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# Study of Surface Properties of Novel Fluorinated Polyurethanes with Fluorine-Containing Pendent Groups

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Novel fluorinated polyurethanes (FPU) with fluorine-containing pendent groups were synthesized from fluorinated polyether glycol (PTMG-*g*-HFP), 1, 6-hexamethylene diisocyanate (HDI) or toluene diisocyanate (TDI) and 1, 4-butanediol (BDO). The structure of the fluorinated polyurethanes was confirmed by the use of Fourier transform infrared spectroscopy (FTIR). The relation between surface components and structure of the fluorinated polyurethanes was investigated by X-ray photoelectron spectroscopy (XPS), contact angle and water resistance measurements. The results from XPS and contact angle studies indicated that the surface of fluorinated polyurethanes was significantly enriched with fluorine groups. The water resistance of polyurethanes was evidently improved by introducing fluorinated groups into PU.

**Keywords:** Fluorinated polyurethane, surface property, XPS, contact angle measurement, water resistance

## 1 Introduction

Fluorinated polyurethane is a new class of functional materials. It combines some virtues of polyurethane and fluorinated polymer, such as high thermal stability, good chemical resistance (to acids, bases and solvents), low water absorptivity and attractive surface properties, excellent resistance to ultraviolet radiation and nuclear radiation, excellent flexibility, good wearability and high weatherability (1–7). Therefore, the study of fluorinated polyurethane has attracted considerable interest in recent years.

Fluorocarbon chains have been incorporated into polyurethanes by fluorinated diisocyanates (8), chain extenders (9–11), polyether glycols (12–15), polyester glycols (16) and end-cappers (17, 18). However, because of the higher synthesizing cost and fewer varieties of fluorinated diisocyanates, the synthesizing route of fluorinated polyurethane with fluorinated diisocyanates was often not used. Owing to the less fluorine content and lower molecular weight of fluorinated alcohols, the improvement of property of fluorinated polyurethane prepared by fluorinated alcohol as end-capper was not evident compared with hydrogenated polyurethane. There

are also some problems with the synthesis of fluorinated polyurethane using fluorinated extenders. These extenders, because of their low molecular weights, do not present the improvement of properties (2). Now, fluorinated polyurethane was mostly synthesized by fluorinated macromolecular diols as soft segment. The fluorinated groups of the macromolecular diols used are mainly distributed in the main chains. Ameduri (19) proposed that the surface properties of fluorinated materials with fluorine-containing pendent groups were better than those with fluorinated groups in the main chains. But the fluorinated polyurethane was seldom synthesized by macromolecular diols as soft segment with fluorine-containing pendent groups.

In our previous work, a new fluorinated polyether glycol (PTMG-*g*-HFP) with fluorine-containing pendent groups was synthesized by radical grafting reaction (20–22). In this paper, we reported the synthesis of novel fluorinated polyurethanes (FPU) with fluorine-containing pendent groups using PTMG-*g*-HFP as chemical intermediates. Two series of polyurethanes containing various amounts of soft segments with fluorinated side chains were then synthesized using a two-step polymerization method. Surface properties of fluorinated polyurethanes were examined by X-ray photoelectron spectroscopy (XPS) and contact angle measurements using goniometry. Effects of fluorine side groups on the surface properties of the fluorinated polyurethanes were also studied. At the same time, the water resistance of fluorinated polyurethanes was investigated.

