

Synthesis and Characterization of Fluorine-Containing Polyester Based on Phthalic Anhydride and Tetrafluoropropyl Glycidyl Ether

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Received 14 July 2011; accepted 12 October 2011

DOI 10.1002/app.36356

Published online 1 February 2012 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Fluorine-containing polyester (FPE) was synthesized by the reaction of phthalic anhydride, epichlorohydrin, and 2,2,3,3-tetrafluoropropyl glycidyl ether (TFGE) at the catalysis of tetraethylammonium bromide using 1,4-butanediol as the initiator. The structure of FPE was characterized by ^1H NMR and ^{19}F NMR, and the result showed that the fluorine in TFGE was introduced into FPE. Fluorine content in FPE was determined by oxygen-flask combustion and fluoride selective electrode. It was found that fluorine content in FPEs increased with the increase of TFGE content. The wettability of water and oil on the cured coating based on FPE was investigated by

contact angle meter. Contact angles of water and diiodomethane on the cured coatings first increased with the increase of the fluorine content in FPEs and then remained constant. The X-ray photoelectron spectroscopic analysis showed that the F/C molar ratio on the coatings surface was much higher than the overall F/C molar ratio, which indicated that fluoroalkyl groups in FPEs had enriched on the coatings surface. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 3068–3075, 2012

Key words: fluorine-containing polyester; synthesis; contact angle; surface tension; enrichment

INTRODUCTION

Polyester powder coating has received much attention in protection of household electrical appliances, chemical equipments, machine parts, and so on, due to its excellent light and weather stability, and good adhesion to substrates.^{1,2} However, the cured coating of common polyester powder coating is apt to be affected by water. The destructive process of the coating can be divided into two steps. First, water penetrates into coating and then ester groups in polyester hydrolyze,³ which results in the decline of the durability and corrosion resistance of the coating.⁴ Moreover, due to the swelling of oil and organic solvent in polyester, oleophobicity of the coating also needs to be further improved.

Fluorine-containing polymer exhibits special physical and chemical properties, such as outstanding thermal and chemical stability,⁵ excellent electric insulation and low dielectric constant,⁶ low surface tension,⁷ solvent resistance, and other features.^{8,9} Therefore, the introduction of fluorine into polyester

is expected to improve the hydrophobicity and oleophobicity of the polyester powder coating.

Wettability of polymer materials mainly depends on their surface properties.¹⁰ Fluoroalkyl groups in polymer materials tend to enrich on the coating surface due to their low surface tension.^{11–21} Therefore, introducing a small amount of fluorine could significantly improve the hydrophobicity and oleophobicity of polymer materials.²²

Previous fluorinated polymer-related studies mainly focused on solvent-borne, water-borne, and liquid solvent-free coatings. Montefusco et al.²³ synthesized the solvent-borne epoxy coating with 2,2,3,3,4,4,5,5-octafluoro-1,6-hexanediol and other monomers. Scheerder et al.²⁴ prepared water-borne fluorinated polymers by the reaction of methyl methacrylate, *n*-butyl methacrylate, and trifluoroethyl methacrylate. van Ravenstein et al.²⁵ prepared the low surface energy coating from a mixture of a hydroxyl-end-capped solventless liquid oligoester, a blocked polyisocyanate, and a fluorinated blocked isocyanate. However, there are few reports about the preparation of the fluorinated polyester, which is expected to apply in powder coating. Therefore, the synthesis of fluorine-containing polyester (FPE) has important theoretical significance and application value.

In this article, FPE was synthesized by the reaction of phthalic anhydride (PA), epichlorohydrin (ECH), and 2,2,3,3-tetrafluoropropyl glycidyl ether (TFGE)

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Contract grant sponsor: Zhejiang Provincial Innovative Research Team; contract grant number: 2009R50004.

at the catalysis of tetraethylammonium bromide using 1,4-butanediol (BDO) as the initiator. The structure of FPEs was characterized by ^1H NMR and ^{19}F NMR. Fluorine content in FPEs was determined by oxygen-flask combustion and fluoride selective electrode. Wettability of the cured coating based on FPEs toward water and oil was investigated by the contact angle meter. X-ray photoelectron spectroscopy was used to study the enrichment of fluoroalkyl groups in FPEs on the coating surface.

