Synthesis and Characterization of Novel Polyurethanes Based on Fluorine-Containing Polyphosphazene

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ABSTRACT: Fluorine-containing poly[bis-(2,2,3,3,4,4,5,5-octafluoro-1-pentanol)$_{1.6}$ (4-hydroxybutaneoxy)$_{0.4}$ phosphazene] (OFHBP) was synthesized and characterized by Fourier transform infrared (FTIR) spectra, nuclear magnetic resonance (NMR), and gel permeation chromatography (GPC). The obtained OFHBP was used as a cross-linker to prepare a series of novel polyurethanes (PUPFs). The composition of the PUPFs was confirmed by FTIR and elemental analysis (EA). The crystalline structure and microstructure of the PUPFs were examined by X-ray diffraction (XRD) and atomic force microscopy (AFM). The thermal and tensile properties of the PUPFs were charac- terized by differential scanning calorimetry (DSC) and tensile testing. In addition, the surface energy of the PUPFs was also evaluated by contact angle measurements (CA). The results showed that glass transition temperature of the PUPF-4 was decreased by 15°C, elongation at break was improved by 61% and a 41% decrease in surface energy in comparison with conventional polyurethane. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 1145–1151, 2011

Key words: polyurethanes; polyphosphazenes; fluorine-containing; glass transition; surface energy

INTRODUCTION

Polyphosphazenes (PPZs) are the inorganic polymers containing alternate phosphorus-nitrogen single and double bonds with two organic side groups being attached to each phosphorus atom.[1,2] Fluorine-containing polyphosphazenes (FPPZs) are perhaps the most important class of phosphazene macromolecules due to their structure variability, synthetic versatility, and wide range of properties.[3–5] However, the inorganic backbone of PPZs is naturally too flexible to obtain necessary mechanical properties.[6] In addition, PPZs have been far proven to be of limited commercial utility due to high production costs.[7] To overcome the limitation, FPPZs have been prepared to several copolymers with poly(propylene glycol),[8] poly(methyl methacrylate),[9] poly(ethylene oxide),[10] and polysiloxane.[11] The results of synthesis of these copolymers were the surface modification and significant improvement of the biocompatibility.

Polyurethanes (PUs) represent an important class of segmented copolymers with excellent mechanical properties including high tensile strength, good tear, and abrasion resistance.[12,13] The modification of the thermal and surface properties of PUs is of outstanding importance.[14–16] For example, hydrophobic PUs (with water contact angles larger than 90°) are useful in many applications such as inert biomaterials, environmentally resistant coatings, and low friction devices.[17]

In this work, to improve the thermal and surface properties of PUs, fluorine-containing poly[bis-(2,2,3,3,4,4,5,5-octafluoro-1-pentanol)$_{1.6}$ (4-hydroxy-butaneoxy)$_{0.4}$ phosphazene] (OFHBP) was synthesized and used as a cross-linker to prepare a series of novel PUs. FPPZs, which have good chain flexibility and low surface energy, were successfully introduced into PUs and led to an excellent improvement of the thermal and surface properties of PUs.

EXPERIMENTAL

Materials

Toluene diisocyanate (TDI, NCO Index = 110) was used as received from Mitsui Takeda Chemicals
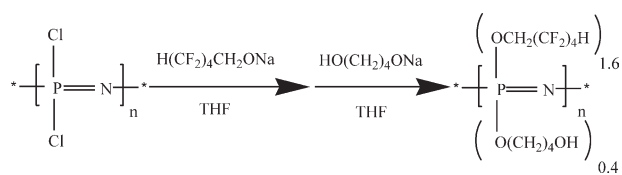
Scheme 1　Synthetic route of OFHBP.

