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Preparation of tetrafluoro-λ⁶-sulfanyl bridged-bonding perfluoroalkyl phenylethyltrichlorosilane and its application on fabric finishing

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Abstract

In this study, one novel perfluoroalkyl silane with tetrafluoro-λ⁶-sulfanyl bridging group named 4-(Tridecafluorohexyl sulfur tetrafluoride) Phenylethyl trichlorosilane (PFSTS) was successfully synthesized via fluorination and hydrolysis. The structure was characterized by FT-IR and NMR. Then, the product and the control subject 1H,1H,2H,2H-perfluoroctyltrichlorosilane (PFOTS) were finished onto PET fabrics through the method of dip-and-pad. The wettabilities of the treated PET fabrics were characterized by Water Contact Angles (WCA) and surface free energies measurements. X-ray Photo electron Spectroscopy (XPS) was used to validate the attachment, together with the chemical composition of the polymers on the surface of treated PET fabrics. The WCAs of PFOTS@PET and PFSTS@PET were 142.2°, 137.3°, while the WCA of untreated PET fabrics is 120° in general, indicating that PFOTS and PFSTS can provide good hydrophobicity by finishing PET fabrics. After the 48 h exposure to accelerated aging UV irradiation, sample of PFSTS@PET show a decreased CA value by 12.5% from 137.3° to 120.1°, while for sample of PFOTS@PET, the percentage of reduction is only 2.8%. It was found that the perfluoroalkyl trichlorosilane that containing –SF₄– bridged group exhibited excellent water-repellency properties and had higher potential to UV degrade as possessing weak bond energy of C–S bond, so the PFSTS might act as an eco-friendly alternative to carbon-chain perfluoroalkyl derivatives in water-repellency areas.

1. Introduction

Long-chain perfluoroalkyl chemicals (PFCs, C ≥ 8) are a group of synthetic fluorinated hydrocarbons, which was produced by 3 M as fluorine-containing surfactants in 1949 [1, 2]. The strong covalent bond between the fluorine and carbon ions allows the eight-carbon backbone to be presented as a sawtooth geometry or comb-like configuration, and the fluorine atoms are situated around the eight-carbon chain in a tight spiral shape [3, 4]. This unique structure makes PFCs possessing a low friction coefficient, low surface energy, chemical inertness and thermal resistance [4–8]. These unique properties contribute to its widespread applications in industry and commerce, such as surfactants, water-and-oil repellents for textiles, flame retardants and aqueous fire-fighting foams [1–4, 9–12]. At the same time, however, it makes these chemicals hard degradation under both chemical and biological conditions and extremely persistent in nature [3, 13, 14]. Although it can be assumed that some fluorinated derived chemicals will degrade to perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) over time, the properties of PFOS and PFOA imply that they are still highly resistant to biodegradation and the elimination half-life of them is even around 3–5 years. Moreover, it has been proved that they can induce male reproductive toxicity, hepatotoxicity, neurotoxicity, immunotoxicity and reprotoxicity and have high potential to be bioaccumulated in organs, such as eye, kidney and testis [2, 15–21]. Therefore, PFOS and PFOA were finally banned in some countries [3].
Most of the current strategies to solve these problems are to use short-chain fluoroalkyl chemicals (C \leq 6) which can be naturally degraded to replace the long-chain polymers and introduce a fluorinated side group on to the carbon–carbon skeleton chain to sustain the positive role in oleophobic behavior [4, 22–26], but the outermost layer that determines the hydrophobic effect is not an ideal closely packed arrangement of fluorinated carbons [4]. Especially in the case of amorphous polymers, there is no organized phase able to force the orientation of the fluorinated groups at the surface of the coating. Besides, due to the rigidity modulus and crystallization of the short-chain perfluoroalkyl is small, even if a stable arrangement is formed at the beginning, the fluorocarbon chain on the surface is easy to be redirected and inverted after contacting with the liquid, which results in the base chain being exposure to the air. Therefore, it is difficult to obtain the ideal liquid repellant performance for these matrix performance [4, 27–33].

