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Preparation of breathable, fluorine-free cotton fabric with robust hydrophobicity

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The fluorine-containing finishing agents commonly used for water repellent modification of cotton textile surfaces have been banned in most countries and regions because they have been proved to be seriously harmful to human beings and the environment, while non-fluorine hydrophobic modification of textiles suffers from the defect of non-durable performance. In this study, we propose a durable, fluorine-free and environmentally friendly approach for hydrophobic modification of cotton textiles: firstly, macromolecular polyurethane hydrophobes with vinyl groups are synthesized; subsequently, electron beam (E-beam) irradiation is used to generate reactive radicals on the surface of cotton fabrics, which triggers the graft polymerization of vinyl-based polyurethane (VPU) hydrophobes on the surface of the fabrics, resulting in the formation of covalently bonded, solid polyurethane hydrophobic layers on the surface of the fabrics. The hydrophobicity of the grafted cotton fabric was significantly improved and remained virtually unchanged after 20 accelerated washing cycles (equivalent to 100 times of household washing), which can be attributed to the robust covalent bonding between the hydrophobic polyurethane groups and the cotton fabric, thereby ensuring long-term stability of the hydrophobic performance. The scanning electron microscope (SEM) characterization and mechanical property test demonstrated that the radiation grafting of the macromolecule urethane hydrophobes had a small effect on the micro-morphology and mechanical properties of the cotton fabrics. The results of air permeability and moisture permeability of textiles proved that the method in this study can give better hydrophobicity to cotton fabric without affecting its air permeability and moisture permeability.

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1. Introduction

Cotton, as a natural textile, is considered to be an ideal substrate for making hydrophobic fabrics due to its low cost, high comfort and skin-friendly breathability.^{1–3} Hydrophobic fabrics exhibit excellent water repellency while maintaining favorable breathability and comfort,^{4,5} rendering them suitable for a wide range of applications in areas such as outdoor equipment, medical protection, and daily apparel.^{6–8} However, it is still a challenge to prepare hydrophobic cotton fabrics that are both environmentally benign and highly durable.

The modification of hydrophobicity of textiles mainly relies on water repellents. Traditional fluorinated repellents⁹ were once widely employed owing to their low surface free energy and high bond energy of C–F bonds,¹⁰ but their use has been banned due to their pollution of the environment, damage to human health and other factors.^{11–13} Current textile water repellents mainly rely on silicone¹⁴ and polyurethane¹⁵ water repellents. Polyurethane water repellents with excellent environmental protection, safety and energy saving are widely used in textile and other fields,^{16–18}

while polyurethane can give excellent water repellency to fabrics and strong adhesion fastness to fabrics. Liu *et al.*¹⁹ prepared a water repellent with adjustable water repellency (GWPUs) and a contact angle of up to 148° using self-emulsification and simple impregnation, however, it was not tested for washing resistance. Wang *et al.*²⁰ used free radical polymerization and impregnation indentation to prepare a water repellent polyurethane agent (WPUA) with a core–shell structure, with a contact angle of up to 151°, but the contact angle showed a decreasing trend with the increase of the number of washes, which indicated that the water repellency effect of the method was not long-lasting. Zhou *et al.*²¹ prepared glycerol monostearate (GMS)-modified hydroxyl-capped polysiloxane waterborne polyurethanes with a contact angle of up to 115.4°, however, due to the uncontrollable nano-particle size of the emulsions, they are not suitable for large-scale production applications. Sheng *et al.*²² prepared stearly acrylate modified waterborne polyurethane water repellents by self-emulsification and free radical copolymerization, with a contact angle of up to 141.5°. However, as the interaction between the water repellent agent and the fabric is based on the physical action of polar chemical bonding, some of the water repellent agent will be detached from the fabric during the washing process, which leads to a decrease in the water repellency of the treated fabric.

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Therefore, it is necessary to prepare a low-cost, long-lasting and environmentally friendly water repellent.

E-beam irradiation technology has significant advantages such as uniform surface treatment, high efficiency and environmental friendliness.²³⁻²⁵ In recent years, this technology has been widely used in textile dyeing,²⁶ antibacterial,²⁷ whitening²⁸ and other fields. This technology triggers the generation of free radicals from cotton by E-beam, which undergoes a graft polymerization reaction with vinyl monomers, resulting in the formation of covalent bonding.²⁹ As a result, cotton fabrics processed by E-beam irradiation technology tend to have better durability.

