Superamphiphobic and flame-resistant cotton fabrics for protective clothing

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Abstract Superamphiphobic and flame-retardant finishing of cotton fabric can significantly improve its protective properties to expand its applications, such as protective clothing. However, creating such materials is still a challenging issue. Herein, we present a facile strategy to fabricate superamphiphobic and flame-retardant cotton fabric (SFC) via step-by-step dip-coating and spraying technology. Ammonium polyphosphate (APP) endows cotton fabric excellent flame retardancy. The robust coating formed by the polymerization product of ethyl 2-cyanoacrylate and 1H,1H,2H,2H-perfluorooctyl trichlorosilane (FOCS) can not only protect APP from being damaged but also trap air to form “air plastron”, which makes SFC have excellent antifouling, chemical repellence and self-cleaning. The resulting SFC exhibited superamphiphobicity and flame retardancy with water contact angle of 161°, oil contact angle of 158° and LOI of 30%. After UV irradiation, mechanical damage, 180 °C oven heating and ultrasonic washing, it still maintains excellent hydrophobicity without loss of flame retardancy. This study expands the potential applications of cotton and provides feasible technologies for improving the overall efficiency of cotton.

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Introduction

Superamphiphobicity is a special surface effect, which is both superhydrophobic and superoleophobic (Chu et al. 2014). Tsujii’s group (Shibuichi et al. 1998; Tsujii et al. 1997) first reported on super water and oil repellent surfaces, which has become one of the most popular research topics in recent years. Researchers have designed different superamphiphobic surfaces (Deng et al. 2012; Liu et al. 2018a, b; Pan et al. 2013; Tuteja et al. 2007) by combining appropriate surface roughness and materials with low surface energy. According to reports, long perfluoroalkyl chains are most commonly used to prepare superamphiphobic surfaces. However, in recent years, it has been discovered that materials containing long perfluoroalkyl groups (R fn, n ≥ 8) accumulate in human and animal tissues, and have a long biological half-life, which has been banned in many countries (Zhao et al. 2018). In view of the above reasons, researchers began to use fluorochemicals with short perfluoroalkyl groups (R fn, ≤ 6) to prepare superamphiphobic surfaces (Pan et al. 2018). As one of the most advanced surface technologies, superamphiphobic finishing has also been applied to the textile field. Fabrics such as cotton (Moiz et al. 2018), polyester (Wang et al. 2013; Zhou et al. 2020), nylon (Li et al. 2017), and aramid (Liu et al. 2021a, b; Siddig et al. 2020) with superamphiphobicity have been manufactured one after another. Researchers have also studied their applications in the fields of chemical protection (Yeerken et al. 2019), anti-fouling (Guo et al. 2017), self-cleaning (Luo et al. 2020), and anti-icing (Pan et al. 2018).

Cotton is one of the most important natural textile fibers, which is widely used in the textile field, but its flammability and high moisture absorption limit its application in special fields. To change these two characteristics together, researchers have proposed some methods for hydrophobic and flame-retardant finishing of cotton fabric. For example, people have prepared multifunctional coatings to prepare cotton fabric with superhydrophobic and flame-retardant (Abdelrahman et al. 2019; Chen et al. 2019; Li et al. 2020; Liu et al. 2020; Hicyilmaz et al. 2019) functions. But the common method is to gradually finish flame-retardant and hydrophobic cotton fabric. First, the flame-retardant fabric was fabricated by dipping flame retardant (such as ammonium polyphosphate Li et al. 2019; Lin et al. 2019; Xue et al. 2016), phytic acid (Liu et al. 2018a, b; Nie et al. 2019) or metal oxides (Ambekar et al. 2020; Wang et al. 2019,2020; Zhang et al. 2015)). Then, use a hydrophobic agent (such as silicone Abdelrahman et al. 2019; Nabispour et al. 2020; Suryaprabha et al. 2018) or fluorosilane (Chen et al. 2015; Lin et al. 2018; Zhang et al. 2015) to perform superhydrophobic finishing on the flame-retardant fabric. Finally, a multi-layered, inside-out composite coating is formed on the surface of the fabric to obtain robust superhydrophobic and flame-retardant properties. However, the superhydrophobicity could prevent the flame retardancy of the fabric from being destroyed by water, but it can do nothing in...
the face of chemical, organic matter, or solvents. In addition, the self-cleaning properties of superhydrophobic fabrics are also limited, because most superhydrophobic surfaces are lipophilic, which makes them susceptible to oil stains. Therefore, superamphiphobic and flame-retardant cotton fabric will have better self-cleaning, anti-fouling, and chemical resistance, but it has not been demonstrated in the research literature.

