

Surface modification of cotton fabric to create water repellence property via atom transfer radical polymerization

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Abstract. To enhance the water repellent property of cotton fabric, cotton was grafted using dodecafluoroheptyl methacrylate (DFHMA) monomer via atom transfer radical polymerization (ATRP) method in aqueous media. The structure of grafted cotton fabric was characterized by scanning electron microcopy (SEM) and X-ray photoelectron spectroscopy (XPS). The results showed that DFHMA was successfully grafted onto the surface of cotton fabric. Compared with the control cotton fabric, the surface contact angle test showed that the water repellence of the grafted cotton fabric was better. The surface contact angle of the grafted cotton fabric could reach 150.0°. Furthermore, the washing durability of the grafted fabric was also investigated. The surface contact angle of the grafted cotton fabric could reach 145.3° after 20 times washing. The whiteness, air permeability and moisture regain of the grafted cotton fabric decreased slightly compared with the control cotton fabric. Cotton fabric with good water repellent property and great washing durability could be obtained, which had little effect on the intrinsic properties of cotton fabric.

1. Introduction

Cellulose, one of the most abundant natural organic materials, has always been the principal fiber for clothing due to its attractive characteristics [1, 2]. The unique structure and versatile properties make cellulose very important as a sporting material. Although cotton has large-scale application in many fields, it has bad water repellent property, which limits the utilization of cotton in wide range of areas. Therefore, it is necessary to improve the water repellent property of cotton fabric.

ATRP has been independently developed by Matyjaszewski and Sawamoto in 1995 [3]. It has been successfully used to prepare a wide variety of well-defined polymeric materials including functional polymers, gradient, and segmented copolymers as well as hybrid materials [4, 5]. The particular advantages of ATRP, well-controlled chain length and low polydispersity, are of great importance for the permanent tailoring of the cellulosic surface.

In this work, cotton was grafted with dodecafluoroheptyl methacrylate (DFHMA) monomer through ATRP in aqueous media [6]. The structure and properties of the grafted cotton fabric were analyzed by different techniques.

2. Results and Discussion.

2.1 Surface morphology.

The SEM images (Fig. 1) show the surface morphology of control and grafted cotton fabric with DFHMA, respectively. It could be seen that control cotton fibers had a typically smooth surface (Fig. 1a). The surface of DFHMA grafted cotton (Fig. 1b-e) was similar to that of the control cotton. And the surface of cotton fabric was also smooth with graft yield increasing gradually. It showed that grafting had almost no effect on the surface of cotton fabric. The homopolymer on the fabric surface in ATRP grafting system was not so much as the traditional radical grafting system. Because in the

ATRP grafting system there was no initiator in the grafting solution, theoretically the monomer could only react with the macroinitiator [7].

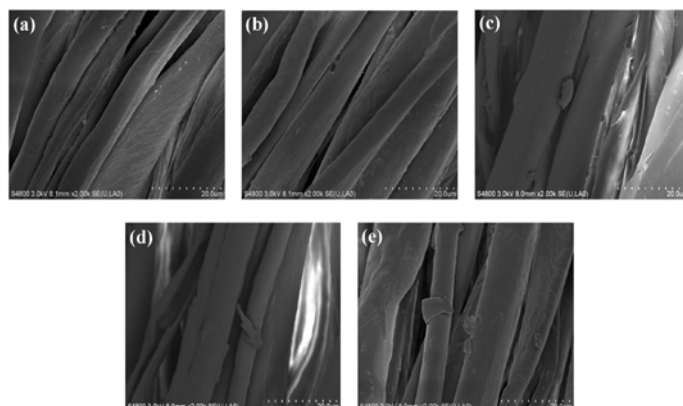


Fig. 1 Scanning electron micrograph of cotton fabric. (a) control cotton sample, DFHMA grafted cotton samples with 10.72% (b), 19.12% (c), 25.87% (d) and 34.42% (e) of graft yield

2.2 XPS.

The respective XPS wide-scan (a) and C1s core-level (b) spectra of the control cotton fabric, and the respective XPS wide-scan (c) and C1s core-level (d) spectra of grafted cotton fabric are shown in Fig. 2.

