

SURFACE STRUCTURE AND BULK PROPERTIES OF FLUORINATED POLY(ETHER URETHANE)S AND POLY(ETHER URETHANE) BLENDS*

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Abstract It has been well known that fluorinated polyurethanes exhibit uniquely low surface energy, biocompatibility and biostability, thermal and oxidative stability and nonsticking behavior. Consequently, these polymers have attracted considerable interest. However, the mechanical properties of fluorinated polyurethanes usually decline with increasing fluorine contents. The blending of fluorinated polyurethanes with normal polyurethane was carried out to achieve balanced mechanical and surface properties. It was found that polyurethane with good mechanical properties and low surface energy can be obtained by adding a small amount of fluorinated polyurethane. The fluorinated side chains can easily migrate to uppermost surfaces of the blends until the fluorine level at the surface becomes almost saturated. It has been shown from contact angle, XPS and AFM measurements that only as little as 0.34 wt% of fluorine level is enough to produce a surface saturated with fluorine, and the fluorine level at the uppermost surface is one hundred times higher than that in the blend bulk. The final outer surface structures of the polyurethane blend were independent of the content of the fluorinated polyurethane in the blends due to the surfaces saturated by fluorine.

Keywords Polyurethane, Fluorinated polyurethane, Blend, Surface structure, Bulk property, Surface dynamics

INTRODUCTION

Polyurethanes (PU) have been widely used for manufacturing medical devices because of their excellent mechanical properties and moderate biocompatibility^[1]. Although polyurethanes used in applications requiring all of the above properties have been successful for short-term use, the problems of long-term thromboresistance and biostability in a biological environment still remain unsolved^[2, 3]. A legitimate approach to improving the properties of polyurethanes is introduction of fluorine, and great attention has been paid to fluorinated polyurethanes due to their unique low surface energies^[4–7], biocompatibility and biostability^[8–11], low water absorptivity, lubricity, thermal and oxidative stability and nonsticking behavior^[12]. It has been demonstrated that this method is efficient for improving blood/material interactions and reducing protein adsorption^[13]. In our previous studies, a series of fluorinated polyurethanes were synthesized with fluorinated side chains attached to hard segments. The fluorine group was found to easily migrate to the surfaces of fluorinated polyurethanes when the amount of fluorinated side chains was small, but the mechanical properties of these fluorinated polyurethanes were obviously decreased. Since most pitting and cracking in relation to biodegradation of polyurethanes occur near the surface in a thickness of 20 μm ^[14], the blending of fluorinated polyurethane with normal polyurethane seems an ideal method for improving performance in biomedical applications of polyurethanes, and an improved mechanical property is also expected.

In this paper, a series of blends of fluorinated polyurethanes with normal polyurethane were prepared via

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solution blending. The bulk properties and the surface structure of the blends were characterized by tensile tests and DSC, XPS, AFM and contact angle measurements. Our results indicate that a polyurethane blend with good mechanical properties and low surface energy can be obtained by adding a small amount of fluorinated polyurethanes

EXPERIMENTAL

Materials

The chain extender 3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluoro-octyloxy)-propane-1,2-diol (PFOPDOL) was prepared from 3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluoro-octyloxymethyl)-oxirane (PDFOMO) via dilute perchloric acid. Fluorinated poly(ether urethane) (FPEU) was synthesized with 0.02 mol methylenebis(phenylene isocyanate) (MDI), 0.01 mol polytetramethyleneoxide $M_w = 1000$ (PTMO), 0.002 mol PFOPDOL, and 0.08 mol 1,4-butanediol (BDO) using two-step bulk polymerization. The structure of FPEU is shown in Fig. 1. Poly(ether urethane) (PEU) was synthesized with MDI, PTMO and BDO (molar ratio 2:1:1) using the same method as for FPEU. The number average molecular weights (GPC) of PEU and FPEU are 5.85×10^4 and 4.58×10^4 , respectively.

