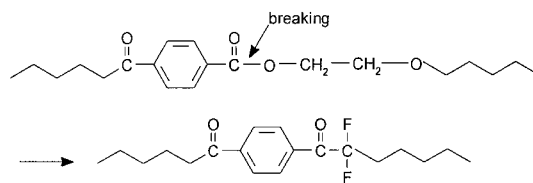


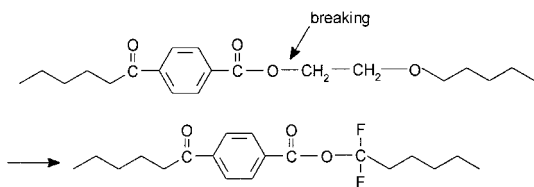
Figure 5 Relationship between contact angle and discharge conditions.

than those at same position in the spectrum of PET, which suggests the possibility of introducing F/C groups in the PET molecule at the interface: the slight increase in width is probably due to the overlap of CF , CF_2 , CF_3 and these quite weak interface signals may arise from partial coverage of the signal from the thicker PET substrate. Moreover, it is noteworthy that a sharp narrow peak centers at $\sim 1720 \text{ cm}^{-1}$ in the spectrum of PET assigned to $\text{C}=\text{O}$ stretch, whereas a double peak appears at the same position in the spectrum of PFCF-PET, which seems to be attributed to cleavage of the peak of $\text{C}=\text{O}$ stretch.²⁰ The reason for this is probably related to the newly formed $\text{F}-\text{C}$ bond on a site of ester group next to the benzene ring. Breaking of the ester group and subsequent substitution of the FC group may occur when fragments arrive at the interface and the film macromolecules start to form. There are two ways to introduce FC group on the ester group next to benzene ring²⁰:



Way 2

The reaction by Way 1 is preferable because of its smaller activation energy and one of the double peaks at higher wave number is thought of as the evidence, indicating the linked ester group by F/C group at the alpha site by Way 1. The other combination of F/C group to ester group by Way 2 should lead to a change in the band at $1770\text{--}1800 \text{ cm}^{-1}$, very weak peak in the spectrum of PET, but no obvious change was observed in this region in the spectrum of FCPF. Accordingly, the combination of FCPF with PET can be contributed by a chemical bond of the $\text{C}-\text{F}$ groups with ester group to some extent by the special way that would enhance the joint strength between film and substrate.



Way 1

Relationship Between Molecular and Hydrophobicity

Figure 5 shows the influence of the power and pressure on the water contact angle. Obviously, the contact angle decreases with increasing power, whereas the contact angle increases with

increasing pressure. The extents of change in the contact angle are different: the drop in contact angle is in the range of 137.5° - 105° , as the power increases from 200 to 600 W; the rise of the contact angle is in the region of 117.5° - 138.5° with increasing pressure (1×10^{-1} to 10×10^{-1} Pa). As is discussed above, the reason arises from a variety of various contents of FC groups. The results are consistent with that obtained by XPS and FTIR analysis.

CONCLUSION

The sputter-coated FCPF have complicated molecular structures and the components here are mostly crosslinked branching containing double bonds and triple bonds

Under given discharge conditions, the F/C ratio of the PFCF remarkably decreases with power, while slightly increases with pressure that attributes to the competition of crosslinked-unsaturated components with the backbone component and end components, and that the change in hydrophobicity of the PFCF is consistent with the change in structure.

The cleavage of the C=O stretch peak in the IR spectra may be attributed to the formed new F—C bond on a certain site of the ester group next to benzene ring, so it may be evidence for chemical bonding between FCPF and PET at the interface.

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