Preparation and properties of hydrophobic filter paper and cotton fabric with reversible solvent response

Chengmin Hou , Mei Wang, Xiaolin Zhang, Na Li , Xueqi Kong and Guangming Zhuo

Faculty of Printing, Packaging Engineering and Digital Media Technology, Xi’an University of Technology, Xi’an 710048, People’s Republic of China

Authors to whom any correspondence should be addressed.

E-mail: 1042067175@qq.com and zxlbmm@sina.com

Keywords: hydrophobic, filter paper, cotton fabric, reversible solvent response, free radical polymerization

Abstract

The preparation of hydrophobic surfaces has been extensively studied, but the reversible responsive hydrophobic surface has received less attention. In this paper, poly(styrene-random-methyl methacrylate-random-acrylic acid) (P(St-r-MMA-r-AA)) was prepared by conventional free radical polymerization, and the filter paper and cotton fabric were immersed in P(St-r-MMA-r-AA) methanol solution to construct a hydrophobic surface. The hydrophobic property, chemical composition and surface morphology of the hydrophobic filter paper and cotton fabric surface were characterized by contact angle, Gibbs free energy, infrared spectroscopy and scanning electron microscopy. The optimum conditions for constructing hydrophobic filter paper and cotton fabric surface were investigated. When the surfaces of hydrophobic filter paper and cotton fabric were treated with methanol, tetrahydrofuran and deionized water respectively, the semihydrophobic-hydrophobic-hydrophilic PAA segment.

1. Introduction

Influenced by the natural phenomenon of hydrophobicity, such as lotus leaf [1, 2], water fly [3], rose petals [4], and butterfly wings [5], the hydrophobic surfaces have been widely studied and attracted widespread attention in scientific research and practical applications due to their good water resistance and self-cleaning properties [1, 2]. Moreover, many super-hydrophobic [1], hydrophobic [6–9], super-hydrophilic [10] and hydrophilic [11] surfaces were studied based on these biomimetic prototypes. The wettability of the material surface is mainly determined by the micro-nano roughness and low surface energy substance. However, these traditional hydrophobic surfaces have only a single wettability, which cannot meet the industrial needs and limit their practical application. Therefore, it is important to achieve a reversible transition of surface wettability under external stimuli.

According to external stimuli [12], the intelligent response surfaces are divided into the following types: light responsive surface [13], temperature responsive surface [14], solvent responsive surface [15, 16], electricity responsive surface [17], and magnetic field responsive surface [18]. Zhang et al. [19] reported that the super-hydrophobic titanium dioxide surface became hydrophilic after 240 min of UV irradiation. Jiang et al. [20] reported that the super-hydrophilic (contact angle <5°) surface of cotton fabric changed into super-hydrophobic (contact angle = 152°) by changing the temperature from 25 °C to 60 °C. Lei et al. [15] achieved that the super-hydrophobic surface was conversed into super-hydrophilic surface by adjusting the pH. Zhang et al. [16] prepared copper surfaces with super-oleophobicity in alkaline solutions, and quasi-super-oleophobicity

© 2020 IOP Publishing Ltd
in acidic solutions. The contact angles of an underwater oil droplet on the resultant surfaces could be reversibly tuned between 157° and 12° by changing the pH of aqueous solutions. Therefore, the reversible conversion of the surface wettability can be better achieved by controlling the chemical composition of the surface [21].

In this paper, poly(styrene-random-methyl methacrylate-random-acrylic) (P(St-r-MMA-r-AA)) was prepared by conventional free radical polymerization, and the filter paper and cotton fabric were immersed in P(St-r-MMA-r-AA) methanol solution to construct a hydrophobic surface. The effects of construction parameters on the surface wettability were investigated, such as the polymer concentration (1%, 3%, 5%, and 7%), immersion time (0.5 h, 1.0 h, 2.0 h, and 3.0 h), drying temperature (70 °C, 80 °C, 90 °C and 100 °C) and drying time (4 h, 5 h, 6 h, and 7 h). The solvent response of hydrophobic filter paper and cotton fabric surface was stimulated by methanol, tetrahydrofuran and deionized water. The Gibbs free energy for every kind of surface were calculated and the morphology of unmodified and modified filter paper and cotton fabric surface were observed by scanning electron microscope (SEM).

