

Preparation and Characterizations of Organic Fluorine–Silicon and Polytetrafluoroethylene Modified Polyester

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ABSTRACT: Hydrophobically modified polyester was synthesized via copolymerization between hydroxy-fluoro-silicone polymer (FGX) and bis(2-hydroxyethyl) terephthalate (BHET), which was named as CMPET. The relations between surface properties of CMPET and FGX viscosity and dosage were studied by contact angle measurements. An optimized synthesis route was determined. b-CMPET with better hydrophobic property was obtained by adding polytetrafluoroethylene (PTFE) into CMPET. A full characterization were given to both CMPET and b-CMPET, including ¹H-NMR, ESCA, mechanical properties, water absorption, contact angle and surface energy analysis. It was found that chemical bondings were formed between

FGX and BHET in c-CMPET via copolymerization. The addition of 12% FGX with viscosity of 2000CP after the system pressure reached the low pressure for 20 min is an optimum condition. The modified polyester (CMPET-12) shows the best hydrophobic effect. Blending a certain amount of PTFE powder with low-surface energy can further enhance the hydrophobic properties of CMPET, due to a strong tendency of PTFE migrate to the sample surface together with organic fluorine–silicon segments. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 2760–2766, 2011

Key words: poly(ethylene terephthalate); copolymerization; blends; hydrophobicity; modification

INTRODUCTION

Due to the excellent anti-fouling, oil repellency, and other special properties, hydrophobic material has broad applications in the daily life, industrial and agricultural production, and military defense. However, most polymer materials do not have good hydrophobic properties. The fluorine–silicon polymers with low surface energy, water- and oil-repellency characteristics show high-thermal stability and low-glass transition temperature. Introducing fluorine- or silicon-containing group into these materials can effectively reduce the materials' surface energy and improve their hydrophobic properties.^{1–3} To date, the development of low-surface energy materials has mainly focused on the introduction of organic fluorine or silicone polymer to improve the materials' hydrophobicity.^{4–7} Among those studies, however, the modified polymers mostly involved with polyurethane, polyethylene, polyacrylate. The study related to hydrophobic modification of polyester has been rarely reported.

In this article, we reported hydrophobic modifications of polyester by the method of co-polymeriza-

tion and blending. Modified polyester (CMPET) was synthesized via polycondensation between bis(2-hydroxyethyl) terephthalate (BHET) and hydroxy-fluorosilicone polymer (FGX), which has the same dihydroxy structure as ethylene glycol. b-CMPET was obtained by adding certain amount of polytetrafluoroethylene (PTFE) powder into CMPET.

EXPERIMENTAL

Materials

Bis(2-hydroxyethyl) terephthalate (BHET), industrial grade; Ethylene glycol (EG), industrial grade; hydroxy-fluorosilicone polymer (FGX) with viscosity of 100CP, 1000CP, 2000CP, 5000CP, and 30000CP, industrial grade; Polytetrafluoroethylene powder (PTFE), particle size <1 μm, industrial grade; Sb₂O₃, analytical reagent (AR) grade; Acetone, AR grade; Ethanol, AR grade were included in this study.

Preparation of samples

Copolymerization

Firstly, the reactants, including BHET, excess EG, and catalyst Sb₂O₃ (accounting for 0.01% mass fraction of BHET), were added into the reactor. During the reaction, modifier FGX (accounting for 6–20% mass fraction of BHET) with different viscosities was

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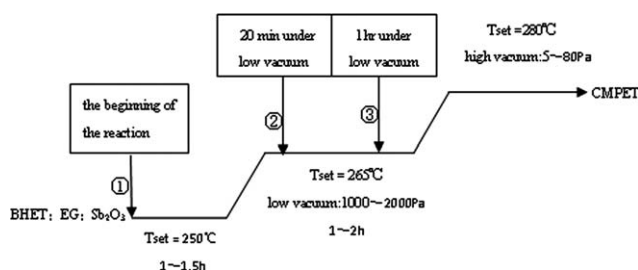


Figure 1 Schematic illustration of synthesis route to CMPET.

added at a certain time, as illustrated in Figure 1. The experiment was carried out under reduced pressure at elevated temperature. The reaction was terminated, when the desired polymerization degree was achieved (determined by the stirring power). The CMPET melt was then cast into strip and cooled in cold water. The different time to add FGX is represented by ①, ②, ③ as shown in Figure 1, respectively. ① refers to the time to add FGX together with the BHET, ② refers to the time to add FGX after the system pressure reduced to 1000–2000 Pa for 20 min, ③ refers to the time to add FGX after the system pressure reduced to 1000–2000 Pa for 1 h.

