

Improving the hydrophobicity of nylon fabric by consecutive treatment with poly(acrylic acid), tetraethylorthosilicate, and octadecylamine

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ABSTRACT: Nylon fabric was consecutively treated with poly(acrylic acid) (PAA), tetraethylorthosilicate (TEOS), and octadecylamine (OA) to improve its hydrophobicity. We proposed that PAA could be used as a mediator between nylon and OA to provide a high density of the carboxyl moiety. TEOS was used to increase the surface roughness of the nylon fabric by hydrolysis and condensation, and OA was used to reduce the surface energy of the nylon fabric with its long alkyl chains. Both the increase in the surface roughness and the reduction in the surface energy contributed to the improvement of the hydrophobicity of the nylon fabric. The hydrophobicity of the treated nylon fabric was evaluated by the measurement of the water contact angle, water resistance to spray, and hydrostatic pressure. Scanning electron microscopy images showed that the surface roughness of the nylon fabric was significantly increased by treatment with TEOS. The nylon fabric with the PAA/TEOS/OA consecutive treatment exhibited a water contact angle of 125°, a resistance to water spray of 90, and a hydrostatic pressure of 275 mm. It was interesting to find that the PAA/TEOS/OA consecutive treatment slightly enhanced the wrinkle recovery but had no apparent effects on the degree of whiteness and the breaking strength of the nylon fabric. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42456.

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INTRODUCTION

In general, a hydrophobic surface has a water contact angle of greater than 90°.^{1–4} Nowadays, hydrophobic materials have found wide applications in agriculture, industry, national defense, and people's daily lives.^{5–7} Bionic research has revealed that plants and organisms exhibit excellent hydrophobicity because of their low-energy surfaces with micro/nano multiscale structures.^{8–12} This has inspired researchers to develop novel hydrophobic materials by reducing the surface energy and increasing the surface roughness with combined chemical treatments.^{13–15}

Nylon has been widely applied for clothing, upholstery, and carpets because of its high tensile strength, good malleability, and high abrasion resistance. However, nylon film has a contact angle around 72°, and nylon fabric with a woven, knitted, or nonwoven structure can be wetted in a few seconds. Because nylon contains reactive groups such as carboxyl (–COOH) and amino (–NH₂) groups, it is possible to improve its hydrophobicity by a dehydration reaction with low-surface-energy chemicals.^{16–18} Octadecylamine (OA) has a low surface energy because of its long alkyl chain, and it can react with nylon by dehydration between the amino group of OA and the nylon carboxyl group on nylon;^{19,20} this results in a hydrophobic nylon fabric.

However, the density of carboxyl groups in nylon is relatively low because of the fact that nylon only has a carboxyl group at the end of its polymer chain. Such a low density of carboxyl groups in nylon limits the quantity of OA grafted onto nylon. Poly(acrylic acid) (PAA) has a high density of carboxyl groups and thus can be used as a mediator between nylon and OA to provide more reactive groups. Additionally, tetraethylorthosilicate (TEOS) can hydrolyze and condense under proper conditions and thus be chemically bonded on nylon to increase the surface roughness.^{21,22} In this study, we proposed that PAA, TEOS, and OA could be combined to treat nylon fabric and greatly improve the hydrophobicity.

EXPERIMENTAL

Materials

A commercial woven nylon fabric (50D*50D/109*81) was used as a substrate for treatments. TEOS was purchased from Yiji, Inc. (Shanghai, China). OA was purchased from Sigma-Aldrich (China). PAA (MV 240,000) was purchased from J&K Chemical Co., Ltd. (China). Ethanol, methanol, acetone, and ammonium hydroxide (NH₄OH) were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). All of the chemicals were used as received without further purification.

Consecutive Treatments of the Nylon Fabric

PAA Treatment. A PAA treatment solution was prepared by the dissolution of 4 g/L PAA in distilled water. A sample of nylon fabric was immersed into the PAA treatment solution at room temperature for 3 h. The sample was padded with 100% wet pickup and cured in an oven at 120°C for 2 min. The PAA-treated nylon fabric was fully cleaned with distilled water three times and oven-dried.

TEOS Treatment. A TEOS treatment solution was prepared by the dissolution of an amount of TEOS in a mixture of ethanol and distilled water. A certain amount of ammonia hydroxide was added to the TEOS treatment solution as a catalyst. The sample of nylon fabric from the PAA treatment was immersed in the TEOS treatment solution at room temperature for 2 h. The sample was padded with 100% wet pickup and cured in oven at 120°C for 2 min. The treated nylon fabric was fully cleaned with acetone three times and oven-dried at 105°C for 2 min.