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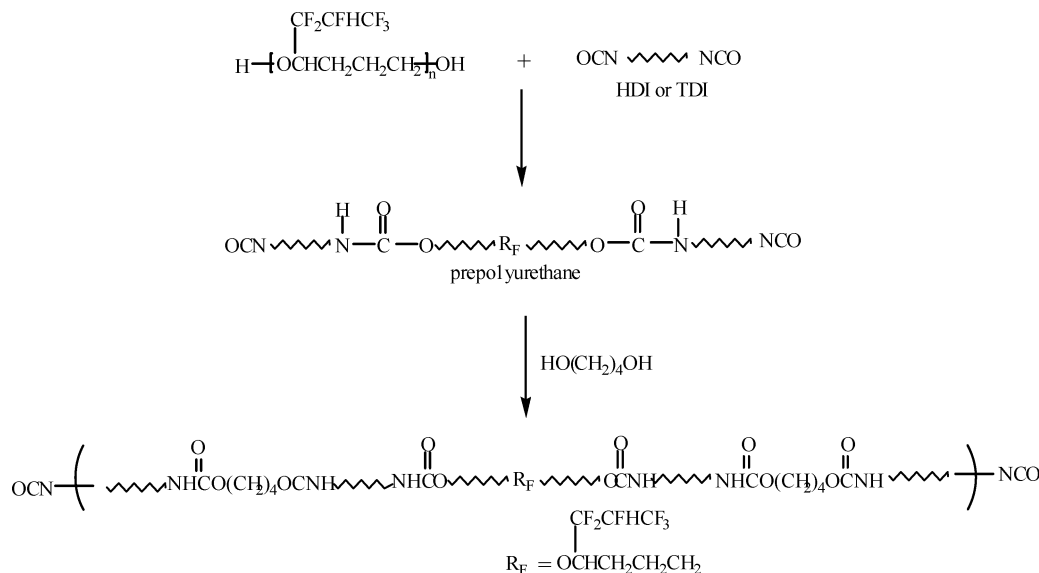


Fig. 1. Reaction scheme of FPU copolymer.

## 2 Experimental

### 2.1 Materials

Polytetramethylene glycol (PTMG,  $M_n = 1500$ ) was purchased from Mitsubishi Chemical and dried under a reduced pressure at  $80^\circ\text{C}$  for 4 h before use. PTMG-*g*-HFP (FPTMG,  $M_n = 1500$ ) was prepared according to the method of References 20–22 and vacuum-dried before reaction. The structure of PTMG-*g*-HFP was fully characterized in the previous work (20–22). PTMG-*g*-HFP spectroscopic data: FTIR/ $\text{cm}^{-1}$ : 3467 (OH stretching), 2940, 2857, 1430 and 1368 ( $\text{CH}_2$  and CH stretching), 1115 (C–O stretching), 1190 and 1287 (C–F stretching), 839 ( $\text{CF}_3$  stretching), 680 ( $\text{CF}_2$  deformation);  $^1\text{H-NMR/ppm}$  ( $\text{CDCl}_3$ ): 4.64–5.15 (m, 1H,  $\text{CF}_2\text{CFHCF}_3$ ), 3.65 (s, 1H,  $\text{CF}_2\text{CHO}$ ), 3.86 (s, 1H, OH), 1.6–1.8 (m, 4H,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 1.9–2.2 (m, 1H,  $\text{CH}_2\text{CH}_2\text{CH}$ ), 3.43 (m, 2H,  $\text{CH}_2\text{O}$ ). 1, 6-hexamethylene diisocyanate (HDI, Aldrich) and toluene diisocyanate (TDI, Bayer) were used as received. Dibutyltindilaurate (DBTDL), 1, 4-butanediol (BDO), acetone (AC) and butanone were purchased from China Medicine, Shanghai Chemical Reagent Corporation. BDO was distilled under vacuum from calcium hydride and then dried over 4 Å molecular sieves prior to use. All the materials mentioned above were used without further purification unless otherwise specified.

