

Solution Blowing of Poly(dimethylsiloxane)/Nylon 6 Nanofiber Mats for Protective Applications*

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Abstract A new strategy was developed to fabricate superhydrophobic nylon 6 nanofibers, in which the blend solutions of poly(dimethylsiloxane) (PDMS) prepolymer and nylon 6 was spun using an innovative solution blowing process, and then the PDMS prepolymer containing nanofibers were cured to obtain PDMS/nylon 6 nanofiber mats. Morphology, surface composition, non-wetting property and protective performance were investigated. The results showed that the addition of PDMS prepolymer improved the spinnability of the spinning solutions, and the PDMS/nylon 6 nanofibers had smooth surfaces and diameters from 100 nm to 350 nm. The presence of PDMS effectively enhanced the hydrophobicity of the nanofiber mats, showing water contact angles of 132° to 161° for PDMS contents of 1 wt% to 3 wt%. The PDMS/nylon 6 mats also possessed excellent protective and transport properties. The results indicated the potential application of the novel nanofiber mats in protective clothing.

Keywords: Nanofiber; Solution blowing; Hydrophobicity; Protective clothing; PDMS.

INTRODUCTION

Nanofiber mats are characterized by their unique properties of having small fiber diameters, small pore sizes, good pore interconnectivity, high specific surface areas and high porosity^[1–4]. These properties can be used in a wide variety of applications such as high performance filters, scaffold in tissue engineering, separation membranes and reinforcement in composite materials^[5–9]. One of the main attractive specifications of nanofiber mats is that they can efficiently remove submicron aerosol particles in filtration systems and protective clothing materials^[10–13]. Ryu *et al.*^[14] investigated the transport properties of electrospun nylon 6 nanofiber mats and the results showed that the filtration efficiency of the nanofilters was superior in comparison to that of a commercialized high efficiency particulate air (HEPA) filter for 0.3 μm particles. Narendiran *et al.*^[15] deposited a layer of electrospun fiber mats on nylon/cotton blended fabric to improve the filtration performance against submicron level aerosol chemical and biological threats. The U.S. Army Natick Soldier Center concluded that a fine layer of electrospun fibers provided good aerosol particle protection, without a significant change in moisture vapor transport of the system^[16].

Solution blowing process has recently been put forward as a new and creative nanofiber fabrication method. In this process, a polymer solution is directly blown and attenuated to the nanofibers by high velocity airflow^[17, 18]. Compared with electrospinning, the solution blowing process is more efficient in producing

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nanofibers because it has a higher solution feed rate, and high voltage equipment is not needed. At present, several polymers, such as poly(methyl methacrylate) (PMMA), polystyrene (PS), poly(lactic acid) (PLA) and cellulose^[19] were successfully spun and the diameters of fibers close to those produced by electrospinning. In our previous study, solution blown nylon 6 nanofiber mats were prepared and they demonstrated superior filtration performance with high efficiency and low resistance^[20].

The non-wettability property is important for many protective applications such as self cleaning and anti-fouling coatings. Various methods have been adopted to obtain superhydrophobic surfaces^[21–25]. Ma *et al.*^[23] synthesized the poly(styrene-*b*-dimethylsiloxane) diblock copolymer and electrospun it from a mixture with polystyrene, and the resulted nonwoven fibrous mats were superhydrophobic with water contact angle (CA) of 163°. Xue *et al.*^[24] fabricated a mechanically stable, self-cleaning web by electrospinning a copolymer of polyhedral oligomeric silsesquioxanes (POSS) and polymethylmethacrylate (PMMA). Ding *et al.*^[25] utilized sol-gel coating of electrospun cellulose acetate with decyltrimethoxysilane (DTMS)/tetraethyl orthosilicate (TEOS) mixture and the coated samples became superhydrophobic with a water CA of 156°.

In the current study, a simple spinning-based method was developed to fabricate superhydrophobic nanofiber mats with excellent protection performance and transport properties. The blend solution of poly(dimethylsiloxane) (PDMS) pre-polymer and nylon 6 was spun to nanofibers via solution blowing process to obtain PDMS/nylon 6 nanofibers after curing. The blend nanofiber mats were hydrophobic because of the presence of low-surface energy PDMS. Compared with the approaches mentioned previously, the developed method in this study is simple and effective.

EXPERIMENTAL

Materials

Nylon 6 pellets were purchased from the Ube Industries, Ltd. (Japan). Poly(dimethylsiloxane) (PDMS) (SYLGARD® 184 Silicone Elastomer KIT) was commercially obtained from Dow Corning Corporation and consisted of liquid components (prepolymer dimethylsiloxane, with vinyl groups) and curing agent (prepolymer dimethylsiloxane with vinyl groups and Si-H groups). Formic acid (98%) was obtained from Tianjin Guangfu Chemical Reagent (China) and used without any further purification.

