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Preparation of novel side-chain fluoroalkyl polyether oligomers with terminal acrylate for emulsion copolymerization and application on cotton fabric finishing

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Abstract

Three novel side-chain fluoroalkyl polyether oligomers with different molecular weight were synthesized base on the ringopening polymerization of 3-perfluoro-*n*-butyl-1,2-epoxypropane, followed by terminal esterification using acryloyl chloride. The oligomer intermediates were used as functional monomers for emulsion copolymerization with methyl methacrylate, butyl acrylate, and hydroxyethyl methacrylate. The produced latexes were used for hydrophobic and oil-phobic finishing on cotton fabric surface and the treated cotton fabrics were tested by scanning electron microscopy and energy-dispersive spectroscopy, combined with chemical composition analysis by X-ray photoelectron spectroscopy. The result showed that fluorinated copolymers were successfully coated on the cotton fibers' surface. Water contact angles was used to evaluate the wettability and the results showed that treated cotton fabrics possessed good hydrophobicity with the contact angle of $139.1 \pm 1^{\circ}$, and the heat resistance of treated cotton fabrics was identified improved through the thermogravimetric analyses (TGA).

Keywords Fluoroalkyl polyether · Emulsion polymerization · Cotton fiber · Oligomer · Hydrophobicity

Introduction

As one of the most widely used consumer products, cotton fabric has many attractive characteristics, such as softness, widespread applicability and easy obtainability. However, the application of cotton fabric is limited in some fields due to the high concentration of hydroxyl groups on the cotton surface, which makes the fabrics easily stained by liquids (Miao et al. 2010; Periolatto et al. 2013; An et al. 2011). Therefore, as one of the most desirable textile properties, the hydrophobic capacity of cotton fiber after modification has become one of the most important domains in current search (Xu et al. 2014; Ferrero et al. 2012; Mohsin et al. 2013; Ferrero and Periolatto 2013). As we know, the surface can be categorized as hydrophilic, hydrophobic or superhydrophobic according to the interaction between water drops and a solid surface. The wettability of the solid surface is characterized by water contact angle measurements generally and a hydrophilic surface shows strong affinity toward water, while a hydrophobic surface strongly repels water. The surface is known to be hydrophobic when the water contact angle is greater than 90° and superhydrophobic when the water contact angle is larger than 150° (Periolatto and Ferrero 2014; Drelich et al. 2011).

Conventionally, hydrophobic surfaces can be fabricated via physical and/or chemical methods (Latthe et al. 2014; Yan et al. 2011; Bhushan et al. 2009; Lafuma and Quere 2003) and many derived methods have been proposed, such as chemical coating (Kim et al. 2013; Xu et al. 2012; Yang et al. 2014; Yan et al. 2013) plasma and chemical etching (Cengiz and Erbil 2014; Cabrales and Abidi 2012; Abidi and Hequet 2005; Ruan et al. 2013; Wang et al. 2013), vapor deposition (Liao et al. 2014; Lau et al. 2003; Aminayi and Abidi 2013) and so on. Surface chemical coating has become a simple and effective technique to manufacture hydrophobic surfaces among all of these methods. Owing to the popularity of chemical coating, there are a large amount of waterproof finishing agents have

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been prepared and applied. Among the finishing agents, fluoropolymers are superior agents and have been widely used in hydrophobic coatings because of their excellent environmental stability, water and oil repellency and low coefficient of friction. Incorporation of fluorine into the polymer main chain or side chain leads to large changes in the surface properties as the fluorinated polymer chains segregate toward the polymer-air interface, resulting in considerable decrease in the surface energy (Aminayi and Abidi 2015; Cheng et al. 2013; Berret et al. 2003; Sauer et al. 1998; Bongiovanni et al. 2000). Therefore, many researchers have reported the synthesis of fluorinated polymers via emulsion polymerization. Generally, the copolymers with longer perfluoroalkyl chains would have lower surface energies (Kim et al. 2002; Kaplánek et al. 2005); however, they have been found to cause a series of problems, such as bioaccumulation, feeble biodegradability, and environmental unfriendliness. Therefore, it is urgent and significant to develop environmentally friendly materials to replace the currently used long-chain fluorinated substances.

Herein, three novel short-chain fluoroalkyl polyether oligomers were synthesized and then esterified with acryloyl chloride. The oligomer acrylates can be used as functional monomers for emulsion copolymerization to give hydrophobic and oil-phobic finishing agent.