### 2.2 Synthesis of Fluorinated Polyurethanes and Hydrogenated Polyurethanes

Fluorinated polyurethanes (FPU) were prepared by a two-step solution polymerization method. The diisocyanate with the stoichiometric amount was dissolved in butanone. The solution was stirred at  $90 \pm 2^\circ\text{C}$  under a dry nitrogen

atmosphere and FPTMG was fed dropwise in 2 h. The reaction mixture was kept for another 2 h at  $90 \pm 2^\circ\text{C}$ . The chain extender BDO with the calculated amount and 0.1 wt% DBTDL were added to the reaction solution while the temperature was kept at  $75\text{--}80^\circ\text{C}$  for 2 h. The reaction completion was monitored by the absence of IR-absorption of the free NCO group at  $2270\text{ cm}^{-1}$ . The whole reaction process is depicted in Figure 1.

Hydrogenated polyurethanes were also prepared for the purpose of comparison. The synthesizing process and reaction conditions of the hydrogenated polyurethanes were almost the same as those of the fluorinated polyurethanes, except using PTMG as a soft segment.

### 2.3 Film Preparation

PU and FPU films were prepared by casting from a 10 wt% AC solution onto glass plates, drying at  $60^\circ\text{C}$  for 48 h, followed by further drying in a vacuum oven at  $60^\circ\text{C}$  for 72 h to remove any residual solvent, and then stored in a desiccator to avoid moisture.

### 2.4 Measurements

Infrared spectra were obtained on a Bruker Equinox 55 FTIR spectrometer in the  $4\text{ cm}^{-1}$  resolution mode. Sixteen scans were averaged for each sample in the range of 4000 to  $500\text{ cm}^{-1}$ . Each sample for infrared analysis was prepared by the coating of a thin film onto a NaCl window from 1 wt% AC solution, and then the solvent was removed by putting the sample in an oven at  $50^\circ\text{C}$  and finally under vacuum.

X-ray photoelectron spectroscopy (XPS) was carried out on a VG-Scientific ESCALAB MK-11 spectroscopy

**Table 1.** Polymer composites

Sample	HDI based	Equivalent Ratio $M^a$ /HDI/BDO	FPTMG $M_n$	Fluorine content (wt%)
HPU-1		1:9:8	—	—
HFPU-1		1:9:8	1500	10.2
HFPU-2		1:7:6	1500	11.8
HFPU-3		1:5:4	1500	14.1
HFPU-4		1:3:2	1500	17.4
HFPU-5		1:2:1	1500	19.7
Sample	TDI based	Equivalent Ratio $M^a$ TDI/BDO	FPTMG $M_n$	Fluorine content (wt%)
TPU-1		1:9:8	—	—
TFPU-1		1:9:8	1500	10.0
TFPU-2		1:7:6	1500	11.6
TFPU-3		1:5:4	1500	13.9
TFPU-4		1:3:2	1500	17.2
TFPU-5		1:2:1	1500	19.6

<sup>a</sup>M = PTMG ( $M_n = 1500$  g/mol) or FPTMG ( $M_n = 1500$  g/mol).

with an MgK $\alpha$  achromatic X-ray source (15 KV, 10 mA). Each sample for XPS was prepared by casting the polymer onto a clean silicon wafer from 10% (w/v) THF. The disks were put into an oven at 40°C for 24 h and 60°C for 24 h under vacuum. Each sample survey scans (0 to 1100 eV binding energy range) were used to identify the surface elemental compositions of polyurethanes. High-resolution scans (15 eV widths) of the C1s were obtained to provide the chemical bonding details of carbon. The C1s of hydrocarbon was taken at 284.8 eV as an internal reference.

Water–air contact angle measurements were used as a measure of the hydrophilicity of the material surface. The polyurethane surfaces were prepared by a dip-coating technique. Glass slides were cleaned with chromic acid and were coated with a PU solution (10% (wt/wt) in AC) and then dried in an oven (dry air-flowing) at 50°C for 12 h. The contact angles were measured by the sessile drop method using telescoping goniometers (Shanghai Zhongchen Digital Technical Equipment Ltd JC2000C1) at room temperature. 5–10  $\mu$ L distilled water was pumped from a microsyringe onto the surface of the PU film, the image was then captured using a telescope fitted with a video camera. All the results were expressed as the average value of at least five independent measurements.