In this study we have prepared a durable hydrophobic cotton fabric using E-beam irradiation technique. Firstly, a VPU was synthesized and subsequently grafted onto cotton fibers under E-beam irradiation, which resulted in covalent bonding between the vinyl-functionalized polyurethane and the cotton fibers. The successful introduction of vinyl groups into the polyurethane was confirmed by ^1H NMR. The grafted cotton fabrics were characterized and analyzed by SEM and FTIR, the hydrophobicity was proved by contact angle test, the hydrophobic durability was tested by accelerated washing, and finally the air permeability and moisture permeability and mechanical properties of the cotton fabrics were tested. The results demonstrate that the proposed approach yields hydrophobic cotton fabrics with strong potential for practical applications.

2. Experimental

2.1 Materials

Pentaerythritol distearate (PEDS), dibutyltin dilaurate (DBTDL), isophorone diisocyanate (IPDI), 4-hydroxybutyl acrylate,

hydroquinone monomethyl ether and ethyl acetate were purchased from Macklin reagent (China). Cotton fabric GB/T7568.2-2008 was purchased from Shanghai Textile Industry Institute of Technical Supervision. All reagents were used without further purification.

2.2 Preparation of VPU

PEDS (6.69 g) was weighed in a 100 ml three-necked flask and dried in an oven at 60 °C for 10 h. Ethyl acetate (7 g) was added and stirred by heating in an oil bath to 70 °C. IPDI (4.4 g) and DBTDL (22 mg) were dissolved in ethyl acetate (5 g) and added into the system at a rate of 1 drop per second, and the prepolymer was prepared by reacting for 2 h after the drop was completed.

4-Hydroxybutyl acrylate (1.44 g), DBTDL (7 mg) and hydroquinone monomethyl ether (7 mg) were dissolved and added into the prepolymer system, and the reaction was continued for 3 h to produce 50% acrylate capped polyurethane. The synthetic route is shown in Fig. 1.

2.3 Preparation of cotton-g-VPUs

The standard cotton samples of 15 cm × 20 cm were cut, washed and dried in an oven at 60 °C for 4 h. A series of grafting solutions with concentration gradients were prepared in a beaker with the mass ratio of the standard cotton cloth to the mass ratio of the ethanol solution (bath ratio) of 1 : 5, and the beaker was placed into an ultrasonic machine for ultrasonication to dissolve the sample, and then the sample of the standard cotton cloth was impregnated with grafting solution fully. Using a padder (P-40), the samples were padded at a pressure of 4 bar and a roller speed of 15 rpm per min.