Experimental

General

All syntheses were carried out under a nitrogen atmosphere in three-neck flask glassware equipped with a Teflon magneton, thermometer, constant pressure separatory funnel and reflux condenser. Perfluorohexyl iodide, 1,3-difluoromethyl benzene (99%) and TEA (triethylamine) were commercialgrade reagents supplied by J&K Chemical Ltd. Methanol, allyl alcohol, acryloyl chloride, AIBN (azobisisobutyronitrile), SDS (surfactant sodium lauryl sulfate) and AEO-9 (fatty alcohol-polyoxyethylene ether) were purchased from Shanghai Aladdin Bio-Chem Technology Co. and used without further purification. BF₃·Et₂O and ammonium persulfate were obtained from TCI (Shanghai) Development Co., Ltd. All other reagents employed were common laboratory materials which were collected from the materials supply center of Soochow University (supplied by Qiangsheng (Jiangsu) Functional Chemicals Co., Ltd.). The reaction route is expressed in Scheme 1.

Synthesis and characterization

Synthesis of 3-perfluoro-n-butyl-2-iodo-l-propanol (FBIP)

34.59 g (0.10 mmol) perfluoro-*n*-butyl iodide was added into a glassware at room temperature and heated to

75 °C. Subsequently, a 35% aqueous solution of Na₂S₂O₅ (17.10 mL) was added and then the mixture was cooled down to 65 °C. 0.50 g (0.30 mmol) AIBN dissolved in 8.70 g (0.15 mol) allyl alcohol was added dropwise with stirring at 80 °C and thus controlling the slightly exothermic reaction for 4 h. After cooling to room temperature, 50.0 mL H₂O was added into the mixture and then worked up. The solid products were isolated by filtration and washed with water. Then the liquid was extracted with Et₂O several times and dried using magnesium sulfate (MgSO₄). Subsequently, the solvent was removed by rotary evaporation to obtain a colorless and transparent oily liquid with 95.0% yield. FT-IR (KBr): ν_{OH} 3386 cm⁻¹, ν_{CF} 1135–1352 cm⁻¹, $\nu_{C=0}$ 1036 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 2.90 (m, 2H, CH₂CHI); 4.43 (tt, 1H, CHI); 3.81 (d, 2H, CH₂O); 2.42 (s br, 1H, OH). 19F NMR (376 MHz, $CDCl_3$): $\delta - 81.7$ (m, 3F, CF₃); -114.3 (q, 2F, CF₂), -125.1 (m, 2F, CF₂), -126.6 (m, 2F, CF₂).

Synthesis of 3-perfluoro-n-butyl-1,2-epoxypropane (FBE)

41.00 g (0.10 mol) of compound *FBIP* was taken in a glassware and heated, while stirring, to 85 °C. Afterward, aqueous NaOH (20%, 30.00 g) was introduced into the dropping funnel. The reaction mixture was stirred for 5 h at 85 °C. After cooling, the mixture was filtered and the organic phase was extracted with Et₂O and washed with H₂O several times. After drying with MgSO₄, the epoxide (a colorless oily liquid) was obtained after evaporating under reduce pressure with a yield of 71%. FT-IR (KBr): ν_{CH} 2938.6–3066.5 cm⁻¹, ν_{C-F} 1422.5 cm⁻¹, ν_{C-O-C} 1023.7–1134.7 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 2.24, 2.39 (2×dm, 2H, CH₂CF₂); 2.60 (dd, IH (a), CH₂); 2.90 (t, 1H (b), CH₂); 3.23 (dq, IH, CH). ¹⁹F NMR (376 MHz, CDCl₃): δ – 81.7 (m, 3F, CF₃); – 114.3 (q, 2F, CF₂), – 125.1 (m, 2F, CF₂), – 126.6 (m, 2F, CF₂).

Synthesis of poly (3-perfluoro-*n*-butyl-1,2-epoxypropane) oligomers (PFBE, *n* = 1, 5, 10)

1.60 g (0.05 mol) of methanol and 0.20 mL BF₃·Et₂O were added into a glassware and the mixture was stirred for 30 min at room temperature. The compound *FBE* (2.76 g, 0.01 mol) was added slowly. The mixture was heated to 90 °C and stirred for 10 h, then the unreacted methanol and BF₃·Et₂O were removed by rotary evaporation to obtain the pure product of *PFBE* (*n*=1) (a colorless oily liquid) with a yield of 90%. FT-IR (KBr): ν_{OH} 3475.9 cm⁻¹, ν_{CH} 2931.2 cm⁻¹, ν_{C-O-C} 1175.4 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 2.10–2.33 (m, 2H, CH₂CF₂); 2.93 (s, 1H, OH); 4.05–4.23 (m, 1H, CHO), 3.33–3.82 (dd, 4H, 2×CH₂O).¹⁹F NMR (376 MHz, CDCl₃): δ – 81.7 (m, 3F, CF₃); –114.3 (q, 2F, CF₂), –125.1 (m, 2F, CF₂), –126.6 (m, 2F, CF₂).