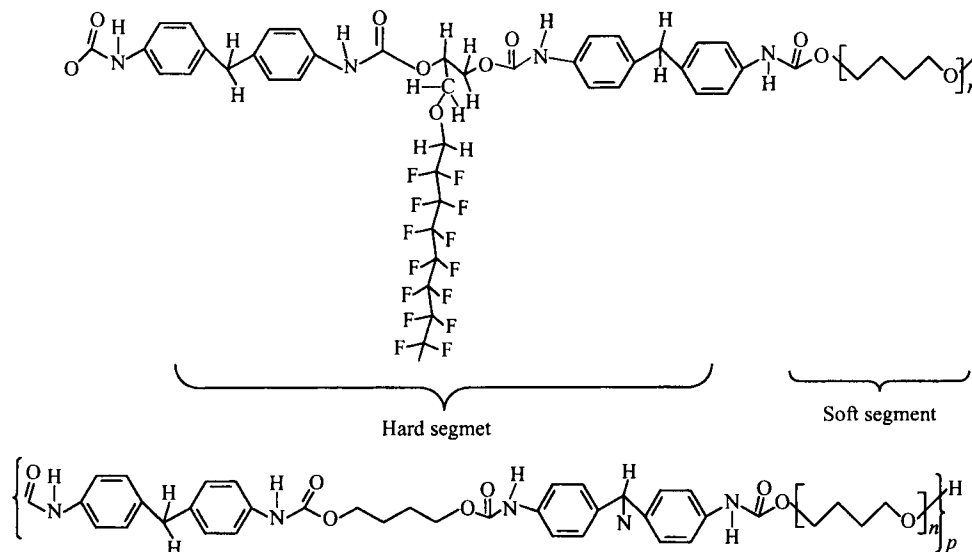


Fig. 1 Schematic structure of fluoropoly(ether urethane and poly(ether urethane)

Fluorine Content Measurement of FPEU Bulk

The polymer sample (20–30 mg) was burnt in an oxygen bomb and the fluorine anion was absorbed by deionized and distilled water. The fluorine content was determined on a Dionex 4500 IHPIC/HPLC using AS4A-SC columns. The mobile phase was 15 mmol/L $\text{Na}_2\text{B}_4\text{O}_7$ aqueous solution, Detector: CDM10MS. The result of fluorine content determination was 3.42 wt% (2.60 atom%).

Sample Preparation

A series of PEU and FPEU blends (Table 1) were prepared in 10% (W/V) solution in THF. The sample films were prepared by casting the solutions onto clean glass disks. The disks were put in an oven at 40°C for 4 h, 50°C for 20 h under vacuum, and the samples were kept at 50°C or 80°C under vacuum conditions till the water contact angle became constant. These films were used for the following measurements.

Table 1. Composition of polyurthanes and fluorinated polyurethane blends

Sample	FPEU (wt%)	PEU (wt%)	F (wt%)
FPEU 10%	10	90	0.342
FPEU 20%	20	80	0.684
FPEU 30%	30	70	1.026
FPEU 50%	50	50	1.71
FPEU 80%	80	20	2.736
FPEU	100	0	3.42

Mechanical Testing

Mechanical testing was carried out at 23°C and relative humidity 50% with an Instron universal testing machine Model 4302. The crosshead speed was 500 mm/min. The cast films were cut into dumbbells of 5 cm in length and 1 cm in width; the narrow section was 2 cm × 0.5 cm in area and 0.3 mm in thickness. The results reported are the mean values of at least five replicates.

DSC Measurements

The polymer samples (17–20 mg) were cut off from the films prepared as described above. The DSC heating data were collected at 10 K/min from –100 to 80°C by TA Instruments 2910 thermal analyzer. During the measurement, dried N₂ gas was purged at a constant flow rate. The temperature reading and calorific measurement were calibrated by using standard indium

X-ray Photoelectron Spectroscopy (XPS)

XPS was carried out on an XSAM-800 electron spectrometer. The spectrometer was equipped with a Mg K α achromatic X-ray source (20 kV, 10 mA) and two take-off angles of 30° and 90° were used with the X-ray source.

Atomic Force Microscopy

AFM sample films were prepared as described above. The AFM measurements of the fluorinated polyurethanes films were performed on an SPA400 apparatus of Seiko Instruments Industry, Co., Ltd. with an SPI3800N controller at room temperature, using the micro-fabrication cantilevers with force constant of approximately 13 N/m. In tapping mode, the topographic and phase data were recorded simultaneously. For our study, the amplitude ratio was adjusted to 0.8–0.9 of the free air amplitude for all the images. Under these light force tapping conditions, phase data are sensitive to local hydrophilicity differences of the phase about 0–5 nm below the surface^[15–17].

Contact Angle Measurements

Contact angles were measured with an Eyma contact angle goniometer. The contact angle data of each sample were obtained at various times of storage. Contact angles were measured on 3 μ L of distilled water at 20°C, and the results reported are the mean values for ten replicates.