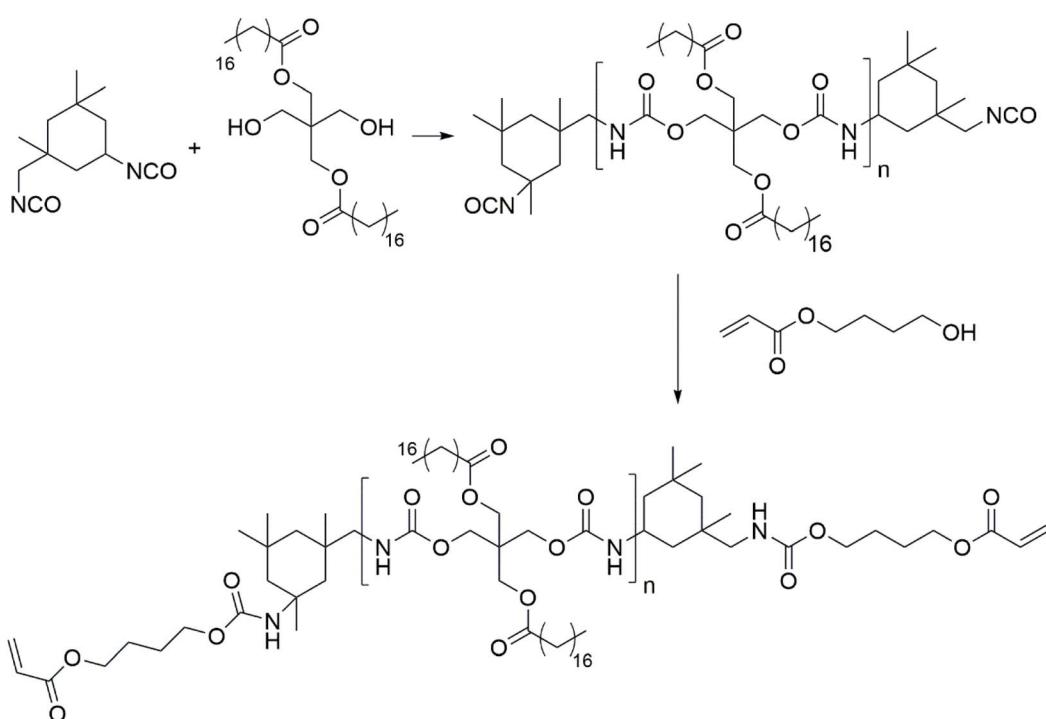


Fig. 1 Synthesis of VPU.

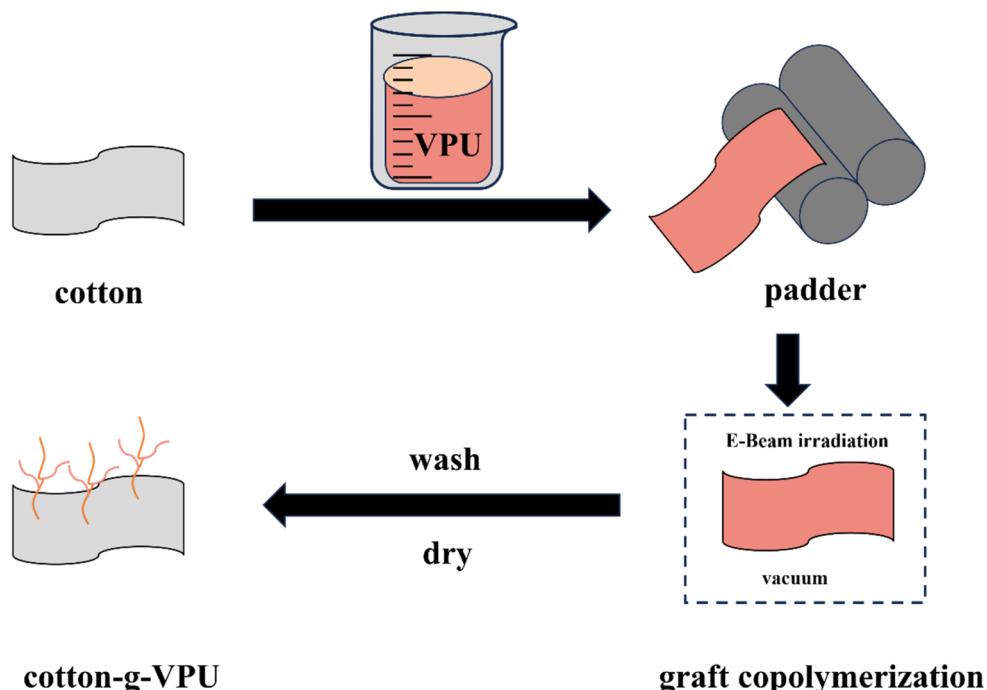


Fig. 2 Preparation of cotton-*g*-VPU by E-beam irradiation.

Subsequently, the padded cotton samples were subjected to E-beam irradiation for grafting under vacuum conditions. After grafting, the cotton samples were washed with ethanol and dried in an oven at 60 °C. The flowchart is shown in Fig. 2. The grafting rate was calculated according to the formula (1):

$$\eta = \frac{m_1}{m_0} \times 100\% \quad (1)$$

where m_0 is the mass of the cotton cloth before grafting, and m_1 is the mass of the cotton cloth after grafting.

Cotton samples dipped and dried in a polyurethane hydrophobic gin were compared with the grafted samples using conventional industrial dyeing and finishing methods, and the comparison samples were recorded as cotton-PU.