OA Treatment. An OA treatment solution was prepared by the dissolution of an amount of OA in methanol at 50°C. A certain amount of ammonia hydroxide was added to the OA treatment solution as a catalyst. The sample of nylon fabric from the PAA/TEOS treatment was immersed in the OA treatment solution at room temperature for 2 h. The sample was padded with 100% wet pickup and cured in oven at 120°C for 2 min. The treated nylon fabric was fully cleaned with acetone three times and oven-dried at 105°C for 2 min.

Measurements

Morphology. The morphology of the treated nylon fabric was observed with a Hitachi SU-1510 scanning electron microscope operated at 5 kV. The roughness and three-dimensional morphology were observed with a Benyuan CSPM 4000 atomic force microscope under ambient conditions.

Fourier Transform Infrared (FTIR) Spectroscopy Characterization. The chemical composition of fabric was examined with a Bruker Tensor 27 FTIR spectrometer.

Particle Size. The size of the particles formed from the condensation of TEOS in the alcohol and water mixture was measured with a Malvern nano-ZS 90.

Water Contact Angle. The water contact angle of the treated nylon fabric was measured with a static sessile liquid drop with a Kruss DSA100 contact angle goniometer under conditions of 20°C and 65% humidity. A volume of 10 μ L of water drops was applied for measurement. The water contact angle was measured five times to obtain an average value.

Resistance to Water Spray. The resistance to water spray of the treated nylon fabric was tested according to AATCC Test Method 22–2010. The testing was performed on a spray tester (model YB-1813, Darong Textile Standard Instruments, China). A sample of the treated nylon fabric was fastened in a metal hoop, which was placed on the stand of the tester. A volume of 250 mL of distilled water was filled into the funnel of the tester, and the water was sprayed onto the sample in 25–30 s. The water spray was evaluated according to the standard.

Hydrostatic Pressure. The hydrostatic pressure of the treated nylon fabric was tested according to AATCC Test Method

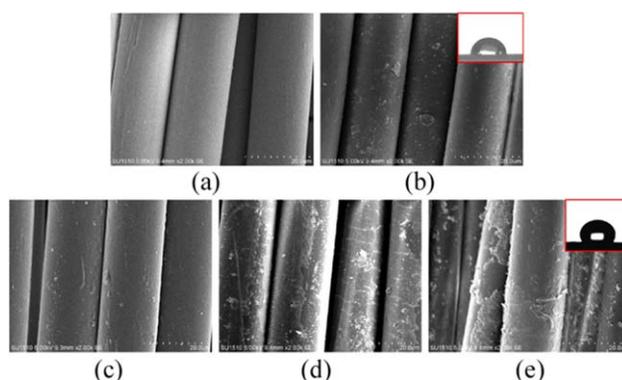


Figure 1. SEM images of the nylon fabrics with (a) no treatment, (b) OA treatment, (c) PAA treatment, (d) PAA/TEOS treatment, and (e) PAA/TEOS/OA treatment (microscopic images of the water contact angles of the nylon fabrics with OA treatment and PAA/TEOS/OA treatment are included in the corresponding SEM images). The nylon fabric was treated in a mixture of water and ethanol with a mass ratio of 3 : 7 with 4 g/L PAA, 3% TEOS, 3% OA, and 1% NH_4OH . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

127–2008. The testing was performed on a hydrostatic pressure tester [model YG (B) 812-120, Darong Textile Standard Instruments, China].

Wrinkle Recovery. The wrinkle recovery of the treated nylon fabric was tested according to GB Standard GB/T 3819-1997. The testing was performed on a wrinkle recovery tester [model YG (B) 5417, Darong Textile Standard Instruments, China].

Tensile Strength. The tensile strength of the treated nylon fabric was tested according to GB Standard GB/T 3923.1–2013. The sample was prepared by cutting the nylon fabric to the size of $20 \times 5.5 \text{ cm}^2$ with the long dimension parallel to the warp or weft and by tearing the edge yarns. Testing was performed on a tensile strength tester [model YG (B) 026D-250, Darong Textile Standard Instruments, China].

