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Radiation induced graft polymerization of a fluorinated acrylate onto fabric

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ABSTRACT

A fluoride acrylate monomer, *1H,1H,2H,2H*-nonafluorohexyl-1-acrylate (denoted as F4), was grafted onto cotton fabric through a simultaneous irradiation induced graft polymerization technique. The grafted cotton fabric (denoted as cotton–F4) is superhydrophobic (SCF) when the degree of grafting (DG) exceeded 10%. The morphology of the cotton fabric was unchanged. In addition, the mechanical properties of the cotton fabric and SCF samples were also studied. The results showed that the decrease in mechanical properties was less than 20%, indicating that the SCF retained good mechanical strength.

1. Introduction

Many strategies have been used to create superhydrophobic surfaces by building micro- and nano-scale rough surfaces on a low surface-energy substance or introducing low surface-energy materials onto existing micro- and nano-scale rough surfaces (Genzer and Efimenko, 2000; Zhao et al., 2007; Li et al., 2007). However, the practicality of superhydrophobic surfaces is hampered by the poor mechanical stability of the microscopic surface topography that plays a key role for very large contact angles (Verho et al., 2011).

Among various superhydrophobic materials, superhydrophobic textiles are considered to be the most promising industrial application in waterproofing clothes (Zimmermann et al., 2008). Cotton fabric is a widely accepted clothing material due to its excellent inherent properties including good breathability, softness and affinity to skin (El-Naggar et al., 2003; Princi et al., 2005; Gowariker et al., 1993). Cotton fabrics, however, are by no means waterproof. A superhydrophobic cotton fabric has extremely good waterproof properties with air-breathability due to the existence of holes between the woven fibers, and has been successfully fabricated via various approaches (Neveu et al., 2010; Yu et al., 2007).

Radiation induced graft polymerization offers an easy and highly efficient way to modify the properties of cotton fabric. In our earlier study, we have reported the laundering durability of a superhydrophobic cotton fabric by radiation induced graft polymerization of *1H,1H,2H,2H*-nonafluorohexyl-1-acrylate (denoted as F4). The covalent bonds formed between cotton and grafted fluorinated polyacrylate chains are the key to maintaining the superhydrophobicity after the laundering test (Deng et al., 2010).

Here we report our study on graft polymerization kinetics and the mechanical properties of superhydrophobic cotton fabrics. Microscope morphology of the cotton fabrics before and after grafting is also studied.

2. Experimental section

2.1. Materials

1H,1H,2H,2H-nonafluorohexyl-1-acrylate was purchased from Fuxin Heng Tong Fluorine Chemicals Co. Ltd. China. Methanol, methyl ethyl ketone (MEK), acetone were all of analytical grade and supplied by Sinopharm Chemical Reagent Co. Ltd. China. All of these chemical agents were used without further purification.

2.2. Simultaneous radiation induced graft polymerization

Cotton fabrics were put into irradiation tubes, then methanol solutions with F4 monomer was added, and the tubes were purged with nitrogen bubbling for 15 min. The glass tubes were sealed and then irradiated by γ-rays from a ^{60}Co source at a definite dose rate for a required period of time. The grafted cotton fabrics were removed and washed with hot MEK. Next, the fabrics were extracted by MEK for 72 h in a Sohxlet apparatus to remove any residual homopolymer. Finally, the cotton fabrics were vacuum dried until a constant weight was obtained.

The DGs were determined by the weight increase according to the following equation:

$$DG(\%) = \frac{Wg - Wo}{Wo} \times 100 \quad (1)$$

where Wg and Wo are the weights after and before grafting, respectively.

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2.3. Characterization and instruments

A morphology study was conducted by means of SEM on a Leo1530vp SEM (Germany). The voltage was set at 25 kV and the current was set at 10 mA.

The mechanical properties were determined by a strip method with an effective gage length of 100 mm and width of 10 mm, at an extension rate of 20 mm/min performed on a computerized tensile testing machine (Shanghai Qingji, China).

3. Results and discussion

3.1. Graft polymerization kinetic study

DG is a key parameter for the preparation of the SCF where only those cotton–F4 samples with a DG higher than 10% are superhydrophobic as reported in our previous work. Fig. 1a presents the relationship between the DG and the monomer concentration (c_{F4}). There is almost a linear relationship between the DG and c_{F4} before c_{F4} exceeded 20%. At a higher monomer concentration range, the DG tends to be saturated and the highest DG can reach 90%. Fig. 1b shows the relationship between the DG and the total absorbed dose. The relationship obeys a Gussain pattern where the peak DG is about 45% at an absorbed dose of 50 kGy. At a higher absorbed dose range, the DG decreases, which can be attributed to the radiation induced chain scission of the graft polymers. The relationship between the DG and the dose rate is presented in Fig. 1c. A high dose rate is unfavorable for graft polymerization. The peak DG is obtained when the dose rate is set at 0.52 kGy/h. A lower dose rate means a longer reaction time, which is uneconomical.

