A study on the stability of superhydrophobic paper reinforced by amino-assisted modified PHFMA-PTSPM polymer

Shangjie Jiang\textsuperscript{1,2}*, Shisheng Zhou\textsuperscript{1,2}, Bin Du\textsuperscript{1,2} and Rubai Luo\textsuperscript{1,2}

\textsuperscript{1} Faculty of Printing, Packaging Engineering and Digital Media Technology, Xi’an University of Technology, Xi’an 710048, People’s Republic of China

\textsuperscript{2} Shaanxi Provincial Key Laboratory of Printing and Packaging Engineering, Xi’an University of Technology, Xi’an 710048, People’s Republic of China

* Author to whom any correspondence should be addressed.

E-mail: xautjsj@126.com

Abstract

In this study, hexafluorobutyl methacrylate (HFMA) and 3-trimethoxysilyl propyl methacrylate (TSPM) were used for polymerization. First, the one-step method is used to prepare a hydrophobic polymer with low surface energy (PHFMA-PTSPM), and then the amino groups on the modified silica surface are used to graft nanoparticles on the polymer to improve the roughness, thereby a new type of high stable super hydrophobic paper was prepared. The further study found that the paper after superhydrophobic treatment has strong hydrophobicity, and its water contact angle reached 156°± 1.6°. In addition, the coating on the surface of the paper after superhydrophobic modification has high transparency, and the effect of the superhydrophobic coating on the color of the paper is within the acceptable range of human eye recognition. Moreover, the modified paper not only has good weather resistance and folding resistance, but also has strong corrosion resistance to strong acids, strong alkalis and organic solvents.

1. Introduction

Cellulose fibers-based paper products have been widely used as packaging materials for their favorable properties such as green environmental protection, good printing, easy access to raw materials, low cost, non-toxic, degradable regeneration, etc [1–3]. However, the hydrophilicity of fibers has largely limited the application and development of paper in many fields. In comparison, superhydrophobic paper with a surface water contact angle higher than 150° has attracted considerable interest in fundamental research and practical applications, as the superhydrophobic surface has been demonstrated not only has the characteristics of self-cleaning and corrosion resistance [4–20], but also has the advantages of biodegradability, regenerability, low cost and softness inherent in fiber materials [9–11]. Therefore, the successful preparation of superhydrophobic paper can greatly exert the potential value of paper and broaden the application range. In recent years, it has attracted the attention of many relevant scientific research workers, and has made certain development of superhydrophobic paper research [12–15]. According to the relevant literature reports, several key points for achieving ideal superhydrophobic paper include excellent water resistance, high transparency and good mechanical durability [16–19]. Nevertheless, the preparation of the reported superhydrophobic paper still has some limitations, such as the properties of excessive preparation conditions, complicated process and low mechanical [20–24].

For example, the following methods have been reported mostly, but they all have certain limitations. First, the superhydrophobic properties can be generated by combining the prepared methyltrichlorosilane with fibers, and forming a polydimethylsiloxane surface with nano-roughness [25–27]. However, this method will form hydrochloric acid during the reaction, and it will chemically react with the fiber, corrode and damage the fiber structure of the substrate, thus reduce its physical properties. Second, the superhydrophobic papers were coated with a polydopamine layer and then immersed in the mixture of polydimethylsiloxane (PDMS) and
hydrophobic-silica nanoparticles, the resultant paper can separate oil-water mixtures under gravity driving conditions, but the preparation process is so cumbersome that not suitable for commercial production and application [28]. Third, the superhydrophobic paper can be obtained by dipping TiO$_2$/sodium alginate (ALG) layer by layer on the surface of the paper through the layer-by-layer self-assembly method (LBL), and then immersing it in anionic colloidal wax emulsion, but the physical properties of the paper may be damaged after multiple soaking [29]. Fourth, the coral-like superhydrophobic coating can be formed by modifying the silica with long-chain alkyl groups for low-surface energy, then forming a composite coating with polystyrene and dipping it on the paper, but the transparency of the formed coating is not ideal in this method [30]. Fifth, the pH-regulated intelligent superhydrophobic surface can be obtained by using capric acid and butyl phthalate to react, immerse the fiber in the reactant to obtain low surface energy, and then use silica for roughness modification [31]. However, this method tends to cause insufficient adhesion between the surface of the polymer and the nano-microsphere, making the polymer or nano-microsphere easy to fall off and the superhydrophobic surface is not stable, which limits its application to some extent [32–34].