The water resistance was determined as follows. The polyurethane films were cut into 3 cm  $\times$  3 cm pieces and dried in a vacuum oven for 24 h to determine their dry weight ( $W_d$ ). Then the film was immersed in distilled water for a time, followed by wiping off the surface water with a piece of filter paper to determine their weight ( $W_t$ ). The water absorption ( $W\%$ ) was then calculated by the formula:

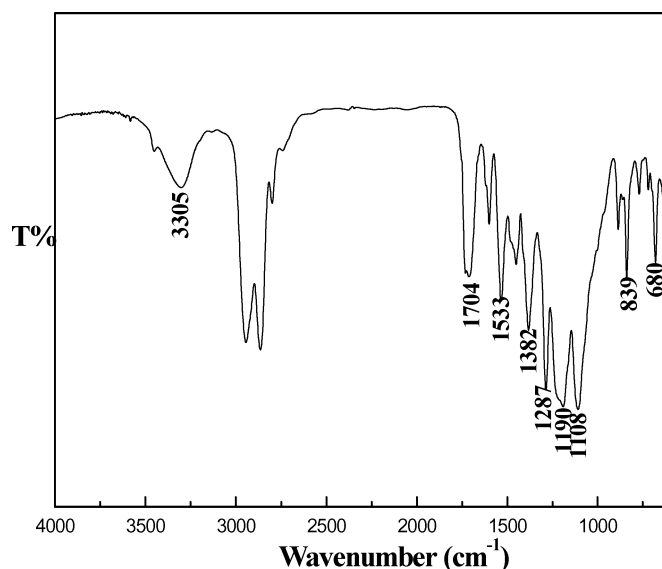
$$W(\%) = \frac{W_t - W_d}{W_d} \times 100$$

### 3 Results and Discussion

According to the above described process, two series of fluorinated polyurethanes were synthesized. The compositions of these polymers are shown in Table 1, in which the details of hydrogenated polyurethanes for the comparison purpose are also included.

#### 3.1 FTIR Characterization

The FTIR spectrum of fluorinated polyurethane based on TDI (TFPU-1) is shown in Figure 2. In the spectrum, there are characteristic peaks of N–H (3305  $\text{cm}^{-1}$ ) and C=O (1700–1730  $\text{cm}^{-1}$ ). C–H aliphatic stretches bands (2945, 2858  $\text{cm}^{-1}$ ) are also observed. The absorption band at 1108  $\text{cm}^{-1}$  originates from C–O–C group. There are phenyl



**Fig. 2.** FTIR spectrum of TFPU-1.

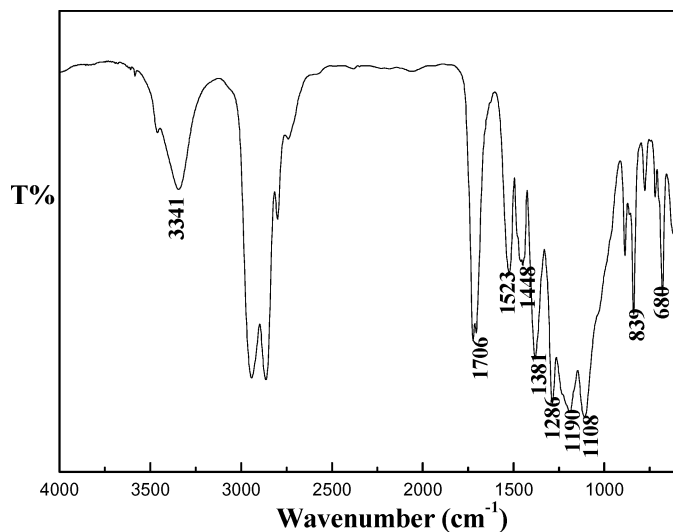


Fig. 3. FTIR spectrum of HFPU-1.