In this work, the fabrication of superamphiphobic and flame-retardant cotton fabric (SFC) was fabricated using a step-by-step dip-coating and spraying technology (Fig. 1). Ammonium polyphosphate (APP) is an eco-friendly and efficient flame retardant, which significantly improves the flame retardancy of flame-retardant cotton fabric (FC). The reactive ethyl 2-cyanoacrylate (ECA, a common instant adhesive) and 1\text{H},1\text{H},2\text{H},2\text{H}-perfluoroctyl trichlorosilane (FOCS) are sprayed onto the FC and then catalyzed by water vapor to form a robust coating. Benefiting from the perfluoroalkyl group of the FOCS, the coating is endowed with a high degree of superamphiphobicity. The PECA formed by ECA polymerization has excellent bonding strength, which ensures the fastness of the combination of cotton fabric and FOCS. As far as we know, there are no similar superamphiphobic and flame-retardant fabrics reported before. The preparation method and mechanism of the superamphiphobic flame-retardant coating proposed in this study have certain guiding and reference significance in improving the functionality and bonding fastness of other textile coatings.

**Experimental section**

**Materials**

Ammonium polyphosphate (APP) was supplied by Yunnan Tianyao Chemical, 1\text{H},1\text{H},2\text{H},2\text{H}-perfluoroctyl trichlorosilane (FOCS) was supplied by Energy Chemical. Ethyl 2-cyanoacrylate (ECA) was supplied by Beijing Chemical Works. 1,1-dichloro-1-fluoroethane was supplied by Juhua Chemical Tech. Ethanol, methanol (MT), acetone, HCl, NaOH, tetrahydrofuran (THF), methyl ethyl ketone (MEK), toluene, N, N-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) were purchased from China National Medicines Co. Ltd. Corn oil was commercially available. All chemicals were used as received without further purification.

Fabrication of superamphiphobic and flame-resistant cotton

The brief procedure to prepare the SFC was schematically illustrated in Fig. 1a. The cleaned cotton fabric was immersed into the prepared APP solution (50 g/L) for 40 min and dried at 70 °C to obtain a flame-retardant cotton fabric (FC). And then 0.4 g of FOCS and 1.6 g of ECA were added into 4 g of 1,1-dichloro-
1-fluoroethane successively to obtain superamphiphobic coating solution. Subsequently, spray the as-prepared solution onto the prepared FC for 2 min to obtain SFC.

Characterization

The element distribution of the fabrics was obtained on an energy dispersive spectrometer (EDS, XMax N20). The surface chemical bonding state of the fabrics was measured by X-ray photoelectron spectroscopy (XPS, Esca lab 250Xi). The Fourier transform infrared (FTIR) spectra of fabrics were recorded on a Fourier transform infrared spectrometer (FTIR Spectrum Two). The morphology of fabrics was observed by a scanning electron microscope (SEM DXS-10ACKT). Thermogravimetric analysis (TGA) was performed with a thermogravimetric tester (TGA4000) under a nitrogen atmosphere, the samples (about 5 mg) were heated from 30 to 600 °C at a linear heating rate of 20 °C/min. The final water contact angle (WCA) and oil contact angle (OCA) were measured using a CA tester (DKSH), liquid drops with a volume of about 5 µL were used. All the contact angle values were average of three measurements. The flammability of the fabric was evaluated by a vertical flammability tester (YG815A) according to the standard of ASTM D6413, the sample with a dimension of (78 × 300) mm² was exposed to a flame for 12 s. The flame retardancy of the samples was measured by LOI tester (LFY605) according to the standard of GB/T 5454–1997. The abrasion resistance was conducted regarding standard GB/T 21,196.2–2007, and the samples were investigated by Martindale Abrasion Tester (YG401E) with a load pressure of 12 kPa and a rotation speed of 47.5 r/min. Ultrasonic cleaner (JAC-4020) was employed to test the washability of the fabrics. The air permeability was measured by an air permeability tester (YG461E) according to the standard of GB/T 5453–1997, the tested air pressure difference is 50, 100, 150, and 200 Pa, respectively. The breaking strength and strain were measured using the testing instrument (Instron 5967) according to standard ASTM D3107-1975, all the fabrics were stretched at a rate of 50 mm/min until breaking with the original dimension of (50 × 150) mm².