The one-step method was used in this study. Above all, TSPM and HFMA were used to polymerize in tetrahydrofuran solution to prepare a high-fluorine and high-silicon-based polymer with low surface energy, then the amino-modified nano-silica was used, and the superhydrophobic coating was successfully obtained by the grafting reaction of prepared polymer and modified silica in solution. Finally, while the coating was sprayed on the surface of the paper to form a film, a superhydrophobic coating was formed on the surface of the paper and after drying, this method has the following advantages: Firstly, the preparation method is simple, efficient, repeatable, and suitable for mass production. Secondly, the method has universal applicability and can be used for surface treatment of various kinds of papers without damaging their fiber structure, and does not require complicated pretreatment of the substrate (such as plasma activation). Thirdly, the prepared superhydrophobic paper surface coating has high transparency, and its influence on paper color and printing effect is within the acceptable range of human eyes. Fourthly, the prepared superhydrophobic paper has good stability, such as acid resistance, alkali resistance, organic solvent resistance, folding resistance, etc., and can be stored for a long time in the air.

2. Experimental section

In this study, based on the adequate preparation of relevant experimental materials, the experimental procedures and ideas as shown in figure 1 were used to prepare the superhydrophobic paper.

2.1. Materials

3-trimethoxysilylpropyl methacrylate (TSPM), Hexafluorobutyl methacrylate (HFMA), Sodium bisulphite, tetrahydrofuran (THF), alumina, potassium bromide, nano-silica, azobisisobutyronitrile (AIBN), absolute ethanol, APTES and triethylamine were purchased from Sigma-Aldrich and used as received.

2.2. One-step preparation of low surface energy polymers

The TSPM was filtered through an alumina chromatography column to remove the polymerization inhibitor. First of all, put TSPM (2.5g), HFMA (10g), AIBN (0.4g) and NaHSO$_3$ (0.4g) into a flask containing tetrahydrofuran (75g) at room temperature, place the flask in liquid nitrogen and freeze, and vacuum after the solution is completely frozen, then thawed by passing nitrogen, and the above procedure was repeated again. Afterwards, nitrogen gas was introduced, and the flask was magnetically stirred for 4.5 h in an oil bath heated at 65°C. A colorless and transparent low surface energy polymer PHFMA-PTSPM was obtained, while after the completion of reaction, and the reactant formed in the vessel was poured out and let it stand at room temperature for 3 h until tetrahydrofuran was evaporated.

2.3. Preparation of amino-modified SiO$_2$

Preparing amino-modified silica require four steps: First, SiO$_2$ (2g) was dispersed in ethanol (100 ml) for ultrasonic dispersion treatment for 45 min to obtain a silicone ethanol dispersion, and triethylamine was gradually added dropwise to the dispersion until the pH reached 9. Second, the liquid was transferred to a three-necked flask, equipped with a condensing reflux device, and a coupling agent APTES (2g) was added to the liquid, heated at 80°C in water bath, and magnetically stirred for 8 h. Third, the obtained dispersion was centrifuged at 3000 rpm for 30 min, the precipitate was washed with absolute ethanol and dried, and the purified amino-modified nano-SiO$_2$ was obtained after repeating the procedure three times. Fourth, the purified amino-modified SiO$_2$ was dried at 80°C for 12 h, and ground to obtain amino-modified SiO$_2$ powder.
2.4. Preparation of superhydrophobic surface
The low surface energy polymer PHFMA-PTSPM was dissolved in tetrahydrofuran, and triethylamine (0.6g) was added to obtain a colorless and transparent alkaline solution. Hereafter, the amino-modified nano-SiO2 was added to the solution, and magnetically stirred at room temperature for 2 h to obtain the superhydrophobic coating (PHFMA-PTSPM-SiO2). Furthermore, the modified solution was sprayed on a 2.5 cm² paper substrate and dried at 70 °C to obtain a superhydrophobic paper.