absorption bands at  $1613\text{ cm}^{-1}$ ,  $886\text{ cm}^{-1}$  and  $770\text{ cm}^{-1}$ . The disappearance of the absorption bands of the NCO group ( $2270\text{ cm}^{-1}$ ) of TDI and the OH group ( $3340\text{ cm}^{-1}$ ) also proves the synthesis of the TFPU. In addition, the absorption bands dealing with the vibration absorption of C–F bond are observed. From the spectrum, it is concluded that the stronger characteristic absorption bands locating at  $1190\text{ cm}^{-1}$  and  $1287\text{ cm}^{-1}$  can be attributed to stretching vibrations of C–F (23) and the absorption bands at  $839\text{ cm}^{-1}$  and  $680\text{ cm}^{-1}$  are resulted from the stretching vibration of  $\text{CF}_3$  and deformation vibration of  $\text{CF}_2$ , respectively (24). From these analyses, it is clear that FPTMG has been introduced into PU.

Figure 3 displays the FTIR spectrum of fluorinated polyurethane based on HDI (HFPU-1). The characteristic peaks of PU are observed in the spectrum. The absorption bands of NCO group and OH group are not found in the spectrum. In addition, the bands caused by the C–F bond are observed, which indicates the presence of the fluorocarbon chains in the polyurethane.

### 3.2 Contact Angle Measurement

Contact angles of hydrogenated polyurethanes and fluorinated polyurethanes with water drops are given in Tables 2

Table 2. Contact angle results of HPU and HFPU samples

Samples	Fluorine content (wt %)	Water contact angle ( $^{\circ}$ )
HPU-1	0	58
HFPU-1	10.2	90
HFPU-2	11.8	95
HFPU-3	14.1	97
HFPU-4	17.4	98
HFPU-5	19.7	98

Table 3. Contact angle results of TPU and TFPU samples

Samples	Fluorine content (wt%)	Water contact angle ( $^{\circ}$ )
TPU-1	0	61
TFPU-1	10.0	92
TFPU-2	11.6	95
TFPU-3	13.9	98
TFPU-4	17.2	99
TFPU-5	19.6	99

and 3. Fluorinated polyurethanes (HFPU and TFPU) showed significantly higher contact angle values as compared to that of the hydrogenated polyurethanes (HPU and TPU). This clearly indicates the generation of a more hydrophobic surface as a result of introducing the fluorinated groups. Fluorinated groups exhibit hydrophobic and unique low surface energy. In general, lower surface free energy component is enriched on the surface in order to minimize the polymer–air surface tension. It is believed that lower surface energy of fluorine atoms provides a thermodynamic driving force for the migration of fluorine to the free surface (25). It is also observed that the contact angle increased with the increasing amount of fluorine incorporated into polyurethanes in Tables 2 and 3. This effect continued until a plateau value was reached at a certain fluorine concentration, indicating a saturation of fluorine at the polyurethane surface. The variance of contact angles of hydrogenated polyurethanes and fluorinated polyurethanes with water drop can be straightly seen from Figure 4.

### 3.3 XPS Analysis

In the XPS measurement, the analysis depth,  $d$  is controlled by the mean free path (26) of the ejected photoelectron according to the following equation (27):