Scheme 1 Synthetic route of the fluorinated polyether acrylate oligomer and its emulsion copolymerization

According to the same procedure, changing the feed ratio of monomer to end-blocking agent from 1:1 to 5:1 and 10:1 (mol/mol), products *PFBE* (n=5, 10) were obtained with yields of 92.9% and 91.6%, respectively. It was expected to control the polymerization and obtain the end-blocking fluoropolyether oligomer with different molecular weight by changing the feed ratio.

Synthesis of poly

(3-perfluoro-*n*-buty-1,2-epoxypropane)-acrylate (PFBEA, *n* = 1, 5, 10)

2.80 g (9.00 mmol) oligomer *PFBE* (n = 1), 30.0 mL 1, 3-difluoromethyl benzene and 1.80 g (18.00 mmol) TBAB dissolved in 15.0 mL H₂O were added into a glassware at room temperature, then the solution was cooled down to -5 °C and stirred for 0.5 h. A THF (20.0 mL) solution of acryloyl chloride (1.20 g, 13.50 mmol) was dropped into the reaction solution slowly; afterward, the temperature of the solution was restored to room temperature and reacted for 6 h. Subsequently, the reactants were washed with distilled water and the organic layer was separated, dried over magnesium sulfate anhydrous and the solvent removed by rotary evaporation to obtain an orange-yellow liquid in 77% yield. FT-IR (KBr): ν_{CH} 2890.2 cm⁻¹, ν_{-COO-} 1734.1 cm⁻¹, $\nu_{C=C}$ 1632.9 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 2.10–2.33 (m, 2H, CH₂CF₂); 3.33–3.75 (m, 4H, 2×CH₂O); 3.8–4.32 (m, 1H, CHO); 6.09–6.41 (m, 2H, –CH=CH₂); 6.67 (d, 1H, –CH=CH₂). ¹⁹F NMR (376 MHz, CDCl₃): δ – 81.7 (m, 3F, CF₃); –114.3 (q, 2F, CF₂), –125.1 (m, 2F, CF₂), –126.6 (m, 2F, CF₂).

Preparation of the fluorinated polyether acrylate copolymer (FPAC) and its application to cotton fiber finishing

The produced *PFBEA* (n = 1, 5, 10) was used as a functional monomer for emulsion copolymerization with methyl methacrylate (MMA), butyl acrylate (BA), and hydroxyethyl methacrylate (HEMA). The specific recipes are shown in Table 1. The amounts of SDS and AEO-9 were, respectively, 1.5% of the total mass of the monomers. All monomers and emulsifiers were pre-emulsified for 15 min at 8000 r/min, then transferred to a three-necked flask, heated to 75 °C

under N_2 gas protection, and the corresponding amount of ammonium persulfate in the table was dissolved in 20.0 mL of deionized water. The pre-emulsion was added dropwise, and the reaction was continued for 3 h. After completion, the gel was removed by filtration to obtain a side-chain fluoroalkyl polyether acrylate copolymer emulsion.

The obtained fluorocopolymer emulsions with different fluorine contents were diluted in deionized water to form 50 g/L finishing agent. The desized and bleached cotton fabrics were immersed in the finishing agent for 15 min and padded through two dips and two nips with pickup 80%. Afterward, the cotton fabrics were dried at 90 °C for 10 min and cured at 150 °C for 5 min.

Characterization

Fourier transform infrared spectroscopic (FT-IR) characterization was carried out using a Nicolet 5700 spectrometer (Thermo Electron, America). The intermediate and monomer specimens were tested by the liquid membrane method: tableting with potassium bromide on the premise that the samples were dry and anhydrous. A certain amount of polymer emulsion was evenly spread in a glass dish and dried at 110 °C to form a film, which was then washed with deionized water and dried at room temperature to obtain a polymer emulsion test sample. ¹H NMR spectra were recorded with a Unity INOVA-400 MHz NMR spectrometer (Varian America) in deuterated chloroform (CDCl₃) with tetramethylsilane (TMS) as the internal standard. ¹⁹F NMR spectra were recorded on a Bruker AC 400 spectrometer (Bruker Optics, Germany) in deuterated chloroform (CDCl₃). The test samples had a mass percentage of 5-10%.

Table 1 Copolymer emulsion polymerization recipes

Constituent (g)	Fluorine content (%)			
	20	25	30	
PFBEA $(n=1)$	15.70	24.09	37.41	
MMA	16.00	16.00	16.00	
BA	4.00	4.00	4.00	
HEMA	1.20	1.20	1.20	
Ammonium persulfate	0.22	0.27	0.35	
PFBEA $(n=5)$	11.20	16.06	22.71	
MMA	16.00	16.00	16.00	
BA	4.00	4.00	4.00	
HEMA	1.20	1.20	1.20	
Ammonium persulfate	0.19	0.22	0.26	
PFBEA $(n = 10)$	10.60	15.14	21.20	
MMA	16.00	16.00	16.00	
BA	4.00	4.00	4.00	
HEMA	1.20	1.20	1.20	
Ammonium persulfate	0.19	0.22	0.25	

Gel permeation chromatography (GPA, TDA-302, American Viscotek Company) was used for measuring the molecular weight and polydispersity index. The concentration of the test specimens was 5 mg/mL and THF was used as the eluent with a flow rate of 1.0 mL/min at room temperature. Particle size and zeta potential were measured by Mastersizer 2000 (Mastersizer, England).