In 2000, Nixon found the water contact angle (106°) of perfluoroalkyl self-assembled monolayer that containing perfluorosulfanyl bridged group (–SF3) was much higher than that (95°) of perfluoroalkyl monolayer, indicating that the –SF3 group has lower surface free energy than the –CF3 [34]. The trifluoromethylthio group (–SCF3) has strong electricity-absorption, oil-affinity and metabolic stability, which is widely used in the field of medicine and agricultural chemicals [35]. The trifluoromethyl tetrafluoroalkyl group (–SF3CF3) is a hydrophobic unit and has better ester-ophilic performance than the –SF3 and –SCF3 groups. Such highly fluorinated compounds have better physical and chemical durabilities [36].

Here, we introduce –SF3− as the bridged group onto the polymer to connect –C6F13 and phenyl units. The introduction of –SF3 group makes the whole chain easy to break at the sulfur-fluorine bond, which destroys the extreme stability of perfluoroalkyl and contributes to the degradation of skeleton. The long-chain perfluoroalkyl may result in better water-repellency properties than short-chain because of the crystallization. Few researches have done with the –SF3− bridged –CnF13 groups as degradable water-repellency ingredient. In this paper, we synthesized 4-[(tridecafluorohexylthio)bromobenzene as intermediate from 4-bromothiophenol and perfluoro-1-iodohexane at first [37]. Then the intermediate was oxidized and fluorinated to 4-[(tridecafluorohexylthio)sulfur tetrafluoride] bromobenzene [38], which further reacted with vinylmagnesium bromide to produce 4-[(tridecafluorohexylthio)sulfur tetrafluoride] styrene [39]. At last, 4-[(tridecafluorohexylthio)sulfur tetrafluoride] phenylethyltrichlorosilane (PFSTS) was performed via hydrosilylation from trichlorosilane and the product of the previous step. To investigate the effect of –SF3− bridged group on degradability of polymers, we finished PFSTS onto the surface of polyethylene terephthalate (PET) through the method of dip-and-pad and employed 1H,1H,2H,2H-perfluorooctyltrichlorosilane (PFOTS) as reference subject. The results may inspire the structure design of degradable water-repellent agent and PFSTS maybe an eco-friendly alternative to carbon-chain perfluoroalkyl groups in water-repellency areas.

2. Experimental

2.1. Materials

Part of the chemical used in this paper were obtained from: Beijing J&K Reagent Company (98% of perfluoro-1-iodohexane, 99% of vinylmagnesium bromide, 97% PFOTS), Shanghai Aladdin Reagent Company (cupric acetate, 98% of manganese dioxide), Shanghai Jingding Chemical Company (97% of 4-bromo thiophenol), Shanghai Macklin Biochemical Technology Company (benzoyl peroxide), Henan Jinsha Chemical Company (highly active potassium cyanide), Shanghai Energy Chemical Technology Company (Pd(dppf)Cl2, TCI Shanghai (anhydrous tetrahydrofuran), Sinopharm Chemical Reagent Co. Ltd (karsedd’s catalyst), Shanghai Lingfeng Chemical Reagent Co. Ltd (Magnesium sulfate, 1,4-dioxane, hexane, anhydrous methanol, acetonitrile, hydrochloric acid). All the above reagents used were of purity grade and used as received.

2.2. Synthesis and characterization

The perfluoroalkyl silane with –SF3− bridged group has been synthesized by our group [40], as shown in Scheme 1, the detailed process was as follows:

2.2.1. Synthesis of 4-[(Tridecafluorohexylthio) Bromobenzene, Br-(C6H4)-S-CnF13 (Product 1)

Bromobenzethiol (10.2 g, 54.0 mmol), perfluoro-1-iodohexane (26.8 g, 60 mmol), cupric acetate (1.1 g, 6.0 mmol) and 1,4-dioxane (200 ml) were taken into a 500-ml three-necked round flask equipped with a magnetic stirrer, thermometer, dropping funnel and a reflux condenser in a nitrogen atmosphere. The reaction mixture turned to yellow gradually during the process of its being heated to 70 °C. Benzoxy peroxide (8.7 g, 36 mmol), which was dissolved in 1,4-dioxane (70 ml), was added dropwise to the mixture then within 1 h. Keeping the temperature at 70 °C for 8 h. After reaction, the mixture was cooled down to room temperature and 1,4-dioxane was removed at a reduced pressure. 500 ml of hexane was added to dissolve the product and then cupric acetate was filtered out. After that the reactant was quenched with sodium carbonate solution and...
deionized water, then dried with anhydrous magnesium sulfate. All volatiles were removed under reduced pressure to give the light-yellow solid Product 1 (9.88 g, yield 36.1%). FT-IR (KBr, cm⁻¹): 3072, 1618, 1561, 1384, 1080, 1067, 1006, 812 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): 7.34 (d, 2H, m-H), 7.43 (d, 2H, o-H). ¹³F NMR (564 MHz, CDCl₃): −80.59 (3F, CF₃), −86.69 (2F, CF₂CF₂), −118.97 (2F, CF₂CF₂CF₂), −121.20 (2F, CF₂(CF₂)₂CH₂), −127.73 (2F, CF₂(CF₂)₃CE₃), −125.86 (2F, CF₃(CF₂)₄CE₂).

2.2.4. Synthesis of 4-(tridecafluorohexyl sulfur tetrafluoride) bromobenzene

Br-(C₆H₄)_3−SF₄−CB₃ (3.9 mmol), dry potassium fluoride (4.7 g, 80.9 mmol) and 150 ml of anhydrous acetonitrile were taken into a 250 ml three-necked round bottom flask equipped with a magnetic stirrer and thermometer. N₂ was passed into the flask to expel air at 0 °C, then Cl₂ was passed into the system slowly and the reaction liquid turned to yellow finally. The mixture was then placed at room temperature and stirred for 20 h. When the reaction finished, pouring a stream of N₂ into the flask to drain the remaining Cl₂. Anhydrous acetonitrile was removed at a reduced pressure. 100 ml of hexane was added to dissolve the product. The reaction was next washed with sodium carbonate solution, followed by deionized water, and then dried over MgSO₄ for 12 h. All volatiles were removed under reduced pressure to give the yellow liquid Product 2 (0.84 g, yield 37.0%). FT-IR (KBr, cm⁻¹): 3093, 1618, 1573, 1325, 1212, 1190, 1096, 1066, 1007, 821 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): 7.79 (d, 2H, m-H), 7.86 (d, 2H, o-H). ¹³F NMR (564 MHz, CDCl₃): 66.69 (4F, CF₂(CF₂)₃CF₂), −80.85 (3F, CE₂), −86.54 (2F, CF₂CF₂), −119.00 (2F, CF₂CF₂CF₂), −121.40 (2F, CF₂(CF₂)₂CF₂), −122.75 (2F, CF₃(CF₂)₃CF₂), −125.84 (2F, CF₃(CF₂)₄CF₂).

2.2.3. Synthesis of 4-(tridecafluorohexyl sulfur tetrafluoride) styrene, CH₂=CH-(C₆H₄)−SF₄−CB₃(CF₃)

The Product 2 (0.6 g, 1 mmol) and Pd(dppf)Cl₂CH₂CH₂ (100 mg, 120 μmol) were dissolved in 20 ml of anhydrous tetrahydrofuran, and vinylmagnesium bromide (4 ml, 4 mmol) was added under N₂. The reaction was allowed to stir for 6 h at room temperature. After that, the reaction was quenched by anhydrous methanol and 30 ml of hexane, which was then filtered and concentrated under reduced pressure to provide a red brown oil Product 3 (0.31 g). FT-IR (KBr, cm⁻¹): 3087, 1628, 1385, 1261, 1223, 1092, 1069, 1008, 809 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): 7.81 (d, 2H, m-H), 7.73 (d, 2H, m-H), 6.48 (d, 1H, CHCH₂), 6.12 (d, 1H, CHCH₂), 5.83 (s, 1H, CHCH₂). ¹³F NMR (564 MHz, CDCl₃): 66.33 (4F, CF₂(CF₂)₃CF₂), −80.77 (3F, CE₂), −86.82 (2F, CF₂CF₂), −119.11 (2F, CF₂CF₂CF₂), −121.39 (2F, CF₂(CF₂)₂CF₂), −122.76 (2F, CF₃(CF₂)₃CF₂), −126.08 (2F, CF₃(CF₂)₄CF₂).