$$d = 3\lambda \sin \theta$$

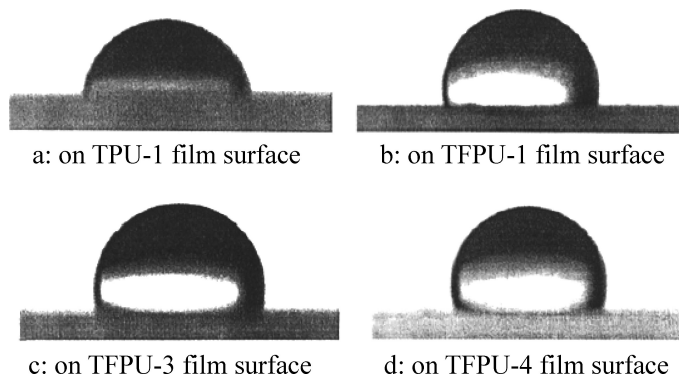
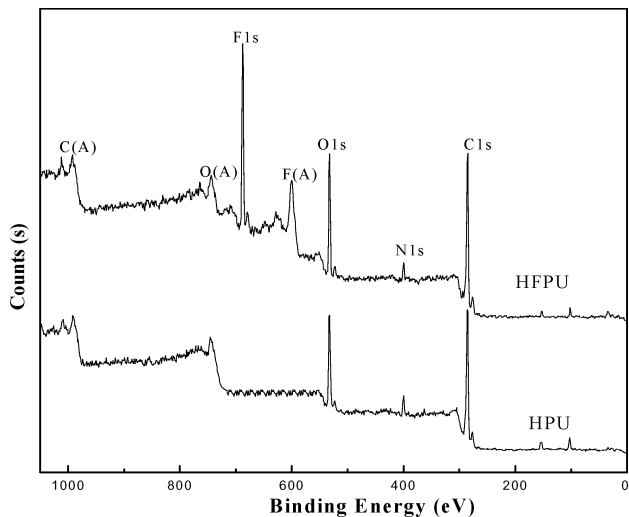


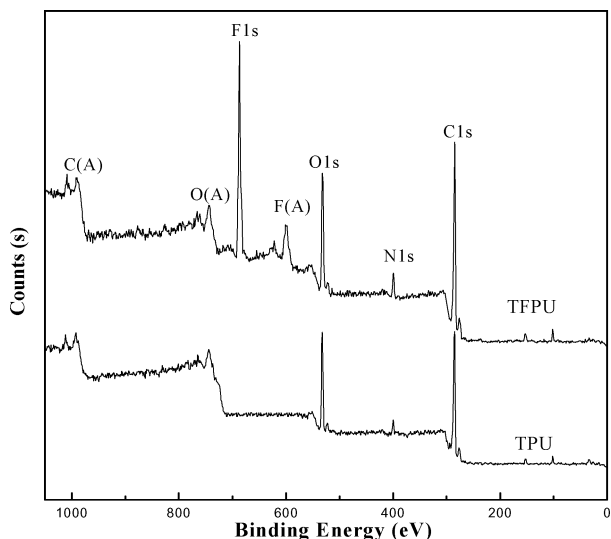
Fig. 4. Shape of water drop on various PU films surface. a: on TPU-1 film surface. b: on TFPU-1 film surface. c: on TFPU-3 film surface. d: on TFPU-4 film surface.



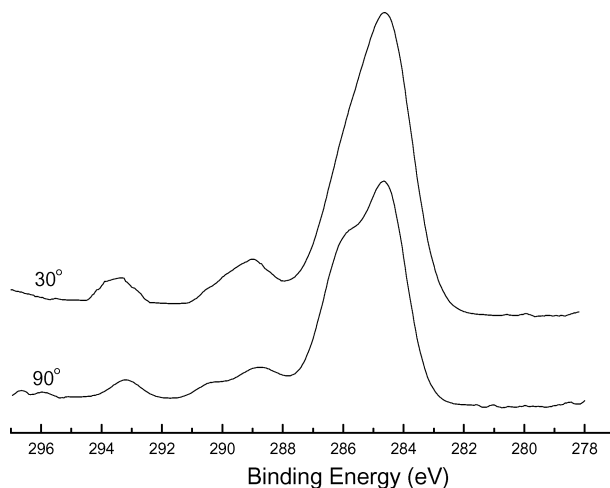
**Fig. 5.** XPS survey spectra of HFPU-1 and HPU (takeoff angle: 30°).

where  $\lambda$  is the inelastic mean-free path of photoelectron in the solids and  $\theta$  is the takeoff angle (determined by sample surface and analyzer lens). To detect possible differences in the chemical compositions between surface and bulk, each sample was measured at 90° takeoff angle and 30° takeoff angle. For typical polymer system, the takeoff angle represents the depth having been detected. 90° is near the surface (10 nm) and 30° is five nanometers away from the surface. Therefore, the higher the takeoff angle, the deeper the layer analyzed.