EXPERIMENTAL

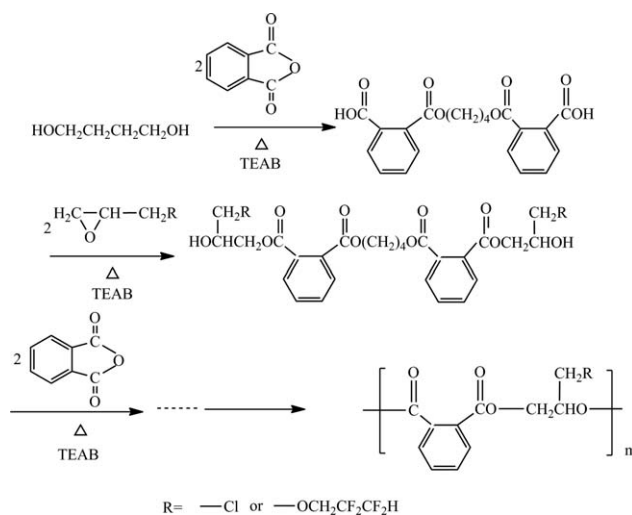
Materials

BDO, AR, was supplied by Shanghai Crystal Pure Reagent Co., Shanghai, China. PA and 2,2,3,3-tetrafluoropropanol (TFPO), AR, were purchased from Aladdin, Shanghai, China. ECH and acetic anhydride (AA), AR, were obtained from Shanghai Lingfeng Chemical Reagent Co., Shanghai, China. Tetraethylammonium bromide (TEAB) and *N,N*-dimethylformamide (DMF), AR, were supplied by Sichuan West Reagent Co., Chengdu, China. Toluene and acetone, AR, were purchased from Hangzhou Reagent Co., Hangzhou, China. Calcium hydride, potassium nitrate, sodium hydrate, methanol, and sodium citrate, CR, were obtained from National Pharmaceutical Group Chemical Reagent Co., Shanghai, China. Sodium fluoride, AR, was purchased from Juhua Reagent Co., Quzhou, China. Curing agent (triglycidyl isocyanurate, TGIC) and CaCO_3 were obtained from Deqing Brilliant Chemical Co., Deqing, China. BYK-361 and NBYK-220S were obtained from Shanghai BYK solutions Co., Shanghai, China. BOD was dried with anhydrous 4\AA zeolite for 24 h and then vacuum distilled. PA was recrystallized in AA and then dried in vacuum oven at 70°C for 12 h. ECH was reflowed with calcium hydride at 145°C for 5 h and then distilled. TEAB was dried in vacuum oven at 70°C for 12 h. DMF was dried with calcium hydride for 24 h and then vacuum distilled. Other reagents were used as received without further purification, unless otherwise stated.

Synthesis of FPE

Synthesis of 2,2,3,3-tetrafluoropropyl glycidyl ether

To synthesize FPE, TFGE was synthesized according to the literature.²⁶ First, 55.5 g (0.6 mol) of ECH, 13.2 g (0.1 mol) of TFPO, 0.105 g (5.000×10^{-4} mol) of TEAB and 10 mL of toluene were charged into a dried 250 mL three-necked round-bottom flask equipped with a mechanical stirrer and condenser. After the mixture was heated to 70°C , sodium hydrate (4.2 g/0.105 mol) was added into the mixture over a period of 5 h during the reaction. After the reaction,



Scheme 1 Synthesis of FPE.

the impure product was first purified by distillation and then the fraction at the boiling point of $135\text{--}145^\circ\text{C}$ was redistilled using a Fischer-Spaltrohr concentric tube distillation apparatus. The fraction ($55^\circ\text{C}/4$ mmHg) was collected and the purity of TFGE was proved by Gas Chromatography (GC) analysis.

Yield: 71%. IR: 2932 cm^{-1} , 3008 cm^{-1} (stretching vibration of methylene); 1463 cm^{-1} (deformation vibration of methylene); 1231 cm^{-1} and 1205 cm^{-1} ($-\text{CF}_2-$), 1109 cm^{-1} ($-\text{O}-$); 834 cm^{-1} (stretching vibration of epoxy group).

