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Water Repellent Treatment of Cotton Fabrics by Electron Beam Irradiation

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Abstract: In this study, traditional dip-pad-cure (DPC) process and electron beam (EB) irradiation were used to graft cotton fabrics with fluorine containing chemical, 1H,1H,2H,2H-perfluorooctyl acrylate (PFA). The grafted cotton fabrics were characterized by FT-IR and SEM. The water repellent properties were measured by contact angle, hydrostatic pressure, and spry test. It was found that there was no significant difference between the grafted cotton fabrics with DPC and EB methods, and the treated fabrics showed good water-resistant properties. The grafted cotton fabrics also showed good washing stability. By measuring the bending rigidity and bending hysteresis, it was found that the cotton fabrics grafted with PFA became softer than untreated samples.

Keywords: Cotton fabric, Water-repellency, Dip-pad-cure process (DPC), Electron beam irradiation (EB)

Introduction

In recent years, functional textiles have attracted much more attentions in academic and industrial areas owing to their potentials for a wide range of applications with functionalities such as antimicrobial property, UV-radiation protection, self-cleaning, anti-wrinkle, superhydrophobicity, and flame retardancy [1,2]. The development trend can be attributed to the various modification techniques available ranging from traditional methods to biological processes [3]. Among these, textile finishing with chemicals is a common method to improve or impart new properties of natural and synthetic fibers [4].

As one of most popular textiles, cotton fabric has specific characteristics of softness, comfortability, superior moisture absorption, biodegradability, air permeability, and good mechanical properties [5,6]. Although cotton fabric has wide range of applications in many fields, the poor water-repellent properties limits its utilization in some areas [7]. Recently, to expand the application of cotton fabric, many attempts have been made to increase the hydrophobicity of cotton fabric. The water-repellent fabrics with high contact angle exhibit a self-cleaning effect, and have a broad application such as carpets, rain coats, umbrellas, shoes, skiing dresses, motorcycle clothes, and jackets [5,8]. Increasing the degree of roughness and lowering the surface energy are two basic ways to fabricate hydrophobic materials [5,9-11]. Introducing some hierarchical structures such as nano-particles TiO_2, SiO_2, and ZnO on the surface of textile fibers could increase the surface roughness [4,9,11]. Methods such as sol-gel chemistry [7,12], gas phase coating [13], and plasma etching [14] have been used to create a relatively rough surface on the materials. Chemical modification of fabrics with hydrophobic substance is another way to prepare hydrophobic materials by lowering the surface energy [4,9]. Fluorine containing chemicals are the current most favorable hydrophobic agents since they have low surface free energy and increase the hydrophobicity of the textile substrates by forming a water-repellent film on the surface [4,5,7]. Wi and his co-workers prepared a type of water repellent cotton fabrics with poly(tetrafluoroethylene) (PTFE) by sputtering technique [15]. Fluoroalkylsiloxanes, which can react with hydroxyl groups on the surface of cellulose, were synthesized and used to produce water- and oil-repellent cotton fabrics [16-18]. To further increase the hydrophobic properties, some fluoromonomers were polymerized to produce fluorinated polymers *in situ* by free radical initiators and then coated onto the cotton fabrics [19-21].

Recently, EB technique has received much attention in surface modification of textiles. Compared with the traditional finishing technique, EB irradiation has advantages of high efficiency, uniform cross-linking, energy-saving, and less environmental hazardousness [22]. Three types of carbon centered radicals can be formed in the cellulose fibers by EB irradiation, which might lead to higher grafting rate than the traditional grafting method by radical initiators. In addition, EB irradiation method has less effect on the physical and mechanical properties of cotton fabrics with irradiation ranging from 20 to 200 kGy. In this study, hydrophobic cotton fabrics were prepared by grafting a fluoromonomer, 1H,1H,2H,2H-perfluorooctyl acrylate (PFA), with electron beam irradiation (EB) and traditional dip-pad-cure process (DPC). The surface of the grafted cotton fabrics with EB were characterized by FT-IR spectra and SEM. The hydrophobicity and durability of the treated cotton fabrics were investigated.