Blending

CMPET was fully mixed with PTFE powder at a certain ratio, and then extruded into film by using HAAKE rheometer at 285°C and 35 rpm. The b-CMPET film was cooled in the air and wound up.

Characterizations

Contact angle (CA) measurement

The modified polyester was melt and pressed into a small piece of plate with a smooth surface. The CA of the plate was measured at room temperature by a contact angle meter (JC98A, Shanghai Zhongchen Economic Developing Co., China). The triple distilled water droplet is of 1 μ L used and the CA value reported in this article was the average of five measurements for each sample.

$^1\text{H-NMR}$ analysis

The $^1\text{H-NMR}$ spectra were obtained from a NMR system (INOVA-500, Varian company, US). CMPET before and after purification were analyzed by $^1\text{H-NMR}$ spectra, respectively. The Purification was especially given to the sample before NMR analysis following the method of dissolution-deposition. The CMPET was dissolved in phenol and tetrachloroethane solvent, and then precipitated in acetone. The precipitate was washed with ethanol several times, and then centrifuged and dried in oven.

Thermogravimetric analysis (TGA)

The thermal properties of the modifier (FGX) was analyzed by TGA (Perkin-Elmer Pyris 1, USA) in nitrogen at a heating rate of 10°C/min within the temperature range of 30–450°C.

Mechanical property test

The mechanical properties of the samples were tested by the universal material testing machine (INSTRON 5500, USA) with the size of 30 mm \times 15 mm \times 0.5 mm.

Water absorption test

The originally dried sample with the mass of m_0 was soaked in distilled water for a period of time and then removed. The sample was wiped quickly for removing water on the surface and then weighed. After that, the sample was soaked in water and weighed out again, until the value of the sample weight (m_1) was stable. The water absorption ratio was calculated by the following equation:

$$A = (m_1 - m_0) / m_0 \times 100\%. \quad (1)$$

Surface morphology observation

The surface morphology of the sample was observed under scanning electron microscopy (SEM) (JSM-6360, JEOL, Japan) at the different magnifications.

Electron spectroscopy for chemical analysis (ESCA)

ESCA data were obtained from a electron spectrometer (K-Alpha, USA). The X-ray source was used under vacuum of 1.33×10^{-6} Pa and current of 15 KV–10 mA. The penetration depth of the tested sample was 10 nm.

RESULTS AND DISCUSSION

Hydrophobicity of modified polyester(CMPET)

Viscosity and adding time of FGX

Figure 2 shows the water contact angle (WCA) of CMPET against the viscosity and adding time of the FGX with 6% mass fraction of BHET. It was found that the WCA increased with the increase of FGX's viscosity. When the viscosity of FGX was 2000CP, the WCA reached its maximum, and then leveled off. By comparison the WCA of CMPET with different adding time of FGX, the best hydrophobic property was found when FGX was added after the system pressure reached low vacuum for 20 min. As a result, FGX with viscosity of 2000CP and adding FGX at the moment of ② was selected as an

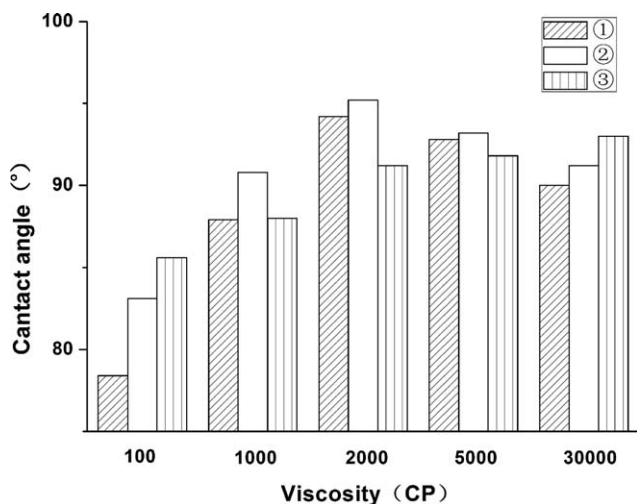


Figure 2 The influence of the viscosity and adding time of FGX on the contact angle of the CMPET.

optimum condition. The product prepared under this condition was named as CMPET-6.