(Tokyo, Japan). Poly(tetramethylene glycol) (PTMG, DuPont, Wilmington, DE) with a molecular weight of 1000, 1,4-butanediol (BDO, AR, purity > 99.5%, Shanghai Chemical Reagents Corp., Shanghai, China), and NH_4Cl (AR, purity > 99.5%, Shanghai Chemical Reagents Corp., Shanghai, China) were dried in vacuum at 100°C for 2 h to remove trace water. Tetrahydrofuran (THF, AR, purity > 99.0%, Shanghai Chemical Reagents Corp., Shanghai, China) was dried and distilled from Na under N_2 atmosphere in the presence of benzophenone (AR, purity > 99.0%, Shanghai Chemical Reagents Corp., Shanghai, China). 2,2,3,3,4,4,5,5-octafluoro-1-pentanol ($H(CF_2)_4CH_2OH$) (AR) and sodium hydride (AR, 60% dispersion in mineral oil) were purchased from Sigma-Aldrich Corp. (St Louis, Mo). PCl_5 (AR, purity > 99.0%), trimethylol propane (TMP, AR, purity > 99.0%) and petroleum ether (60–90°C, AR) were received from Shanghai Chemical Reagent Corp. (Shanghai, China) and used without further purification.

Synthesis of OFHBP

Linear poly(dichlorophosphazene) (PDCP) was synthesized by one-step method as described by Carriedo et al.[18] PDCP (10.0 g) was dissolved in 100 mL of THF in a three-neck flask. The solution of $H(CF_2)_4CH_2ONa$ was made from addition of sodium hydride (5.5 g, 138 mmol) to a solution of $H(CF_2)_4CH_2OH$ (32.0 g, 138 mmol) in 100 mL of THF. The solution was reacted at 50°C for 2 h, which was then added to the PDCP solution. The mixture was stirred at 50°C for 12 h. After removal of the insoluble hydrochloride salts by filtration, poly[bis-(2,2,3,3,4,4,5,5-octafluoro-1-pentanol)$_{1.6}$ (chloro)$_{0.4}$ phosphazene] (PFCP) solution was isolated by vacuum evaporation at 30°C on a rotary evaporator.

The mixture of sodium hydride (1.4 g, 34 mmol) and THF (50 mL) was added dropwise into a solution of $HO(CH_2)_4OH$ (3.1 g, 34 mmol) in 50 mL of THF, and the resulting solution was stirred at 0°C for 2 h. The solution was then added to the above PFCP solution and stirred at 50°C for 24 h. The product was first purified following the procedures similar to that of PFCP. The product was further purified by dissolution in THF and precipitation into deionized water three times, respectively. The yellow polymer was dried in vacuum. The yield was about 34.5%.

Preparation of PUPFs

TDI (3.5 g, 20 mmol) was charged to a flask and PTMG (10.0 g, 10 mmol) was added dropwise. The reaction was maintained at 70°C for 2 h to obtain isocyano (—NCO) terminated PU prepolymer. According to the —NCO content (determined by dibutylamine titration) of PU prepolymer, the exact amount of BDO, TMP, and OFHBP were calculated from the following equations:

$$[-NCO]_{PU prepolymer} = [-OH]_{BDO} + [-OH]_{TMP}$$
$$+ [-OH]_{OFHBP} \quad (1)$$
$$[-OH]_{OFHBP} = m_{OFHBP}/1126 \quad (2)$$

Where "[]" defines the mole values and 1126 represents grams per mole of hydroxyl in OFHBP.

BDO was added to PU prepolymer in drops and reacted at 70°C for 0.5 h. Then the mixture of OFHBP and TMP was added and intensively stirred for several minutes. Afterwards, the product was poured to Teflon mold to produce polyurethane (PUPF) at 80°C for 6 h. Finally, PUPF was placed at 110°C oven for 1 h. Conventional polyurethane (CPU) was prepared with a two-step process similar to PUPFs, which was cross-linked by TMP.