Degree of Whiteness. The degree of whiteness of the untreated and treated nylon fabrics were measured according to GB Standard GB/T 23774-2009. The measurement was performed on a spectrophotometer (WSD-III, Kang Guang Spectrophotometer, Ltd., China). The degree of whiteness was calculated with the Hunter whiteness formula.

RESULTS AND DISCUSSION

PAA/TEOS/OA Treatments

Nylon fabric was consecutively treated by PAA, TEOS, and OA. Figure 1 shows the morphology of the nylon fabric after the consecutive treatment and the microscopic images of the water contact angles of the treated nylon fabrics. The roughness and three-dimensional morphology of fabric were observed with atomic force microscopy (AFM), as shown in Figure 2. Untreated nylon, PAA-treated nylon, PAA/TEOS-treated nylon, PAA/TEOS/OA-treated nylon, and OA-treated nylon fabrics were found to have root-mean-square roughness values of 9.09, 18.7, 90.3, 60.2, and 13.7 nm, respectively. As shown in Figures 1 and 2, the untreated nylon fabric had a comparatively smooth surface, whereas the TEOS treatment resulted in an increase in

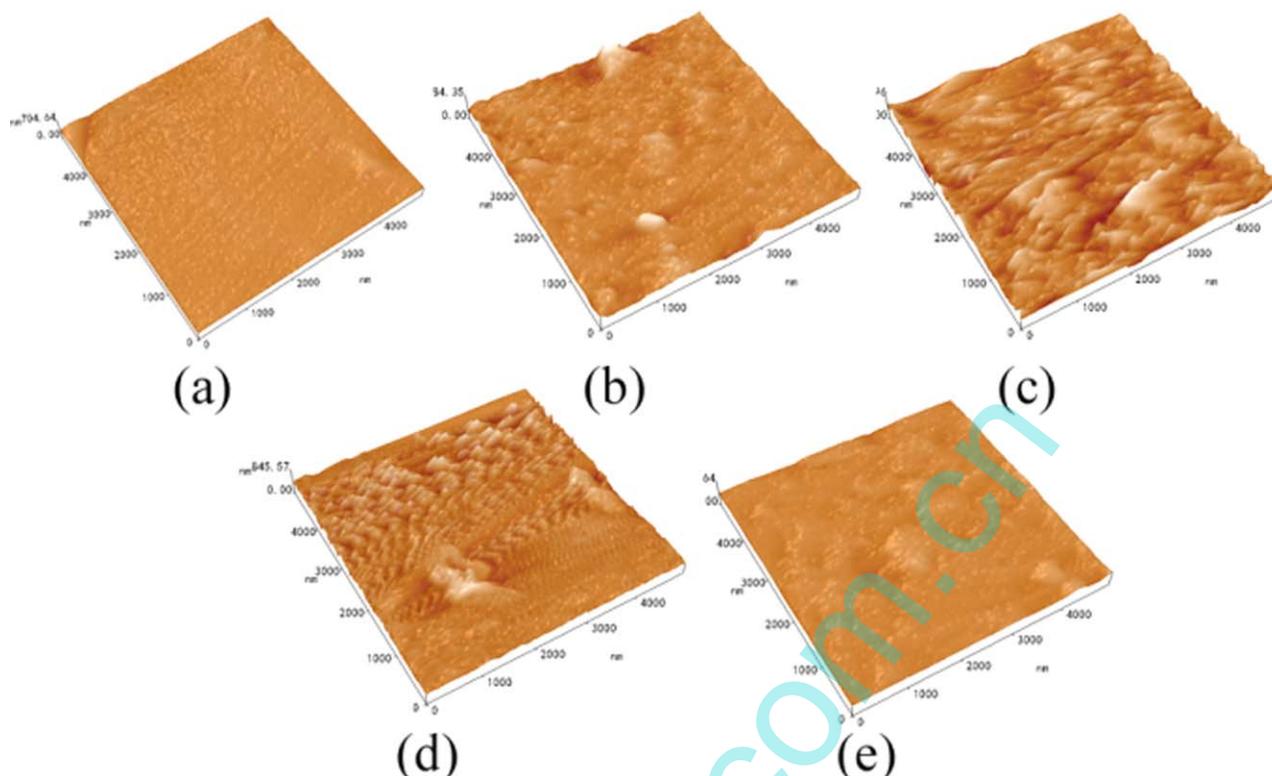


Figure 2. AFM images of the nylon fabrics with (a) no treatment, (b) PAA treatment, (c) PAA/TEOS treatment, (d) PAA/TEOS/OA treatment, and (e) OA treatment. The nylon fabric was treated in a mixture of water and ethanol with a mass ratio of 3 : 7 with 4 g/L PAA, 3% TEOS, 3% OA, and 1% NH_4OH . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the surface roughness of the nylon fabric. As shown in Figure 1, the nylon fabric with OA treatment exhibited a water contact angle around 90° , whereas the nylon fabric with the PAA/TEOS/OA treatment exhibited a water contact angle of 125° . The improvement in the water contact angle of the nylon fabric was ascribed to the subsequent PAA treatment, which introduced more carboxyl groups onto the nylon for reaction with OA, and the TEOS treatment, which increased the roughness of the nylon surface.