RESULTS AND DISCUSSION**Bulk Properties**

Polyurethanes containing a repeating urethane linkage and having alternating hard and soft segments, exhibit a typical two-phase microstructure. With the domains of the hard segments serving as a reinforcing filler as well as a thermally reversible multifunctional crosslink, dispersed in a soft segment elastomeric matrix, polyurethanes have good mechanical properties. The changes of mechanical properties of polyurethane by adding fluorinated poly(ether urethane) are listed in Table 2. The data show that the fluorinated polyurethane has much lower tensile strength and modulus compared with those of the polyurethane, but they have the same glass transition temperature. For the blends, there is no remarkable effect of the fluorinated polyurethane on tensile strength and modulus of the blends at a content level of 10 wt%, but the tensile strength and modulus were obviously decreased when the content of fluorinated polyurethane is 50 wt%. The change of glass transition temperature with addition of fluorinated polyurethane may give a hint of the observed change of mechanical properties, as shown in Fig. 2 and Table 2. PEU and FPEU have the same glass transitions, and incorporation of 10% FPEU

into PEU (sample FPEU10%) did not affect the glass transition, including the onset temperature and width of the glass transition. However, FPEU 50% has a wider glass transition region than that of other samples and the T_g of FPEU 50% is the highest among the four samples. An increase in the phase mixing of the blends can be represented by an increase in the T_g of the soft segment^[18], and the T_g width has been shown to reflect the phase heterogeneity^[19]. So a phase separated structure between polyurethane and fluorinated polyurethane exists most likely in sample FPEU 50%, which causes a remarkable deterioration of mechanical properties. On the other hand, a less phase separated structure is expected for sample FPEU 10%, resulting in mechanical unchanged properties. In fact, a slight increase of tensile strength and modulus are seen for FPEU 10% compared with PEU. At the same time, one observes a decrease of glass transition temperature in this case. It appears contradictory. More work is needed to find out the reason.

Table 2. Mechanical properties and glass transition of the polyurethane blends

	Ultimate tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)	T_g (°C)
PEU	43.7	24.0	675.3	-45.7
FPEU 10%	45.5	27.5	556.7	-47.3
FPEU 50%	33.5	10.0	854.7	-40.1
FPEU	24.6	9.0	870.6	-45.3

Surface Dynamics

The water contact angle can be a reflection of the surface hydrophobicity of the polymer blends^[20], and it increases with the content of fluorine on the outer surface^[21–23]. The long-term behavior of the blends and FPEU surfaces was assessed by contact angle measurements after various times of storage at 50 °C or 80 °C under vacuum conditions, and this is shown Fig. 3. The data are obtained after storage at 50 °C under vacuum conditions within two weeks. The contact angles of these samples increase markedly within the first week, then the contact angle almost levels off at a constant value (Table 3). The time at which the contact angles achieve stabilized values decreases with increasing content of fluorinated polyurethanes in the blends (Table 3). The rate of change of the contact angles depends also very much on the storage temperature. The higher temperature of storage speeds up the migration of fluorinated side chains, and thus shortens the time for achieving the stabilized value of the contact angles, but the leveling off contact angle keeps constant (Fig. 4). It should be noted that the final contact angles measured at 80 °C are somewhat lower than that obtained at 50 °C for all the blends. This may be caused by the re-organization (aggregation) of fluorinated side chain on the surface at higher temperature, or due to the migration of soft segments onto the surface at high temperature^[24, 25]. It can be safely concluded that the fluorinated side chains can easily migrate to the top layer of the blends with a constant content value, and the time of obtaining the surface saturated with fluorine decreases with increasing fluorine content and storage temperature.