Characterization

The Fourier transform infrared (FTIR) spectra were recorded on a Paragon 1000 instrument (PerkinElmer, Wellesley, MA) on the range of 4000–500 cm^{-1}. Nuclear magnetic resonance spectrum (^{1}H-NMR) was recorded on Varian DRX 400 NMR spectrometer (Varian NMR Instruments) with the operating frequency at 400 MHz. Gel permeation chromatography
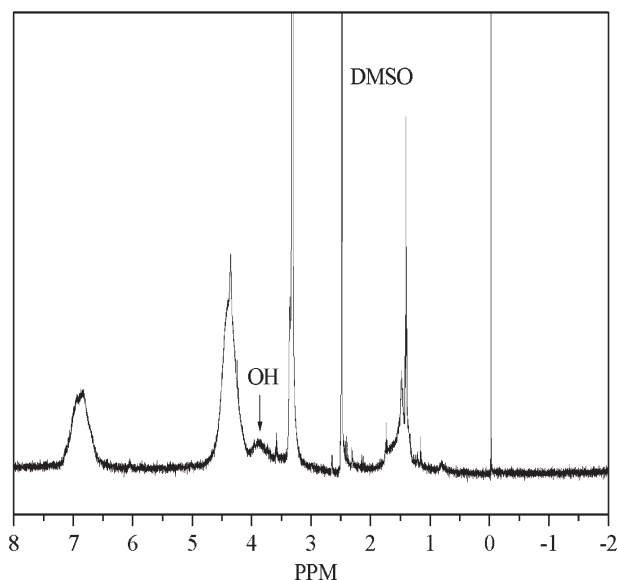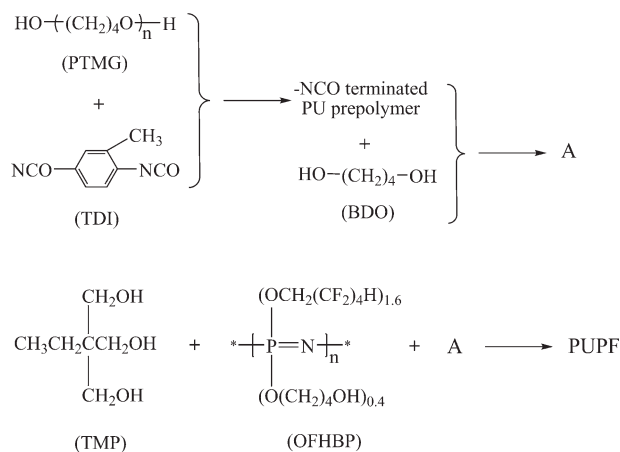

**Figure 1**　^{1}H-NMR spectrum of OFHBP.

Scheme 2 Preparation of PUPFs.

(GPC) was obtained with the use of a PE Series-200 instrument (PerkinElmer, Wellesley, MA). Elemental analysis (EA) was performed on 2400 series II CHN/O analyzer (PerkinElmer, Wellesley, MA). Differential scanning calorimetry (DSC) was carried out on a Pyris DSC analyzer (PerkinElmer, Wellesley, MA) from -70 to $110°C$ at rate of $10°C$ min^{-1} under nitrogen flow. X-ray diffraction (XRD) patterns were taken on a XRD-6000 diffractometer (Shimadzu, Kyoto, Japan) with Cu/Ka target (40 kV, 15 mA), and the scanning rate was $6°$ $min^{-1.}$ Tensile properties were conducted on the INSTRON 4465 Universal Testing System with a crosshead speed of 500 mm $min^{-1.}$ The results reported are the mean values for five replicates. Atomic force microscopy (AFM) was recorded with a tapping mode on Nanoscope IIIa scanning probe microscope (Digital Instruments). Water contact angles (CA) was measured at $25°C$ using a sessile drop method (OCA 20 contact angle system, Dataphysics, Instruments GmbH, Germany). The results were the mean value of five determinations.