3.2. Morphology analysis

The low range SEM images of the cotton fabric and the SCF given in Fig. 2a and b indicate that the microstructure of the fabrics is the same before and after the graft polymerization. The woven structure is retained, which makes it breathable and comfortable while being water-repellent. The SEM images focusing on the fiber for the cotton fabric (Fig. 2c) and the SCF (Fig. 2d) indicate that there are some cracks that are a few nanometers in width, which can be attributed to the accumulation of fluoride polyacrylate graft chains on the surface due to the phase separation. The roughness of fiber after graft polymerization, however, is much lower than that of the prior one.

3.3. Mechanical properties

A superhydrophobic cotton fabric must withstand the stretching and wearing forces encountered during its application. A certain amount of degradation in the cellulose macromolecules does occur, however, due to the gamma ray irradiation and graft polymerization. Fig. 3a and b shows the mechanical properties of the samples under stretching. From the relationship between stress and strain, the mechanical strength of the cotton–F4 declines slightly compared to that of pristine cotton fabric. Fig. 3b shows that decreases in the load and elongation of cotton fabric is about 10% and 25%, respectively, after the irradiation and graft polymerization. This is attributed to a slight degradation of the cellulose macromolecules of the cotton fabric.

4. Summary

1H,1H,2H,2H-nonafluorohexyl-1-acrylate (F4) was successfully grafted onto a cotton fabric by simultaneous radiation induced graft polymerization, and the obtained cotton–F4 fabric shows superhydrophobicity when the DG exceeded 10%. Graft polymerization kinetics were studied and the woven structure was unchanged after the graft polymerization. The decrease in the mechanical properties is less than 20% indicating that the SCF retains good mechanical strength. In conclusion, the results

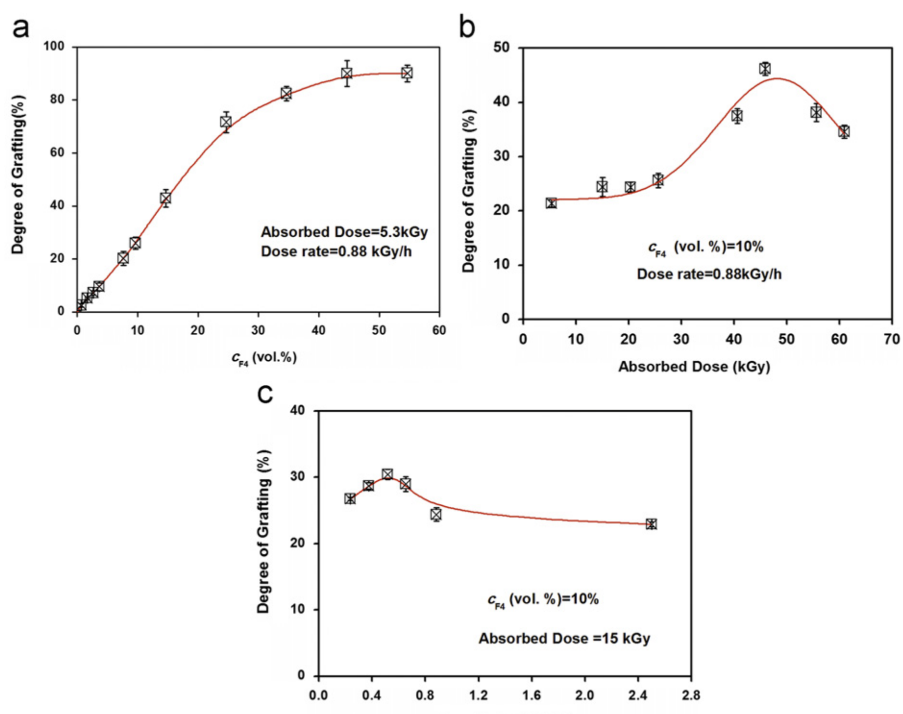

Fig. 1. Kinetic study result of the relationship between the DG and the experimental parameters of (a) concentration of F4 at dose rate of 0.88 kGy/h and total absorbed dose of 5.3 kGy, (b) absorbed dose at c_{F4} of 10% and dose rate of 0.88 kGy/h and (c) dose rate at c_{F4} of 10% and total absorbed dose of 15 kGy.