2.5. Characterization
The surface wettability of the modified cellulose fibers were measured using Contact angle measuring instrument DS100 by sessile drop method with 5 μl volume of deionized water droplet at ambient humidity and temperature. The water droplet was gently dropped onto the testing paper sample surface using a micro-syringe, and the water contact angle (CA) was recorded at a contact times of 60 s. The values of CA were measured in five different positions and the average values of the CA were reported. Scanning electron microscopy (SEM) images and the energy dispersive spectroscopy (EDS) were obtained on a JSM-6701F field emission scanning electron microscope, the sample was pre-sprayed before the microtopography was observed. Fourier transform infrared (FTIR) spectra were collected on a Bruker IFS66 V/S spectrometer at a resolution of 2 cm⁻¹. Thermogravimetric analysis (TG) was performed with an STA449 CTG thermogravimetric analyzer. Samples were heated at a ramp rate of 10 °C/min in air, with a temperature range from room temperature to 600 °C. Reflectance spectra of the fabric samples (3 × 3 cm) were determined using a Perkin-Elmer Lambda 35 UV–vis spectrophotometer. Air was used as the reference, the spectra were recorded in the range of 400–700 nm. The three coordinates (L*, a* and b*) of the CIELAB color system and the color difference (ΔE2000) of the fabrics were measured by colorimetry software.

3. Results and discussion
3.1. Effect of SiO2 content on contact angle
Figure 2 shows the morphology and contact angle of the coating of amino-modified SiO2 and polymer (PHFMA-PTSPM) at different mass ratios. While SiO2 is not added to the polymer (PHFMA-PTSPM), the surface of the coating is smooth and flat, showing good hydrophobicity, and the contact angle is 92° ± 1.6°, as showed in figure 2(a). With the addition of amino-modified SiO2, the silica particles attract each other to form micro-nano-sized aggregates and protrusions. Therefore, as the mass ratio of the amino-modified SiO2 to the polymer PHFMA-PTSPM is increased, the surface roughness of the coating is enhanced, and the hydrophobicity of the coating surface also continuously enhanced (it can be seen from figures 2(a) to (c)). according to the Cassie model [35], with the continuous increase of SiO2, the roughness of the coating surface will be greater, and this rough surface coating structure allows the water droplets to contact the coating and capture air between the solid-liquid interfaces to form a composite contact, so that the water droplets do not wet the coating surface [36]. While the mass ratio of the amino-modified SiO2 to the polymer reaches 0.2, the contact angle of the coating surface reaches 152° ± 1.9°, which is superhydrophobic, as showed in figure 2(c) and (e). However, with the continued addition of SiO2, a large amount of silica will destroy the continuity of the PHFMA-PTSPM film formation, causing the coating to break. although these cracks can capture air and make the surface of the coating still have good hydrophobicity, the crack of the coating will affect the appearance and other properties of the substrate, as showed in figure 2(d). Therefore, the mass ratio of the amino-modified SiO2 to the polymer (PHFMA-PTSPM) is preferably 0.2.
3.2. Surface morphology

Figure 3 shows the microscopic morphology of the original paper and superhydrophobic paper that observed by scanning electron microscopy (SEM). Figures 3(a) and (b) shows the fibers of original paper have smooth fiber structure. Figures 3(c) and (d) shows, a large amount of protrusions is apparently formed on the surface of the fiber after the superhydrophobic treatment, and the nano-scale surface roughness is imparted. by comparison, the superhydrophobic coating adhered uniformly on the surface of the fiber, and there was no aggregated block, the fiber edge was still clearly identifiable, so the morphology of the fibers has not changed significantly after modification.