RESULTS AND DISCUSSION

Synthesis and structural characterization of OFHBP

The procedure for preparing of OFHBP is illustrated in Scheme 1. At first, linear PDCP was synthesized through a simple one-pot method. Co-substituted
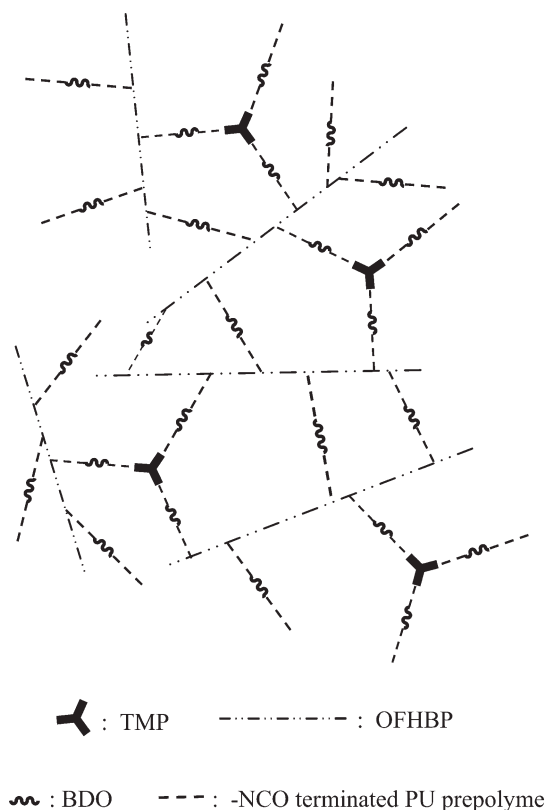
Scheme 3 A representative chemical structure of PUPF.

OFHBP was accomplished by introduction of $NaOCH_2(CF_2)_4H$, followed by excess of $NaO(CH_2)_4OH$ in an attempt to generate an approximate 4 : 1 molar ratio of substituent. OFHBP has good solubility in organic solvents, such as THF, dimethylsulphoxide (DMSO), 1-methyl-2-pyrrolidinone (NMP), N,N-dimethylformamide (DMF), and dimethylacetamide (DMAC), etc. OFHBP was characterized by FTIR, ^{1}H-NMR, and GPC.

The FTIR spectrum of OFHBP shows that the characteristic peaks for —OH, C—F, and P=N can be seen at 3400, 1260, and 1220 cm^{-1}, respectively. The ^{1}H-NMR spectrum of OFHBP (Fig. 1) shows CF_2H protons at $\delta = 6.8$ ppm (s, 1H), $O—CH_2—CF_2$ protons at $\delta = 4.4$ ppm (s, 8H), OH protons at $\delta = 3.9$ ppm (s, 1H), $P—O—(CH_2)_3$ protons at $\delta = 3.3$ ppm (s, 6H), and $P—O~CH_2—O$ protons at $\delta = 1.5$ ppm (d, 2H). The data indicates the OFHBP structure is the same as

TABLE I
Chemical Composition of PUs

Code	TDI (g)	PTMG (g)	BDO (g)	TMP (g)	OFHBP (g)
CPU	3.48	10.00	0.81	0.09	–
PUPF-1	3.48	10.00	0.81	0.07	0.49
PUPF-2	3.48	10.00	0.81	0.04	1.24
PUPF-3	3.48	10.00	0.81	0.02	1.75
PUPF-4	3.48	10.00	0.81	–	2.25

Figure 2 FTIR spectra of CPU and PUPF-4.

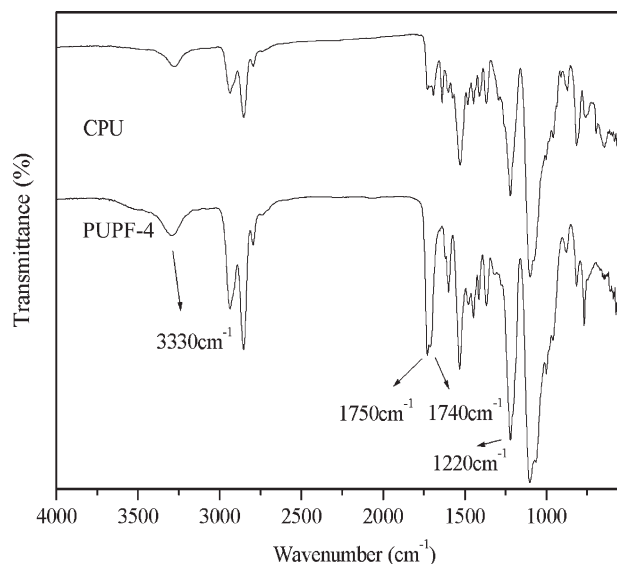**Figure 3** XRD curves of PUs.