2. Experimental

2.1. Materials
Styrene (St, 98% purity), methyl methacrylate (MMA, 98% purity) and acrylic acid (AA, 98% purity) were purchased from Aladdin and used as monomers for the synthesis of polymer. These monomers were purified by passing through the based alumina columns. Azobisobutyronitrile (AIBN, 98% purity) and sodium hydrogen sulfite (NaHSO₃, 98% purity) were purchased from Tianjin Fuyu Fine Chemical Co., Ltd and used as initiator and catalyst for polymerization of St, MMA and AA. Tetrahydrofuran (THF, 98% purity), n-hexane (98% purity), and anhydrous methanol (98% purity) were purchased from Tianjin Fuyu Fine Chemical Co., Ltd and used as received.

2.2. Preparation of hydrophobic filter paper and cotton fabric
Hydrophobic filter paper and cotton fabric were prepared by immersing these materials into polymer P(St-r-MMA-r-AA) methanol solution which was synthesized by traditional radical polymerization of monomers St, MMA, and AA.

The synthesis of P(St-r-MMA-r-AA) was carried out as follow: monomers St 6.21 g (59.6 mmol), MMA 3.01 g (30.1 mmol), AA 2.23 g (30.9 mmol) and 12 ml THF were added into a 50 ml single-necked flask. Then NaHSO₃ 0.3748 g (3.6 mmol) and initiator AIBN 0.5915 g (3.6 mmol) were added to the flask and the flask were sealed. The oxygen was removed by blowing nitrogen for 30 min, and the mixture was heated at 65 °C for 1 h. The polymer P(St-r-MMA-r-AA) was purified by precipitation in n-hexane for three times, and dried at 70 °C for 10 h.

0.15 g of polymer P(St-r-MMA-r-AA) was dissolved in 5 ml of anhydrous methanol, and magnetically stirred for 30 min to make P(St-r-MMA-r-AA) completely dispersed to prepare a polymer methanol solution. A 2 cm × 2 cm filter paper and cotton fabric were immersed in the polymer methanol solution and stirred for 5 h to construct a hydrophobic surface on the filter paper and cotton fabric. At last, the modified filter paper and cotton fabric were washed with THF, and dried at 80 °C for 15 h.

The effects of construction parameters on the surface wettability were investigated, such as the polymer concentration (1%, 3%, 5%, and 7%), immersion time (0.5 h, 1.0 h, 2.0 h, and 3.0 h), drying temperature (70 °C, 80 °C, 90 °C and 100 °C) and drying time (4 h, 5 h, 6 h, and 7 h). The effect of the reaction conditions was studied by varying one parameter while maintaining the others constant.

The solvent-response of hydrophobic filter paper and cotton fabric surface was stimulated by methanol, tetrahydrofuran and deionized water. The surface of the obtained hydrophobic cotton fabric and filter paper was immersed in methanol for 1 min, and then dried at 100 °C for 7 h. The contact angle of water was measured, and the surface energy was calculated; then, it was immersed in THF for 1 min, and baked at 100 °C for 7 h. The contact angle was measured and the surface energy was calculated. Finally, it was immersed in water for 1 min, and baked at 100 °C for 7 h. The contact angle was measured, and the surface energy was calculated. This procedure was cycled for 10 times. The samples were investigated for 10 times like this.

3. Characterization

3.1. Gel permeation chromatograph
The molecular weight of the P(St-r-MMA-r-AA) (Mn) and its distribution (Mn/Mw) were determined on a Waters 1515 Gel Permeation Chromatograph(GPC). The mobile phase was THF and DMF (VTHF: VDMF = 1:1), and the flow rate of mobile phase was 1.0 ml min⁻¹.
3.2. Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR, FTIR-8400S, Shimadzu Corporation, Japan) was used for polymer structure analysis. 0.4 mg of P(St-r-MMA-r-AA) and 0.1 g of purified KBr were mixed and milled to a thickness of 0.3 mm transparent sheet. FTIR spectrum range is 4000 – 400 cm⁻¹, scanning resolution is 4 cm⁻¹, and scanning times is 40 times.