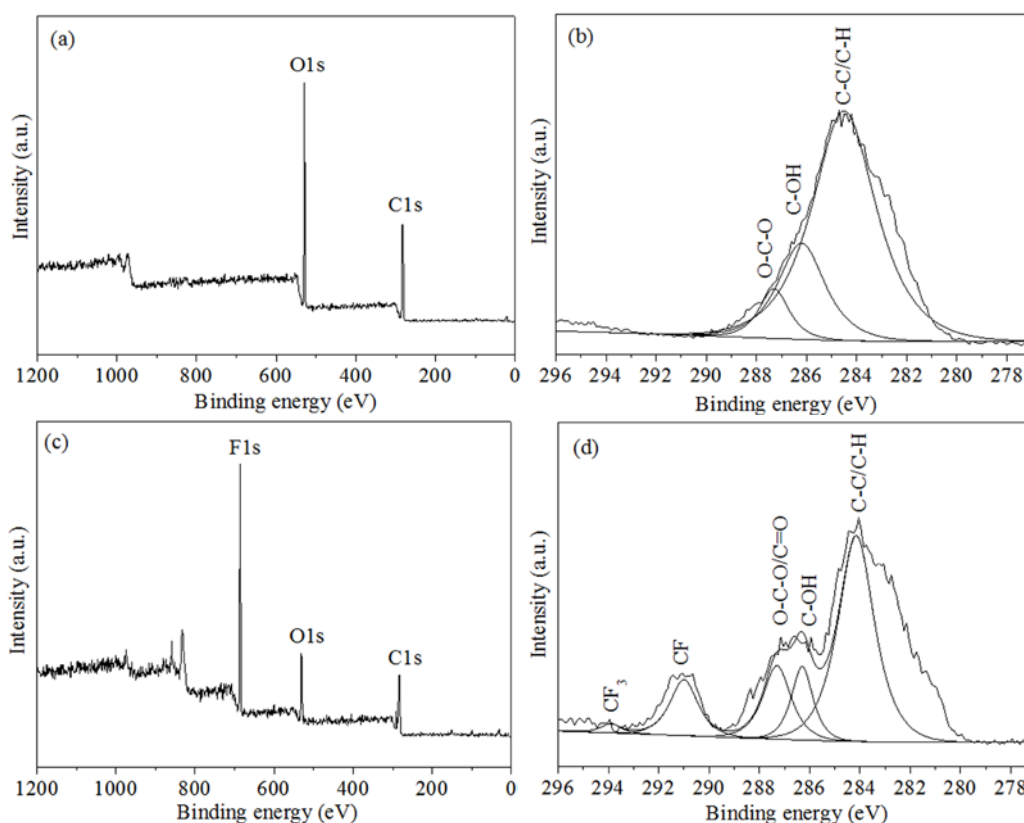


Fig. 2 X-ray photoelectron spectroscopy wide-scan and C1s core-level spectra of control cotton fabric (a and b) and grafted cotton fabric(c and d, 27.19 % of graft yield)

Compared with the typical wide-scan XPS spectrum of control cotton fabric, two major binding energy peaks at 284.9 eV for C1s, 531.7 eV for O1s were almost unchanged. A new peak at 688.2 eV of binding energy occurred for the wide-scan spectrum of grafted cotton fabric, which was attributed to C-F bond. In addition, the C1s core-level spectrum of the control cotton showed three distinct peaks at 284.4 eV (-C-C-), 286.0 eV (-C-OH), and 287.3 eV (-O-C-O-). These peaks were attributed

to the bonds present in the cotton. After grafting treatment, the C1s spectra showed the peaks at 287.3 eV (-C=O), 290.9eV (-CF), and 293.8 eV (-CF₃) [8, 9]. The XPS indicated that fluorine containing side chain covered or distributed onto cotton fabric surface.

2.3 Surface contact angle.

The surface contact angle of cotton fabrics are listed in Table 1. As graft yield increasing gradually, the water contact angle of cotton fabric increased. When graft yield was 34.42%, the surface contract angle of DFHMA grafted cotton fabric was 150.0°, which indicated that the grafted cotton fabric obtained good water repellence property. And the surface contact angle of DFHMA grafted cotton fabric did not increase when graft yield achieved 38.87%. The grafting occurred mainly in the amorphous region of cotton, and DFHMA might block certain hydrophilic groups of cotton macromolecules, which decreased the hygroscopic properties of cotton fabrics. In addition, the fluorine containing long carbon chain was surrounded by the fluorine atoms, and the fluorine-containing segment spread onto the fabric surface. It formed a special brush-like structure which could reduce the surface tension of the fabric and formed more remarkable space shielding effect. When the graft yield increased to a certain degree, it had no promoting effect to the surface contact angle because the density of cotton fabric surface fluoride groups reached saturation. The results of washing fastness testing after 0, 5, 10, 15 and 20 times of washing show that the surface contact angle of the grafted cotton fabrics have better water repellence compared with the control fabric. With the washing times increasing, the surface contact angle just slightly decreased, which can be explained by the fact that the washing would not affect the covalent bond between cotton and DFHMA. Consequently, the grafted cotton fabrics had a great washing durability.

Table 1 Water contact angles of cotton fabrics with various washing times

Samples	Graft yield (%)	Surface contact angle (°)				
		after 0 times washing	after 5 times washing	after 10 times washing	after 15 times washing	after 20 times washing
Control	0	0	0	0	0	0
DFHMA graft	12.92	143.5	140.5	139.6	139.1	138.4
	27.50	149.0	148.3	147.8	145.5	144.7
	34.42	150.0	148.6	147.4	146.1	145.3
	38.87	140.1	138.3	137.8	136.5	134.2

2.4 Physical Properties.

It can be seen from Table 2 that the whiteness, air permeability and moisture regain of grafted cotton fabric slightly decreased compared with the control sample.

Table 2 Whiteness, permeability and moisture regain of cotton fabric

Samples	Graft yield (%)	Whiteness (%)	Air permeability (mm/s)	Moisture regain (%)
Control	0	81.8	119.0	9.4
DFHMA graft	12.92	69.9	89.2	5.3
	27.50	67.2	80.9	5.0
	34.42	64.5	79.2	3.8
	38.87	61.3	72.9	4.4

With the increase of graft yield, the air permeability of the grafted cotton fabric decreased. This was due to the pore size between the interstices of cotton fibers became smaller, which derived from the grafting of DFHMA monomer onto the cotton fabric. A decrease of whiteness of grafted cotton fabric was noticed owing to the influence of TEA and metal catalyst after the grafting treatment. The decline of moisture regain was attributed to the decrease of grafted cotton surface hydrophilic groups and the space shielding effect of fluoride groups. However, under the circumstances of less affecting

the intrinsic properties of cotton fabric, cotton with good water repellence property could be obtained by properly controlling the graft yield.

3. Conclusions.

In this study, DFHMA was covalently bonded onto the surface of cotton fabric via ATRP method. The SEM and XPS analysis results confirmed that DFHMA was successfully grafted on the surface of the cotton fabric. The surface contact angle of the grafted cotton fabric could reach 150.0°, and the contact angle of grafted cotton fabric increased with the graft yield increasing. The grafted cotton fabric had a good washing durability. Cotton fabric with good water repellent property was successfully obtained, which had little effect on the fabrics wear ability.

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