Synthesis of FPE

FPE was synthesized via the reaction of PA, ECH and TFGE at the catalysis of TEAB using BDO as the initiator. 0.36 g (4.0×10^{-3} mol) of BDO, 14.8 g (0.1 mol) of PA, 0.21 g (1.0×10^{-3} mol) of TEAB, 0.1 mol of the mixture of ECH and TFGE, and 4 mL of DMF were charged into a dry 250 mL three-necked round-bottom flask equipped with a mechanical stirrer, condenser, and nitrogen inlet and outlet. The mixture was heated to 100°C and reacted for 1 h under nitrogen (Scheme 1). Then, the mixture was diluted with acetone and precipitated with water. The product was purified by reprecipitation from acetone solution into a 1 : 1 (V : V) mixture of water and methanol for three times. The collected solid was dried in vacuum oven (1.3×10^3 Pa) at 100°C for 10 h. FPEs with various fluorine contents were obtained by varying ECH and TFGE contents (Table I). Yields: 88% for FPE-0, 91% for FPE-1, 87% for FPE-2, 90% for FPE-3 and 86% for FPE-4, respectively.

Preparation of polyester powder coating

A 65 g of FPEs, 30 g of CaCO_3 , 4 g of curing agent (TGIC), 0.5 g of flattening agent (BYK-361N), and 0.5 g of wetting agent (BYK-220S) were blended in a

TABLE I
Content of ECH and TFGE in Synthesis of FPEs

Species	ECH (g) (mol)	TFGE (g) (mol)
FPE-0	9.25 (0.1)	0.00 (0.0)
FPE-1	9.0 (9.733×10^{-2})	0.5 (2.674×10^{-3})
FPE-2	8.755 (9.465×10^{-2})	1.0 (5.347×10^{-3})
FPE-3	8.260 (8.930×10^{-2})	2.0 (1.070×10^{-2})
FPE-4	7.766 (8.396×10^{-2})	3.0 (1.604×10^{-2})

banbury mixer for 10 min at 100°C and 80 rotor/min. The product was smashed and sifted through a 180 mesh stainless steel sieve.

Spray and cure of the polyester powder coating

Polyester powder coating was sprayed on a 100 mm × 50 mm × 0.5 mm iron plate treated by degreasing and decontamination with a static spraying gun. The coating was cured for 20 min at 180°C, and the curing reaction was shown in Scheme 2.

Characterizations

The structure of FPEs was characterized by NMR. ¹H NMR (300 MHz) and ¹⁹F NMR (282 MHz) spectra were recorded with a Bruker AVANCE II spectrometer using acetone-*d*₆ as solvent. The hydroxyl value of FPEs was determined according to Ref. 29, and from the hydroxyl value the molecular weight of FPEs was calculated.

Fluorine content in FPEs was determined by oxygen-flask combustion and fluoride selective electrode.²⁷ The solution with the known fluoride concentration was measured by fluoride selective electrode, and the working curve between the fluoride ion concentration and potential was obtained. Then, FPEs were burnt completely under oxygen atmosphere in oxygen-flask, and the organic fluoride

in FPEs was transferred into inorganic fluoride after being absorbed by NaOH solution. Then, the potential of the solution was measured by fluoride selective electrode.

Contact angle measurement was carried out with an OCA-20 contact angle meter equipped with a videocamera at room temperature with ion-exchanged water and diiodomethane. A drop of liquid (3 μL for water and 1.5 μL for diiodomethane) was placed on the coating, and the contact angle was determined after 30 s. The contact angle reported is the average value for 3 times, and the difference was within 3°.