3.3. Contact angle

Water contact angle (WCA) was obtained by using the static droplet contact angle/interfacial tension tester (JC2000A, POWEREACH). The liquid used was deionized water, and the volume of the droplet was 2 uL. Each sample was measured for 5 times, and the average value was the final WCA.

3.4. Sanning electron microscopy

The surface morphological analysis of the filter paper and cotton fabric was scanned by scanning electron microscopy (SEM). The surface of the sample was tested. The sample was first sprayed with gold and then placed in a vacuum chamber for scanning. The accelerating voltage was 1 kV and 2 kV, and the magnifications were 5 000 times, 10 000 times and 30 000 times, respectively.

4. Results and discussion

4.1. Synthesis and characterization of P(St-r-MMA-r-AA)

In order to construct a solvent-responsive hydrophobic surface on the surface of cotton fabric and filter paper, the polymer P(St-r-MMA-r-AA) was synthesized by free radical polymerization, wherein PS was a hydrophobic segment, PAA was a hydrophilic segment, and PMMA was a semi-hydrophobic segment. The feeding molar ratio of St, MMA and AA was 2:1:1. The molecular weight and structure of obtained polymer P(St-r-MMA-r-AA) was characterized by GPC and FTIR spectra as shown in figure 1.

we performed a gel permeation chromatography (GPC) test on the product and the results showed that the molecular weight of the product was about 150 thousand((figure 1(a)). As show in figure 1(b), the C=O vibration absorption peak of MMA was appeared at 1700 cm⁻¹, and the C–O vibration absorption peak of MMA was strong and wide, and appeared at 1075 cm⁻¹–1360 cm⁻¹. These two peaks indicated that MMA was present in polymer P(St-r-MMA-r-AA). The peaks at 1450 cm⁻¹, 1500 cm⁻¹, 1550 cm⁻¹ and 1600 cm⁻¹ were the C=C skeleton stretching vibration of St segment. There was also the C–H vibration absorption peak in St in the range of 2980 cm⁻¹ and 3140 cm⁻¹. These two peaks indicated the presence of St in the polymer P(St-r-MMA-r-AA). The peak at 1625 cm⁻¹ was the vibration absorption peak of C=O in AA, and there was the peaks for O-H vibration absorption peak of AA at 2500 cm⁻¹–3550 cm⁻¹. There was also the O-H bending vibration absorption at 1400 cm⁻¹ and 980 cm⁻¹. These three kinds of peaks demonstrated the presence of AA in the polymer P(St-r-MMA-r-AA). All these information showed that P(St-r-MMA-r-AA) was successfully synthesized by free radical copolymerization of monomers St, AA and MMA.

4.2. Optimum parameters for constructing hydrophobic filter paper and cotton fabric surface

In order to construct a solvent-responsive hydrophobic surface on the surface of cotton fabric and filter paper, the cotton fabric and filter paper were immersed into polymer P(St-r-MMA-r-AA) methanol solution. The effect of constructing conditions on the hydrophobic performance of cotton fabric and filter paper was explored by varying the the polymer concentration (from 1% to 7%), immersion time (0.5 h, 1.0 h, 2.0 h, and 3.0 h), drying...
Figure 2. The effects of constructing parameters on hydrophobic performance of modified filter paper and cotton fabric surface. (a) the effect of polymer concentration on hydrophobic filter paper; (b) the effect of polymer concentration on hydrophobic cotton fabric; (c) the effect of soaking time on hydrophobic filter paper; (d) the effect of soaking time on hydrophobic cotton fabric; (e) the effect of drying temperature of hydrophobic filter paper; (f) the effect of drying temperature on hydrophobic cotton fabric; (g) the effect of drying time on hydrophobic filter paper; and (h) the effect of drying time on hydrophobic cotton fabric.
temperature (70 °C, 80 °C, 90 °C and 100 °C) and drying time (4 h, 5 h, 6 h, and 7 h). The hydrophobic performance of cotton fabric and filter paper was evaluated by water contact angle.