Thermogravimetric analysis (TGA) was carried out from room temperature to 600° with heating at a rate of 10°/min using a Perkin Elmer Diamond 5700 thermogravimetric analyzer (Elmer Platinum, USA) under nitrogen atmosphere. The nitrogen flow rate was 20 mL/min and the test samples were 0.8 g of crumb-like fabrics placed in a ceramic crucible.

The surface morphologies of the cotton fibers were investigated using a scanning electron microscope (SEM, S-4800, Japan Hitachi Company) equipped with an energy-dispersive spectroscopy (EDS) detector and the test specimens were gold-spray fabrics with a length and a width of 0.5 cm, fixed on the electron microscope stage by a conductive adhesive.

X-ray photoelectron spectroscopy (XPS) measurement was carried out using a Kratos Axis Ultra HAS photoelectron spectrometer (Shimadzu, Japan). The samples were dried fabrics with a length and width of 0.5 cm and kept for 2 h in a vacuum oven to remove all volatile substances before the XPS analysis.

Contact angle (CA) measurements were evaluated at room temperature and ambient humidity on the Krüss DSA100 instrument (Dataphysics, Germany). The volume of each water droplet was 3 μ L, and the value was the average of five separate measurements made on different areas. It was estimated by the instrument software according to the fitting method, and the experimental errors of the measurements were within $\pm 2^{\circ}$. The water repellency of the fabric was tested on a YB813 fabric water immersion meter (Drake Instrument Co., LTD, China) according to the AATCC-22 standard invented by Dupont. The test samples were dried fabrics having a length and a width of 3 cm and 1 cm, respectively, fixed on a glass slide by a double-sided tape.

Results and discussion

Structure characterization of intermediates and target products

In Fig. 1, curves 1 and 2 show the spectra of FBIP and FBE, respectively. The peaks at 3386.6 cm⁻¹, 2879.5 cm⁻¹ and 1427.7 cm⁻¹ for FBIP, correspond to O–H stretching vibration, symmetric –CH stretching vibration and antisymmetric –CH stretching vibration, respectively. The absorption peaks at 1228.8 cm⁻¹ and 1132.5 cm⁻¹ belong to C–F stretching vibration, and the absorption peak at 1042.7 cm⁻¹



Fig. 1 FTIR spectra (left) and ¹H-NMR spectra (right). Curve 1: FBIP, curve 2: FBE

is attributed to the in-plane blending vibration peak of C–O. We can see that the C=C peak of the reactant allyl alcohol completely disappeared after the addition reaction. FBE showed absorption peaks at 3012.7 cm⁻¹ (symmetric stretching vibration of C–H), 1422.5 cm⁻¹ (antisymmetric stretching vibration of C–H) and 1234.9 cm⁻¹ (stretching vibration of C–F). The disappearance of the O–H stretching vibration peaks at 3386.6 cm⁻¹ and the new appearance of the stretching vibration peaks of –C–O–C– at 1134.7 cm⁻¹ and 1023.7 cm⁻¹ indicate the successful synthesis of the epoxy compound. The ¹H-NMR spectrum gives the same result, in which the O–H peak at 2.42 ppm completely disappeared and the new appearance of –CH–O–CH₂–C at 3.23 ppm

after the cyclization reaction, combined with ¹⁹F NMR data, confirm that the FBE was synthesized successfully.

In Fig. 2, it can be seen from the infrared absorption spectrum that PFBE showed absorption peaks at 3475.9 cm^{-1} (stretching vibration of O–H) and 2931.2 cm^{-1} (symmetric stretching vibration of –C–H). The peak at 1175.4 cm⁻¹ can be assigned to the stretching vibration of the –C–O–C bond produced by ring-opening reaction. From the infrared absorption spectrum of curve 4, we can see that the absorption strength of O–H decreased sharply and the newly appeared peaks at 1734.1 (vibration absorption of C=C) indicated the occurrence of esterification reaction. In curve 3, the



Fig. 2 FTIR spectra (left) and ¹H-NMR spectra (right). Curve 3: PFBE (n=1), curve 4: PFBEA (n=1)



Fig. 3 FTIR spectra (left): FPAC film; ¹⁹F NMR spectra (right): FBE

Table 2 Molecular weight and molecular weight distribution of a series of polymers synthesized by cationic ring-opening polymerization