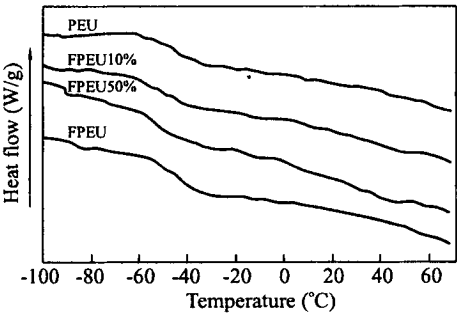


Fig. 2 DSC curves of PEU, FPEU and their blends

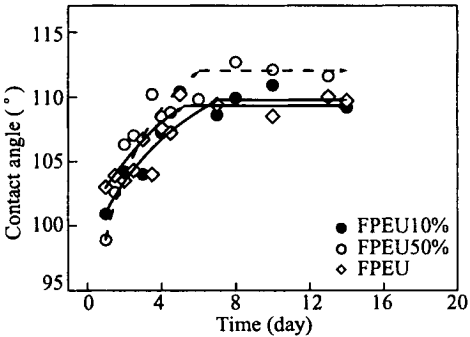


Fig. 3 Contact angle versus time curves of FPEU, FPEU 10% and FPEU 50% films

Table 3. Balance water contact angles and time of fluorine migration

	FPEU 10%	FPEU 20%	FPEU 30%	FPEU 50%	FPEU 80%	FPEU
Contact angle	109.6°	111.06°	111.9°	112.0°	110.8°	109.3°
Balance time (h)	168.2	167.5	156.9	144.5	144.0	123.4

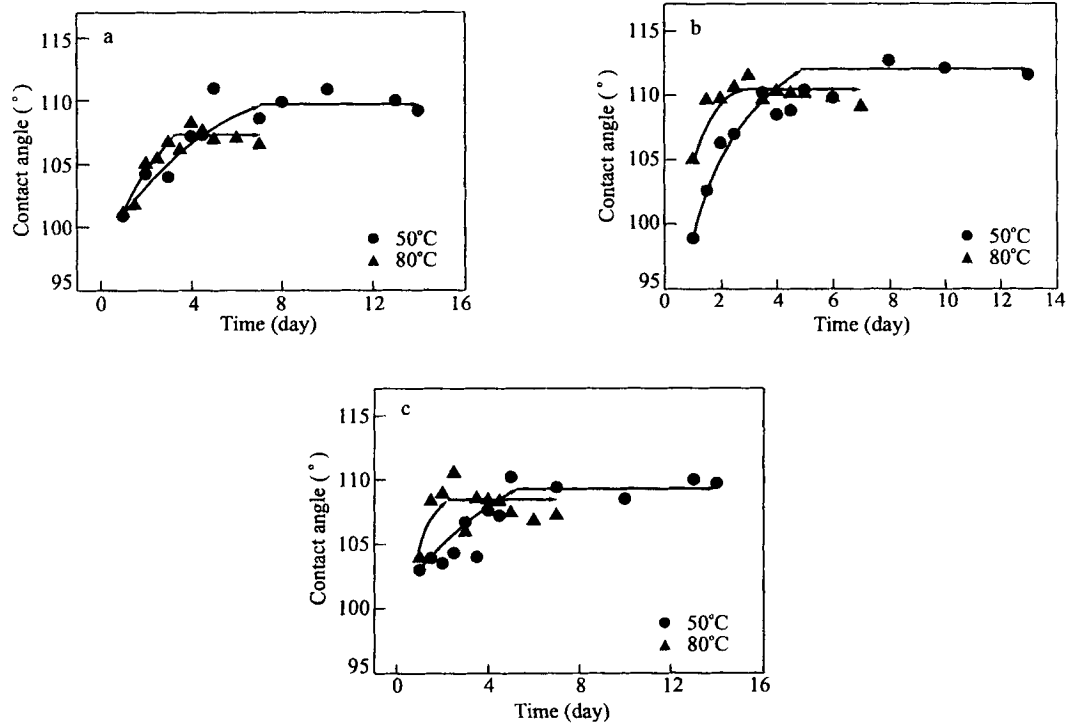


Fig. 4 Contact angle versus time curves of FPEU10% (a), FPEU50% (b) and FPEU (c) film storage at 50°C and 80°C

Structure of Surface Saturated with Fluorine

XPS analysis

If the surface is really saturated with fluorine, as suggested by water contact angle measurements, the outer surfaces of the blends should have almost the same distribution of the element. To prove this, an XPS experiment was carried out. In the XPS measurement, the sample of interest is irradiated with Mg K α achromatic X-rays as the kinetic energy of the emitted photoelectron is recorded. The analysis depth d is controlled by the mean free path^[26] of the ejected photoelectron according to the following equation^[27].