The dosage of FGX

The contact angle and the surface energy of polymer indirectly reflect the wetting properties of solid surface. To determine the surface energy of a material, Fowkes proposed that the solid surface free-energy (γ) of organic compounds consists of dispersion component (γ^d) and polar component (γ^p). Namely:

$$r = r^d + r^p. \quad (2)$$

Owen and Wendt⁸ developed Fowkes' theory and put forward the following formula,

$$r_{lv}(1 + \cos \theta) = 2(r_{sv}^d \times r_{lv}^d)^{1/2} + 2(r_{sv}^p \times r_{lv}^p)^{1/2} \quad (3)$$

where θ is the contact angle. γ_{lv} and γ_{sv} represent the surface tension of liquids and the surface energy of solids, respectively.

If the surface tension, dispersion component, and polar component of any two different liquids are known, the dispersion component, polar component, and surface energy of an unknown solid surface can be calculated after measuring its contact angle. Water and hexadecane are selected to measure the contact angle of samples. The dispersion component and polar component of the water are 22.1 mN m^{-1} and 50.7 mN m^{-1} . Those of hexadecane are 26.0 mN m^{-1} and 0.0 mN m^{-1} , respectively.

The relations between the dosage of FGX and the contact angle as well as surface energy of the CMPET-6 were studied as shown in Figure 3. It reveals that the contact angle increased and the surface energy reduced as the FGX increased. When the weight fraction of FGX is 6%, the contact angle of

CMPET-6 is 95.2° and its surface energy of CMPET-6 is 24.65 mJ m^{-2} . As the mass fraction of FGX is 12%, the contact angle of CMPET-12 increased to 97.2° and the surface energy of CMPET-12 reduced to 23.4 mJ m^{-2} , which approaches the surface energy of modifier $\text{CH}_2\text{—CF}_3$ of 20 mJ m^{-2} . Keep on increasing the amount of FGX, the contact angle changes slightly. It is mainly because that the intermolecular forces between the molecules on the surface are different from that in bulk. That is the reason for the existing surface energy of materials. According to the surface thermodynamic theory, for an isothermal system with constant volume, it has a strong tendency to adjust its state by itself until its Helmholtz free energy reach its minimum value.⁹ Compared with molecular chains of PET, fluorine-silicon containing chain segments have a lower surface energy. It is possible to reduce the surface energy of PET if introducing a certain amount of FGX. It was reported in some literatures that organic silicon chain and fluoroalkyl chains have the tendency to migrate to the surface of the material.^{10–12} The results also showed that, with the increase of FGX, the fluorinated chain segments tended to accumulate on the surface of the CMPET, so that the surface tension decreased and its hydrophobicity increased. When the fluoride content on the surface of CMPET reached a certain value, the surface energy of CMPET reached the similar level to that of FGX. That was the reason why there was no significant change in both contact angle and surface energy with increase of fluoride content after exceeding the threshold value.

¹H-NMR analysis

Qualitative analysis

Figure 4 shows the ¹H-NMR spectroscopy for the PET and the CMPET. The typical spectrum of PET is

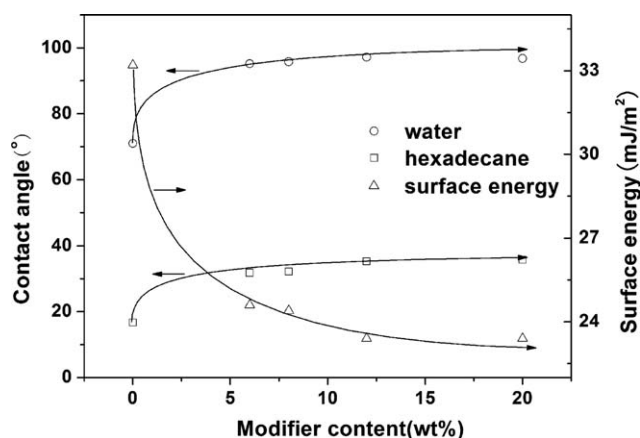


Figure 3 The relations between the dosage of FGX and contact angle as well as surface energy of CMPET.