Firstly, the effects of polymer concentration was studied. 0.5 g, 0.15 g, 0.25 g and 0.35 g of polymer P(St-r-MMA-r-AA) was dissolved in 5 ml of anhydrous methanol, and magnetically stirred for 30 min, respectively. A 2 cm × 2 cm filter paper and cotton fabric were immersed in the polymer methanol solution and stirred for 2 h. At last, the modified samples were washed with THF, and dried at 80 °C for 5 h. The results were shown in figure 2(a) for filter paper and 2(b) for cotton fabric. For figure 2(a), the water contact angle increased first and then decreased with the concentration of the polymer increased. When the polymer concentration was 3%, the initial water contact angle was 75 ± 1.6°, which was maximum. When the polymer concentration was 7%, the initial water contact angle was 68 ± 2.8°, which was minimum. When the polymer concentration was 1% and 5%, the initial water contact angle were at 71 ± 3.0° and 72 ± 4.2°. For figure 2(b), the same trend was observed for modified cotton fabric. When the polymer concentration was 3%, the initial water contact angle was 79 ± 3.6°, which was the maximum. When the polymer concentration was 7%, the contact angle was 73 ± 1.1°, which was minimum. When the polymer concentration was 1% and 5%, the initial water contact angle were 75 ± 4.3° and 74 ± 2.1°. This is because that the amount of the polymer attached to the surface of the filter paper and the cotton fabric was small, and the surface cannot be completely covered when the polymer concentration was 1%. As the polymer concentration increased, the polymer completely covered the surface and formed a rough surface. When the polymer concentration was 5% and 7%, the rough pleats constructed by the polymer overlap each other too much, so that the surface of the hydrophobic filter paper and the cotton fabric became relatively smooth. Therefore, the hydrophobic effect of the hydrophobic filter paper and cotton fabric surface increased first and then decreased with the increase of polymer concentration. The hydrophobic filter paper and cotton fabric surface constructed with the polymer concentration of 3% have the best hydrophobic effect.

Secondly, the effects of immersion time was studied. 0.15 g of polymer P(St-r-MMA-r-AA) was dissolved in 5 ml of anhydrous methanol, and magnetically stirred for 30 min A 2 cm × 2 cm filter paper and cotton fabric were immersed in the polymer methanol solution and stirred for 0.5 h, 1.0 h, 2.0 h, 3.0 h, respectively. At last, the modified samples were washed with THF, and dried at 80 °C for 5 h. The results were shown in figure 2(c) for filter paper and 2(d) for cotton fabric. It was shown that the water contact angle increased first and then decreased with the immersion time increased. For figure 2(e), the initial water contact angle was 27 ± 3.9° when the soaking time was 0.5 h. The initial contact angle increased to 55 ± 3.6° when the soaking time was 1 h. And the contact angle reached 75 ± 1.6° and 74 ± 1.7° when the soaking time was 2 h and 3 h. For figure 2(d), the initial water contact angle changed from 29 ± 1.5° to 58 ± 3.6° when the soaking time increased from 0.5 h to 1 h, and reached 79 ± 3.6° and 80 ± 3.4° when the soaking time was 2 h and 3 h. This was because the polymer absorbed on the surface of the hydrophobic filter paper and the cotton fabric was less when the immersion time was 0.5 h. With the immersion time increased to 1 h, the polymer absorbed gradually increased. When the soaking time was 2 h and 3 h, the polymer absorbed was saturated. Therefore, the hydrophobic effect of hydrophobic filter paper and cotton fabric surface increased first and then remained unchanged with the increase of soaking time. The hydrophobic filter paper and cotton fabric surface constructed by the soaking time of 2 h had the best hydrophobic effect.