designed. The average molecular weight of OFHBP was determined by GPC, M_n (number average) = 2.16×10^4 g mol^{-1} and M_w/M_n (polydispersity) = 1.61.

Preparation and chemical composition analysis of PUPFs

The preparation of PUPFs is outlined in Scheme 2. At first, the —NCO terminated PU prepolymer was synthesized, which subsequently chain extended by BDO and finally cross-linked by the mixture of OFHBP and TMP. A representative chemical structure of PUPF is shown in Scheme 3. The chemical composition of PUs is listed in Table I. Hereafter, the abbreviations PUPF-1, PUPF-2, PUPF-3, and PUPF-4 have been used to donate different contents of OFHBP, respectively.

FTIR spectra of CPU and PUPF-4 are displayed in Figure 2. In the spectra, typical PU absorption bands include the following: 3300 and 1160 cm^{-1} bands indicate the existence of N—H and C—O groups, respectively; 1740 and 1750 cm^{-1} bands denote C=O groups because of the presence of H-bonding.[19] Compared to CPU, the spectrum of PUPF-4 shows a more intense peak at 1220 cm^{-1}, which is
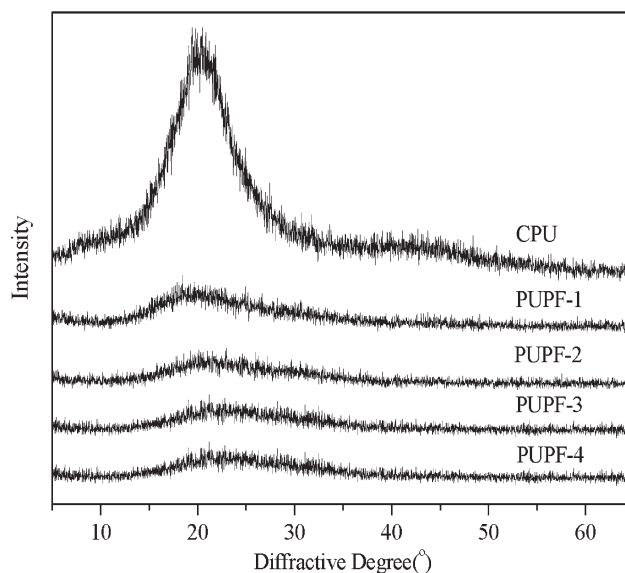
attributed to P=N groups absorption. It indicates that OFHBP had been successfully introduced into PU. In addition, no absorption at 2270 cm^{-1} appears in the spectrum which indicates that —NCO groups in PU prepolymer had completely reacted with chain extender and cross-linkers. Moreover, the results of EA also give additional evidence for the composition of PUPFs. The results of EA are listed in Table II.

Crystalline structure and microstructure of PUPFs

The XRD patterns of PUs are showed in Figure 3. A diffused diffraction peak of CPU pattern appears around 20°, which is attributed to the short-range-order arrangement of chain segments of CPU. It is probable that PTMG chains are very flexible and subject to form microcrystals. However, this diffused diffraction peak becomes weaker in PUPFs patterns indicating that PUPFs are almost amorphous. The main reasons could be the short-chain-length of branched OFHBP attaching to PU chains, and then the branched structure could hinder and weaken crystalline ability of PUPFs.