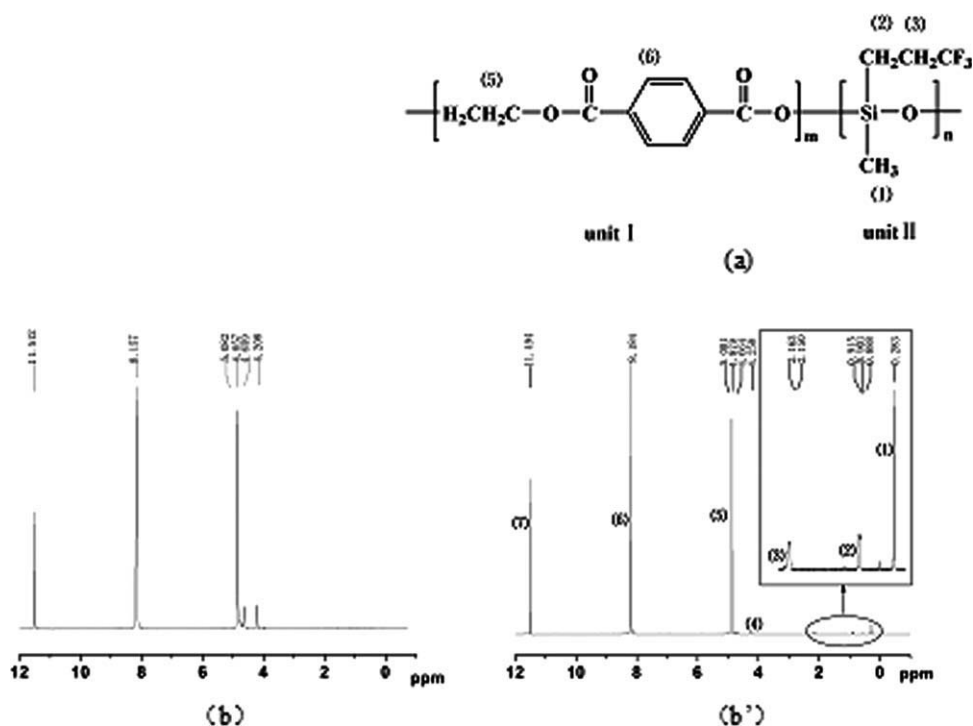


Figure 4 $^1\text{H-NMR}$ spectroscopy of PET and CMPET-6: (a) The chemical formula of CMPET; (b) $^1\text{H-NMR}$ spectrum of PET; (b') $^1\text{H-NMR}$ spectrum of CMPET-6.

shown in Figure 4(b), which shows the characteristic signals at $\delta_{\text{H}}=8.157$ ppm (benzene ring hydrogen), $\delta_{\text{H}}=4.659\text{--}5.082$ ppm (methylene hydrogen), and at $\delta_{\text{H}}=4.208$ ppm (hydroxyl hydrogen). The spectrum including peak assignment of CMPET is shown in Figure 4(b'), in which there are some new characteristic peaks compared with that of PET, such as $\delta_{\text{H}}=2.150\text{--}2.163$ ppm (C-CH₂-CF₃ hydrogen), $\delta_{\text{H}}=0.888\text{--}0.915$ ppm (Si-CH₂-C hydrogen), and at $\delta_{\text{H}}=0.289$ ppm (Si-CH₃ hydrogen). The protons peak of C-CH₂-C is at $\delta_{\text{H}}=1.25$ ppm. The electronegativity of Si is so weak that the electron cloud density of protons in the methylene connected with Si increases, and the deshielding effect weakens, which results in a shift of the protons peak to the high-field. In contrast, because the electronegativity of the F is the strongest in all atoms, the protons around the F are strongly induced, which results in a decrease in the electron cloud density and a peak shift to the low-field.¹³ By comparison of the $^1\text{H-NMR}$ spectroscopy of PET, the characteristic peaks of the FGX are found in the spectrum of CMPET, which indicates that the CMPET has been synthesized successfully.