2.4 Characterization

Nuclear magnetic resonance spectroscopy (NMR, Advance III 400, Germany) was used to characterize the H atoms on the double bonds in the polyurethane. Scanning electron microscopy (SEM, ZEISS Sigma 300, Germany) was used to observe the surface morphology. Fourier transform infrared spectroscopy (FTIR, Thermo Scientific Nicolet iS20, America) was used to characterize the surface chemistry. Hydrophobicity was determined by contact angle meter (DSA30, Germany). The tensile properties of the textiles were tested by a microcomputer-controlled electronic universal testing machine (CMT6103, China).

2.5 Hydrophobicity and laundering durability test

Laundering durability evaluation was carried out according to AATCC (American Association of Textile Chemists and Colorists) test method 61-2006. The cotton-*g*-VPU and cotton-PU of

size 5 cm × 10 cm were cut and laundered in a rotary closed cylinder containing 0.15% (w/w) AATCC standard WOB (without optical brightener) detergent in 150 ml of deionized water. The rotating closed cylinder contains 50 stainless steel balls, a thermostatic water bath at 50 °C, and 40 ± 2 rpm. An accelerated wash lasts 45 minutes, which is equivalent to 5 domestic laundering cycles. The washed samples were dried in an oven at 60 °C and the contact angles were tested to compare the contact angles before and after washing.

2.6 Air and moisture permeability test

The water vapor transmission test is conducted according to the national standard GB/T 8170, and the water vapor transmission rate is calculated according to formula (2):

$$WVT = \frac{(\Delta m - \Delta m')}{A \times t} \quad (2)$$

where: Δm is the difference in mass between two weighings of the specimen combination, $\Delta m'$ is the difference in mass of the blank test (when no water is added, usually 0), A is the effective test area (0.00283 m², corresponding to the inner diameter of the permeability cup of 60 mm), t is test time.

The air permeability test was carried out according to GB/T 5453 standard.

2.7 Mechanical performance test

According to the national standard GB/T 3923.1-2013 standard for fabric tensile strength test.



3. Results and discussion

3.1 ^1H NMR characterization of vinyl groups in polyurethanes

From the ^1H NMR of VPU in Fig. 3, which shows peaks for three hydrogen atoms in the vinyl group, it is clear that the polyurethane has been successfully prepared. Unlike existing water-repellent materials,³⁰ vinyl acts as a reactive group in water-repellent materials and is an important feature in the preparation of non-fluorinated water-repellent materials. A clear carbon–carbon double bond peak appears between the chemical shifts of 5.8 ppm and 6.6 ppm, indicating that a carbon–

carbon double bond has been successfully introduced into the polyurethane. The presence of vinyl in the water repellent material is key to achieving hydrophobic firmness.

3.2 Infrared characterization

From the FTIR of VPU in Fig. 4a, the peak at 1637 cm^{-1} is considered to be a vinyl stretching vibration,³¹ which is due to the influence of conjugation effect of the neighboring carbonyl group. Comparing with cotton, VPU and cotton-g-VPU have obvious stretching vibration of C–H bond at 2914 cm^{-1} and 2851 cm^{-1} , which indicates the successful preparation and successful grafting of VPU onto cotton.³² From Fig. 4b, it can