Results and discussion

We designed the superamphiphobic and flame-resistant cotton fabric according to the following criteria: (1) the fabric should be highly effective flame retardant; (2) the surface of the fabric should be superamphiphobic to resist harmful substance; (3) the coatings of fabric must be mechanically robust and durable to withstand common damages. As schematically depicted in Fig. 1b, FC was first fabricated by dipping the APP aqueous solution, then SFC was obtained by spraying the mixed solution of FOCS and ECA. Briefly, APP is combined with cotton fiber through the weak force, which is easy to fall off. After spraying, water vapor in the air is mainly used as a nucleophilic initiator to cause anionic polymerization of ECA to form PECA, and it can also be used as a catalyst to accelerate the polymerization of FOCS to form PFOCS (Fig S1), forming a superamphiphobic coating to protect APP and cotton fibers. The carboxyl group in APP and the hydroxyl group in cellulose and FOCS all contain lone electron pairs that are nucleophilic groups. By taking advantage of the binding ability of them to ECA, the coating covalently binds to the fabric Fig. 2. In addition, the huge amount of ester groups and Si–O-Si groups of the coating form strong hydrogen bonds with the hydroxyl groups of the cellulose to ensure that they are firmly fixed on the surface of the fabric.

![Fig. 2 Schematic illustration of chemical bonds between coatings and fabric](image-url)
Chemical compositions and surface morphology

The chemical composition of the fabric surface plays an important role in its wettability. EDS analysis was carried out to observe the chemical composition of the fabrics. As shown in Fig. 3a and Fig S2, after introducing APP on the cotton fabric, the content of P and N increased to 4.75 at% (atomic percentages) and 7.25 at%, while the content of O and C changed to 37.87 at% and 50.13 at%, respectively. Further, after spraying the superamphiphobic coating solution (Fig. 3b), the percentages of newly introduced F and Si elements were 10.91 at% and 0.67 at%, respectively, while the P and N on the surface of the fabric reduce to 2.39 at% and 5.05 at%, respectively, which indicates that the coating formed after spraying covers APP. In Fig. 3c and Fig S3, the EDS mapping images showed that the four elements of F, Si, P, and N were uniformly distributed on the surface of the fiber, suggesting the uniform coverage of flame retardant and low surface energy materials on the cotton fabric.

XPS could not only investigate the composition ratio of chemical elements on the surface but also verify whether new chemical bonds were formed. As shown in Fig. 3d, e, S4, and S5, compared with FC, the P and N elements on the surface of SFC decreased from 2.9 at% and 4.73 at% to 0.21 at% and 0.54 at%, respectively. However, a large amount of F (52.05 at%) and Si (3.43 at%) elements have been added. The main reason for the large difference between the F and

![Fig. 3](image-url)  
**Fig. 3** EDS of a FC and b SFC. c EDS mapping images of SFC. XPS spectra of d FC and e SFC. Schematic illustration f of the distribution of flame retardant (APP) adhesive (PECA) and amphiphobic agent (PFOCS) on cotton fabric. High-resolution g C 1s and h Si 2p spectrum of SFC. FTIR spectra i of cotton fabric, FC, and SFC.
P elements in the XPS and EDS analysis results of SFC is that the detection depth of the XPS test is about 10 nm, while the EDS is much deeper. This indicates that a large amount of F elements have migrated to the outermost layer of the fabric, thereby forming a low surface energy material to wrap the flame-retardant material, and completely cover the cotton fabric (Fig. 3f). To investigate the chemical bond structure in the superamphiphobic coating, we analyzed the high-resolution C1s and Si2p spectra of SFC (Fig. 3g, h). The C1s spectrum could be deconvoluted into six peaks centered at 284.58, 285.68, 286.58, 289.58, 292.28, and 294.48 eV, which corresponded to the C atoms in C–C, C–O, C=O, COO, C–F_2, and C–F_3, respectively. The appearance of two new peaks of C–F_2 and C–F_3 verified the successful wrapping of long fluorinated hydrocarbon chains from FOCS, indicating the robust superamphiphobicity of SFC. The Si2p spectrum could be deconvoluted into three peaks centered at 103.88, 102.48, and 101.78 eV, corresponding to Si–O–Si, Si–O–R, and Si–C, respectively. The appearance of the new Si–O–Si peak indicates that the FOCS has undergone a polymerization reaction to form a polymerized FOCS, which is defined as PFOCS.

The fabrics were analyzed by FTIR, and the result was presented in Fig. 3i. Compared to cotton, new peaks at 1441 and 1244 cm\(^{-1}\) belong to the P=O stretching peak. Those peaks indicate that FC was successfully fabricated. After the introduction of superamphiphobic coating solution, the peaks at 1212 and 1146 cm\(^{-1}\) appear, corresponding to the stretching vibration modes of CF_3 and CF_2 respectively. The peak at 1750 cm\(^{-1}\) is ascribed to stretching vibration of the mode of -COO- from PECA, and the peak at 1020 cm\(^{-1}\) is assigned to stretching vibration of the mode of Si–O–Si from PFOCS.