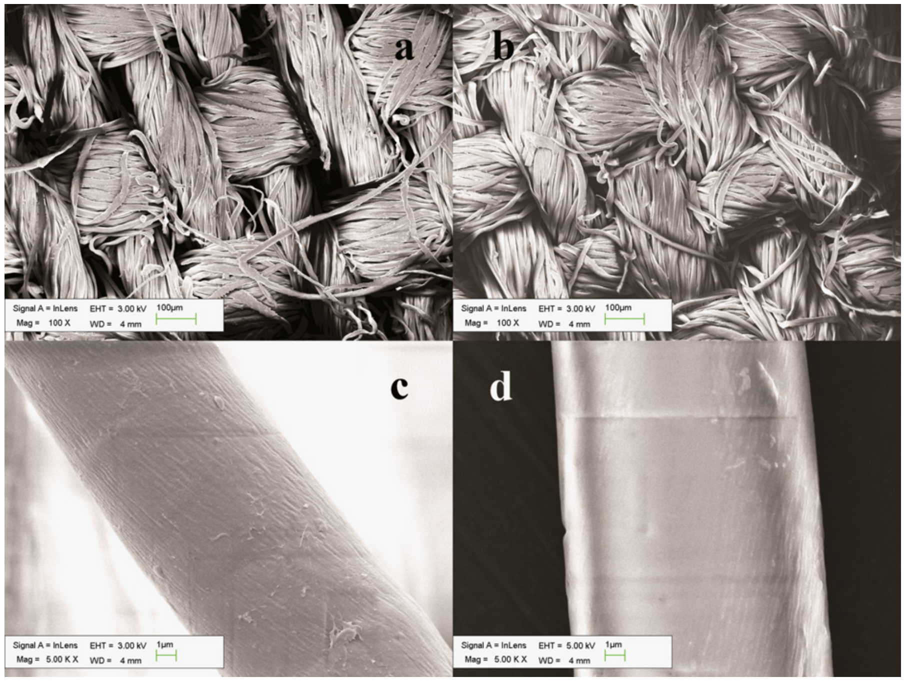

Fig. 2. Low range SEM image (magnified to 100 ×) of (a) the pristine cotton fabric and (b) the cotton–F4 with a DG of 28%. The SEM image of (c) a single fabric of the pristine cotton fabric and (d) a single fabric of the cotton–F4 with a DG of 28%.

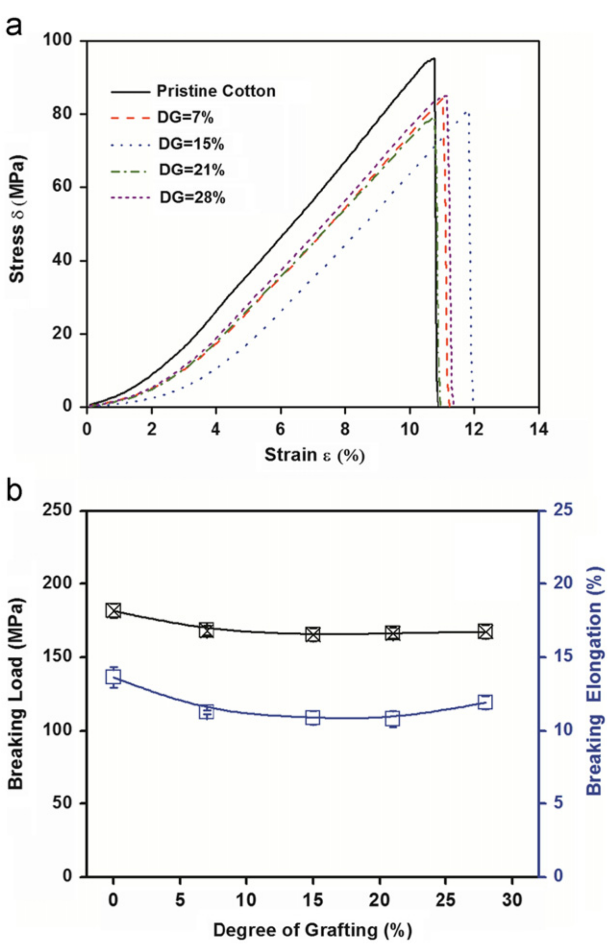

Fig. 3. Mechanical properties of the fabrics: (a) the relationship between stress and strain of the pristine cotton fabric and cotton–F4 with different DG($\delta \sim \varepsilon$), and (b) the breaking load and breaking elongation of the pristine cotton fabric and cotton–F4 with different DG.

indicated that the radiation did not damage the cotton fabric significantly and the SCF retains a comparable mechanical property to that of pristine cotton fabric.

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