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

where λ is the inelastic mean free path of electron and θ is the take-off angle (between the film surface and the axis of the analyzer lens). In our experiments, the take-off angle is 30° and 90°, and the detection depth is then around 5 nm and 10 nm, respectively. The XPS result is listed in Table 4. It can be seen that the surface of PEU is distinctly changed by incorporation of fluorinated polyurethanes, and the measured surface fluorine content of the blend films is much larger than the theoretical calculated average value in the bulk. The ratio of surface fluorine content and the theoretical value ($F_{\text{surface}}/F_{\text{bulk}}$) is about 92–121 for FPEU 10% and 20–23 for FPEU 50%, and the blend films have much higher $F_{\text{surface}}/F_{\text{bulk}}$ compared with FPEU. Indeed, one finds that the blend films have the same element composition on the uppermost surfaces (around 5 nm), in agreement with the result of water contact angle. However, a sharper gradient of fluorine distribution into the film is seen for FPEU 10%. This result indicates a higher mobility of fluorinated side chains for FPEU 10% compared with FPEU 50%. Only

a fluorine level in bulk as low as 0.34 wt% (FPEU 10%) is enough to produce a surface saturated with fluorine, and the fluorine level at the uppermost surface is one hundred times higher than that in the blend bulk. The final outer surface structures of the polyurethane blend were independent of the content of the fluorinated polyurethane in the blends due to the saturation phenomenon of fluorine in surfaces.

AFM measurement

The AFM technique has been used to study the microdomains of polyurethanes lying underneath the uppermost surface layer by moderate force tapping^[28–30], and the phase imaging at moderate tapping of the ratio of amplitudes in the range 0.4–0.7 provides information about surface stiffness variation related to changes in Young's modulus^[15, 29]. However, the phase imaging at light force tapping of the ratio of amplitudes in the range 0.8–0.9 derives the chemical resolution from hydrophilicity differences of the phase at the surface^[15–17]. For some fluorinated polymer surfaces, the fluorine level at about 5 nm depth is about tens-fold above their stoichiometric level and the concentration profile of fluorine exhibits a steep gradient normal to the surface^[28, 31]. In this study, it has been known from XPS and water contact angle experiments that fluorinated side chains attached to the hard block can easily migrate to the surfaces of the blends and were mainly enriched about 0–5 nm below the surface. In order to further understand the distribution of fluorinated side chain attached to a hard segment on the uppermost surface of the blends, the light tapping mode AFM was used to study the surface of these blends. Figure 5 shows the topographic and phase images of PEU, FPEU 10%, FPEU 50% and FPEU samples in a 1000 nm scan region. For these blends, they give apparent topographical data on the surface where the hydrophobic patches (rich fluorine patches) appear as low spots, and the hydrophilic areas appear as high spots (Fig. 5b, c). The phase data for the hydrophobic patches are bright and the hydrophilic areas are dark^[16, 17]. Moreover, these images are coincident with those of FPEU (Fig. 5d). The PEU surface exhibits apparent hydrophobic areas based on the topography and phase images because there is only the polyether soft segment on the uppermost surface and it has the high C/O atomic ratio (Table 4, Fig. 5a). However, the blends show significant roughness and height differences when compared to PEU and FPEU (Fig. 6, Table 5). It was suggested that the fluorinated polyurethanes migrated to the surfaces and masked the surfaces of the polyurethanes so as to result in an unequal dispersion of fluorinated polyurethanes in the blends^[32].

Table 4. Atomic percentage of carbon, fluorine, oxygen and nitrogen at the depth of about 5 nm and 10 nm on the blend film surfaces

Sample	Take-off angle	F%	C%	O%	N%	$F(30^\circ/90^\circ)$	Theoretical $F\%$ *	$F_{\text{surface}}/F_{\text{bulk}}$ *
PEU	30°	0	94.0	6.0	0.0	–	0.0	–
	90°	0	93.5	5.8	0.7			
FPEU 10%	30°	36.4	51.8	9.7	2.2	1.31	0.3	121.3
	90°	27.7	57.8	11.7	2.8			
FPEU 50%	30°	34.6	53.7	9.9	1.8	1.13	1.5	23.1
	90°	30.4	55.4	11.8	2.5			
FPEU	30°	40.3	48.8	9.0	1.9	1.14	2.6	15.2
	90°	35.2	51.5	10.7	2.6			

* Data from theoretical value

Table 5. Surface roughness of the PEU, FPEU and their blend films in $2\ \mu\text{m} \times 2\ \mu\text{m}$ size by AMF measurements

Sample	PEU	FPEU10%	FPEU50%	FPEU
RMS* (nm)	5.49	14.91	19.27	4.49
Rz* (nm)	27.00	50.49	81.75	25.22

* Root-mean-square surface roughness.

* Mean height of ten points.