Figure 3 shows the FTIR spectra of the untreated nylon, PAA-treated nylon, PAA/TEOS-treated nylon, PAA/TEOS/OA-treated nylon, and OA-treated nylon. In the FTIR curves of the nylon fabrics, the peak at 1633 cm^{-1} was the characteristic absorption of $\text{C}=\text{O}$ of amide. The peaks at 3085 and 3293 cm^{-1} were the associated vibrations of $\text{N}-\text{H}$ of nylon. The peaks at 2857 and 2931 cm^{-1} were the stretching vibrations of $-\text{CH}_2-$. These peaks became stronger for both the PAA/TEOS/OA-treated and OA-only-treated nylon fabrics after OA grafting because of the long alkyl chain of OA. No new peaks appeared for the PAA-treated nylon compared with the untreated one. This may have been caused by the thin coating of PAA. However, the scanning electron microscopy (SEM) images [Figure 1(a,c)] and AFM images [Figure 2(a,b)] proved that the PAA-treated nylon fabric exhibited a rougher surface than the untreated one. This indicated that PAA was successfully grafted onto the nylon fabric. For the TEOS-treated nylon fabric, the peak at 1072 cm^{-1} was the symmetrical stretching vibrations of $\text{Si}-\text{O}-\text{Si}$ bonds.

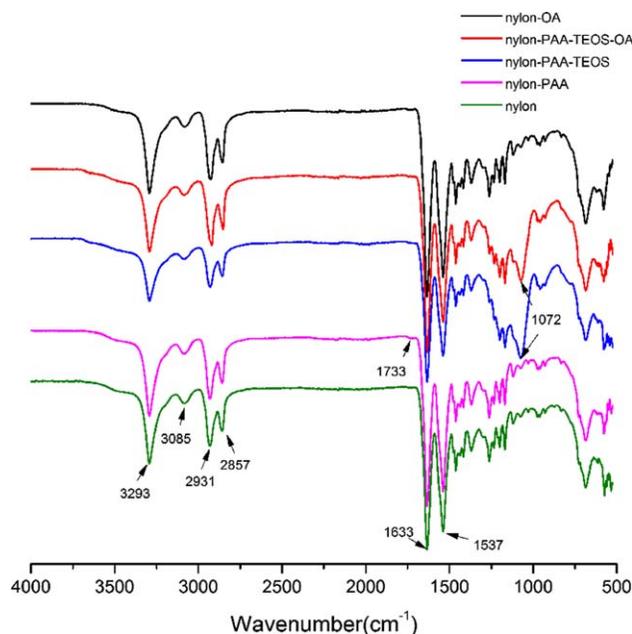
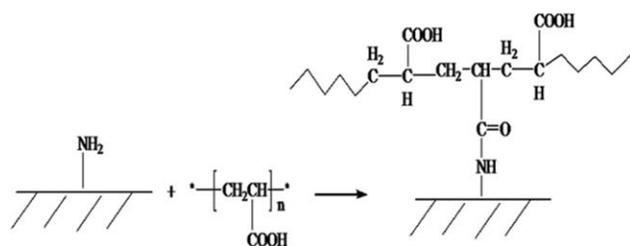


Figure 3. FTIR spectra of the fabrics with no treatment, PAA treatment, PAA/TEOS treatment, PAA/TEOS/OA treatment, and OA treatment. The nylon fabric was treated in a mixture of water and ethanol with a mass ratio of 3 : 7 with 4 g/L PAA, 3% TEOS, 3% OA, and 1% NH_4OH . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Scheme 1. PAA treatment of the nylon fabric by a dehydration reaction.

The peaks at 1072, 2857, and 2931 cm^{-1} suggested that TEOS and OA were grafted onto the nylon fabric.