3.3. Preparation of functionalized SiO₂ nanoparticles

Figure 4 shows the TEM images of as-prepared bare and amino modified SiO₂ nanoparticles. as can be seen from the comparison of figures 4(a) and (c), the silica particles before and after the modification exhibited spherical particles of the same diameter, indicating that the modification reaction did not affect the appearance of the silica particles [37]. According to the comparison of figures 4(b) and (d), the distribution between the silica

![Figure 2. SEM images and water contact angle of hybrid coatings with different mass ratio of Amino-modified SiO₂ to PHFMA-PTSPM. (a) 0; (b) 0.1; (c) 0.2; (d) 0.5; (e) is a line graph of the mass ratio of the amino-modified silica to the polymer (PHFMA-PTSPM) and the contact angle.](image-url)
particles before modification is relatively uniform, only a small agglomeration phenomenon occurs, and a large agglomeration phenomenon occurs between the modified silica particles. This is owing to the silica particles themselves have a negative charge, and the interaction between the particles is relatively balanced, while the
surface of the modified silica contains amino groups, the interaction between the amino group and the negative charge on the exposed portion of the functionalized silica surface results in agglomeration, which indicating that the amino group can be complexed to the silica surface.

3.4. FTIR analysis

Figure 5 shows the FTIR spectra of bare SiO$_2$ and amino modified SiO$_2$. The spectrum of bare SiO$_2$ exhibited the absorption peaks at 472 cm$^{-1}$ and 811 cm$^{-1}$ are at tribute to the Si–O bending vibration and stretching vibration respectively [38], the peak at 1109 cm$^{-1}$ is as signed to the Si–O–Si stretching vibration [39], O–OH stretching vibration at around 1622 cm$^{-1}$. In addition to the basic characteristic peaks of the curve a, curve b exhibited two adsorption peaks at 1450 cm$^{-1}$ and 2937 cm$^{-1}$ in both spectra, which stem from CH$_3$ and CH$_2$ bending vibrations and stretching vibrations, respectively. The new peak at 1562 cm$^{-1}$ due to N–H bending vibration. Which indicates that SiO$_2$ has reacted with the amino group of APTES.

The FTIR spectra of HFMA and PHFMA-PTSPM are presented in figure 6. The spectrum of HFMA exhibited CH$_3$ and CH$_2$ stretching vibrations at around 2972 cm$^{-1}$ and 2937 cm$^{-1}$ respectively, C=O stretching vibration at 1736 cm$^{-1}$, C–O stretching vibration at around 1235 cm$^{-1}$, C=C stretching vibration at 1640 cm$^{-1}$, and strong peak at 1190 cm$^{-1}$ is the stretching vibration of C–F. For low surface energy polymer (PHFMA-PTSPM), the new peaks at 794 cm$^{-1}$ and 473 cm$^{-1}$ is the bending vibration and stretching vibration of Si–O. The peak intensity at 1050 cm$^{-1}$–1200 cm$^{-1}$ markedly increases due to the stretching vibration of Si–O–C appears near 1080 cm$^{-1}$, and the coincidence with the C–F stretching vibration makes the characteristic peak widen. In addition, the new peak at 2963 cm$^{-1}$ and 2845 cm$^{-1}$ indicate the introduction of hydrocarbon of TSPM. Moreover, C=C stretching vibration disappeared at 1640 cm$^{-1}$. These observations chemically confirms that the polymerization has conducted successfully.
3.5. Elemental analysis of superhydrophobic paper

The chemical composition of the surface of superhydrophobic paper was analyzed by EDX spectroscopy (figure 7). The spectrum of the pristine paper showed peaks for carbon and oxygen, and the weight percentage of C and O is 50.24% and 49.76%. However, the EDX spectrum of the superhydrophobic treated paper have yielded carbon, oxygen, fluorine and silicon peaks, and the weight percentage of F and Si is 10.64% and 3.45%. Due to the introduction of the two elements, the surface of the paper has good hydrophobicity.