Thirdly, the effect of drying temperature was studied. 0.15 g of polymer P(St-r-MMA-r-AA) was dissolved in 5 ml of anhydrous methanol, and magnetically stirred for 30 min. A 2 cm × 2 cm filter paper and cotton fabric were immersed in the polymer methanol solution and stirred for 2 h. At last, the modified samples were washed with THF, and dried at 60 °C, 70 °C, 80 °C, 90 °C and 100 °C for 5 h, respectively. The results were shown in figure 2(e) for filter paper and 2(f) for cotton fabric. The water contact angle increased with the drying temperature increased. For figure 2(e), the initial water contact angle was 73 ± 3.0°, which was the lowest, when the drying temperature was 70 °C. The initial water contact angle increased sequentially to 75 ± 1.6° and 77 ± 3.2°, when the drying temperature increased to 80 °C and 90 °C. When the drying temperature was 100 °C, the initial water contact angle was 80 ± 2.7° to reach the maximum. For figure 2(f), the initial water contact angle was 77 ± 1.3° when the drying temperature was 70 °C. The initial water contact angle increased to 79 ± 3.6° and 81 ± 3.2° when the drying temperature was 80 °C and 90 °C. When the drying temperature was 100 °C, the initial water contact angle reached 84 ± 2.6°. This is the higher the drying temperature, the greater the bonding strength of P(St-r-MMA-r-AA) to the surface of the filter paper and the cotton fabric. Therefore, the hydrophobic effect of the surface of the hydrophobic filter paper and the cotton fabric increased with the increase of the drying temperature, and the hydrophobic filter paper and the surface of the cotton fabric had the best hydrophobic effect when the drying temperature was 100 °C.

At last, the effect of drying time was studied. 0.15 g of polymer P(St-r-MMA-r-AA) was dissolved in 5 ml of anhydrous methanol, and magnetically stirred for 30 min. A 2 cm × 2 cm filter paper and cotton fabric were immersed in the polymer methanol solution and stirred for 2 h. At last, the modified samples were washed with THF, and dried at 100 °C for 4 h, 5 h, 6 h and 7 h, respectively. The results were shown in figure 2(g) for filter
paper and 2(h) for cotton fabric. The water contact angle increased with the drying time increased. For figure 2(g) the initial water contact angle was 78 ± 1.9° when the drying time was 4 h. With the drying time increased to 5 h and 6 h, the initial water contact angle increased sequentially to 80 ± 2.7° and 81 ± 3.3°, respectively. When the drying time was 7 h, the initial water contact angle reached 83 ± 1.5°. For figure 2(h), the initial water contact angle was 83 ± 2.6° when the drying time was 4 h. The initial water contact angle increased sequentially to 84 ± 2.6° and 86 ± 2.8° with the increasing of the drying time to 5 h and 6 h. The initial water contact angle reached 87 ± 2.5° when the drying temperature was 7 h. This is because the longer the drying time, the greater the bonding strength of P(St-r-MMA-r-AA) with the surface of the filter paper and the cotton fabric. Therefore, the hydrophobic effect of the hydrophobic filter paper and cotton fabric surface increase with the drying time. The hydrophobic filter paper and the cotton fabric surface have the best hydrophobic effect when the drying time is 7 h.

In figure 2, the water contact angle gradually decreases with testing time. This is because the retention time of water droplets on the surface of the filter paper and the cotton fabric increases as the testing time increases. The force of the water droplets with the surface fibers and the PAA segment in the polymer increases, and the surface becomes more and more hydrophilic. Moreover, when studying the effect of the polymer concentration, the immersing time, the drying temperature and drying time, the water contact angle of the hydrophobic filter paper under each parameter was smaller than that of hydrophobic cotton fabric, because a plurality of fibers in cotton fabric are interlaced and overlapped and the surface of the cotton fabric has a higher roughness, compared with the surface of the filter paper.