2.2.4. Synthesis of 4-(Tridecafluorohexyl sulfur tetrafluoride) Phenylenetri chlorosilane, SiCl₃−C₆H₄−SF₄−C₆H₄ (PFSTS)

Product 3 obtained from the above procedure (0.3 g, 0.6 mmol) was dissolved in anhydrous toluene, followed by one drop of karseld’s catalyst in a 25 ml three-necked round bottom flask. The reaction was warmed to 70 °C and chlorosilane (0.3 g, 2.3 mmol, dissolved in 5 ml of toluene) was added dropwise. After stirring for 2 h, the reaction was concentrated under reduced pressure to provide Product 4 (0.52 g) as a red brown oil. FT-IR (KBr, cm⁻¹): 3021, 2964, 2853, 1630, 1385, 1261, 1092, 1069, 1006, 808 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): 7.87 (d, 2H, o-H), 7.78 (d, 2H, m-H), 2.49 (d, 2H, SiCH₂CH₂), 1.62 (d, 2H, SiCH₂CH₂). ¹³F NMR (564 MHz, CDCl₃): 66.37 (4F, CF₂(CF₂)₃CF₂), −80.74 (3F, CE₂), −86.78 (2F, CF₂CF₂), −119.12 (2F, CF₂CF₂CF₂), −121.37 (2F, CF₂(CF₂)₂CF₂), −122.72 (2F, CF₃(CF₂)₃CF₂), −126.06 (2F, CF₃(CF₂)₄CF₂).
2.3. Characterization

Fourier Transform Infrared (FTIR) spectra were processed on Thermo Electron Corporation Nicolet 5700 FTIR spectrometer (Thermo Nicolet, USA), which was recorded with 12 scans at resolution of 4 cm$^{-1}$.

$^1$H Nuclear Magnetic Resonance (NMR) and $^{19}$F NMR spectra were obtained on an AvanceIII-400MHz spectrometer (Bruker, Switzerland) with 8 scans were accumulated for each spectrum and deuterated chloroform (CDCl$_3$) with tetramethyl silane (TMS) was served as the internal standard.

X-ray Photoelectron Spectroscopy (XPS) spectra were collected at Axis Ultra DLD photoelectron spectrometer (Shimadzu, Japan) with amono chromatic AlK$_\alpha$ (1486.6 eV) radiation source at 12 kV and 15 mA. The binding energy of CH$_2$ peak at 285.0 eV was used as the reference to compensate for sample charging. The records were gathered at raw pressure of 4.0 × 10$^{-9}$ Pa, photo electron takeoff angle of 90°, and 0.9–1.3 eV full widths at half-maximum through using an analyzer pass energy of 20 eV. Approximately 0.1 eV of error was allowed to delimit the position of absorption peaks. All the parameters were processed using XPS PEAK software.

Contact Angle (CA) measurement was carried out at RM and ambient humidity on an optical contact angle goniometer (OCAH200, Dataphysics Inc.). Water, hexadecane as well, was adopted as the reference liquid for the analysis. 3 μL of each liquid drop was allowed. Each sample was measured three times. Average values were recorded after calculations.

Scanning Electron Microscope (SEM) was done by TM3030 desktop SEM and S-4800 field emission SEM further. The samples were treated with gold spraying in advance.

2.4. Synthesis of poly(vinyl acetate) emulsion and Pre-treatment of PET fabric

(1) pre-emulsification: vinyl acetate (83.0 g), butyl acrylate (8.0 g), methyl methacrylate (5.0 g), acrylic acid (2.8 g), N-Methylolacrylamide (1.2 g), compound emulsifier (OP-10: sodium dodecyl sulfate = 2: 1, 3 g) and deionized water were taken into a beaker and dispersed by a high-shear dispersion homogenizer at a speed of 13 000 r min$^{-1}$ for 10 min to form a stable pre-emulsion (solid content = 40%).