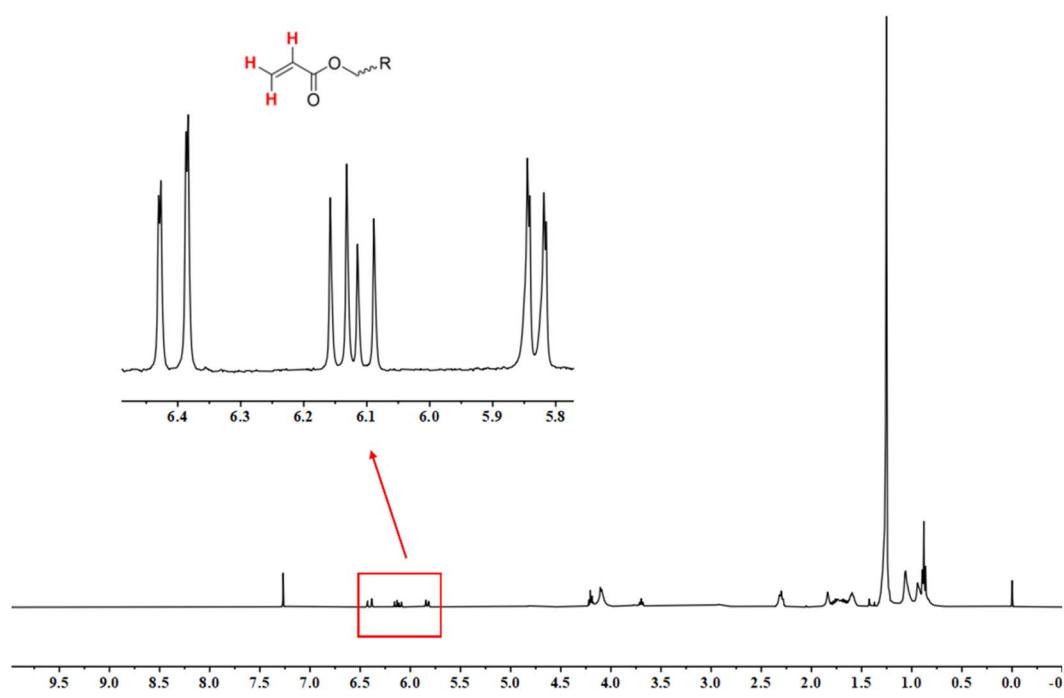


Fig. 3 ^1H NMR of VPU.

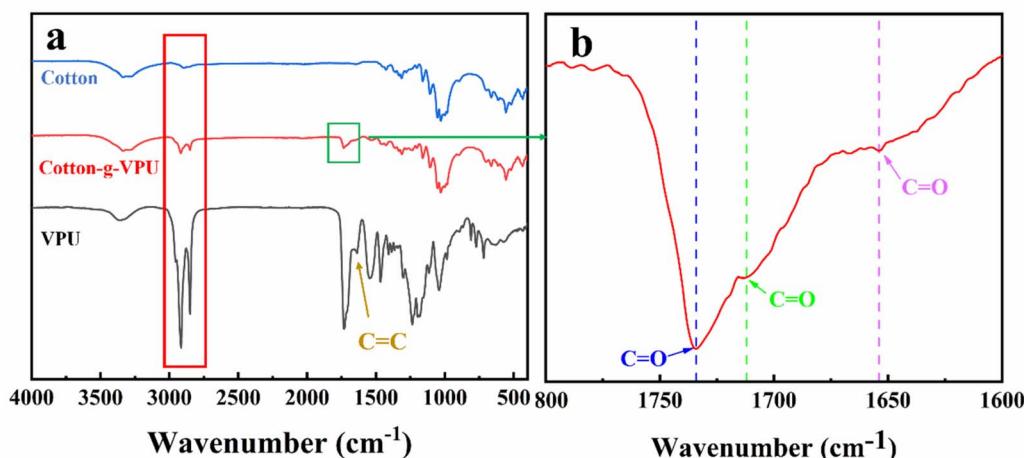


Fig. 4 (a) FTIR of VPU, cotton and cotton-g-VPU. (b) Local magnification of carbonyl group in cotton-g-VPU.