4.3. Solvent responsiveness and surface energy of hydrophobic filter paper and cotton fabric surface

By using the interface energy relationship model of the solid, liquid and gas, and the Young’s equation, the solid surface energy can be calculated [22]. In 1805, Young [23] proposed a qualitative formula (1) based on the concept of tension balance of three-phase contact points (solid, gas, liquid) to describe the degree of wetting. This formula presents the relationship between the solid surface energy ($\gamma_{SG}$), the liquid surface energy ($\gamma_{LG}$), the interface energy of liquid and solid ($\gamma_{SL}$) and the contact angle. Fowkes [24] considers that the interface energy of liquid and solid ($\gamma_{SG}$) to be the sum of the solid surface energy and the liquid surface energy minus the geometric mean of the dispersion component of the two surface energies, as shown in equation (2). The simultaneous equations (1) and (2) can obtain the equation (3). The calculation is made simpler by simplifying the $\gamma_{SL}$. Here, the $\gamma_{LG}$ and $\gamma_{SG}^d$ are the surface energy and the dispersion component of surface energy of the ionized water at 25 °C, and these theoretical values can be obtained by consulting the literature. The $\gamma_{LG}$ and $\gamma_{LG}^d$ are 72.0 and 21.8 mN m$^{-1}$. Moreover, $\gamma_{SG}$ and $\gamma_{SG}^d$ are equal for the filter paper and cotton fabric. It is only necessary to measure the contact angle of the ionized water to calculate the surface Gibbs free energy of the filter paper and the cotton fabric (the surface energy).

$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG} \times \cos \theta$$

(1)

$\gamma_{SG}$ is the solid surface energy, $\gamma_{SL}$ is the solid-liquid interface energy, and $\gamma_{LG}$ is the liquid surface energy.

$$\gamma_{SL} = \gamma_{SG}^d + \gamma_{LG} - 2 \times \sqrt{\gamma_{SG}^d \times \gamma_{LG}^d}$$

(2)

$\gamma_{SG}^d$ is the dispersion component of the solid surface energy, and $\gamma_{LG}^d$ is the dispersion component of liquid surface energy.

$$\gamma_{SG}^d = ((\gamma_{LG} \times \cos \theta + \gamma_{LG}) / 2) / \gamma_{LG}^d$$

(3)

The solvent-response of hydrophobic filter paper and cotton fabric surface was stimulated by methanol, tetrahydrofuran and deionized water. The water contact angle was tested and the solid surface energy $\gamma_{SG}$ was calculated, and the results were shown in figure 3. For hydrophobic filter paper, the water contact angle changed from 83 ± 1.5°, 122 ± 2.6°, to 28 ± 3.7° under the stimulation of methanol, tetrahydrofuran and deionized water. After calculation, the solid surface energy was 74.8 ± 2.5 mN m$^{-1}$, 13.1 ± 1.6 mN m$^{-1}$, and 210.8 ± 2.7 mN m$^{-1}$. For hydrophobic cotton fabric, the water contact angle was 87 ± 2.5°, 136 ± 1.7°, and 30 ± 2.2° under the stimulation of methanol, tetrahydrofuran and deionized water. Correspondingly, the surface energy was 65.8 ± 3.2 mN m$^{-1}$, 4.7 ± 4.2 mN m$^{-1}$, and 207 ± 3.6 mN m$^{-1}$, respectively. If the contact angle is larger, the surface energy is lower. The contact angle of the hydrophobic cotton fabric is larger than that of hydrophobic filter paper. According to the change of surface energy, the principle of solvent-response is as follows: when the filter paper and cotton fabric surface was treated with methanol, PS, PMMA and PAA in P(St-r-MMA-r-AA) are exposed to the air. After THF (28.8 mN m$^{-1}$) treatment, St with low surface energy migrates to the surface of hydrophobic filter paper and cotton fabric. The amount of St exposed to air is greater than that of MMA and AA, and the hydrophobic effect is better. However, after treatment of deionized water (72.7 mN m$^{-1}$), AA migrates to the surface of hydrophobic filter paper and cotton fabric. The amount of St and MMA exposed to air are less than AA, and the hydrophilic effect better.
The hydrophobic filter paper and the cotton fabric repeatedly stimulated with methanol, tetrahydrofuran and water for 10 times and the results of water contact angle were shown in figure 4. After each treatment with methanol, the water contact angle was greater than 80°. After each treatment with THF, the contact angle of the surface of the substrate with water was greater than 120°, which has hydrophobic properties. After the deionized water treatment was completed, the contact angle of the surface of the substrate with water was less than 32°, and had hydrophilic properties. These behaviors indicated that the wettability of the filter paper and cotton fabric surface was greatly altered after stimulation with methanol, THF and water.