Hydrophobic nylon can be prepared by methods such as the mixing or grafting of chemicals before nylon spinning or film formation instead of nylon fabric formation.^{23,24} Perfluoro chemicals can be applied to nylon to give it a water contact angle of greater than 150° but cause environmental problems.^{17,25,26} Additionally, techniques such as plasma, microwaves, and femtosecond lasers are used to improve the hydrophobicity of nylon by the creation of a rough surface or through the induction of a chemical reaction. However, these techniques are limited by the machine costs and the treatment parameters, including the power, and nylon fabrics undergo the risk of reduced breaking strength with high-energy treatments.^{25–29} Michielsen and Lee¹⁷ used OA to obtain hydrophobic nylon fabric, for which 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride was used to trigger the reaction, but this was more expensive than the NH_4OH used as a catalyst in this study. In this study, nylon fabric was treated by PAA (4 g/L, 120°C , 2 min of curing), TEOS (3% TEOS, 4% NH_4OH), and OA (3% OA, 1% NH_4OH) with a traditional dipping–padding–curing process under mild conditions (e.g., 120°C for 2 min). After treatment, the nylon fabric was found to be hydrophobic and to have a water contact angle of 125° . It was also found that the treatment had no apparent effect on the degree of whiteness and the breaking strength of the fabric. The consecutive PAA/TEOS/OA treatment was convenient and provided uniform products compared to the treatments with plasma, microwaves, and femtosecond lasers. OA with a long alkyl chain was adopted to provide a low surface energy to nylon and to prevent the environmental problem caused by perfluoro chemicals. Therefore, the consecutive PAA/TEOS/OA treatment of nylon may be interesting to academia and industry.

PAA Treatment

Nylon has a limited number of reactive sites for improving its hydrophobicity by chemical treatment as $-\text{COOH}$ and $-\text{NH}_2$ groups only appear at the end of the polymer chain. PAA contains a carboxyl group in each repeat unit. Such a high density of $-\text{COOH}$ groups in PAA could be used to increase the reactive sites by dehydration reactions between the $-\text{COOH}$ group in PAA and the $-\text{NH}_2$ group in nylon, as shown in Scheme 1. Once the $-\text{NH}_2$ groups in nylon reacted with the $-\text{COOH}$ groups in PAA, the nylon fibers would have been covered with the PAA chains; this could provide excessive $-\text{COOH}$ groups for further hydrophobicity improvement. As shown by the SEM and AFM images, the nylon fibers with PAA treatment [Figure 1(c) and 2(b)] exhibited rougher surfaces than the untreated nylon fibers.

This indicated that PAA was successfully grafted onto the nylon fabric and could be used as a mediator to enhance the dehydration reaction between the $-\text{COOH}$ and the $-\text{NH}_2$ groups.

TEOS Treatment

We assumed that TEOS could hydrolyze [eqs. (1) and (2)] and condense [eqs. (3) and (4)] in the presence of water to form nanoscale or microscale particles, which would deposit on the nylon fabric to create surface roughness. An alkali or acid is often used as a catalyst for the hydrolysis and condensation of TEOS. In this study, NH_4OH was used as an alkali in TEOS treatment because of the fact that the amide groups of nylon hydrolyzed under acidic conditions at a high temperature. The TEOS treatment was carried out in a mixture of water and ethanol because of the fact that TEOS is slightly soluble in water but readily dissolves in ethanol:

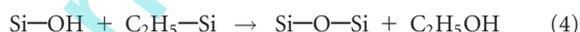
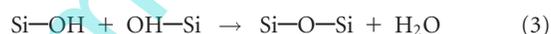
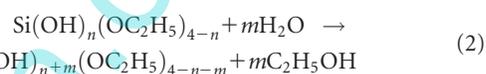


Figure 4 shows the size of the particles formed by the hydrolysis and condensation of TEOS in the mixture of water and ethanol with various mass ratios. As shown, the particle size increased with increasing proportion of water in the TEOS treatment solution, and the largest particle size of 631 nm was achieved at a 3 : 7 mass ratio of water to ethanol. This was mainly due to the fact that water is an essential reactant for the hydrolysis of TEOS, as demonstrated by eqs. (1) and (2). The increase in the proportion of water was enhanced the hydrolysis of TEOS; this provided more $-\text{SiOH}$ groups, which subsequently underwent a condensation reaction to form bigger particles in solution. However, too high a proportion of water in the TEOS treatment solution resulted in a quick hydrolysis of TEOS, and a great number of $-\text{SiOH}$ groups was thus produced in a short period of time. These generated $-\text{SiOH}$ groups condensed to form a