(2) emulsion polymerization: 20% of pre-emulsion and deionized water were taken into a 500 ml three-necked round flask that equipped with a magnetic stirrer, dropping funnel, reflux condenser and thermometer. Initiator (sodium persulfate, 0.5 g) and buffer agent (sodium bicarbonate, 0.3 g) were dissolved in water to form a mixture. When the pre-emulsion was heated to 75 °C, the mixture was added dropwise to take seed emulsion polymerization. After the emulsion turning to blue, the rest of the pre-emulsion was added within 4 h. Then the reaction was stirred at 75 °C over 1 h and the product formed after cooling.

(3) Pre-treatment of PET fabric: Poly(vinyl acetate) emulsion (PVAc, 40% of solid content) was diluted 50 times. As can be seen in figure 1, the PET fabric (3 × 7 cm$^2$, $m_1$) was soaked in the above solution, followed by two dips and two pads (wet pick-up 60%). Then, the treated fabric was taken into the air to remove part of the water. After losing some water, recording the weight of the treated fabric as $m_2$ and controlling the water content (W) as 20%. $W = [(m_2-m_1)-m_1G_S]/m_1*100\%$, where $m_1$ is the weight of untreated PET fabric; $m_2$ is the weight of final treated PET fabric; G is the wet pick-up as 60% in this treatment; S means the solid content of polyvinyl acetate emulsion that diluted 50 times, which is less than 1%.

Figure 1. The process of grafted PET fabric.
2.5. Application of R-SiCl₃ absorbers to PVAc-PET fabric

As can be seen in figure 2, 100 ml of petroleum ether was taken into a 100 ml beaker that equipped with a stir bar, which was then placed into a 250 ml beaker on the magnetic stirrer. PET fabric that pre-treated by PVAc was dipped into the petroleum ether quickly and 300 μl of R-SiCl₃ was next added with a syringe. Glass cover was used to prevent the dust in the air from entering into the mixture and decrease the volatilization of petroleum ether. The reaction was stirred slowly at room temperature for 2 h. After that, the grafted PET fabric was washed thoroughly with petroleum ether, then pre-dried in an oven at 120 °C for 5 min and cured at 150 °C for 3 min.

3. Results and discussions

The perfluoroalkyl silane with –SF₄– bridged group has been successfully synthesized and characterized by our group [40]. Figure 3 shows the ¹H and ¹⁹F NMR spectrogram of the products. The peak ascription was signed in the figure and described in the experiment part. Here we mainly focus on the application of the tetrafluoro-λ⁴-sulfanyl bridged-bonding perfluoroalkyl phenylethyltrichlorosilane on fabric finishing, such like the photodegradable properties, water repellent properties, and the inner relation between those phenomena.

3.1. X-ray photoelectron spectroscopy (XPS)

XPS showed graduate changes of surface structure and chemical compositions, from untreated PET fabric to PET fabrics treated by 1H,1H,2H,2H-Perfluorooctyloctyltrichlorosilane (PFOTS@ PET) and that finished by 4-(Tridecafluorohexyl sulfur tetrafluoride) Phenethyl trichlorosilane (PFSTS@ PET). As is vividly shown in...
Figure 4. XPS survey scans of (a) PFOTS@PET, (b) PFSTS@PET and (c) untreated PET fabric.

Figure 5. SEM images of (a) PFOTS@PET, (b) PFSTS@PET.

3.2. Scanning electron microscopy (SEM)
SEM was used to observe the surface morphologies of PET fabrics, the morphology images of PET fabrics finished by 1H,1H,2H,2H-Perfluoroalkyltrichlorosilane (PFOTS@PET) and that finished by 4-(Tridecafluoroethyl sulfur tetrafluoride) Phenylethyl trichlorosilane (PFSTS@PET) were pictured in figure 5. As can be seen, there was a thin polymer film covered on both finished PET fabrics. Because of the finishing of PFSTS or PEOTS, the surface free energy decreased, resulting of the water-repellency properties of the PET fabrics.