In addition to the chemical composition of the surface, the roughness of the fabric can enhance the wettability of the fabric. The surface morphology of cotton fabric, FC, and SFC were characterized by SEM, as shown in Fig. 4a, b, the cotton fibers have a smooth surface and a rod-like structure. Both the WCA and OCA on cotton fabric become 0° within 5 s and 1 s, respectively. Figure 4c, d clearly shows that after flame-retardant finishing, the APP particles are attached to cotton fibers and covers the individual cotton fibers. Since APP is water-soluble, the moisture absorption of cotton fabric was obviously enhanced, then the WCA on FC becomes 0° within 3 s (Fig S6). In contrast, as shown in Fig. 4e, f, the superamphiphobic coating completely covered the cotton fiber and APP after spraying, and the WCA and OCA of SFC can reach up to 161° and 158°, respectively (Fig. 4g–i).

**Thermal performance**

The thermal stability of the pristine cotton fabric, FC, and SFC were studied by TG analysis. As shown in Fig. 5a. The weight loss of cotton fabric and FC were around 4% below 150 °C, which was caused by evaporating adsorbed water of the cellulose. The first stage of degradation of cotton fabric occurred in the range of 305–400 °C, and the maximum weight loss was at 380 °C. The reason is the cellulose of cotton decomposed into volatile gases and aliphatic char (Gao et al. 2019). After 405 °C was the second stage, the weight decreased slowly, and the residual amount at 600 °C is 19.5%. In this stage, aliphatic char was converted into aromatic structures and released gases such as water, methane, carbon monoxide, and carbon dioxide. As shown in Fig. 5b, the degradation of FC and SFC mainly occurred in the range of 253–349 °C, the maximum weight losses were at 326 °C, 319 °C with weight losses of 24.8%, 31.1%, respectively. The reasons may be that the polyphosphoric acid produced by the dehydration of APP after about 253 °C is a strong dehydrating agent, which promoted the dehydration of cellulose and coatings into carbides. As the temperature rises further, the generated non-volatiles such as phosphorus oxides and polyphosphoric acid covered the surface of the fabric and isolated the air to achieve flame retardancy. The residual amount of FC and SFC at 600 °C was 44.5% and 34.8%. It suggested that APP could improve the thermal stability of cotton and more char residues were formed at high temperature, then the thermal stability of SFC was higher than that of cotton fabric.

**Flame-resistant properties**

The flame retardant property of cotton, FC, and SFC were investigated by LOI and vertical flammability test. It is generally believed that LOI < 20% belongs to flammable materials, and LOI > 27% belongs to flame-retardant materials. As shown in Fig. 5c, the cotton fabric is flammable material with an LOI value
Fig. 4  SEM images of a, b cotton fabric, c, d FC, e, f SFC. Photographs of water droplet (\( \sim 5 \, \mu L \)) contact angle (g) and corn oil droplet (\( \sim 5 \, \mu L \)) contact angle (h) on SFC. Digital photos of water, oil, ethanol, and DMF on SFC (i).

Fig. 5  a TG and b DTG curves of cotton, FC, and SFC. c LOI, d Char lengths and char of cotton, FC and SFC.
of 18.2%, and it was completely burnt during the vertical burning test (Fig S7). The afterburn time, afterglow time, and residual weight of the cotton fabric were 16 s, 21 s, and 0.5% (Fig. 5d), respectively. FC and SFC treated with APP achieved flame retardancy, with LOI values of 31.1 ± 0.4% and 30 ± 0.2% (Fig. 5c), respectively. When the fire source left the fabric, the flames on FC and SFC were immediately extinguished, the afterburning time and afterglow time were both 0, the remaining weight is 37.8 ± 1.6% and 27.6 ± 2.2%, and the char length was 11.6 ± 0.2 and 12.4 ± 0.2 cm, respectively (Fig. 5d). The char length of SFC was less than 13 cm, which met the required maximum char length value (10–15 cm) and passed the vertical burning test. The combustion residue was analyzed by SEM (Fig S8), and it was found that there were a large number of bubbles on the surface of the carbon layer, which was similar to the related research results of some previous scholars (Gao et al. 2019). The possible flame retardant mechanism is that APP can decompose at high temperature to produce free radicals (HPO2, PO, PO2, etc.), phosphoric acid and NH3. Free radicals can capture H/C1 and OH/C1, thus inhibit gas phase combustion reactions. Phosphoric acid can catalyze the dehydration of cotton fibers and PECA to cause carbonization. The released non-combustible gases, NH3, can foam carbon to form a dense physical barrier layer, which has the effect of shielding heat and oxygen. (An et al. 2020).