3.6. Thermogravimetric analysis

Figure 8 shows the TGA curves of samples $A_0$, $A_1$, $A_2$. Among the three samples, $A_0$ is the original paper sample, $A_1$ is a paper sample after spraying amino-modified silica, and $A_2$ is a paper sample after spraying PHFMA-PTSPM-SiO$_2$. In this study, the three samples were gradually heated to 600 °C in air to observe the weight loss rate, in order to reveal the influence of the sample surface coating on the thermal stability of the material. The results showed that: When the temperature is between air temperature and 200 °C, the weight loss rate of the three samples is approximately the same. And when the temperature is heated to about 200 °C-300 °C, since the hydroxyl and amino groups on the silica surface of the $A_1$ and $A_2$ begin to rapidly degrade, the weight loss rate of these samples is also faster than that of $A_0$. However, when the temperature is heated to above 300 °C, the surface coatings of $A_1$ and $A_2$ have been completely degraded, and the samples still contain residual substances such as silica, so the weight loss rate of these two samples is generally slower than that of $A_0$. Especially when the temperature is heated to above 450 °C, the weight loss rate of $A_0$ is almost close to 100%, while $A_1$ and $A_2$ still retain more than 4.47% and 3.97% of the original weight respectively. This indicates that the silica coating
on the paper and the composite recombination of PHFMA-PTSPM on the surface of the modified silica particles have a certain effect on the thermal stability of the material [40].

3.7. Performance of superhydrophobic paper

It can be seen from figure 9(a) that due to the large number of hydroxyl groups on the surface of the fiber, and the fiber exhibits superhydrophilicity, which makes the water droplets absorb and disappear quickly on the surface of the paper. However, in the superhydrophobic treated paper, water droplets can form spherical water droplets on the surface of the paper, and the water droplets can stand on the surface of the paper and roll off easily. In this case, the contact angle reaches 156° ± 1.6°, as shown in figure 9(b). Figures 9(c)–(g) shows a series of images taken during the rise and fall of the paper, and it found that the water droplets did not stay on the horizontal surface of the paper. While the paper is raised from (d) to (e), the water droplets do not wet the surface of the paper, but roll off to the side. In addition, while the paper is lowered, the water droplets are detached from the surface of the paper and suspended on the dropper, as figures (f)–(g) shows. It indicates that the prepared paper has excellent hydrophobic properties.

In the actual production and application, Superhydrophobic paper will be affected by external factors such as acid, alkali or organic solvent corrosion, or repeated bending, leading to the insufficient hydrophobicity of the surface. Therefore, the stability is an important indicator of the performance of superhydrophobic paper. Accordingly, this article focuses on paper durability, resistance to acid, alkali and organic solvent, and folding resistance.

Superhydrophobic paper is susceptible to UV light, dust and oil during use, which reduces surface hydrophobicity. Consequently, good durability is an important factor in evaluating the performance of superhydrophobic paper. Figure 10 shows the effect of exposure time on the hydrophobic properties of the paper. It can be seen from the figure that even if the exposure time is up to three months, the contact angle of the paper remains substantially unchanged. Considering from the coating structure, the polymer (PHFMA-PTSPM) contains high bond energy silicon oxide bonds and low surface energy fluorine atoms, and the chemical properties of the silica particles are relatively stable, so the superhydrophobic surface has good durability.

Since paper maybe corroded by acids, alkalis or organic solvents during application, acid and alkali resistance and organic solvents are important factors influencing the service life of superhydrophobic paper. As showed in figure 11, the effect of the pH of water droplets on the hydrophobic properties of superhydrophobic paper is discussed. It can be seen from the figure that when the pH of the water droplets is 1, 7, and 14, respectively, the water droplets can appear spherical on the surface of the paper. The contact angle of water droplets at different pH values on the surface of the paper remains substantially unchanged and both are greater than 150°, so that the prepared superhydrophobic paper has good acid and alkali resistance.