### 4.4. Analysis of surface morphology of filter paper and cotton fabric

After the filter paper and cotton fabric were modified with P(St-r-MMA-r-AA), the surface morphologies were shown in figure 5. The surface of the filter paper and cotton fabric before modification were very smooth, without any substance and rough structure. The surface of the modified hydrophobic filter paper and cotton fabric were covered with a thin, micro-nano rough protrusion structure. And the outer contour of the fiber after modification was clear, and no adhesion to other fibers was occurred. This information indicates that the apparent properties of the hydrophobic filter paper and cotton fabric treated with P(St-r-MMA-r-AA) were not...
affected. Compared with the surface of the modified hydrophobic filter paper, the surface of the modified hydrophobic cotton fabric has more concave and convex structures, and more micro-nano roughness structure, which also explains the hydrophobic effect of the hydrophobic cotton fabric was better than that of the hydrophobic filter paper.

5. Conclusion

The polymer poly(styrene-random-methyl methacrylate-random-acrylic acid) (P(St-r-MMA-r-AA)) was prepared by conventional radical polymerization of monomers St, MMA and AA, and the structure of P(St-r-MMA-r-AA) was characterized by FTIR spectra. It showed that P(St-r-MMA-r-AA) was successful synthesized. The effect of constructing parameters on the hydrophobic performance of modified filter paper and cotton fabric surface were investigated, and the optimal conditions were 3% of polymer concentration, 2 h of soaking time, 100 °C of drying temperature and 7 h of drying time. The water contact angle of the hydrophobic filter paper can be freely converted from 83°, 122°, to 28° under the stimulation of methanol, tetrahydrofuran and deionized water. With the same treatment, the water contact angle of the hydrophobic cotton fabric can be freely converted from 87°, 136°, to 30°. After the hydrophobic filter paper and cotton fabric surface were repeatedly stimulated with methanol, tetrahydrofuran and water for 10 times, the water contact angle did not change significantly, and the hydrophobic effect of the hydrophobic cotton fabric was better than that of the hydrophobic filter paper.

Acknowledgments

This work was supported by the National Nature Science Foundation of China (no. 51803167), the Nature Science Foundation of Shaanxi Province (no. 2016JQ2029), the Construction Science and Technology Plan Project of Xi’an (no. SJW2015-024), the Scientific Research Program Founded by Shaanxi Provincial Educational Department (Grant No. 18JK0586), and the Science and Technology Association Project of Shaanxi Province (no. 20160116).

ORCID iDs

Chengmin Hou  https://orcid.org/0000-0002-8072-7431
Na Li  https://orcid.org/0000-0001-9026-8550
Guangming Zhuo  https://orcid.org/0000-0001-5264-0673

References

[1] Cao M, Guo D, Yu C, Li K, Liu M and Jiang L 2016 Water-repellent properties of superhydrophobic and lubricant-infused 'slippery' surfaces: a brief study on the functions and applications ACS Appl. Mater. Interfaces 8 3615–23