TABLE II
Elemental Analysis Results of PUPFs

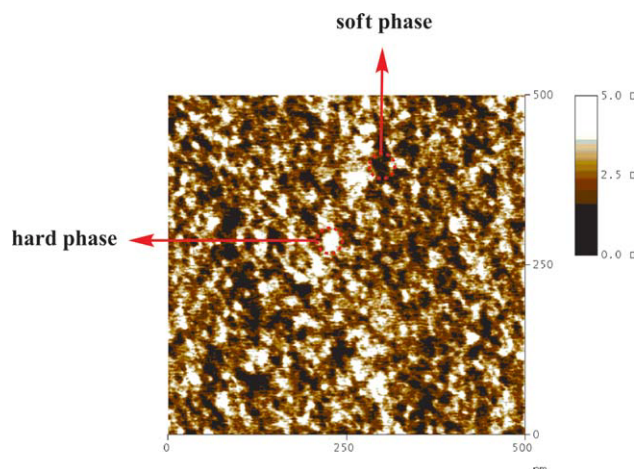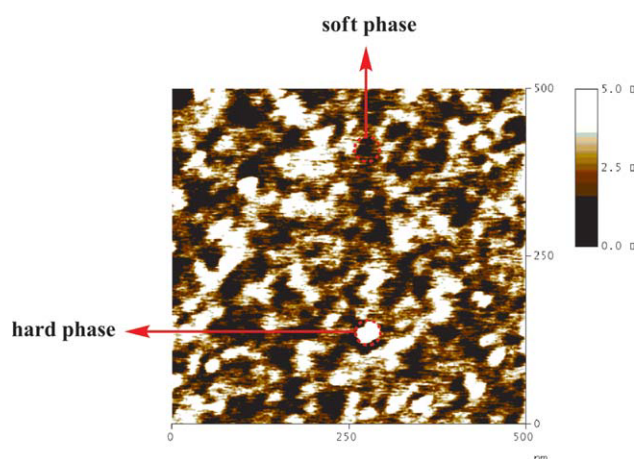| Code	C (%)		H (%)		N (%)		O (%)	
	Test.	Calc.	Test.	Calc.	Test.	Calc.	Test.	Calc.
PUPF-1	63.5	63.4	9.0	9.0	3.9	3.9	21.5	21.4
PUPF-2	61.6	61.8	8.6	8.7	3.8	3.8	20.6	20.8
PUPF-3	60.5	60.7	8.4	8.4	3.8	3.9	20.0	19.8
PUPF-4	59.5	59.7	8.2	8.3	3.8	3.8	19.5	19.3

Test., tested values; Calc., calculated values.

Figure 4 AFM image of CPU. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 6 DSC curves of PUs.

AFM has been proved to be an important tool to characterize microstructure.[20] Generally, the scales of AFM phase images are set so that the harder phase induces a higher phase offset and appears lighter whereas the softer phase appears darker. AFM images of CPU and PUPF-4 are shown in Figures 4 and 5, respectively. According to the images, the hard segment sizes of PUPF-4 are larger than CPU, which cause the hard segments of PUPF-4 to distribute more unevenly into the soft segments; that is the area of interface between hard and soft segments became smaller. Therefore, microseparation of PUPF-4 is higher than CPU. This may be attributed to two reasons: (1) difference in solubility parameters of polyphosphazenes (about 20 (cal mL^{-1})$^{1/2}$)[21] and polyurethanes (about 10 (cal mL^{-1})$^{1/2}$);[22] (2) N—H groups would form hydrogen bonds with fluorine atoms, which resulted a corresponding

decrease the hydrogen bond density between the soft and hard segments.[23] Although the degree of appropriate microseparation remains unclear from AFM, it is probable that some properties of PUPFs are affected by high degree microseparation.

Thermal properties and tensile properties of PUPFs

The thermal properties were determined by DSC. According to DSC thermograms (Fig. 6), it could be seen that glass transition temperatures (T_g)s of PUPFs are lower than that of CPU. The T_g of CPU is about $-26°C$, in comparisons with it, the T_g of PUPF-1 decreased by about 8°C, and a greater deterioration in T_g (about 15°C) was achieved for PUPF-4. The deterioration in T_g may be attributed to flexible OFHBP turned the PU chains mobility readily, further lead to the decreased T_g, that is, PUPFs could be used in a lower range of temperature.