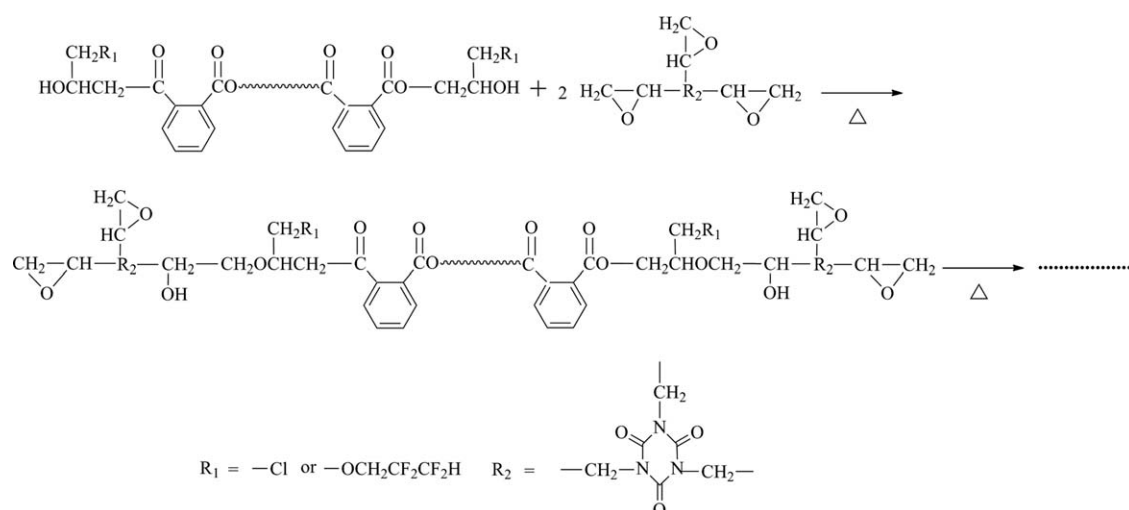
Enrichment of fluoroalkyl groups in FPEs on the coatings surface was investigated by VG ESCALAB MARK II X-ray photoelectron spectroscopy equipped with a MgK_α X-ray source ($h\nu = 1253.6$ eV). Spectra were obtained at a photoelectron takeoff angle of 0° corresponding to the coating surface.²⁸ Sample chamber pressure kept at 1×10^{-8} mmHg. Survey and detail scan (C, F) spectra were recorded for each sample. All spectra were acquired at 50 eV pass energy. Survey spectrum was recorded at 0–1060 eV with a step internal of 0.5 eV to determine the surface chemical composition. For detail scan spectrum a step internal of 0.2 eV was used.

RESULTS AND DISCUSSION

Synthesis and structure of FPE

To improve the hydrophobicity and oleophobicity of polyester powder coating, FPE was synthesized by the reaction of PA, ECH, and TFGE at the catalysis of TEAB using BDO as the initiator (Scheme 1).

The possible structure unit of FPE was shown in Table II. Figure 1 showed the ¹H NMR spectra of FPEs, which corresponded well to its molecular structure. For instance, the peaks at 7.5–8.0 ppm



Scheme 2 Curing reaction of FPEs with TGIC.

TABLE II
The Possible Structure Unit of FPEs

Backbone	End group

were assigned to the hydrogen atoms of substituted benzene (a). The characteristic peaks at 6.15–6.5 ppm proved the existence of the hydrogen atoms of $-\text{CF}_2\text{H}$ (h). The peaks at 5.5–5.6 ppm were assigned to the hydrogen atoms of $-\text{CHO}-$ (d). The peak at 4.5–4.7 ppm was ascribed to the hydrogen atoms of methylene (b). The proton peak of $-\text{OH}$ (i) was found at 4.2–4.3 ppm. The proton peak for $-\text{CH}_2\text{Cl}$ (e) was found at 3.8–4.0 ppm. The peaks at 3.65–3.72 ppm were assigned to the hydrogen atoms of methane (j) connected to OH. There were no peaks assigning to the hydrogen atoms of carboxyl at 12–13 ppm, indicating that the end group of FPEs was hydroxyl. It was also found that the intensity of the proton peak of $-\text{CF}_2\text{H}$ (h) at 6.15–6.5 ppm increased from FPE-0 to FPE-4, indicating that the fluorine

content in FPEs increased with the TFGE content in reactants.

The ^{19}F NMR spectrum of FPE-1 was given in Figure 2. The fluorine resonances of $-\text{CF}_2-$ (l) and $-\text{CF}_2\text{H}$ (m) were found at -127 ppm and -141.5 ppm, respectively. The ratio of integrals of peaks l to m was about 1, which further proved that fluorine in TFGE had been successfully introduced into polyester.

The number-average molecular weight (M_n , g/mol) of FPEs was calculated according to eq. (1),²⁹ and the result was shown in Table III.

$$M_n = \frac{1}{\text{hydroxyl value} \times (2 \times 40 \times 1000)} \quad (1)$$

M_n^* was the theoretical molecular weight estimated from the recipes by assuming complete conversions of all reactions.

The number-average molecular weight of FPEs obtained by experiment was lower than the theoretical one, which may be ascribed to that the trace water in DMF and ECH was involved in ring-opening reaction of PA.