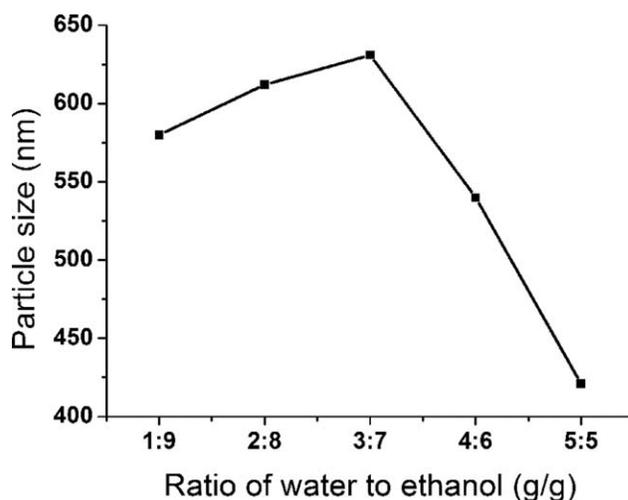


Figure 4. Size of the particles formed by the hydrolysis and condensation of TEOS in mixtures of ethanol and water at various mass ratios. The solutions contained 3% TEOS and 1% NH_4OH .

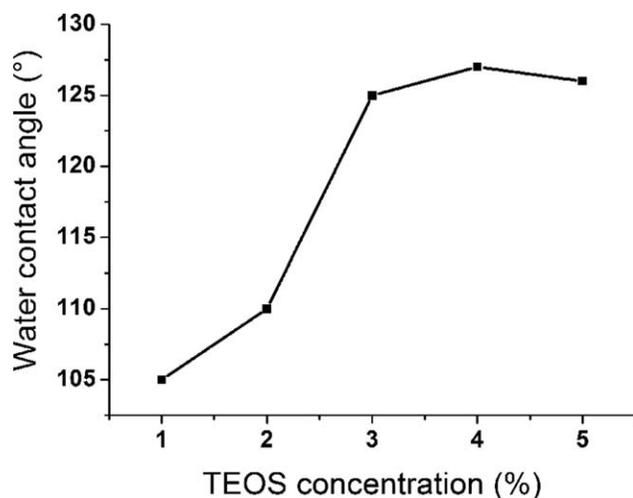


Figure 5. Water contact angles of the nylon fabric with the PAA/TEOS/OA treatment with various concentrations of TEOS. The nylon fabric was treated in a mixture of water and ethanol with a mass ratio of 3 : 7 with 4 g/L PAA, 3% OA, and 1% NH_4OH .

high number of particles, and this was responsible for the small particle size. Hence, it was reasonable, as shown in Figure 4, that the particle size decreased as the mass ratio of water to ethanol increased from 3 : 7 to 5 : 5.

The particles formed by the hydrolysis and condensation of TEOS were responsible for the surface roughness of the nylon fabric. As shown in Figures 1(d) and 2(c), the surface roughness of the nylon fibers was greatly increased after the TEOS treatment. With the assumption that an increase in the surface roughness contributed to an improvement in the hydrophobicity of the nylon fabric, it was possible to optimize the hydrophobicity performance by increasing the concentration of TEOS. Figure 5 shows the water contact angle of the nylon fabric with the PAA/TEOS/OA treatment, for which various concentrations of TEOS were applied. As shown in Figure 5, the

water contact angle of the nylon fabric increased to the greatest value as the concentration of TEOS increased to 3% and was kept to relatively constant in the concentration range of greater than 3%. This indicated that the TEOS treatment improved the hydrophobicity of the nylon fabric by increasing the surface roughness of the nylon fibers, but there was a limit on the concentration of TEOS.

The concentration of TEOS was also found to have an effect on the time that sediment visibly appeared in the treatment solution. As shown in Figure 6, visible sediment appeared in the treatment solution in a shorter time as the concentration of TEOS increased. This was most likely because a higher concentration of TEOS resulted in a faster hydrolysis and, as such, the condensation of TEOS in the treatment solution.