The tensile properties of PUs are shown in Table III. From the table, it can be noted that break elongation of PUPFs was improved, but tensile strength was slightly decreased. Such as PUPF-4, break elongation was improved by 61%, and tensile strength was decreased by 18% in contrast to CPU. As we know, the hard domains provide both physical crosslink

Figure 5 AFM image of PUPF-4. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE III
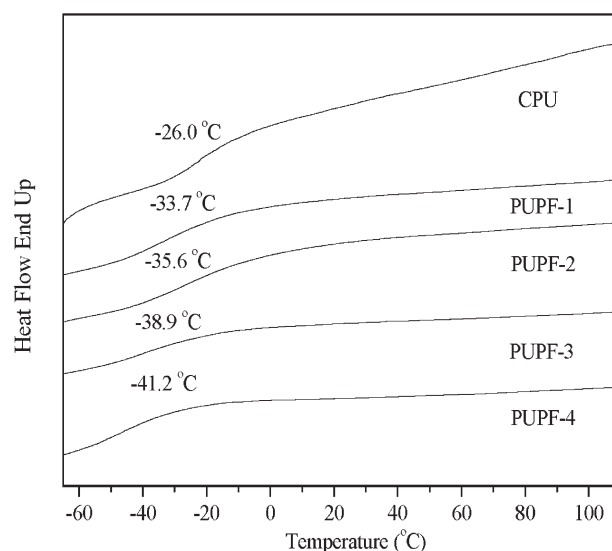### Tensile Properties of PUs

Code	Stress at 100% strain (MPa)	Ultimate strength (MPa)	Elongation at break (%)
CPU	6.7 ± 0.2	18.4 ± 0.3	328 ± 10
PUPF-1	6.2 ± 0.1	16.8 ± 0.1	399 ± 10
PUPF-2	5.8 ± 0.1	16.7 ± 0.1	455 ± 8
PUPF-3	5.6 ± 0.1	15.3 ± 0.2	488 ± 12
PUPF-4	5.4 ± 0.2	15.0 ± 0.2	527 ± 10

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TABLE IV
Contact Angles and Surface Energies of PUs

Code	Contact angle (°)		Surface energy (mN m^{-1})		
	H$_2$O	CH$_2$I$_2$	γ^d	γ^p	γ
CPU	74.8	55.5	23.1	15.1	38.2
PUPF-1	90.6	64.1	21.7	8.2	29.9
PUPF-2	99.1	71.3	20.1	5.3	25.4
PUPF-3	105.8	72.9	22.2	0.4	22.6
PUPF-4	110.1	74.7	22.5	0.0	22.5

sites and filler-like reinforcement to the soft segment matrix, so it is not strange that tensile strength of PUPFs was slightly reduced because of the decrease of soft segments proportions with increasing the OFHBP content. On the other hand, the incorporation of OFHBP obviously increased elongation at break due to PUPF chains became flexible as the introduction of OFHBP.

Surface energy investigation results

The surface energy of PUs could be evaluated from contact angle measurements using water and diiodomethane as probe liquids, based on the following equations:[24]

$$(1 + \cos\theta_{H_2O})\gamma_{H_2O} = 4\left(\frac{\gamma^d_{H_2O}\gamma^d}{\gamma^d_{H_2O} + \gamma^d} + \frac{\gamma^P_{H_2O}\gamma^P}{\gamma^P_{H_2O} + \gamma^P}\right) \quad (3)$$

$$(1 + \cos\theta_{CH_2I_2})\gamma_{CH_2I_2} = 4\left(\frac{\gamma^d_{CH_2I_2}\gamma^d}{\gamma^d_{CH_2I_2} + \gamma^d} + \frac{\gamma^P_{CH_2I_2}\gamma^P}{\gamma^P_{CH_2I_2} + \gamma^P}\right)$$