Fluorine content in FPEs

To investigate the relationship between the fluorine content in FPEs and wettability of water and oil on the cured coatings based on FPEs, it was important to determine the fluorine content in FPEs. Due to the inaccuracy of chemical titrimetry under low fluorine content in FPEs, the more sensitive fluoride selective electrode was used. The solution with the known fluorine ion concentration (C_F , mg/L) was measured with fluoride selective electrode and the

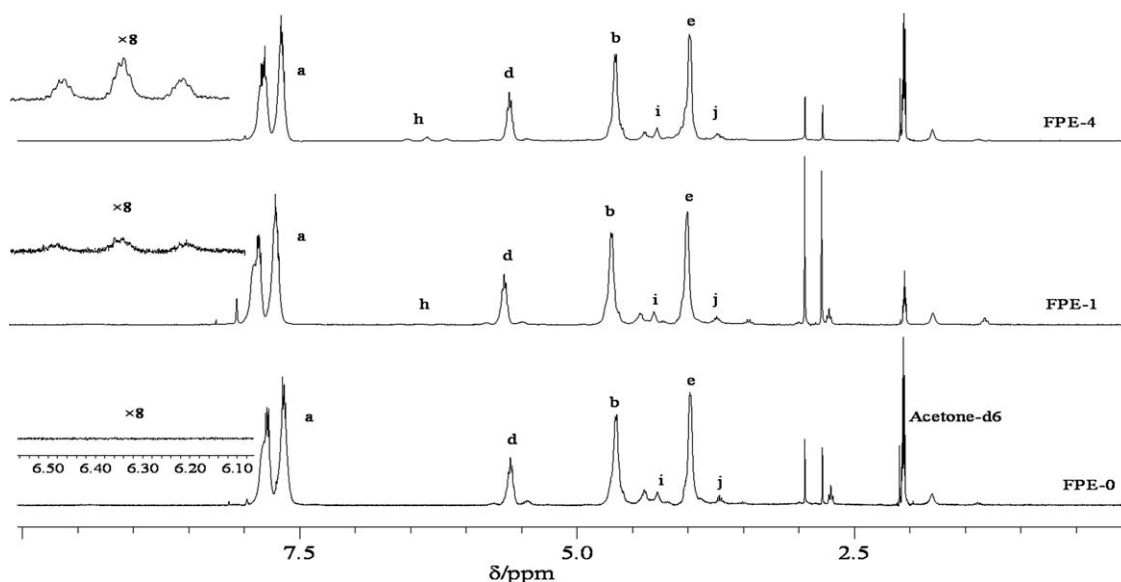


Figure 1 ^1H NMR spectra of FPEs (inset: the enlarged spectra at 6.1–6.5 ppm).

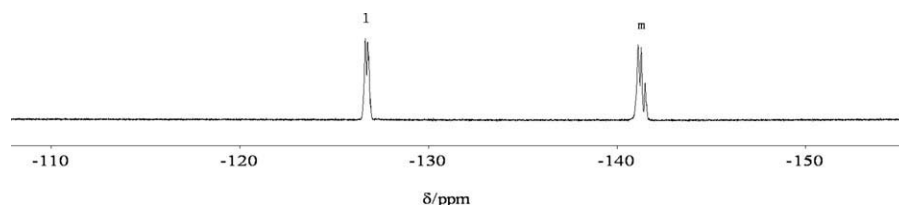


Figure 2 ^{19}F NMR spectrum of FPE-1.

potential (E , mV) was obtained. Equation (2) showed the relationship between E and c_F (correlation coefficient was 0.9983). According to the measured potential (E), c_F of FPE was determined by eq. (2), and the fluorine content (W_m , wt %) in FPEs was calculated by eq. (3).

$$E = 116.09 - 55.51\lg(c_F) \quad (2)$$

$$W_m = \frac{c_F \times V}{m_R} \times 100 \quad (3)$$

where V and m_R represented the volume of fluorine ion solution (L) and weight of FPEs (mg), respectively.

Table III showed the fluorine content in FPEs. It was found that fluorine content in FPEs increased with the increase of TFGE content and FPEs with various fluorine contents were obtained by varying the molar ratios of ECH to TFGE.