In the TEOS treatment of the nylon fabric, NH_4OH was selected as a catalyst. As shown in Figure 7, the water contact angle of the nylon fabric increased as the concentration of NH_4OH increased. This was ascribed to the fact that a higher amount of OH^- was dissociated with an increase in the concentration of NH_4OH and nucleophilically attacked the Si—O bond to cleave the ethoxyl group ($-\text{OC}_2\text{H}_5$); this, thereby, induced the reactions, as demonstrated in eqs. (1–4).

OA Treatment

A material with an alkyl chain ($-\text{CH}_2\text{CH}_2-$) may have a surface energy as low as 31 mN/m; this is greatly lower than that of nylon fabric, that is, 46 mN/m. OA contains a long alkyl chain, which can thus be used to reduce the surface energy of nylon fabric. As shown in Figure 8, the water contact angle of the nylon fabric increased steeply as the concentration of OA increased to 3%, but it increased slightly when the OA concentration was higher than 3%. This indicated that OA was grafted onto nylon by a dehydration reaction between amino and carboxyl groups, and a certain amount of OA was required to achieve a satisfactory water contact angle.

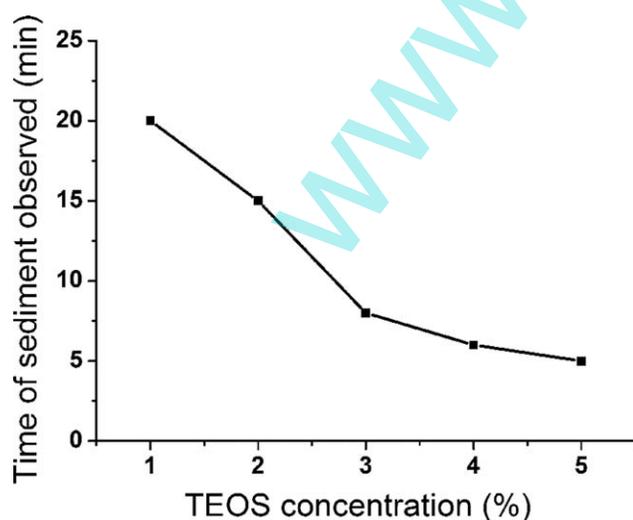


Figure 6. Plot of the sediment appearance time in the treatment solution against the TEOS concentration. The solutions contained 3% TEOS and 1% NH_4OH .

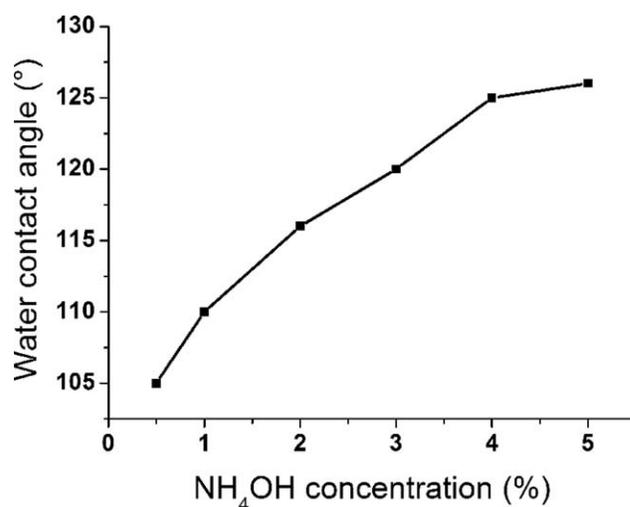


Figure 7. Water contact angle of the nylon fabric with PAA/TEOS/OA treatment with various concentrations of NH_4OH in TEOS treatment. The nylon fabric was treated in a mixture of water and ethanol with a mass ratio of 3 : 7 with 4 g/L PAA, 3% OA, and 3% TEOS.

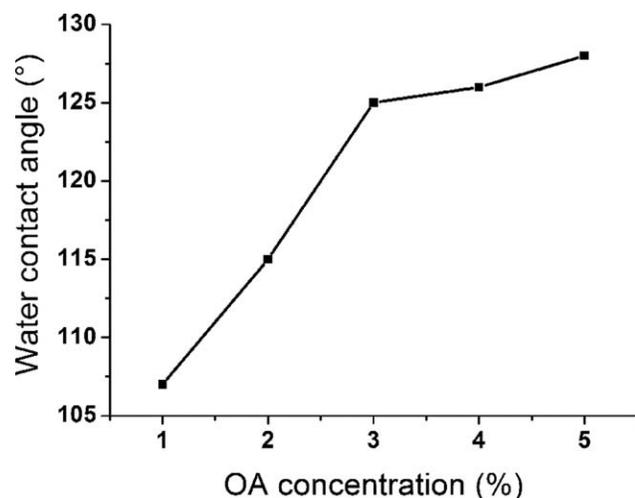


Figure 8. Effect of the concentration of OA on the water contact angle of the nylon fabric with PAA/TEOS/OA. The nylon fabric was treated in a mixture of water and ethanol with a mass ratio of 3 : 7 with 4 g/L PAA, 3% TEOS, and 1% NH_4OH .