Self-cleaning and anti-fouling properties

As shown in Fig. 6a, the self-cleaning test of SFC was carried out using ash as a model pollutant. In this test, the fabrics were fixed on a glass slide with a tilted angle of ~ 20°, then a layer of ash was sprinkled on the surface of cotton fabric, FC, and SFC, respectively. When water and corn oil were continuously dropped onto the polluted surface, ash still stay on the cotton fabric and FC, and the pollution of the fabrics were aggravated (Fig S9). But the ash on the SFC was easily carried away by water and corn oil flow (Fig. 6a). Therefore, SFC could protect the fabric from soiling by letting ash roll off under a small force with liquid droplets.

Cotton fabric, FC, and SFC were separately submerged into different liquids by an external force to test their anti-fouling ability. After SFC was immersed into the liquid, a bright silvery sheen layer can be observed, called an air plastron (Shirtcliffe et al. 2006), which could reduce the interaction between the surface and liquid (Fig. 6b). Studies have shown that the thickness of air plastron is related to the chemical composition of the material surface and the surface tension of the liquid, while the stability of the air plastron of the surface determined the working effect of the SFC when it is applied in prolonged contact with liquids (Liu et al. 2021a, b). After taking them out of the liquids, the surface of the cotton fabric was wetted and soiled (Fig S10), but as illustrated in Fig. 6c, SFC remained entirely dry and clean. The above tests showed that SFC has excellent self-cleaning and anti-fouling properties, which can significantly reduce the number of washing cycles.

Chemical protective properties

The chemical protective properties of the fabrics were explored via chemical resistance tests to acids, alkalis, and organic solvents. For protective clothing, the long-term chemical repellence and stability are key indicators that determine their performance and application feasibility. Figure 7a, b illustrated the shape change of representative organic solvents droplets (THF and DMF) sitting on the top of the SFC against the contact time. During the test, the shape of the droplets gradually became smaller. After a long time of contact, until the solvents were completely volatilized, the length of the contact interface between the droplets and the SFC did not change, indicating the chemical repellency of SFC was excellent. As shown in Fig. 7c, The contact angles of methanol, ethanol, DMF, DMSO, acetone, THF, toluene, and MEK all were above 130°. In addition, SFC was immersed in 1 M HCl and 1 M NaOH respectively, and the contact angle was tested every 25 min to prove its chemical stability. As shown in Fig. 7d, WCA and OCA of SFC display no significant change, after being immersed in HCl for 100 minutes. And Fig. 7e showed, after 100 min in NaOH, contact angles of SFC remain over 150°. It can be proved that SFC can effectively avoid the occurrence of acid and alkali corrosion.

Durability and robustness

Although introducing superamphiphobic coatings on the surface of cotton fabric could efficiently enhance
superamphiphobicity, the robust mechanical performance, water resistance, and aging resistance are still major challenges. Generally, these fluorine-containing materials do not efficiently resist the deformation and...
abrasive due to that the low surface energy materials did not firmly adhere to the membranes. The mechanical durability of SFC was assessed by an abrasion resistance test. As shown in Fig. 8a, after being tested 400 cycles, WCA and OCA remain 153.1 ± 2.4° and 147.6 ± 2.2°, respectively. The washing resistance of SFC was tested by ultrasonic washing with a frequency of 40 kHz. Figure 8b showed that after 60 min test, WCA and OCA were changed from 159.1 ± 1.7°, 154.2 ± 3.0° to 154.5 ± 1.2°, 150.8 ± 3.6°, respectively.

UV irradiation and heat usually have a critical effect on the stability of the fabric and will cause it to age. As shown in Fig. 8c, SFC is exposed to 1000 W UV for 15 min each time, and its WCA and OCA were maintained above 158° and 152°, respectively, after 4 tests. Thermal endurance test was conducted by heating the SFC at different temperatures for 15 min. After 60 min heat treatment at 180 °C, WCA and OCA remained over 158° and 152°, which showed no significant change (Fig. 8d).

The FC finished with APP alone did not efficiently resist the erosion of water or polar solvents because the excellent water solubility of APP cannot resist being dissolved by solvents. However, the superamphiphobic coating greatly improves the flame-retardant stability of SFC. The flame retardancy of SFC after 400 cycles of abrasion, 60 min of ultrasonic washing, 60 min of UV irradiation, and 60 min of heating, respectively, were investigated by LOI test. As shown in Fig. 8e, after testing, the LOI value of SFC remained above 29%. And both of them extinguished immediately after leaving the flame, still maintaining excellent flame retardancy.