Surface properties of the coatings based on FPEs

The value of the contact angle reflects the surface wettability. The contact angle of water and diiodomethane on the cured coatings based on FPEs was measured and the results were shown in Figure 3. It was found that the contact angle of water on the cured coatings based on FPEs first increased with the increase of the fluorine content in FPEs and reached the maximum value (108°) at a fluorine content of about 2.43 wt %. Further increase of the fluorine content did not make any difference on the contact angle. A similar trend of the contact angle of diiodomethane on the cured coatings was also observed. The equilibrium contact angles of water and diiodomethane on cured coatings based on FPEs were close to those on smooth polytetrafluoroethyl-

ene surface (118° ³⁰ and 77° ³¹ respectively), which indicated that the introduction of a small amount of fluorine into polyester significantly improved the hydrophobicity and oleophobicity of polyester powder coating and fluoroalkyl groups may be enriched on the coatings surface.¹⁵

The surface tensions can be estimated by the geometric mean method [eqs. (4), (5),³² and (6)³³] on the basis of contact angles of two liquids.

$$(1 + \cos\theta_{\text{H}_2\text{O}})\gamma_{\text{H}_2\text{O}} = 2(\gamma_{\text{H}_2\text{O}}^d \gamma^d)^{\frac{1}{2}} + 2(\gamma_{\text{H}_2\text{O}}^p \gamma^p)^{\frac{1}{2}} \quad (4)$$

$$(1 + \cos\theta_{\text{CH}_2\text{I}_2})\gamma_{\text{CH}_2\text{I}_2} = 2(\gamma_{\text{CH}_2\text{I}_2}^d \gamma^d)^{\frac{1}{2}} + 2(\gamma_{\text{CH}_2\text{I}_2}^p \gamma^p)^{\frac{1}{2}} \quad (5)$$

$$\gamma = \gamma^d + \gamma^p \quad (6)$$

In which γ was surface tension, γ^d represented dispersive component of surface tension, γ^p stood for polar component of surface tension, $\theta_{\text{H}_2\text{O}}$ and $\theta_{\text{CH}_2\text{I}_2}$ were contact angles of water and diiodomethane on the cured coatings based on FPEs, respectively. The values of $\gamma_{\text{H}_2\text{O}}$, $\gamma_{\text{CH}_2\text{I}_2}$, $\gamma_{\text{H}_2\text{O}}^d$, $\gamma_{\text{H}_2\text{O}}^p$, $\gamma_{\text{CH}_2\text{I}_2}^d$, and $\gamma_{\text{CH}_2\text{I}_2}^p$ were shown in Table IV.³⁴ Figure 4 showed the change of surface tension of the cured coatings based on FPEs with the fluorine content in FPEs. The surface tension, dispersive component and polar component of the cured coatings based on FPEs first decreased with the increase of the fluorine content and then remained constant at a fluorine content

TABLE III
Molecular Weight and Fluorine Content of FPEs

Species	OH value (mgNaOH/g)	M_n^* (g/mol)	M_n (g/mol)	Fluorine content (wt %)
FPE-0	15.3	6000	5229	0
FPE-1	15.8	6000	5063	0.62
FPE-2	16.5	6000	4848	1.24
FPE-3	15.3	6000	5229	2.43
FPE-4	15.1	6000	5300	3.57

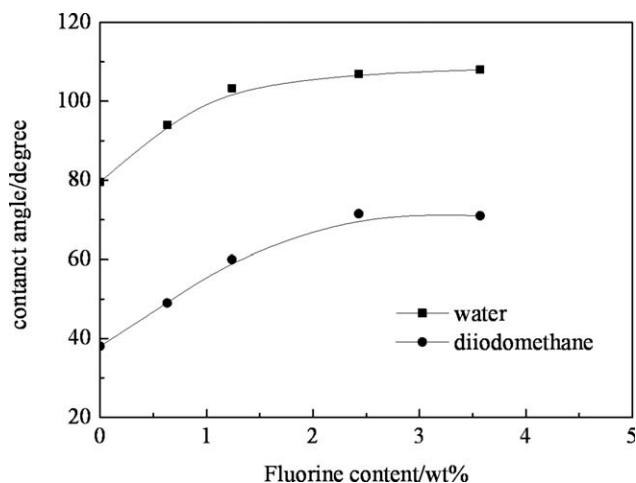


Figure 3 Change of the contact angle of water and diiodomethane on cured coatings based on FPEs with fluorine content in FPEs.