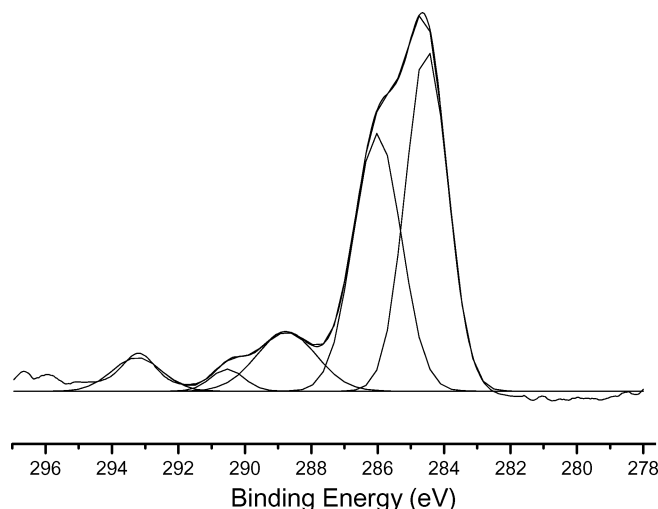
To study the surface compositions and structure of the hydrogenated polyurethanes and fluorinated polyurethanes, the XPS analysis of them was carried out. The XPS survey spectra of two groups of the hydrogenated



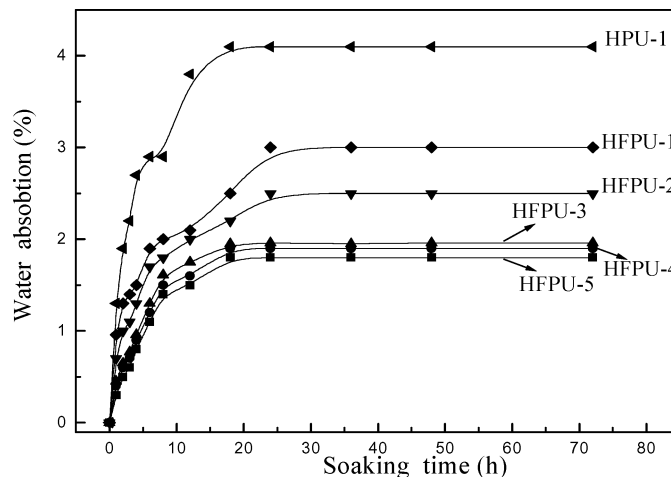
**Fig. 6.** XPS survey spectra of TFPU-1 and TPU (takeoff angle: 30°).



**Fig. 7.** High resolution XPS spectra of the C 1s region for HFPU-1.



**Fig. 8.** Fitting C1s curve of HFPU-1 at 90° takeoff angle.



**Fig. 9.** The relationship between the soaking time and the water absorption of PU films based on HDI.

**Table 4.** Surface element molar percents and bulk element molar percents of two FPU

Sample	Takeoff angle	Depth (nm)	C% Surface/bulk	O% Surface/bulk	N% Surface/bulk	F% Surface/bulk
HFPU-1	90°	10	52.85/66.05	16.01/19.06	3.64/7.05	27.50/7.84
	30°	5	50.70/66.05	14.36/19.06	3.81/7.05	31.13/7.84
TFPU-1	90°	10	52.32/67.21	15.69/18.41	3.77/6.81	28.22/7.57
	30°	5	50.76/67.21	13.26/18.41	3.93/6.81	32.05/7.57

polyurethanes and fluorinated polyurethanes are shown in Figures 5 and 6, respectively.