Sample	[I]/[M]	1411	Mn (GPC)	Mw (GPC)	PDI	A %
FPACP $(n=5)$	1:5	1411	1319	1495	1.13	93.48
$\frac{\text{FPACP}(n=10)}{2}$	1:10	2791	2740	3072	1.19	98.27

reappearance of the O–H peaks (2.93 ppm) combined with the appearance of the –CH=CH₂ peaks (5.02–5.44 ppm, 5.73–6.13 ppm) in curve 4 also indicated that PFBE and PFBEA were successfully synthesized. The FTIR spectra in Fig. 3 are the ATR–FTIR of the fluorinated acrylate copolymer film. The peaks at 2956.8 cm⁻¹ and 1732.6 cm⁻¹ are attributed to the –C–H stretching vibration and the C=O stretching vibration, respectively, and the disappearance of the C=C stretching vibration absorption (1632.9 cm⁻¹) indicates that the polymerization was complete and FPAC was successfully prepared. It can also be seen in Fig. 3 (right) that the target product showed four sets of peaks representing –CF₂– (–81.03 ppm), –CF₂– (–109.60 ppm), –CF₂– (122.86 ppm) and –CF₃ (– 125.66 ppm), which demonstrate the presence of perfluorobutyl.

Fluorinated polyether acrylate copolymer and its latexes

Gel permeation chromatography of fluorinated polyether acrylate copolymer

The molecular weight and molecular weight distribution of oligomers FPAC (n = 5, n = 10) were determined by GPC using THF as an eluent. From the results (in Table 2), we can see that the number-average molecular weight (Mn, GPC) meets well the theoretical value (Mn, Theo.) predicted from



Fig. 4 GPC traces of FPAC with different molar ratios

the ratio of initiator/monomer ([I]/[M]). Figure 4 lists the unimodal GPC curves of FPAC (n=5, n=10) with a relatively low PDI of 1.13 and 1.19, respectively. This proved that the polymerization degree of cationic ring-opening polymerization of fluorine containing epoxide monomers was controllable and the molecular weight distribution of the obtained products was narrow (Zhong et al. 2008).

Size, zeta potential of fluorinated polyether acrylate copolymer latexes

To identify the emulsion stability, the particle size of fluorinated polyether acrylate copolymer latexes was investigated and is shown in Fig. 5a. It clearly showed that the latex particle sizes increased gradually with the increase in fluorine content, and the increments of oligomer chain length enlarged the particle size. This is because the increase in fluorine segments enhances the hydrophobic interactions around the particles, which induces the aggregation of particles formed at the early stage and further leads to particle size enlargement (Hansen et al. 2007).

As another representation of the emulsion stability, the zeta potentials of fluorinated polyether acrylate copolymer latexes (the data were the absolute values of tested zeta potentials) are shown in Fig. 5b. It clearly showed that the zeta potential of these polymer latexes was decreased with the increase in fluorine content, which demonstrated that the stability of the copolymer latexes decreased, consistent with the effect of fluorine content on the particle size. The zeta potential was further found similarly to decrease with the increment of oligomer molecular weight in the side chain in copolymers.

The application of fluorocopolymer latexes on cotton fabrics

X-ray photoelectron spectroscopy

The changes in chemical compositions on the surface of treated cotton fabrics were analyzed by XPS. Figure 6 shows the typical wide scan spectra of pristine cotton and coated cottons (FPAC-cotton, n=1, 5, 10) with 30% fluorine content. A strong peak with binding energy of 688.9 eV corresponding to F_{1s} was found in the spectra of coated cotton

fabrics (Fig. 6b–d) except for the pristine cotton (Fig. 6a). The results proved that the surface of the cotton fabric was covered by a flurocopolymer film, which provided lower surface free energy and water repellency.

Surface morphology of fluorocopolymer films on cotton substrates

The chemical composition and morphology of the fibers' surface have a major impact on the surface properties of fabrics. When the fiber surface is covered with a fluoroalkyl polymer, the side chain will migrate toward the film–air interface to reduce the surface free energy of the film and thus to form a hydrophobic surface. When watching the surface of the pristine cotton fiber (Fig. 7a), many natural pleats and uneven gullies can be found, which were fully covered



Fig. 6 XPS survey scans of pristine cotton (**a**), FPAC (n=1)-cotton (**b**), FPAC (n=5)-cotton (**c**) and FPAC (n=10)-cotton (**d**)



Fig. 5 Effect of fluorine content on the emulsion particle size (a) and zeta potential (b)

by polymer, in Fig. 7b–d, after finishing, and the surface became relatively smooth and flat. The fluoropolymer provides liquid repellency by cross-linking on the fiber surface. In addition, in the finished cotton fabrics, the elements and element distributions, as in Fig. 8, were identified by EDS. The fluorine element distributed uniformly and evenly in the film on the surface of the fibers, demonstrating that the fluoropolymer had been successfully coated on the surface of the fibers. This provides the treated fabrics good water repellency, which was found to be durable as shown in Fig. 9, as the finished cotton fabrics still possess good hydrophobicity and oleophobicity after 20 cycles of water washing.