TABLE IV
Surface Tension, Dispersive Component and Polar Component of Water and Diiodomethane

	γ (dyn/cm)	γ^d (dyn/cm)	γ^p (dyn/cm)
Water	72.8	22.1	50.7
Diiodomethane	50.8	50.4	0.4

over 2.43 wt %, which may be ascribed to the saturation of fluoroalkyl groups on the coatings surface. The equilibrium surface tension of the cured coatings based on FPEs was similar to that of smooth polytetrafluoroethylene surface (18.6 dyn/cm),³⁵ indicating that the cured coatings based on FPEs exhibited the excellent hydrophobicity and oleophobicity. In addition, the decrease of surface tension was mainly due to the decrease of the dispersive component, which was consistent with the previous studies about the fluorine-containing films.^{36,37}

Enrichment of fluoroalkyl groups in FPEs on the coatings surface

Surface properties of polymer materials have an affinity with the surface chemical composition. Literatures reported that fluoroalkyl groups preferred to enrich on the surface.¹¹⁻²¹ The chemical composition and surface enrichment of fluoroalkyl groups were investigated by XPS.

Figure 5 showed the XPS survey scan spectra of the cured coatings based on FPEs. In the case of the cured coatings based on FPE-1,2,3,4, peaks at 195.1 eV, 284.7 eV, 527.3 eV, 598.1 eV, and 684.5 eV were observed and ascribed to Cl_{2p} , C_{1s} , O_{1s} , F_{KLL} , and F_{1s} , respectively. However, there were no peaks at 598.1 eV and 684.5 eV for the cured coating based on FPE-0. The results further indicated that fluorine had been introduced into FPEs.

The high-resolution detail scan spectra of C_{1s} and F_{1s} for the cured coatings based on FPEs were also

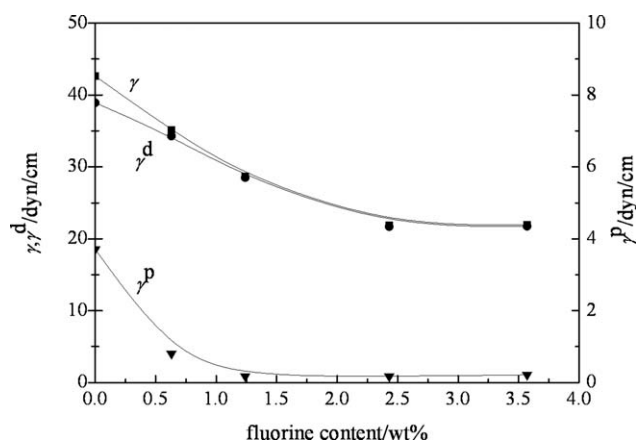


Figure 4 Relationship between surface tension and fluorine content in FPEs.

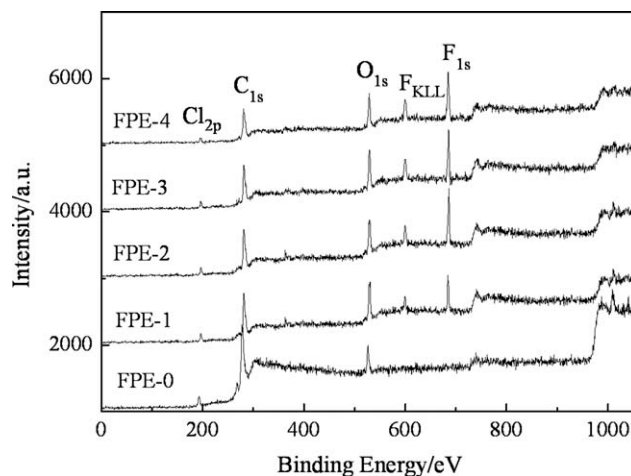


Figure 5 XPS survey scan spectra of the cured coatings based on FPEs.

collected, and Figure 6 showed the curve-fitting spectra of C_{1s} region for the cured coating based on FPE-1.

The shape of the measured C_{1s} spectrum of FPE-1 was a composite of different carbon atoms. The curve-fitting analysis of C_{1s} region of FPE-1 indicated the presence of five kinds of carbon atoms (284.7 eV (aromatic hydrocarbons), 286.4 eV ($-\text{CH}_2\text{OC}(\text{O})-$), 288.7 eV ($-\text{CH}_2\text{OC}(\text{O})-$), 292.4 eV ($-\text{OCH}_2\text{CF}_2-$) and 293.4 eV ($-\text{C}_2\text{F}_4-$)).