The results show that the above four tests have no significant effect on the superamphiphobicity and flame retardancy of SFC. According to SEM observation, the test has almost no damage to the structure of the SFC coating, except for abrasion. The damaged SFC was characterized using EDS (Fig. 8f). The proportions of C, N, O, F, Si and P elements are 49.75 at%, 6.21 at%, 30.59 at%, 9.54 at%, 0.65 at% and 3.26 at%, respectively. Compared with before abrasion, the ratio of each element hardly changed. And all elements are still evenly distributed on the surface of the fabric (Fig. 8g and S11). Furthermore, even SFC was severely damaged by the blade, water droplets and oil droplets remain spherical on the seriously worn-out area (Fig. 8h), and the SFC surfaces remained superamphiphobicity. It can be seen that the superamphiphobic coating has penetrated the interior of the fabric to protect the internal APP from being damaged.
Cellulose

(a) Experiment 1: Abrasion vs. WCA and OCA over 400 cycles.
(b) Experiment 2: Ultrasonic vs. WCA and OCA over 60 minutes.
(c) Experiment 3: UV exposure vs. WCA and OCA over 60 minutes.
(d) Experiment 4: Heating vs. WCA and OCA over 60 minutes.
(e) Flame retardant testing showing linear increase in LOI (%).
(f) Elemental analysis chart showing percentages of C, N, O, F, Si, P.
(g) Imaging of F, P, Si, N distribution.
(h) Sample images of cotton fiber, APP, coatings, airholes.

Mechanical force applied to cotton fiber, resulting in structural changes.
When damaged by an external force, as the wear area expands, the outer coating and fibers fall off, and the superamphiphobic coating embedded in the fiber gaps would be exposed, so that the fabric maintains the superamphiphobicity and flame retardancy (Fig. 8i).

### Wearability

The wearing comfort of the fabric ought to be taken into consideration in protective clothing. As shown in Fig. 9a, the bending length of SFC was tested using the inclined plane method, which increased from 2.6 to 8.5 cm. We used an intuitive method to prove the moisture permeability of SFC (Fig. 9b). First, covering the SFC on the top of the beaker containing hot water, then placing color-changing silica gels on the surface of the SFC, and finally covering it with a large beaker. After 8 min, the color-changing silica gels changed from dark blue to pink due to moisture absorption, and the droplet size on the surface of the SFC hardly changed, indicating that SFC has excellent moisture permeability. Figure 9c shows that the air permeability of cotton, FC, and SFC was 48.8, 39.9, and 37.2 mm/s, respectively, with a difference of 11.6 mm/s under the pressure difference of 50 Pa. As it increases to 200 Pa, the air permeability increases to 271.1, 146, and 125.9 mm/s, respectively, and the difference reaches 145.2 mm/s. This is because the superamphiphobic coating wraps the fibers in the fabric, but does not completely block the gap between them. The breaking strength (Fig. 9d) of FC and SFC reduced from 26.3 to 24.2 and 20.5 MPa, while the elongation at break decreased from 22.1% to 19.9% and 16.9%. These results indicate that the SFC still has satisfactory flexibility air permeability and mechanical behavior for protective clothing.

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**Fig. 8** WCA and OCA of SFC under a ultrasonic, b abrasion, c UV irradiation, and d Heating treatment. e LOI% of SFC after ultrasonic, abrasion, UV irradiation, and Heating treatment. EDS f of damaged SFC, EDS mapping images g of damaged SFC, h water and oil droplets on the damaged SFC i Schematic illustration of cotton fiber shedding and the arrangement of superamphiphobic coating on SFC during mechanical force

**Fig. 9** a Bending length of cotton, FC, and SFC. b Measurement method of moisture permeability. c Air permeability of cotton, FC, and SFC in different air pressure. d Typical breaking stress–strain curves of cotton, FC, and SFC

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Conclusions

We have demonstrated a simple and feasible strategy for the preparation of SFC through a step-by-step dip-coating and spraying technology. FOCS and ECA were coated onto the surface of FC covered with APP to construct a highly amphiphobic surface. As a result, SFC achieved integrated properties with WCA of 161°, OCA of 158°, LOI of 30%, and good wearability, which can provide a high level of protection as well as comfort. Furthermore, the superamphiphobicity also has endowed SFC with excellent self-cleaning, anti-fouling, and chemical protective properties. SFC still showed superamphiphobicity and flame-retardance after 400 cycles of abrasion, 60 cycles of ultrasonic washing, 60 min of UV irradiation (1000 W), and 60 min of heat treatment (180 °C), which lays a foundation for its large-scale applications. We believe that SFC is a promising candidate for the next generation materials of high-end protections. We believe that SFC is a promising candidate which lays a foundation for its large-scale applications. The authors thank the National Key R&D Program of China (2016YFC0802802), National Natural Science Foundation of China (51963020).