Figure 12 shows the original paper and the superhydrophobic paper are respectively fixed on a glass slide, placed in a cup filled with organic solvent for a while. It can be clearly observed from the figure that the unmodified paper has been completely wetted, and the surface of the modified paper forms a mirror-like bright layer, which called silver mirror layer. The wet state between the liquid and the substrate is distinguished by the presence of the silver mirror layer. This phenomenon occurs is owing to the surface of the superhydrophobic

![Figure 9](image-url) (a) Colored water droplets sitting on pristine and PHFMA-PTSPM-SiO₂ treated paper. (b) Goniometer images for 5 μl droplets. Series of images taken during ascending (c)(d)(e) and descending (f)(g) of superhydrophobic paper surface.
paper repels the organic solvent, so that the air layer trapped on the surface of the paper separates the fibers and the liquid, resulting in the surface of the paper not being wetted and the air layer reflects incident light to form a shiny silver mirror layer. The paper soaked in the organic solvent is taken out, and after drying, the surface of the paper is subjected to a hydrophobicity test. Figure 12(b) shows the paper still has good hydrophobicity, and the contact angle is measured to be $156^\circ \pm 1.9^\circ$. These phenomena indicate that the modified paper has good corrosion resistance to organic solvents.

For superhydrophobic paper, the effect of deformation and bending when turning on the page on hydrophobicity is an important factor in the application. Figure 13 shows the relationship between paper surface wettability and multiple bending cycles. The paper is bent forward to backward, in other words from $-90^\circ$ to $90^\circ$, and this process is defined as a cycle. After the paper is folded over 100 cycles, the surface still shows excellent
Figure 12. (a) Photographs of pieces of pristine and PHFMA-PTSPM-SiO$_2$ treated paper immersed in organic solvents. (b) Colored water droplets sitting on the superhydrophobic paper after soaking in organic solvent.

Figure 13. Effects of bending cycles of water droplet on the water contact angle of superhydrophobic paper.

Figure 14. (a) Reflection spectra of red-colored paper before and after PHFMA-PTSPM-SiO$_2$ coating. (b) Photographs of water droplets on the printed superhydrophobic paper.
hydrophobicity with a contact angle of 153°± 1.5°, indicating that the superhydrophobic paper has good mechanical stability.

Generally, superhydrophobic modification of paper not only changes the wettability of the paper, but also changes the color of the paper. However, it can be seen from the reflection spectra of figure 14(a), the treated paper has a spectral reflectance similar to the original paper in range of 400–600 nm, and slight deviation in the red spectral region of 600–700 nm. The $L^\ast$, $a^\ast$, and $b^\ast$ values, quantitatively characterizing the color of the samples, are reported in table S1 (available online at stacks.iop.org/7/MRX/105301/mmedia). The color difference $\Delta E_{2000} < 2 (\Delta E_{2000} = 1.9)$ is measured, so the effect of the superhydrophobic coating on the color of the paper is within the acceptable range from the perspective of human eye recognition [41]. It can be seen from figure 14(b) that after superhydrophobic treatment of the printed paper, not only the visibility of the printed writing remains unchanged, but also the spraying of the superhydrophobic coating does not smudge the ink.

4. Conclusion

In this study, we demonstrated the low surface energy polymer PHFMA-PTSPM is successfully synthesized by one-step method. During the experiment, while the inorganic nanoparticles are introduced to increase the roughness of the paper, and the amino groups on the surface of the modified silica are used to bond the nanoparticles to the polymer to improve the stability of the superhydrophobic coating, the superhydrophobic paper with a contact angle of 156° ± 1.6° is obtained by spraying. The research shows that superhydrophobic paper not only has good transparency, but also exhibits excellent stability and high corrosion resistance to acids and bases and organic solvents. In addition, since the method does not require harsh and complicated experimental synthesis conditions and the preparation method is simple, easy to implement and high repeatability, it can be used for mass production and practical application.

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ORCID iDs

Shangjie Jiang https://orcid.org/0000-0003-1304-3395
Bin Du https://orcid.org/0000-0003-1302-1348

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