Hydrophobicity Performance

The nylon fabric with the PAA/TEOS/OA treatment was characterized by the measurement of the water contact angle, resistance to water spray, and hydrostatic pressure, as summarized in Table I. As observed, the water drop penetrated into the untreated nylon fabric within 3 s, and the water contact angle was measured to be 0° , whereas the water drop was globular on the nylon fabric with the PAA/TEOS/OA treatment [shown in Figure 1(e)], and the water contact angle was measured to be 125° . After it was sprayed with 250 mL of water, the untreated nylon fabric was completely wetted, and its resistance to water spray was rated to be 0, whereas the nylon fabric with the PAA/TEOS/OA treatment had a resistance to water spray with a grade of 90. The hydrostatic pressure of nylon fabric was increased from 200 to 275 mm after the PAA/TEOS/OA treatment. All these results suggest that the hydrophobicity performance was greatly enhanced by the PAA/TEOS/OA treatment.

Effects of the PAA/TEOS/OA Treatment on the Physical Properties of the Nylon Fabric

The main objective of the PAA/TEOS/OA treatment was to improve the hydrophobicity of nylon fabric without a sacrifice of the physical properties, such as breaking strength, wrinkle recovery angle, and degree of whiteness. As shown in Table II, there was no apparent change in the breaking strength of the nylon

Table I. Hydrophobicity of the Nylon Fabric with the PAA/TEOS/OA Treatment

Nylon fabric	Water contact angle ($^\circ$)	Resistance to water spray	Hydrostatic pressure (mm)
Without treatment	0	0	200
With treatment ^a	125	90	275

^aThe nylon fabric was treated in a mixture of water and ethanol with a mass ratio of 3 : 7 with 4 g/L PAA, 3% TEOS, 3% OA, and 1% NH_4OH .

Table II. Effect of the PAA/TEOS/OA Treatment on the Physical Properties of the Nylon Fabric

Nylon fabric	Breaking strength (N)		Wrinkle recovery angle ($^\circ$)		Degree of whiteness
	Warp	Weft	Warp	Weft	
Without treatment	720	525	113	118	89.91
With treatment ^a	718	505	138	133	91.50

^aThe nylon fabric was treated in a mixture of water and ethanol with a mass ratio of 3 : 7 with 4 g/L PAA, 3% TEOS, 3% OA, and 1% NH_4OH .

fabric after the PAA/TEOS/OA treatment. This indicated that the PAA/TEOS/OA treatment did not cause any breaking strength loss in the nylon fabric. It was interesting that in the nylon fabric, the wrinkle recovery angle increased after the PAA/TEOS/OA treatment. Hence, the nylon fabric with PAA/TEOS/OA treatment was more resistant to wrinkles because of the fact that Si—O bonds were formed by the polycondensation of TEOS, in which the bond angle could change under external force and recover once the force was released. The PAA/TEOS/OA treatment had no apparent effect on the degree of whiteness of the nylon fabric.

CONCLUSIONS

The PAA/TEOS/OA treatment was carried out to enhance the hydrophobicity of the nylon fabric. The treatment was optimally performed in 4 g/L PAA first, then in a mixture of water and ethanol with a mass ratio of 3 : 7 with 3% TEOS and 4% NH_4OH , and finally in methanol with 3% OA and 1% NH_4OH . The PAA treatment provided nylon with more carboxyl groups, which enhanced the reaction with OA. The TEOS treatment made the nylon fiber surface rougher, and this was effective for improving the hydrophobicity of the nylon fabric. The nylon fabric with the PAA/TEOS/OA treatment exhibited a water contact angle of 125° , a resistance to water spray of 90, and a hydrostatic pressure of 275 mm. It was interesting to find that the PAA/TEOS/OA treatment gave rise to no apparent reduction in the breaking strength or degree of whiteness but an increase in the wrinkle recovery angle of the nylon fabric.

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