The F/C molar ratio on the coatings surface was calculated according to the detail scan spectra by comparing the F_{1s} and C_{1s} peak intensities [eq. (7)].²⁸

$$\frac{n_F}{n_C} = \frac{I_F/S_F}{I_C/S_C} \quad (7)$$

where I_C and I_F represented the areas of C_{1s} and F_{1s} peak, respectively. S_C and S_F were the sensitivity factors of C and F (0.296 for C and 1.00 for F),

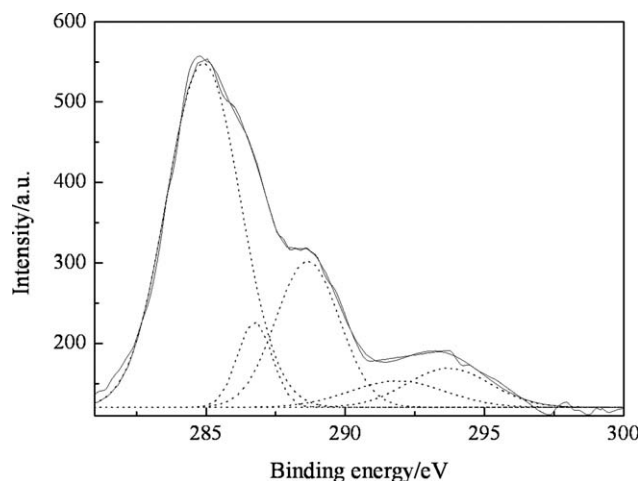


Figure 6 Detail scan and curve-fitting spectra of C_{1s} region of the cured coating based on FPE-1.

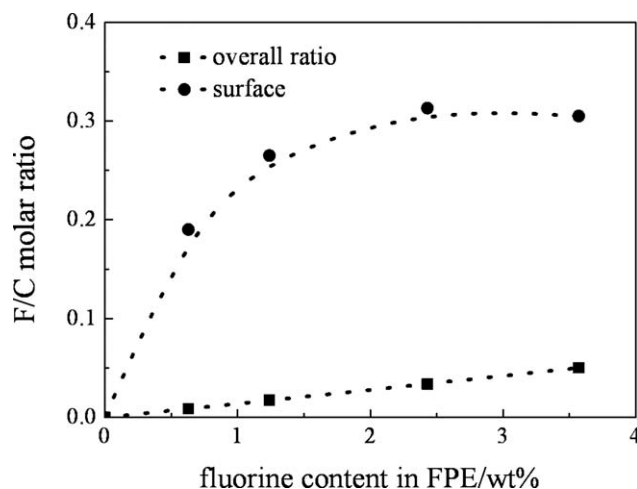


Figure 7 Change of the F/C molar ratio on the coatings surface based on FPEs with the fluorine content in FPEs (the overall F/C molar ratio was estimated from the recipes by assuming complete conversions of all reactions).

respectively.

Change of the F/C molar ratio of the coating surface based on FPEs with the fluorine content was presented in Figure 7. The F/C molar ratio on the coatings surface increased with the increase of the fluorine content in FPEs. When the fluorine content in FPEs was 2.43 wt %, the F/C atomic ratio on the coatings surface was 0.31, which was much higher than the overall F/C atomic ratio of the cured coatings (0.035). The results confirmed that fluoroalkyl groups in FPEs had enriched on the coatings surface. When the fluorine content in FPEs was over 2.43 wt %, the F/C molar ratio on the coatings surface remained constant, suggesting that fluoroalkyl groups in FPEs were saturated on the coatings surface and the results were in agreement with the contact angle. Therefore, introducing a small amount of fluorine into polyester could significantly improve the hydrophobicity and oleophobicity.

Uragmi et al.³⁸ synthesized the fluorine-containing graft copolymer (additive) and found that the surface tension of a microphase-separated PDMS-PMMA membrane decreased to 19 dyn/cm after the addition of a small amount of the additive. In this study, the F/C molar ratio on the membrane surface was about 0.3, which was far higher than the overall F/C molar ratio. The enrichment results of fluoroalkyl groups in our study were similar to those in Uragmi's results.

CONCLUSIONS

By using a novel fluorine-containing monomer-TFGE, together with a conventional ECH and PA, FPE was synthesized. The introduction of fluorine into polyester significantly improved the hydropho-

bicity and oleophobicity of polyester powder coating. The X-ray photoelectron spectroscopy analysis showed that the F/C molar ratio on the coatings surface increased with the increase of fluorine content in FPEs. When the fluorine content in FPEs was 2.43 wt %, the F/C molar ratio (0.31) on the coatings surface was much higher than the overall F/C molar ratio (0.035), which indicated the enrichment of fluoroalkyl groups in FPEs on the coatings surface.

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