Contact angles of cotton fabrics coated with fluorinated copolymer and its water repellency

The surface wettability of the FPAC-cotton fabric was estimated through contact angle test in Fig. 10. It can be seen from the figure that the surface contact angle of the finished fabric gradually increases as the fluorine content increases. In addition, when controlling the fluorine content at the same level, the surface contact angle of the finished fabric treated with longer side-chain fluoroalkyl polymer is significantly higher than that treated with the short-chain polymer. The WCAs of FPAC (n=1)-cotton (b), FPAC (n=5)-cotton (c) and FPAC (n=10)-cotton (d) were found to be 128.8°,

 134.7° and 139.1° , respectively. In addition, when the fluoropolymer with higher fluorine content was used as finishing agent, a better water repellency can be obtained. The result is shown in Table 3 when controlling the concentration at 50 g/L.

Thermal property analysis

The curves of TGA of pristine cotton and FPAC-cotton at a heating rate of 10°/min in N2 are presented in Fig. 11. It can be seen that all the cotton fabrics present three stages of decomposition before and after finishing. The first stage of weight loss is between 50 and 300 °C. This process caused less weight loss of about 10% by the dehydration of the glucose group in the cellulose, accompanied by a decrease in the degree of fiber polymerization. In the second stage, the rapid weight loss between 300 and 400 °C was as high as 70%, which corresponded to the decomposition of carbon chains and mainly due to the fact that the cellulose macromolecules pyrolyzed into combustible small molecules (Ayeni et al. 2013). The last stage is the residue oxidation stage of the fibers with a weight loss of about 10%. The residue was aromatically cyclized and gradually carbonized to form a graphite structure.

The initial decomposition temperature of pristine cotton fabric was 298 °C. However, the values of FPAC



Fig. 7 SEM micrographs of pristine cotton (a), FPAC (n=1)-cotton (b), FPAC (n=5)-cotton (c) and FPAC (n=10)-cotton (d)



Fig.8 Low-resolution electron micrograph and elemental distribution of the FPAC (n = 10)-cotton surface (**a**) and the corresponding elemental energy spectrum of the sample (**b**)

(n = 1)-cotton (b), FPAC (n = 5)-cotton (c) and FPAC (n = 10)-cotton (d) increased to 315 °C, 316 °C and 318 °C, respectively, after treating with fluoropolymer, revealing that the thermal stability of coated cotton fabrics was enhanced due to the introduction of fluorinated polyether acrylate copolymer. At the same time, the coated

cotton fabrics exhibited more residue compared to the pristine cotton fabric at the complete decomposition stage, which increased from 2.76 to 4.67%. The results may be attributed to the presence of fluoroalkyl chains, which have tightly packed and high energy C–F bonds (Xu et al. 2013). All of the results indicate that the thermal stability







Fig. 10 Water contact angles of FPAC (n=1)-cotton, FPAC (n=5)-cotton and FPAC (n=10)-cotton with different fluorine contents

and the heat resistance of the fabric are improved after finishing.

Conclusions

In this study, the fluorine-containing polyether oligomers were synthesized by ring-opening reaction using short fluoroalkyl propylene oxide as materials. The oligomers were then esterified with acryloyl chloride to give the

Table 3 Hydrophobicity of treated fabric with different fluorine contents

DP	Fluorine content (%)	Hydrophobic level (points)
n=1	20	70
	25	70
	30	80
n = 5	20	80
	25	80
	30	90
<i>n</i> = 10	20	80
	25	80
	30	90

fluoropolyether acrylates, followed by copolymerizing with MMA, BA, and HEMA to obtain the fluoropolymer emulsion. The latex particle size increases with the increase in fluorine content, while the emulsion stability decreases accordingly. Controlling the concentration of the finishing agent at 50 g/L and the fluorine content at 30%, the copolymers FPAC, whose side-chain length was 1, 5 and 10, were coated on cotton fabrics to give contact angles of 128.8°, 134.7° and 139.1°, respectively. In addition, the initial decomposition temperatures of the finished cotton treated with FPAC (n = 1, 5, 10) were 315 °C, 316 °C and 318 °C, which were higher than that of pristine cotton (298 °C). This indicates that the thermal stability of



Fig. 11 TG curves of pristine cotton, FPAC (n=1)-cotton, FPAC (n=5)-cotton and FPAC (n=10)-cotton

cotton fibers can be enhanced by finishing with fluorinated copolymers.