3.3. Water contact angles (WCAs)
Contact Angle (CA) was measured to detect the wettability of PET fabrics. The WCAs of treated PET fabrics were showing separately in the corner of figures 4(a) and (b). As can be seen, the WCAs of PFOTS@PET and PFSTS@PET were 142.2°, 137.3°, while the WCA of untreated PET fabrics is 120° in general, indicating that the surface hydrophobicity of PET fabrics can be improved through being finished by PFOTS and PFSTS. The mechanism of microphase separation was usually employed to demonstrate this phenomenon, on a more
concrete basis is that the perfluoroalkyl chains migrated from interior to surface during the process of curing, and then the water-repellency of PET fabrics surface was improved.

3.4. Photodegradation analysis
Photodegradation test was applied to study the effect of –SF₄– bridged group in PFSTS@PET on photodegradation properties by comparing to PFOTS@PET. Accelerated aging of the treated PET fabrics (PFOTS@PET, PFSTS@PET) were performed in an Accelerated Aging Xenon Test Chamber (Q-SUN, Xe-3HS) for different period in a 12 h basis continuously. The test chamber is equipped with a precision light control system which allows the choice of the desired level of irradiance. Irradiance is monitored and controlled at 320 nm and optical density is 1 mW/cm². Temperature monitoring and control is performed by a black panel temperature sensor which controls the specimen’s surface temperature and simultaneously by the chamber air temperature control to give the ultimate determination of the specimen temperature. The operating temperature was set up as 50°C.

The analysis of the water contact angle values of the PET samples during the experimental period reveals that in both samples WCA decreases under the UV light. As is can be seen in figure 6, after the 48 h exposure to accelerated aging conditions, sample of PFSTS@PET show a deceased CA value by 12.5% from 137.3° to 120.1°, while for sample of PFOTS@PET, the percentage of reduction of the CA value is only 2.8%. Fₐ is the equatorial F atoms of –SF₄– and lies nearly opposite the C atom. With a corresponding contraction of the intermolecular, there is a stretch in this S–Fₐ bond, and this stretch correlates with the overall binding energy [41]. Therefore, as a bridged group with weak binding energy, –SF₄– breaks easily after absorbing enough energy from UV light, which eventually leads to the destruction of tight and regular arrangement between perfluoroalkyl chains in PFSTS@PET. This is the reason why the surface water repellency of the PFSTS@PET decreased significantly.

3.4.1. Surface free energy
The surface energy of a material is determined by the chemical composition and structure of its outermost layer [42]. When the surface of the material is covered with fluoroalkyl compounds, the material has lower surface energy, therefore, we can judge the degradation of fluoroalkane film by studying the change of free energy on the surface of fabric before and after UV irradiation. The surface free energy can be calculated by equations (1) and (2):

\[
\gamma_{LV}(1 + \cos \theta) = 2\sqrt{\gamma_{SV}^d \gamma_{LV}^d} + 2\sqrt{\gamma_{SV}^p \gamma_{LV}^p}
\]

\[
\gamma_{SV} = \gamma_{SV}^d + \gamma_{SV}^p
\]

Figure 6. Variation of water contact angle for each sample by different irradiation time.

In equation (1), \( \theta \) is the contact angle of water or ethylene glycol; \( \gamma_{LV} \) means the surface tension of liquid, (72.8 mN m\(^{-1}\) for water, 48 mN m\(^{-1}\) for ethylene glycol); the dispersion of liquid, \( \gamma_{LV}^d \) (water of 21.8 mN m\(^{-1}\), ethylene glycol of 29 mN m\(^{-1}\) ); the polar components for liquid \( \gamma_{LV}^p \) (water of 51.0 mN m\(^{-1}\), ethylene glycol of 19 mN m\(^{-1}\) ). According to equation (2), the surface free energy \( \gamma_{SV} \) of PFSTS@PET can be calculated by its dispersing component \( \gamma_{SV}^d \) and polar component \( \gamma_{SV}^p \).
After measuring the water and ethylene glycol contact angles, the surface free energy of PFOTS@PET and PFSTS@PET were calculated and manifested in Table 1. The surface free energy of PFOTS-12h, PFOTS-28h and PFOTS-48h were all at a low level and showed a downward trend, while that of PFSTS-12h, PFSTS-28h, PFSTS-48h exhibited an upward trend. After 48 hours of UV irradiation, its surface free energy reached 32.9 mN m\(^{-1}\), which was much higher than before (6.4 mN m\(^{-1}\)). This illustrates the weak bond in PFSTS is collapsed after taking in large quantities of energy and the orientation of fluoroalkanes is disrupted. Hence the surface free energy of PFSTS@PET increases.