$$(4)$$

Where γ is surface energy, superscript d refers to dispersion component, p refers to polar component,

in which $\gamma = \gamma^d + \gamma^P$, $\gamma^d_{H_2O} = 22.1$ mN m^{-1}, $\gamma^p_{H_2O} = 50.7$ mN m^{-1}, $\gamma^d_{CH_2I_2} = 44.1$ mN m^{-1}, $\gamma^p_{CH_2I_2} = 6.7$ mN m^{-1}, and θ_{H_2O} is the contact angle of water-polymer, $\theta_{CH_2I_2}$ is the contact angle of diiodomethane-polymer.

The results of contact angles and surface energies are listed in Table IV. The water contact angles of PUs are shown in Figure 7. With the addition of OFHBP, the water contact angles of the PUPFs are enhanced, as shown in Figure 7. The results demonstrate that the PUPFs surfaces have significant water and oil repellency. In addition, in comparisons with the surface energy of CPU, the surface energy of PUPF-1 decreases by about 8 mN m^{-1}, and a greater decrease (about 16 mN m^{-1}) is achieved for PUPF-4. The surface energies of PUPFs decrease by 22–41% comparing with that of CPU. The reason comes mainly from the chemical structure of OFHBP, which has polyphosphazene and fluorine groups synchronously. OFHBP has a flexible backbone imparting fluorine groups to align to form an ordered structure which contributes to low surface energies.

CONCLUSIONS

In this study, fluorine-containing OFHBP had been successfully synthesized and characterized. A series of novel PUPFs were prepared in a two-steps way. FTIR and EA confirmed that OFHBP had been successfully introduced into PUPFs. Studies on crystalline structure and microstructure of the PUPFs have found that PUPFs are amorphous and higher microseparation than CPU. Addition of OFHBP has greatly affected the properties of PUPFs. The excellent properties of PUPFs displayed in decreasing the T_gs and surface energies. In comparison with CPU, the T_g and surface energy of the PUPF-4 was decreased by
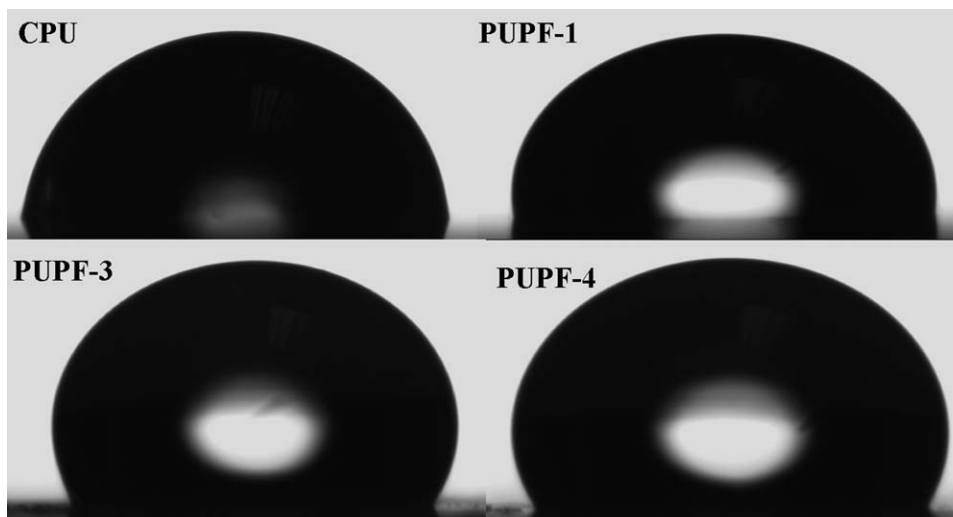
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Figure 7 Shape of water drops on PUs surfaces.

15°C and 16 mN m^{-1}, respectively. Besides, elongation at break was improved by 61% in contrast to CPU. The novel PUs is ideal for development in self-cleaning materials, biomaterials, and anti-ultraviolet materials.

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