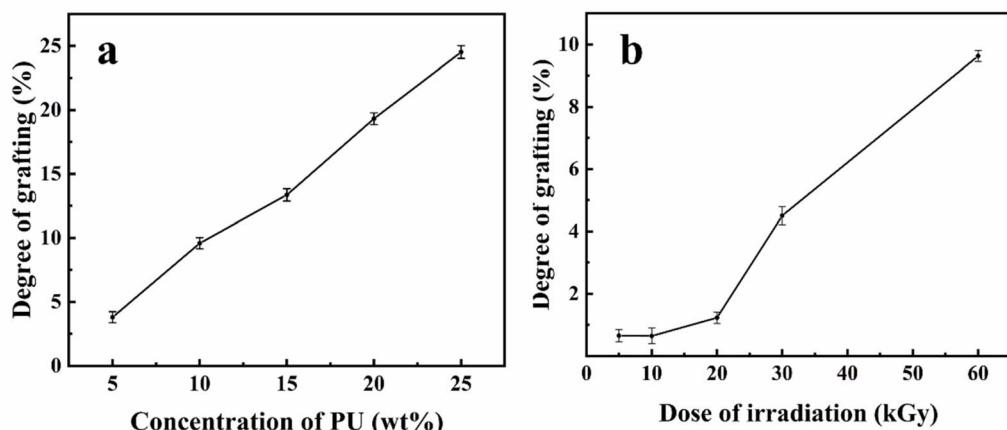


Fig. 5 Effect of VPU concentration (a) and absorbed dose (b) on grafting rate.

be seen that the stretching vibration of $\text{C}=\text{O}$ bond was considered at 1734 cm^{-1} , 1712 cm^{-1} and 1653 cm^{-1} , which proves that cotton-*g*-VPU has been successfully prepared.³³

3.3 Irradiation grafting kinetics

As can be seen in Fig. 5, the grafting rate of the fabrics increased with both the polyurethane concentration and the absorbed dose. However, the optimum mass concentration of VPU is 10%, this is because the higher the concentration of VPU, there will be more VPU sticking to the surface of the

cotton fabric and uneven distribution, resulting in the contact angle of the cotton fabric will not increase and the water repellency effect is not stable. The optimum absorbing dose is 60 kGy, because when the absorbing dose is lower than 60 kGy, only a small amount of VPU is grafted onto the surface of the fabrics, which results in a poor water repellency effect; and the absorbing dose is higher than 60 kGy, which results in the reduction of the strength of the cotton fabrics. So the optimal experimental conditions are a polyurethane concentration of 10 per cent and an absorbed dose of 60 kGy.

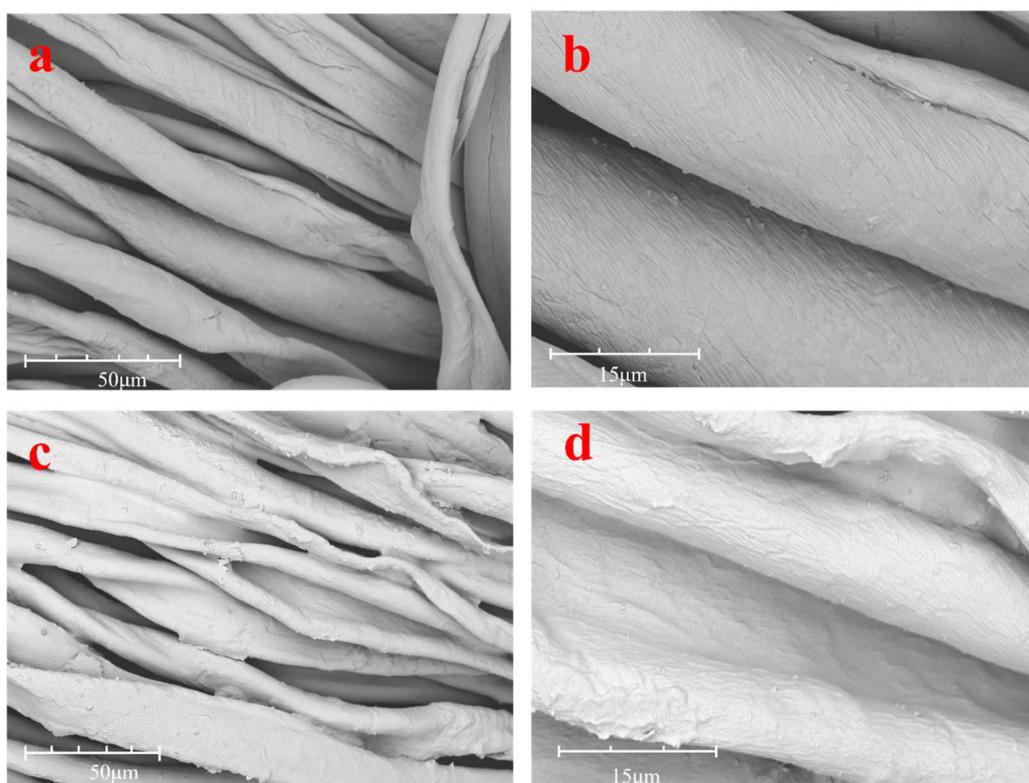


Fig. 6 (a) SEM image of cotton. (b) SEM image of cotton (10 000 \times). (c) SEM image of cotton-*g*-VPU. (d) SEM image of cotton-*g*-VPU (10 000 \times).