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References

- Abidi N, Hequet E (2005) Cotton fabric graft copolymerization using microwave plasma II. Physical properties. J Appl Polym Sci 98:896–902. https://doi.org/10.1002/app.22195
- Aminayi P, Abidi N (2013) Imparting super hydro/oleophobic properties to cotton fabric by means of molecular and nanoparticles vapor deposition methods. Appl Surf Sci 287:223–231. https:// doi.org/10.1016/j.apsusc.2013.09.132
- Aminayi P, Abidi N (2015) Ultra-oleophobic cotton fabric prepared using molecular and nanoparticle vapor deposition methods. Surf Coat Technol 276:636–644. https://doi.org/10.1016/j.surfc oat.2015.06.005
- An QF, Wang KF, Jia Y (2011) Film morphology, orientation and performance of dodecyl/carboxyl functional polysiloxane on cotton substrates. Appl Surf Sci 257:4569–4574. https://doi. org/10.1016/j.apsusc.2010.12.032
- Ayeni NA, Adeniyi A, Abdullahi NN, Bernard E, Ogunleye AO (2013) Thermogravimetric and kinetic study of methylolmelamine phosphate treated—cotton fabric. Bayero J Pure Appl Sci 5:51–55. https://doi.org/10.4314/bajopas.v5i2.9
- Berret JF, Calvet D, Collet A, Viguier M (2003) Fluorocarbon associative polymers. Curr Opin Colloid Interface Sci 8:296–306. https ://doi.org/10.1016/S1359-0294(03)00048-7
- Bhushan B, Jung YC, Koch K (2009) Micro-, nano-, and hierarchical structures for superhydrophobicity, self-cleaning and low adhesion. Philos Trans R Soc A 367:1631–1672. https://doi. org/10.1098/rsta.2009.0014
- Bongiovanni R, Beamson G, Mamo A, Priola A, Recca A, Tonelli C (2000) High resolution XPS investigation of photocured films

containing perfluoropolyether acrylates. Polymer 41:409–414. https://doi.org/10.1016/S0032-3861(99)00203-7

- Cabrales L, Abidi N (2012) Microwave plasma induced grafting of oleic acid on cotton fabric surfaces. Appl Surf Sci 258:4636– 4641. https://doi.org/10.1016/j.apsusc.2011.12.130
- Cengiz U, Erbil HY (2014) Superhydrophobic perfluoropolymer surfaces having heterogeneous roughness created by dip-coating from solutions containing a nonsolvent. Appl Surf Sci 292:591– 597. https://doi.org/10.1016/j.apsusc.2013.12.013
- Cheng DF, Masheder B, Urata C, Hozumi A (2013) Smooth perfluorinated surfaces with different chemical and physical natures: their unusual dynamic dewetting behavior toward polar and nonpolar liquids. Langmuir 29:11322–11329. https://doi. org/10.1021/la402398y
- Drelich J, Chibowski E, Desheng Meng D, Terpilowski K (2011) Hydrophilic and superhydrophilic surfaces and materials. Soft Matter 7:9804–9828. https://doi.org/10.1039/c1sm05849e
- Ferrero F, Periolatto M (2013) Application of fluorinated compounds to cotton fabrics via sol-gel. Appl Surf Sci 275:201–207. https ://doi.org/10.1016/j.apsusc.2013.01.001
- Ferrero F, Periolatto M, Udrescu C (2012) Water and oil-repellent coatings of perfluoro-polyacrylate resins on cotton fibers: UV curing in comparison with thermal polymerization. Fiber Polym 13:191–198. https://doi.org/10.1007/s12221-012-0191-z
- Hansen NML, Jankova K, Hvilsted S (2007) Fluoropolymer materials and architectures prepared by controlled radical polymerizations. Eur Polym J 43:255–293. https://doi.org/10.1016/j.eurpolymj.2006.11.016
- Kaplánek R, Paleta O, Michálek J, Přádný M (2005) Perfluoroalkylated diblock-alkyl methacrylate monomers for biomedical applications: wettability of their copolymers with HEMA and DEGMA. Fluor Chem 126:595–600. https://doi.org/10.1016/j. jfluchem.2005.01.004
- Kim YS, Lee JS, Ji Q, McGrath JE (2002) Surface properties of fluorinated oxetane polyol modified polyurethane block copolymers. Polymer 43:7161–7170. https://doi.org/10.1016/S0032 -3861(02)00458-5
- Kim B, Kim H, Kim J, Cho CS, Lee J (2013) Superhydrophobic polytetrafluoroethylene surface obtained using reactive ion etching and duplication with polydimethylsiloxane mould. Micro Nano Lett 8:691–695. https://doi.org/10.1049/mnl.2013.0266
- Lafuma A, Quere D (2003) Superhydrophobic states. Nat Matter 2:457–460. https://doi.org/10.1038/nmat924
- Latthe SS, Terashima C, Nakata K, Fujishima A (2014) Superhydrophobic surfaces developed by mimicking hierarchical surface morphology of lotus leaf. Molecules 19:4256–4283. https://doi. org/10.3390/molecules19044256
- Lau KKS, Bico J, Teo KBK, Chhowalla M, Amaratunga GAJ, Milne WI, McKinley GH, Gleason KK (2003) Superhydrophobic carbon nanotube forests. Nano Lett 3:1701–1705. https://doi. org/10.1021/nl034704t
- Liao RJ, Zuo ZP, Guo C, Yuan Y, Zhuang AY (2014) Fabrication of superhydrophobic surface on aluminum by continuous chemical etching and its anti-icing property. Appl Surf Sci 317:701–709. https://doi.org/10.1016/j.apsusc.2014.08.187
- Miao H, Bao FF, Cheng LL, Shi WF (2010) Cotton fabric modification for imparting high water and oil repellency using perfluoroalkyl phosphate acrylate via γ-ray-induced grafting. Radiat Phys Chem 79:786–790. https://doi.org/10.1016/j.radphysche m.2010.01.017
- Mohsin M, Carr CM, Rigout M (2013) Novel one bath application of oil and water repellent finish with environment friendly cross-linker for cotton. Fiber Polym 14:724–728. https://doi. org/10.1007/s12221-013-0724-0
- Periolatto M, Ferrero F (2014) Cotton and polyester surface modification by methacrylic silane and fluorinated alkoxysilane via sol-gel