References

Abdelrahman MS, Khattab TA (2019) Development of one-step water-repellent and flame-retardant finishes for cotton. ChemistrySelect 4:3811–3816. https://doi.org/10.1002/slct.201900048
Ambekar RS, Deshmukh A, Suarez-Villagran MY et al (2020) 2D Hexagonal boron nitride-coated cotton fabric with self-extinguishing property. ACS Appl Mater Interfaces 12:45274–45280. https://doi.org/10.1021/acsami.0c12647
An W, Ma J, Xu Q et al (2020) Flame retardant, antistatic cotton fabrics crafted by layer-by-layer assembly. Cellulose 27:8457–8469. https://doi.org/10.1007/s10570-020-03556-7
Chen S, Li X, Li Y et al (2015) Intumescent flame-retardant and self-healing superhydrophobic coatings on cotton fabric. ACS Nano 9:4070–4076. https://doi.org/10.1021/acsnano.5b00121
Chen T, Hong J, Peng C et al (2019) Superhydrophobic and flame retardant cotton modified with DOPO and fluorine-silicon-containing crosslinked polymer. Carbohydr Polym 208:14–21. https://doi.org/10.1016/j.carbpol.2018.12.023
Chu Z, Seeger S (2014) Superamphiphobic surfaces. Chem Soc Rev 43:2784–2798. https://doi.org/10.1039/C3CS60415B
Deng X, Mammen L, Butt H-J et al (2012) Candle soot as a template for a transparent robust superamphiphobic coating. Science 335:67–70. https://doi.org/10.1126/science.1207115
Gao D, Zhang Y, Lyu B et al (2019) Nanocomposite based on poly (acrylic acid)/attapulgite towards flame retardant of cotton fabrics. Carbohydr Polym 206:245–253. https://doi.org/10.1016/j.carbpol.2018.10.113
Guo X-J, Xue C-H, Jia S-T et al (2017) Mechanically durable superamphiphobic surfaces via synergistic hydrophobization and fluorination. Chem Eng J 320:330–341. https://doi.org/10.1016/j.cej.2017.03.058
Hicyilmaz SA, Altin Y, Bedeloglu A (2019) Polyimide-coated fabrics with multifunctional properties: flame retardant, UV protective, and water proof. J Appl Polym Sci 136:47616. https://doi.org/10.1002/app.47616
Li G, Lee HJ, Michielsen S (2017) Design of abrasion resistant super-antiwetting nylon surfaces. New J Chem 41:13593–13599. https://doi.org/10.1039/C7NJ02807E
Li S, Lin X, Li Z et al (2019) Hybrid organic-inorganic hydrophobic and intumescent flame-retardant coating for cotton fabrics. Compos Commun 14:15–20. https://doi.org/10.1016/j.jccc.2019.05.005
Li S, Huang S, Xu F et al (2020) Imparting superhydrophobicity and flame retardancy simultaneously on cotton fabrics. Cellulose 27:3989–4005. https://doi.org/10.1007/s10570-020-03041-9
Lin D, Zeng X, Li H et al (2018) Facile fabrication of superhydrophobic and flame-retardant coatings on cotton fabrics via layer-by-layer assembly. Cellulose 25:3135–3149. https://doi.org/10.1007/s10570-018-1748-9
Lin D, Zeng X, Li H et al (2019) One-pot fabrication of superhydrophobic and flame-retardant coatings on cotton fabrics via sol-gel reaction. J Colloid Interface Sci 533:198–206. https://doi.org/10.1016/j.jcis.2018.08.060
Liu H, Wang Y, Huang J et al (2018a) Bioinspired surfaces with superamphiphobic properties: concepts, synthesis, and applications. Adv Funct Mater 28:1707415. https://doi.org/10.1002/adfm.201707415
Liu L, Huang Z, Pan Y et al (2018b) Finishing of cotton fabrics by multi-layered coatings to improve their flame retardancy and water repellency. Cellulose 25:4791–4803. https://doi.org/10.1007/s10570-018-1866-4
Liu J, Dong C, Zhang Z et al (2020) Multifunctional flame-retarded and hydrophobic cotton fabrics modified with a cyclic phosphorus/polyisiloxane copolymer. Cellulose 27:3531–3549. https://doi.org/10.1007/s10570-020-03016-w
Liu G, Xia H, Zhang W et al (2021a) Photocatalytic superamphiphobic coatings and the effect of surface microstructures on superamphiphobicity. ACS Appl Mater Interfaces 13:12509–12520. https://doi.org/10.1021/acsami.0c022982
Liu X, Chen J, Shao Q et al (2021b) Robust, flame retardant and colorful superamphiphobic aramid fabrics for extreme conditions. Sci China Tech Sci 64:1765–1774. https://doi.org/10.1007/s11431-020-1781-y
Luo G, Wen L, Yang K et al (2020) Robust and durable fluorinated 8-MAPOSS-based superamphiphobic fabrics with buoyancy boost and drag reduction. Chem Eng J 383:123125. https://doi.org/10.1016/j.cej.2019.123125
Moiz A, Padhye R, Wang X (2018) Durable superomniphobic surface on cotton fabrics via coating of silicone rubber and fluoropolymers. Coatings 8:104. https://doi.org/10.3390/coatings8030104