Experimental

Materials and Instruments

Cotton fabrics were provided by Zhejiang Guangdong Printing & Dyeing Company, Zhejiang, China. 1H,1H,2H,2H-

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Perfluorooctyl acrylate (PFA) was bought from Silworld Chemical Co., Ltd., Wuhan, China. Other chemicals used in this study were obtained from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. The grafted cotton fabrics were characterized by a Nicolet iS 10 FT-IR spectrometer (Thermo Scientific, USA) and a SU1510 scanning electron microscope (Hitachi, Japan).

Preparing of Water-repellent Cotton Fabrics

DPC Process

In a typical run, cotton fabrics were soaked in the finishing solution containing 4 % PFA and 0.16 % 2,2'-azobis(2-methylpropionitrile) (AIBN) for 15 min, followed by two dips and two pads (wet pick-up 75 %). Then the cotton fabrics were dried at 110 °C for 120 s and cured at 180 °C for 120 s. The treated cotton fabrics were washed thoroughly with alcohol and distilled water to remove the homopolymer, and dried in an oven.

EB Irradiation

The cotton fabrics were soaked in the solution containing 4 % PFA for 15 min, followed by two dips and two pads (wet pick-up 75 %). Then, the cotton fabrics were irradiated by EB (22 kGy), and dried at 120 °C for 120 s. The treated cotton fabrics were washed thoroughly with alcohol and distilled water to remove the homopolymer, and dried in an oven.

Evaluation of Water Resistance Properties

The water repellency properties of the grafted cotton fabrics were measured with the following three methods.

Spray Test

According to AATCC 22, the test samples were fastened securely in the hoop, and the surface of the sample was exposed to the water spray for 25-30 s.

Water Contact Angle

The contact angle was determined in a JC2000D contact angle meter. Five duplicates were detected and their average value was calculated to evaluate the hydrophobic properties of the grafted cotton fabrics.

Hydrostatic Pressure Test

According to AATCC 127, hydrostatic pressure test was performed to measure the force required by water to penetrate through textile material under a constantly increasing water pressure until three leakage points appeared on its surface. Five readings were read and the average was recorded.

Washing Stability of the Treated Cotton Fabric

The washing stability of the grafted cotton fabrics was determined according to AATTC 135-2000 standard. The fabrics were cut into 1×2 in^2. The prepared samples were placed in stainless steel canisters containing 50 stainless steel balls and 150 m*l* of 0.15 % AATCC detergent water solution. After washed for the equivalents of 5 and 10 machine washes in a Launder-Ometer, samples were taken out and dried before contact angle was measured.

KES Bending Properties Test

The softness was measured by detecting bending rigidity and hysteresis in a KES-FB2-AUTO-A automatic bending test machine.

Results and Discussion

Characterization of the PFA-Grafted Cotton Fabrics

To confirm PFA successfully grafted onto the cotton fibers with methods of DPC and EB processes, the FT-IR spectra of untreated cotton fabrics (A), PFA-grafted cotton fabrics with DPC process (B), and PFA-grafted cotton fabrics with EB process (C) were obtained and the results were presented in Figure 1. Compared with the untreated cotton fabric, the peaks appearing at 1742 cm^{-1} in the PFA grafted cotton fabric with DPC and EB processes were corresponding to carbonyl bond of PFA. The additional peaks at 1251 cm^{-1}, 1247 cm^{-1}, 800 cm^{-1}, and 798 cm^{-1} were due to the introduction of C-F bond to the cotton fabrics. There was no significant difference between the PFA grafted cotton fabrics with DPC and EB processes, which indicates that PFA could be grafted onto cotton fabrics with the two methods.

The surface micrographs of untreated cotton fabrics (A), PFA-grafted cotton fabrics with DPC process (B), and PFA-grafted cotton fabrics with EB process (C) were shown in Figure 2. Unlike the smooth surface of untreated samples, the PFA grafted cotton fabrics with DPC and EB processes had rough coverage on the surface, which provides evidence that the water repellent agent PFA was attached onto the surface of cotton fabrics.