and UV-curing coupled process. Surf Coat Technol 271:165–173. https://doi.org/10.1016/j.surfcoat.2014.12.048

- Periolatto M, Ferrero F, Montarsolo A, Mossotti R (2013) Hydrorepellent finishing of cotton fabrics by chemically modified TEOS based nanosol. Cellulose 20:355–364. https://doi.org/10.1007/ s10570-012-9821-2
- Ruan M, Li W, Wang B, Deng B, Ma F, Yu Z (2013) Preparation and anti-icing behavior of superhydrophobic surfaces on aluminum alloy substrates. Langmuir 29:8482–8491. https://doi.org/10.1021/ la400979d
- Sauer B, Mclean RS, Thomas RR (1998) Tapping mode AFM studies of nano-phases on fluorine-containing polyester coatings and octadecyltrichlorosilane monolayers. Langmuir 14:3045–3051. https://doi.org/10.1021/la971334d
- Wang Z, Li Q, She Z, Chen F, Li L, Zhang X, Zhang P (2013) Facile and fast fabrication of superhydrophobic surface on magnesium alloy. Appl Surf Sci 271:182–192. https://doi.org/10.1016/j.apsus c.2013.01.158
- Xu W, An QF, Hao LF, Zhang D, Zhang D (2012) Synthesis and characterization of s elf-crosslinking fluorinated polyacrylatesoap-free latices with core–shell structure. Appl Surf Sci 268:373–380. https://doi.org/10.1016/j.apsusc.2012.12.104
- Xu L, Xu L, Dai WS, Tsuboi TJ, Xie HD (2013) Preparation and characterization of a novel fluoro-silicone acrylate copolymer by semicontinuous emulsion polymerization. J Fluor Chem 153:68–73. https://doi.org/10.1016/j.jfluchem.2013.05.01
- Xu W, An QF, Hao LF, Zhang D, Zhang M (2014) Synthesis of selfcrosslinking fluorinated polyacrylate soap-free latex and its

waterproofing application on cotton fabrics. Fiber Polym 15:457–464. https://doi.org/10.1007/s12221-014-0457-8

- Yan YY, Gao D, Barthlott W (2011) Mimicking natural superhydrophobic surfaces and grasping the wetting process: a review on recent progress in preparing superhydrophobic surfaces. Adv Colloid Interface Sci 169:80–105. https://doi.org/10.1016/j. cis.2011.08.005
- Yan ZL, Liu WQ, Gao N, Wang HL, Su K (2013) Synthesis and properties of a novel UV-cured fluorinated siloxane graft copolymer for improved surface, dielectric and tribological properties of epoxy acrylate coating. Appl Surf Sci 284:683–691. https://doi. org/10.1016/j.apsusc.2013.07.156
- Yang X, Zhu LQ, Chen YC, Bao CQ, Xu JL, Zhou WW (2014) Surface properties and self-cleaning ability of the fluorinated acrylate coatings modified with dodecafluoroheptyl methacrylate through two adding ways. Appl Surf Sci 295:44–49. https://doi. org/10.1016/j.apsusc.2013.12.177
- Zhong LT, Zhang SS, Li YJ, Lu GL, Huang XY (2008) Synthesis and characterization of perfluorocyclobutyl aryl ether-based amphiphilic diblock copolymer. Polymer 49:4534–4540. https://doi. org/10.1016/j.polymer.2008.08.033

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