Quantitative analysis

Base on the $^1\text{H-NMR}$ spectrum, a quantitative calculation can be carried out to calculate the molar ratio

(α : β) of unit I and unit II in CMPET. The calculation of the copolymerization ratio is based on the integral area ratio of the proton peak. The proton peak of benzene ring is at $\delta_{\text{H}}=8.184$ ppm, whose integral high is defined as h_1 ; the proton peak of -O(CH₂)₂O- is at $\delta_{\text{H}}=4.664\text{--}5.001$ ppm, whose integral high is defined as h_2 . The two peaks are the characteristic proton peak of PET. The proton peak of methyl which connected with the silicon is at $\delta_{\text{H}}=0.289$ ppm, whose integral high is defined as h_3 . According to eq. (4), the hydrogen content ratio of -O(CH₂)₂O- to benzene ring is nearly 1 : 1 in the

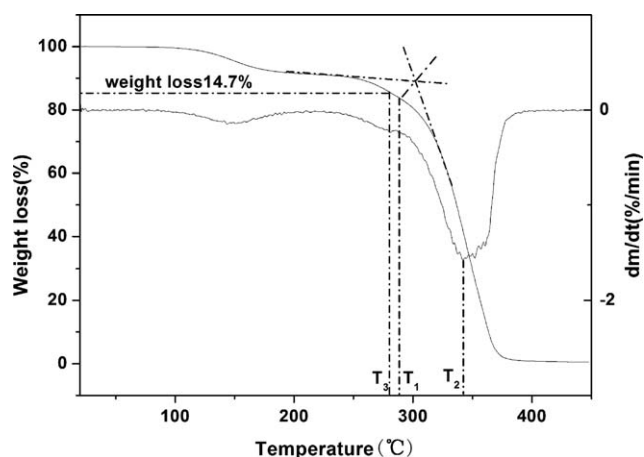


Figure 5 TG analysis of FGX.

TABLE I
The Content of FGX in CMPET

	FGX ¹ /BHET (wt%)	FGX ² /BHET (wt%)	FGX/R (wt%)	Conversion ratio (%)
CMPET-6 (pure)	6	5.12	2.48	56.5
CMPET-6 (impure)			4.39	
CMPET-12 (pure)	12	10.24	5	56.8
CMPET-12 (impure)			8.8	

FGX¹, the actual feeding amount of FGX; FGX², the FGX after removing low molar mass substances; R, $-\text{CH}_2\text{CH}_2\text{O}-\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{O}-$ in CMPET.

CMPET, which indicated that the data of ¹H-NMR is reliable.

$$n(\text{benzene ring hydrogen}) : n(-\text{O}(\text{CH}_2)_2\text{O}-) = \frac{h_1}{4} : \frac{h_2}{4} \quad (4)$$

$$\alpha(\text{unit I}) : \beta(\text{unit II}) = \frac{h_1}{4} : \frac{h_3}{3} \quad (5)$$

The TG analysis was also given to FGX as shown in Figure 5. It was found that initial decomposition temperature is at 288°C (T₁) and the maximum decomposition occurs at 342°C (T₂). When the temperature reaches 280°C, the weight loss is 14.7%, corresponding to substances with low molar mass, which play a trivial role in hydrophobicity modification by using FGX. The FGX content in purified CMPET and non-purified CMPET are listed in Table I. From the table, we can see that in the purified CMPET, the copolymerization ratio of FGX and BHET is less than the actual feed ratio, which may be related to difference in the reactivity FGX and BHET. In the non-purified CMPET, the chain segment ratio of FGX and BHET is the similar to the feed ratio, which illustrates that most FGX reacted with BHET and the rest of FGX was blended in the CMPET. Both of them can play an effective role in lowering the surface energy of the materials.

Hydrophobicity of modified PET by both copolymerization and blending

Effect of PTFE powder addition on the hydrophobic properties of b-CMPET

Compared with CMPET-6, the amount of FGX was doubled in CMPET-12, but the contact angle only increased 2°. Considering the contribution of FGX and the cost of production, the CMPET-6 was chosen as a control polymer for this blending study. When the dosage of FGX is fixed as 6%, it is found that the addition of PTFE powder has an obvious influence on properties of the modified material. Table II showed that the hydrophobic performance of the b-CMPET enhanced but the mechanical properties decreased with the increase of the amount of PTFE powder.