Water Resistance Properties

Despite many superior characteristics, the poor water

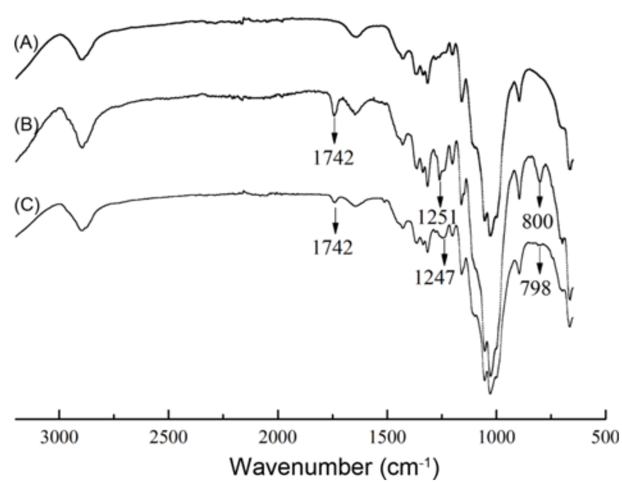

Figure 1. FTIR spectra of (A) cotton fabrics, (B) PFA-grafted cotton fabrics with DPC process, and (C) PFA-grafted cotton fabrics with EB process.

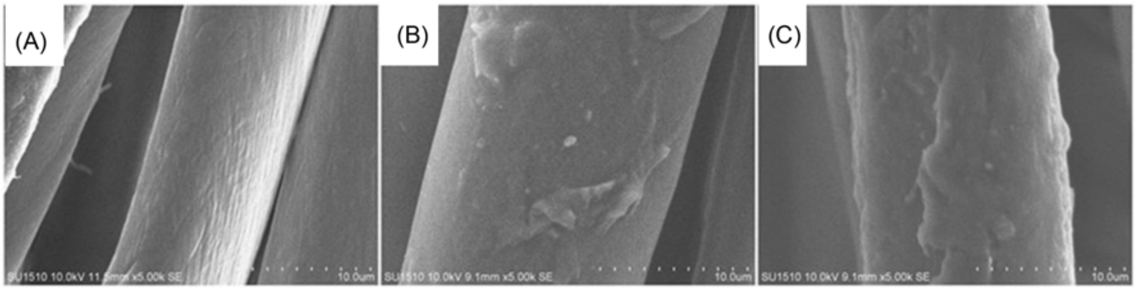

Figure 2. SEM micrographs of (A) cotton fabrics, (B) PFA-grafted cotton fabrics with DPC process, and (C) PFA-grafted cotton fabrics with EB process.

Table 1. The results of spry and hydrostatic pressure tests

Samples	Water repellent grade[a]	Hydrostatic pressure (mm H_2O)
Control	50	200
PFA-cotton-DPC[b]	100	251
PFA-cotton-EB[c]	100	244

[a]Water repellent grade was measured by spry test, [b]PFA-cotton-DPC: PFA-grafted cotton fabrics with DPC process, and [c]PFA-cotton-EB: PFA-grafted cotton fabrics with EB process.

repellency of cotton fabric restricted its application in some areas. Water repellent finishing is a good way to solve the problem. Over the past decades, fluorine containing chemicals have been widely used in cotton fabric finishing because fluorine containing chemicals have low surface free energy which makes them the most important water and oil repellents [23,24]. In this study, cotton fabrics were grafted with fluorine containing water repellent agent PFA with the DPC process and EB irradiation. The water repellency of the PFA grafted cotton fabrics was measured by three test methods: spray test, hydrostatic pressure test, and contact angle test.

To evaluate the water-repellent properties under more real condition like rain, the spray and hydrostatic pressure tests were carried out. The experimental results were presented in Table 1. Compared with control samples (rated at 50), both the PFA grafted cotton fabrics by process DPC and EB irradiation showed good water repellency with rate of 100. It could be confirmed that the efficient hydrophobic property could be attained and the treated fabrics could withstand higher water pressure until the leakage points appeared.

The wettability of the treated cotton fabrics was investigated by water contact angle, and the results were shown in Figure 3. The control cotton can be completely wet by water (Figure 3(A)) due to abundant amount of hydroxyl groups in the fibers. Most of the hydrophilic groups can be blocked and the surface energy of fabrics decreased sharply after grafting with fluorine containing chemicals, and the grafted cotton fabrics became difficult to wet. Compared with untreated samples, the PFA grafted cotton fabrics prepared by DPC and EB methods showed high water contact angles of 140 ^{o} and 137 ^{o}, respectively (Figure 3(B) and 3(C)).