Nabipour H, Wang X, Song L et al (2020) Hydrophobic and flame-retardant finishing of cotton fabrics for water–oil separation. Cellulose 27:4145–4159. https://doi.org/10.1007/s10570-020-03057-1

Nie S, Jin D, Yang J et al (2019) Fabrication of environmentally-benign flame retardant cotton fabrics with hydrophobicity by a facile chemical modification. Cellulose 26:5147–5158. https://doi.org/10.1007/s10570-019-02431-y

Pan S, Kota AK, Mabry JM et al (2013) Superomniphobic surfaces for effective chemical shielding. J Am Chem Soc 135:578–581. https://doi.org/10.1021/ja310517s

Pan S, Guo R, Björnalm M et al (2018) Coatings super-repellent to ultralow surface tension liquids. Nat Mater 17:1040–1047. https://doi.org/10.1038/s41563-018-0178-2

Shibuichi S, Yamamoto T, Onda T et al (1998) Super water-and oil-repellent surfaces resulting from fractal structure. J Colloid Interface Sci 208:287–294. https://doi.org/10.1006/jcis.1998.5813

Shirtcliffe NJ, McHale G, Newton MI et al (2006) Plastron properties of a superhydrophobic surface. Appl Phys Lett 89:104106. https://doi.org/10.1063/1.2347266

Siddig E, Xu Y, He T et al (2020) Plasma-induced graft polymerization on the surface of aramid fabrics with improved omniphobicity and washing durability. Plasma Sci Technol 22:055503. https://doi.org/10.1088/2058-6272/ab55d8

Suryaprabha T, Sethuraman MG (2018) Fabrication of superhydrophobic and enhanced flame-retardant coatings over cotton fabric. Cellulose 25:3151–3161. https://doi.org/10.1007/s10570-018-1757-8

Tsujii K, Yamamoto T, Onda T et al (1997) Super oil-repellent surfaces. Angew Chem Int Ed 36:1011–1012. https://doi.org/10.1002/anie.199710111

Tuteja A, Choi W, Ma M et al (2007) Designing superoleophobic surfaces. Science 318:1618–1622. https://doi.org/10.1126/science.1148326

Wang H, Zhou H, Gestos A et al (2013) Robust, superamphiphobic fabric with multiple self-healing ability against both physical and chemical damages. ACS Appl Mater Interfaces 5:10221–10226. https://doi.org/10.1021/am4029679

Wang B, Peng S, Wang Y et al (2019) A non-fluorine method for preparing multifunctional robust superhydrophobic coating with applications in photocatalysis, flame retardance, and oil–water separation. New J Chem 43:7471–7481. https://doi.org/10.1039/C9NJ01318K

Wang W, Wang J, Wang X et al (2020) Improving flame retardancy and self-cleaning performance of cotton fabric via a coating of in-situ growing layered double hydroxides (LDHs) on polydopamine. Prog Org Coat 149:105930. https://doi.org/10.1016/j.porgcoat.2020.105930

Xue C, Zhang L, Wei P et al (2016) Fabrication of superhydrophobic cotton textiles with flame retardancy. Cellulose 23:1471–1480. https://doi.org/10.1007/s10570-016-0885-2

Yeerken T, Yu W, Feng J et al (2019) Durable superamphiphobic aramid fabrics modified by PTFE and FAS for chemical protective clothing. Prog Org Coat 135:41–50. https://doi.org/10.1016/j.porgcoat.2019.05.022

Zhang M, Zhang D, Shi J et al (2015) Superhydrophobic cotton textile with robust composite film and flame retardancy. RSC Adv 5:67780–67786. https://doi.org/10.1039/C5RA09963C

Zhao J, Wang X, Liu L et al (2018) Human skin-like, robust waterproof, and highly breathable fibrous membranes with short perfluorobutyl chains for eco-friendly protective textiles. ACS Appl Mater Interfaces 10:30887–30894. https://doi.org/10.1021/acsami.8b10408

Zhou X, Sun S, Zhang C et al (2020) Facile fabrication of durable superamphiphobic PET fabrics. J Coat Technol Res 17:711–718. https://doi.org/10.1007/s11998-019-00289-0

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