3.4 Microcosm

From the SEM images of cotton fabrics in Fig. 6a and b, it can be seen that the surface of the original cotton fabrics is smooth on the whole, and the direction of the fiber texture can be seen clearly in the magnification of 10 000 times of the electron microscope. From the SEM images of cotton cloth in Fig. 6c and d, it can be seen that the surface of the grafted cotton cloth becomes rough and the VPU is uniformly adhered to the surface of the cotton cloth. This is due to the polymerization reaction between VPU and free radicals generated from the cotton cloth under radiation conditions, forming grafted chains that cover the surface of the cotton cloth fibers. The fiber texture is not clear in the electron microscope magnification of 10 000 times, which indicates that the grafted chains cover the surface of the cotton cloth uniformly and obscure its original fiber morphology. The uniform coverage of the graft chains on the surface of the cotton fiber also ensures the stability of water repellency.

3.5 Hydrophobicity and washing resistance

From Fig. 7a and d, it can be seen that the contact angle of Cotton-g-VPU is 142° both before and after washing, which is different from the conventional impregnation and coating techniques (Fig. 6b and e), which suggests that the VPU can be firmly bonded with the cotton fiber by irradiation grafting, and thus the grafted water repellency cotton fabrics have a long lasting water resistance. From Fig. 7c and f, it can be seen that the wetting time of cotton before and after washing is <1 s, which is almost instantaneous. The comparison can prove that cotton-g-VPU has a long-lasting water repellent effect.

3.6 Breathability and moisture permeability

As can be seen in Fig. 8, cotton-g-VPU showed a slight increase in water vapor permeability and air permeability over cotton, indicating that the air and moisture permeability of the cotton

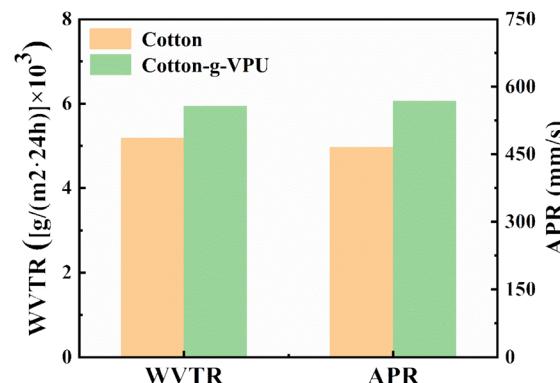


Fig. 8 Water Vapor Transmission Rate (WVTR) and Air Permeability Rate (APR) of cotton and cotton-g-VPU.

fabric was hardly affected after grafting. This is due to the fact that radiation grafting only introduces graft chains uniformly on the surface of cotton, without significantly damaging the microstructure of cotton.

3.7 Mechanical characterization

Fig. 9 shows the tensile strength of cotton and cotton-g-VPU. the tensile breaking strength of cotton is 25 MPa, however, the tensile breaking strength of cotton-g-VPU is increased to 35 MPa, which indicates that the irradiation with E-beam at 60 kGy did not reduce the tensile breaking strength of cotton fabric, but increased it, which is related to the enhancement of the loading. This is related to the enhanced load carrying capacity of VPU, which can improve the ability of cotton-g-VPU to resist damage. The elongation at break of cotton is 25%, while the elongation at break of cotton and cotton-g-VPU is 20%, which indicates that the original cotton fabrics maintain good flexibility, which is reduced after irradiation, which may be related to the polyurethane bonding on the surface of cotton fibers.