The increase in hydrophobicity of b-CMPET is possibly because of the immiscibility of component having different values of solubility parameter. The solubility parameter of PTFE and the FGX is about 12.7 J^{1/2} cm^{-3/2} and 10 J^{1/2} cm^{-3/2}, respectively. However, the solubility parameter of polyester is 21.9 J^{-1/2} cm^{-3/2}. The large difference in solubility parameter could induce microphase separation in the bulk of b-CMPET. According to the Thermodynamic Theory of Miscibility,¹⁴ PTFE powder tends to accumulate in the surrounding of fluorine-silicon chains. And fluorine-silicon chains trends to migrate to the surface of the material. During the process of

TABLE II
The Properties of Modified PET with Different Amount of PTFE Powder

Sample	Content of FGX (%)	Content of PTFE (%)	Tensile strength (Mpa)	Water absorption ratio (%)	Water contact angle (°)	Surface energy (mJ m ⁻²)
PET	0	0	45.60	0.82	78.0	33.23
CMPET-6	5.12	0	37.57	0.81	95.2	24.65
b-CMPET-1	5.12	1	36.13	0.80	99.0	23.39
b-CMPET-2	5.12	3	30.12	0.69	102.0	22.65
b-CMPET-3	5.12	5	29.30	0.60	102.1	21.96
b-CMPET-4	5.12	10	14.02	0.58	100.3	21.68
b-CMPET-5	5.12	15	17.18	0.55	103.5	20.55
b-CMPET-6	5.12	20	12.91	0.48	104.0	20.06
b-CMPET-7	5.12	25	12.04	0.43	105.8	19.97

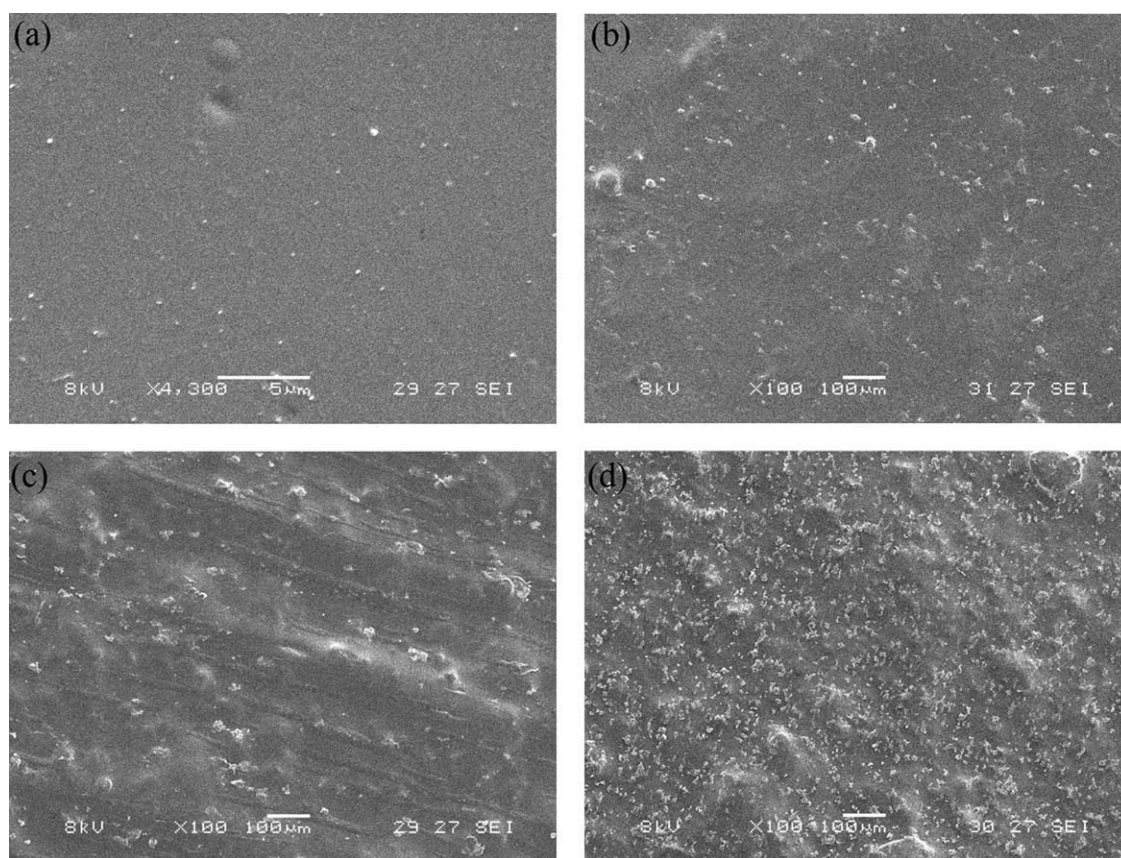


Figure 6 SEM micrographs of the samples: (a) b-CMPET-1; (b) b-CMPET-3; (c) b-CMPET-5; (d) b-CMPET-7.

migration, PTFE powder moved to the material surface together with FGX. Therefore, water contact angle further increased. The combined effect of PTFE powder and FGX results in a material with better hydrophobic property. It was also found that too much addition of PTFE powder will weaken the mechanical properties of modified material. As shown in Table II, there are no obvious changes in mechanical properties when the powder addition is less than 5%. However, when the amount of powder exceeds 5%, the sample became brittle and its tensile strength decreased greatly.