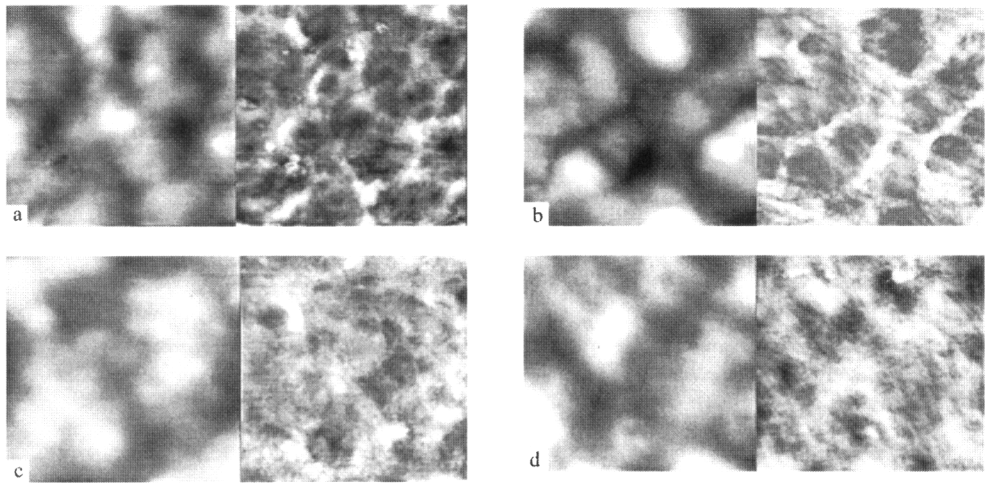


Fig. 5 Topography and phase images of PEU a), FPEU10% b), FPEU50% c), and FPEU d) at 1 μ m scan sizes

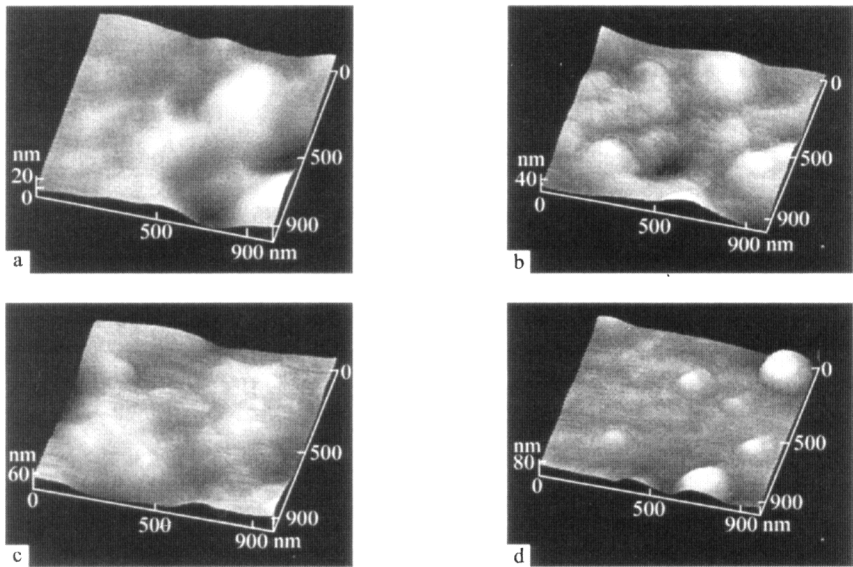


Fig. 6 Atomic force microscopy 3D images of PEU a), FPEU10% b), FPEU50% c) and FPEU d)

CONCLUSION

It has been demonstrated in this paper that surfaces with high fluorine content could be produced by blending a small amount of fluorinated polyurethane with polyurethane, due to the migration of fluorinated polyurethane on the surface. It was found that high storage temperature could improve the rate of this migration. It has been shown from contact angle and XPS measurements that only as low as a 0.34 wt% of fluorine level in blends is enough to produce a surface saturated with fluorine, and the fluorine level at the uppermost surface is one hundred times higher than that in the blend bulk. The final outer surface structures of the polyurethane blend were independent of the content of the fluorinated polyurethane in the blends due to the saturation of fluorine in the surfaces. Meanwhile the good mechanical properties can be maintained when the content of fluorinated polyurethane is small (say 10 wt%). Our results indicate that blending in a small amount of fluorinated polyurethane is a very efficient way to obtain polyurethanes with good mechanical properties and low surface

energy.

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