| Samples   | \(\theta_{\text{water}}(\degree)\) | \(\theta_{\text{ethanol}}(\degree)\) | \(\gamma_{SV}(\text{mN m}^{-1})\) |
|-----------|----------------------------------|----------------------------------|----------------------------------|
| PFOTS     | 142.2                            | 126.4                            | 4.1                              |
| PFOTS-12h | 141.3                            | 123.8                            | 5.3                              |
| PFOTS-28h | 139.8                            | 127.1                            | 2.9                              |
| PFOTS-48h | 138.2                            | 126.6                            | 2.6                              |
| PFSTS     | 137.3                            | 119.3                            | 6.4                              |
| PFSTS-12h | 134.4                            | 108.9                            | 15.1                             |
| PFSTS-28h | 127.1                            | 101.2                            | 18.5                             |
| PFSTS-48h | 120.1                            | 92.9                             | 32.9                             |

Figure 7. SEM morphology images of PFSTS@PET under different UV irradiation times.

After measuring the water and ethylene glycol contact angles, the surface free energy of PFOTS@PET and PFSTS@PET were calculated and manifested in Table 1. The surface free energy of PFOTS-12h, PFOTS-28h and PFOTS-48h were all at a low level and showed a downward trend, while that of PFSTS-12h, PFSTS-28h, PFSTS-48h exhibited an upward trend. After 48 hours of UV irradiation, its surface free energy reached 32.9 mN m\(^{-1}\), which was much higher than before (6.4 mN m\(^{-1}\)). This illustrates the weak bond in PFSTS is collapsed after taking in large quantities of energy and the orientation of fluoroalkanes is disrupted. Hence the surface free energy of PFSTS@PET increases.

### 3.4.2. Surface morphology

The surface morphology of PFSTS@PET fabrics was measured by SEM and is shown in Figure 7. Figure 6(a) shows the surface appearance of PFSTS@PET fabric without ultraviolet irradiation and Figure 7(b) is that of PFSTS@PET under 48 h of UV light. From Figure 7(a), we see that the fibers surface was covered by an intact and tight membrane and the space between PET fibers was also filled with PFSTS. However, after 48 h of ultraviolet radiation, the perfluoroalkyl film cracked in the interstitium between fibers and the film roughness on fibers decreased visibly. This phenomenon might be expected from the embedded SF\(_4\) bridging group, which acted as a reactive site and broke under UV irradiation.

Perfluorohexyltetrafluorosulfuranylienyltrichlorosilanes (PFSTS) was successfully prepared through introducing the \(-\text{SF}_4\)-bridged group into perfluoroalkyl chain by using bromobenzenethiol, perfluoro-1-iodohexane, potassium fluoride, vinylmagnesium bromide and trichlorosilane as raw materials. Then the two perfluoroalkysilane films, Perfluorohexyltetrafluorosulfuranylienyltrichlorosilanes (PFOTS) and PFSTS, were grafted onto the PET fabrics by the method of two dips-and-pads. The changes of surface elements, morphology and surface free energy of PET fabrics were conducted by XPS, SEM and WCAs respectively. The WCAs of PFOTS@PET and PFSTS@PET were 142.2°, 137.3°, while the WCA of untreated PET fabrics is 120°, indicating that the finished PET fabrics can obtained good surface hydrophobicity by PFOTS and PFSTS. After the 48 h exposure to UV, sample of PFSTS@PET show a decreased CA value by 12.5% from 137.3° to 120.1°, while for sample of PFOTS@PET, the percentage of reduction of the CA value is only 2.8%. Studies on photodegradation abilities of PFOSTS@PET and PFSTS@PET revealed that the introduction of tetrafluoro-\(\lambda^6\)-sulfanyl group made it easier for perfluoroalkysilane chains on PFSTS to cleavage. The decrease of CA value indicates that this compound has good photo-degradation properties and might act as an eco-friendly alternative to carbon-chain perfluoroalkyl materials.
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