The surface morphology of b-CMPET mixed with a certain amount of PTFE powder was observed under SEM, as seen in Figure 6. It is clear that the surface roughness of b-CMPET increased by increasing the amount of PTFE. By covering with PTFE, a material with lower surface energy could be obtained. According to the theory of relations between the roughness and contact angle proposed by Wenzel,¹⁵ we can see that increasing the surface roughness of hydrophobic CMPET can further enhance the hydrophobic properties of the material. The PTFE powder can improve the hydrophobic properties of the material from combining its special property of low-surface energy and increasing the surface roughness of modified material.

Effect of thermal treatment on surface properties of b-CMPET

The samples were annealed for 12 h at the temperature of 95°C in a vacuum oven. The effect of annealing on the surface properties of b-CMPET is shown in Table III. It was found that the water contact angle of annealed samples increased obviously, which indicated an enhancement of hydrophobic property in annealed samples. This is mainly due to the migration of fluorinated chains toward the surface is a thermodynamic equilibrium process. During the thermal treatment, the annealing temperature

TABLE III
The Influence of Thermal Treatment on the Surface Property of Blended Copolymer

Sample	Content of FGX (%)	Content of PTFE (%)	Water contact angle (°)	Water contact angle (annealed) (°)
CMPET-6	5.12	0	95.2	97.5
b-CMPET-1	5.12	1	99.0	103.0
b-CMPET-2	5.12	3	102.0	104.5
b-CMPET-3	5.12	5	102.1	106.0
b-CMPET-4	5.12	10	100.3	103.3
b-CMPET-5	5.12	15	103.5	106.2
b-CMPET-6	5.12	20	104.0	107.0
b-CMPET-7	5.12	25	105.8	110.3

TABLE IV
Surface Element Composition of the Samples

sample	Experimental atom percentage (%)			Theoretical atom percentage (%)		
	C	Si	F	C	Si	F
CMPET-6	81.60	3.89	1.84	70.50	0.37	1.11
b-CMPET-1	69.44	5.89	10.63	70.20	0.37	1.66
b-CMPET-2	66.37	9.04	10.18	69.62	0.36	2.71
b-CMPET-3	57.14	8.69	19.46	69.04	0.35	3.73

is 95°C, which is above the glass transition temperature of the samples. The internal chain segments of the b-CMPET can obtain high enough energy to move around. In order to decrease the system energy and achieve thermodynamic equilibrium state, the organic fluorine and silicone chain segment with the lower surface energy prefer to migrate to the surface. And PTFE nano-particle with low-surface energy also migrate to the surface together with the fluorine and silicone chain segments.^{16,17}

Electron spectroscopy for chemical analysis (ESCA) of modified PET

The chemical composition of the hydrophobically modified PET was analyzed via ESCA. The penetration depth of X-ray beam is around 10 nm. The results are listed in Table IV. By comparison of experimental and theoretical atomic percentage on the surface, it is found that experimental values of the F and Si atom are much greater than the theoretical values, indicating the occurrence of F and Si atom migration to the surface of the modified material.

4. CONCLUSION

The synthesis route of CMPET was optimized by investigating the relations between contact angle and the viscosity and dosage of the FGX. CMPET with low-fluorine content and excellent hydrophobic performance was prepared under optimum conditions.

b-CMPET with further enhanced hydrophobic properties was made by blending a certain amount of PTFE powder into CMPET. The further improved

hydrophobicity is thought to be related to the micro-phase separation of each component with different solubility parameters. Organic fluorine–silicon segments and PTFE have strong tendency to migrate to the sample surface in order to lower the system energy. The migration of PTFE powder onto the sample surface also lead to the increase of surface roughness, which has a positive contribution to increase the hydrophobicity. The contact angle of modified PET increases some degrees after thermal treatment at 95°C, which is also due to the migration of PTFE and fluorine–silicon chain segments.

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