Washing Durability of Water Repellent Properties

The washing durability of the water repellent properties needs to be investigated in the practical application of hydrophobic textiles. The surface contact angles of cotton fabrics before and after grafted with PFA by the two methods were listed in Table 2. It can be seen that the PFA grafted cotton fabrics had much better water repellence properties compared with the control. Even after 10 washing cycles, the contact angle of the grafted fabrics was around 130 ^{o}, and good water repellence property was maintained. The PFA grafted cotton fabrics with DPC and EB methods showed the same results, and the surface contact angle

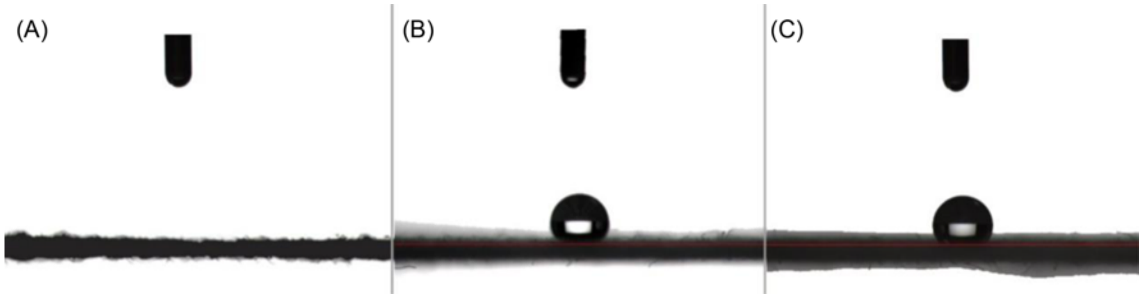

Figure 3. Contact angles of (A, 0 ^{o}) cotton fabrics, (B, 140 ^{o}) PFA-grafted cotton fabrics with DPC process, and (C, 137 ^{o}) PFA-grafted cotton fabrics with EB process.

Table 2. Water contact angles of samples with various washing cycles

Washing cycles	Contact angles (°)		
	Control	PFA-cotton-DPC[a]	PFA-cotton-EB[b]
0	0	140	137
5	0	133	135
10	0	128	132

[a]PFA-cotton-DPC: PFA-grafted cotton fabrics with DPC process and [b]PFA-cotton-EB: PFA-grafted cotton fabrics with EB process.

Table 3. KES bending properties of cotton fabrics and the PFA grafted cotton fabrics

Samples	Bending rigidity ($cN \cdot cm^2/cm$)		Bending hysteresis ($cN \cdot cm^2/cm$)	
	Warp	Weft	Warp	Weft
Cotton	0.0779	0.0269	0.0352	0.0158
PFA-cotton-DPC[a]	0.0359	0.0142	0.0213	0.0104
PFA-cotton-EB[b]	0.0364	0.0135	0.0246	0.0114

[a]PFA-cotton-DPC: PFA-grafted cotton fabrics with DPC process and [b]PFA-cotton-EB: PFA-grafted cotton fabrics with EB process.

decreased slightly with the increase of washing cycles. The covalent bonds between cotton fibers and PFA were very stable to the continuous washing, and the grafted cotton fabrics had a great washing durability.

KES Bending Properties

The softness of the grafted cotton fabrics was determined by measuring the bending rigidity and bending hysteresis with KES bending test machine. The bending rigidity and bending hysteresis affect the handle of the treated fabrics. The lower the bending rigidity and bending hysteresis are, the higher softness of the fabrics was obtained [25]. The bending properties of the cotton fabrics were changed after the water-repellent finishing. Table 3 showed the bending properties (bending rigidity and bending hysteresis) of untreated cotton fabric and the PFA grafted cotton fabrics with DPC and EB methods. The results indicated that the bending rigidity and bending hysteresis decreased after the treatment, which indicates that the PFA grafted cotton fabrics were softer than control sample. There is no significant difference between the fabrics treated with DPC and EB regarding to bending rigidity and bending hysteresis.

Conclusion

Fluorine containing hydrophobic agent, 1H,1H,2H,2H-perfluorooctyl acrylate (PFA), was grafted onto the cotton fabrics to prepare superhydrophobic materials with DPC and EB irradiation processes. The grafted cotton fabrics with the two methods showed good water-resistant properties and washing durability. Even after 10 washing cycles, the grafted cotton fabrics still showed good water repellency. It was also found that the grafted cotton fabrics had lower bending rigidity and bending hysteresis, which indicates that the PFA grafted cotton fabrics were softer than control samples. Compared with traditional DPC process, the same result can be obtained by EB irradiation process under lower temperature and without initiator.

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