The XPS measurements showed the photoionization peaks of carbon, oxygen, nitrogen and fluorine in the HFPU and TFPU survey spectra. No peak attributable to the fluorine was detected in the HPU and TPU survey spectra. Table 4 lists the bulk element molar percents and surface element molar percents obtained by XPS elemental analysis of two FPU. For the two fluorinated polyurethanes, the surface fluorine contents are higher than the bulk fluorine contents. In the mean time, the smaller of takeoff angle is, the higher of surface fluorine content is. The dependence of decreasing takeoff angle confirms fluorine enrichment toward the outermost surface. Similar observations were made by Han et al. (28) when they grafted a perfluorodecanoic acid onto polyurethane. It should be noted that the amount of elemental nitrogen represents the amount of hard segment. The amount of surface elemental nitrogen increases with decreasing the depth profile of FPU films. The reason can be that the hydrogen bond interaction between fluorine on C–F of FPTMG and proton on the N–H of the urethanes groups (11) is generated. As a result, the parts of hard segments can be pulled to the surfaces with the help of fluorinated side chains. It can be also seen that the surface carbon and oxygen contents are lower than the bulk contents in Table 4.

Figure 7 shows the carbon (1s) region at 90° takeoff angle and 30° takeoff angle for HFPU-1 film. The difference between two spectra is larger. The peak of C1s is resulted from the effect of carbon atoms in four chemical environments, which are aliphatic carbon atoms, ether carbon atoms, urethane carbon atoms and the atoms of CF, CF<sub>2</sub> and CF<sub>3</sub>. The binding energy of C–C, C–O, –HNCOO, –CF, –CF<sub>2</sub> and –CF<sub>3</sub> are 284.8 eV, 286.6 eV, 289 eV, 288.8 eV, 290.9 eV and 293.2 eV, respectively (29–30). The peaks of –CF and –HNCOO are very adjacent and difficult to distinguish. Therefore, these two peaks were dealt with the same peak

**Table 5.** Surface chemical functionalities calculated from XPS C1s fitting spectrum of HFPU-1

Takeoff angle	Depth (Å)	C1s composition (% molar percent)				
		C–C	C–O	NCOO(C–F)	CF <sub>2</sub>	CF <sub>3</sub>
90°	~ 100	56.38	28.17	7.84	2.02	5.59
30°	~ 50	60.16	17.01	9.35	3.73	9.75

when the peak of C1s is separated and fitted. The result of peak separation and fitting of the C1s peak at 90° takeoff angle is shown in Figure 8. The fitted curve is identical with the original curve. Table 5 reports a description of the chemical bond relative to each of the fit components and the relative atomic concentration. It can be seen that the amount of –CF<sub>2</sub> and –CF<sub>3</sub> is higher close to the surface of HFPU-1 film in Table 4. This shows a fluorine-rich layer has been developed.

### 3.4 Water Resistance

The water absorption is an important factor of characterizing the hydrophobic property of polymer surface. Figure 9 shows the relationship between the water absorption and the soaking time. It was found that the water absorption increased with the soaking time, then leveled off. On the other hand, the water absorption of the films decreased with increasing the fluorine content. When the fluorine content exceeded 14.1 wt%, this phenomenon is not evident. This is consistent with the analysis of contact angle measurement with water for FPU. These results show the water resistance of PU can be improved by the incorporation the fluorinated groups into PU.

## 4 Conclusions

Novel fluorinated polyurethanes with fluorinated pendant groups were successfully synthesized from PTMG-*g*-HFPU, HDI or TDI and BDO. The incorporation of fluorinated polyether glycol into the polyurethane backbone showed a significant effect on the surface property of PU. XPS and contact angle measurements showed that there was an obvious mobility of fluorinated groups to the surface of fluorinated polyurethane films and a fluorine-rich phase was formed at higher fluorine contents. Furthermore, the surface enrichment of fluorine atoms increased the water resistance of PU.

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