Figure 5. SEM image of filter paper and cotton fabric (a) unmodified cotton fabric (b) modified cotton fabric (c) unmodified filter paper (d) modified filter paper.
[2] Qu M, Zhao G, Cao X and Zhang J 2008 Biomimetic fabrication of lotus-leaf-like structured polyaniline film with stable superhydrophobic and conductive properties Langmuir 24 4185–9
[3] Gao X and Jiang L 2004 Biophysics: water-repellent legs of water striders Nature 432 36
[4] Ghosh U U, Naira S, Dash A, Mukherjee R and DasGupta S 2019 Replicating and resolving wetting and adhesion characteristics of a Rose petal Colloid Surf. A-Physicochem. Eng. Asp. 561 9–17
[5] Shao C, Chi J, Chen Z, Cai L and Zhao Y 2019 Superwettable colloidal crystal micropatterns on butterfly wing surface for ultrasensitive detection J. Colloid Interface Sci. 546 122–9
[6] Lu F, Cao Z, Yang F, Wang S and Zhong H 2019 Fabrication of hydrophobic coating on electrolytic manganese surface for enhancing corrosion resistance Prog. Org. Coat. 132 579–87
[7] Lalehganiz, Ramazani S A A, Tamsillian Y and Shirazi M 2019 Inverse emulsion polymerization of triple monomers of acrylamide, maleic anhydride, and styrene to achieve highly hydrophilic–hydrophobic modified polyacrylamide J. Appl. Polym. Sci. 136 47753
[8] Khodaparast S, Boulogne F, Poulard C and Stone H A 2017 Water-based peeling of thin hydrophobic films Phys. Rev. Lett. 119 154502
[9] Gailus T, Krah H, Kuhnel V, Rupprecht A and Kaatze U 2018 Carboxylic acids in aqueous solutions: hydrogen bonds, hydrophobic effects, concentration fluctuations, ionization, and catalysis J. Chem. Phys. 149 244503
[10] Zhao J, Guo J, Shrotriya P, Wang Y, Hand Y, Dong Y and Yang S 2019 A rapid one-step nanosecond laser process for fabrication of super-hydrophilic aluminum surface Opt. Laser Technol. 117 134–41
[11] Yang G, He X, Cheng S, Li X, Yang S, Wei H and Ding Y 2018 A CO2-triggered hydrophobic/hydrophilic switchable polyurethane Appl. Surf. Sci. 456 270–5
[12] Jiao K, Zhou C, Becerra-Mora N, Fiske J and Kohliet P 2016 Vapor-enhanced covalently bound ultra-thin films on oxidized surfaces for enhanced resolution imaging J. Mater. Chem. C 4 8634–47
[13] Chen K, Gou W, Wang X, Zeng C, Ge F, Dong Z and Wang C 2018 UV-cured fluoride-free polyurethane functionalized textile with pH-induced switchable superhydrophobicity and underwater superoleophobicity for controllable oil/water separation ACS Sustain. Chem. Eng. 6 10616–28
[14] Shi Y, Yang W, Bai J, Feng X and Wang Y 2014 Fabrication of flower-like copper film with reversible superhydrophobicity–superhydrophilicity and anticorrosion properties Surf. Coat. Technol. 253 148–53
[15] Lei Z, Zhang G, Dong Y and Wang C 2017 Surface modification of melamine sponge for pH-responsive oil absorption and desorption Appl. Surf. Sci. 416 798–804
[16] Zhang J, Yong J, Yang Q, Chen F and Hou X 2019 Femtosecond laser-induced underwater superoleophobic surfaces with reversible pH-responsive wettability Langmuir 35 3295–301
[17] Xu L, Chen W, Mulchandani A and Yan Y 2005 Reversible conversion of conducting polymer films from superhydrophobic to superhydrophilic Angew. Chem.-Int. Edit. 117 6163–6
[18] Hong X, Gao X and Jiang L 2007 Application of superhydrophobic surface with high adhesive force in no lost transport of superparamagnetic microdroplet J. Am. Chem. Soc. 129 1478–9
[19] Zhang X, Jin M, Liu Z, Tryk D A, Nishimoto S, Murakami T and Fujishima A 2007 Superhydrophobic TiO2 surfaces: preparation, photocatalytic wettability conversion, and superhydrophobic-superhydrophilic patterning J. Phys. Chem. C 111 14521–9
[20] Jiang C, Wang Q and Wang T 2012 Thermoresponsive PNIPAAm-modified cotton fabric surfaces that switch between superhydrophilicity and superhydrophobicity Appl. Surf. Sci. 258 4888–92
[21] Rather A M, Mahato S, Maji K, Gogoi N and Manna U 2017 ‘Reactive’ nano-complex coated medical cotton: a facile avenue for tailored release of small molecules Nanoscale 9 16154–65
[22] Flynn Bolte K T, Balaraman R P, Jiao K, Tustison M, Kirkwood K S, Zhou C and Kohli P 2018 Probing liquid–solid and vapor–liquid–solid interfaces of hierarchical surfaces using high-resolution microscopy Langmuir 34 3720–30
[23] Young T 1805 An essay on the cohesion of fluids Proc. R. Soc London, 95 65–87
[24] Fowkes F M 1964 Attractive forces at interfaces Ind. Eng. Chem. 56 40–52