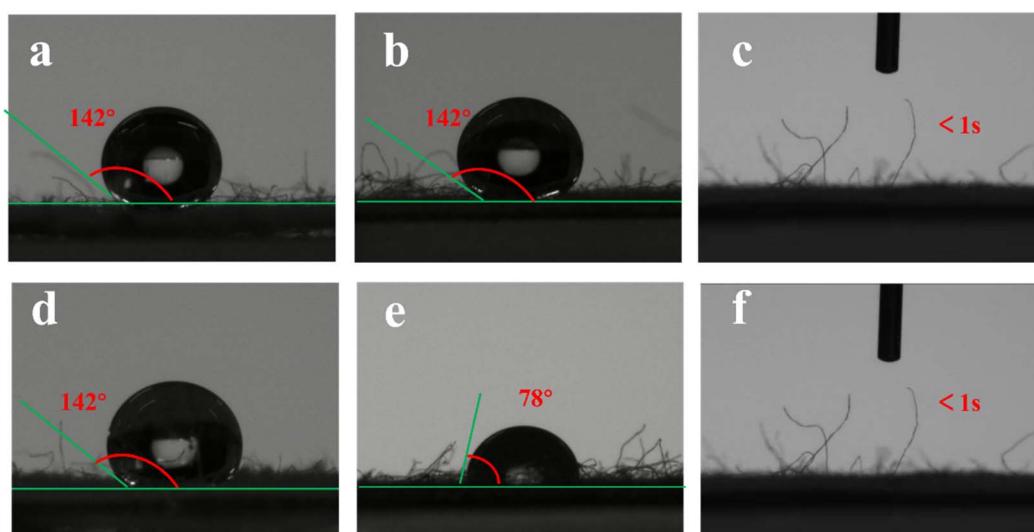


Fig. 7 (a) Cotton-g-VPU contact angle before washing. (b) Cotton-PU contact angle before washing. (c) Cotton contact angle. (d) Cotton-g-VPU contact angle after washing. (e) Cotton-PU contact angle after washing. (f) Cotton contact angle after washing.



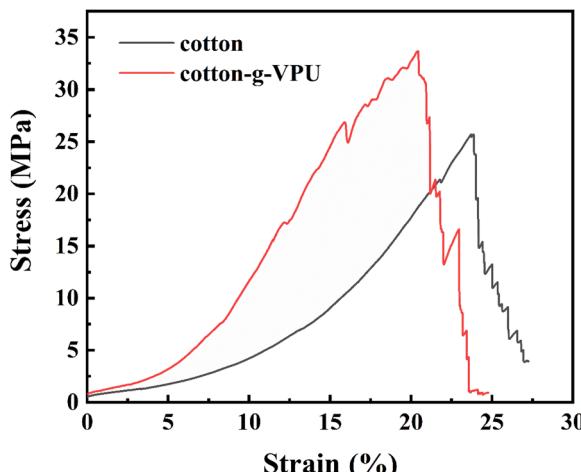


Fig. 9 Strain–stress curve of cotton and cotton-g-VPU.

3.8 Comparison with conventional fluorination processes

Historical production of perfluoropolymers was around 9 kilotonnes per year, current production is unknown, and they can accumulate in living organisms through the food chain,³⁴ resulting in health effects, whereas polyurethanes are non-toxic.³⁵ Fluorinated hydrophobes often require high temperature curing to prepare hydrophobic materials,³⁶ whereas E-beam irradiation techniques can be performed at room temperature.

4. Conclusions

In this study, vinyl-functionalized polyurethane (VPU) hydrophobes were synthesized and grafted onto cotton fabrics *via* E-beam irradiation, forming robust covalent bonds that impart durable hydrophobicity. The effects of VPU concentration and absorbed dose on the grafting rate were investigated by a systematic irradiation grafting kinetic study. Characterization by FTIR and ¹H NMR proved the successful synthesis of VPU. The excellent water repellency of cotton-g-VPU was demonstrated by SEM, FTIR and contact angle test. While having good water repellency, the modification method in this study has less effect on the mechanical properties, air permeability and moisture permeability of the cotton-g-VPU. The contact angle test after accelerated washing proved that the modified cotton fabric prepared in this study has excellent and long-lasting water repellency. This research expands energy efficient, environmentally friendly and durable functional textiles. The use of this technology is promising for large scale industrial production of functionalized textiles.

Conflicts of interest

There are no conflicts to declare.

Data availability

All data that support the plots within this paper and other findings of this study are available in the main text.

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