Preparation of PDMS/Nylon 6 Blend Solutions

Nylon 6 was dissolved in formic acid at 16 wt% content at room temperature to form a homogeneous solution. Then, a calculated amount of PDMS pre-polymer together with the curing agent (10:1) was added to the solution dropwisely and dispersed with ultrasonic to achieve a designed weight ratio of PDMS pre-polymer and nylon 6. The PDMS content was designed as 1 wt%, 2 wt% and 3 wt% of the whole polymer, and they were marked as 1% PDMS/nylon 6, 2% PDMS/nylon 6 and 3% PDMS/nylon 6, respectively.

Solution Blowing of Nanofiber Mats

The schematic of solution blowing apparatus is illustrated in Fig. 1, as described in our previous works^[19]. It consisted of a high velocity compressed air supply, a spinning die, a spinning cabinet and a collector. The spinning die was composed of a cylindrical steel nozzle with diameter of 0.5 mm which was coaxially surrounded by a gas cavity, and the high velocity airflow was supplied to the gas cavity. The spinning solution was supplied to the nozzle and formed a solution stream, and it was subsequently blown and attenuated into ultrafine fibers, accompanied with the evaporation of the solvent. The nanofibers were collected on nylon net to form a nonwoven mat.

In the process, a variety of conditions including solution concentrations, gas pressure, feed rate and collecting distance affect the solution blown nanofibers. In this experiment, the optimum parameters were fixed as follows: gas pressure was 0.1 MPa, feed rate of solution was 16 mL/h, collecting distance was 50 cm.

After the nanofiber mats were spun, they were put in a drying oven at 100 °C for 45 min for removing the residual solvent and post curing treatment.

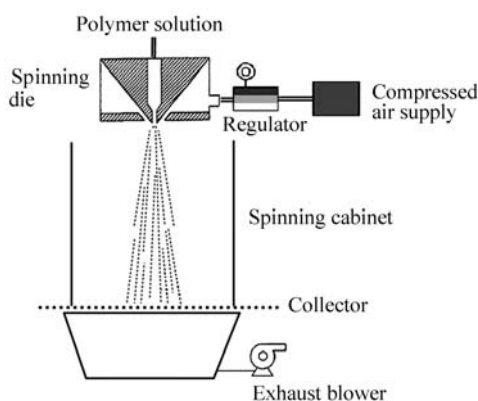


Fig. 1 Schematic of solution blowing apparatus

Measurements and Characterization

Viscosity of solutions was measured at room temperature using an NDJ-79 rotary viscometer (Shanghai Changji Geological Instruments Co., Ltd., Shanghai, China). Surface tension of solutions was tested using a BZY-2 automatic surface/interface tension (Shanghai Hengping Instrument & Meter factory, Shanghai, China) at room temperature.

The morphology of the nanofiber mats was observed using a Field Emission Scanning Electron Microscopy (FE-SEM) (S-4800, Hitachi Co., Japan) after 2 min gold coating (E1045, Hitachi ion sputter, Japan). The EDX spectrum of a PDMS/nylon 6 nanofiber mat was also recorded with the same FE-SEM instrument. The fiber diameters were identified by Image-Proplus analyzer (ipwin32, Soft Imaging System).

Hydrophobic property of the nanofiber mats was determined by measuring the water contact angle (CA) using a video contact angle system (JYSP-180, Beijing Jinshengxin Testing Machine Co., Ltd. China).

The element composition of nanofibers was determined by X-ray photoelectron spectra (XPS) (Bruker AXS D8 discover). Monochromatic Al K α X-rays were employed.

Protection performance of nanofiber mats was assessed by a Filter Media Tester (SX-L1050, Suxin Cleanroom Equipment Factory, China). The monodispersed polystyrene (PS) aerosol (particles size: 0.3 μm) was employed. The penetrating velocity was 5.33 cm/s and the area of the sample was 100 cm².

Transport properties were investigated by measuring the air permeability and water vapor transmission. The air permeability was tested by YG461E-III Fully Automatic Air Permeability Tester (Ningbo Textile Instrument Factory, China) in accordance with GB/T 5453-1997. The moisture vapor transmission rate (MVTR) was measured according to GB/T 12704-91.

RESULTS AND DISCUSSION

Morphology of Solution Blown Nanofiber Mats

Figure 2 shows the SEM images of solution blown nanofiber mats of nylon 6 and PDMS/nylon 6 nanofiber mats with different PDMS contents. From the SEM images, the solution blown fibers were three-dimensional curly which made a loose construction. The fibers were smooth and no beads were observed. The diameter of nylon 6 nanofibers ranged from 200 nm to 450 nm with an average diameter of 268.02 nm (Fig. 2a). While the PDMS/nylon 6 blend nanofibers were from 100 nm to 350 nm in diameter, and their average diameters decreased slightly to 208.91 nm, 182.13 nm and 178.95 nm, respectively. Table 1 shows the viscosity and surface tension of PDMS prepolymer/nylon 6 blend solutions. From the data, the addition of PDMS pre-polymer decreased the viscosity of the blend solutions, which resulted in the lower resistance offered by the polymer chains to the drag forces of the high velocity gas flow, thus resulting in the formation of nanofibers with smaller diameters^[17, 18]. Meanwhile, the surface tension of PDMS prepolymer/nylon 6 blend solutions sharply decreased accordingly, which also played an important role in the formation of thinner fibers and favored the formation of fibers without beads^[26–28].

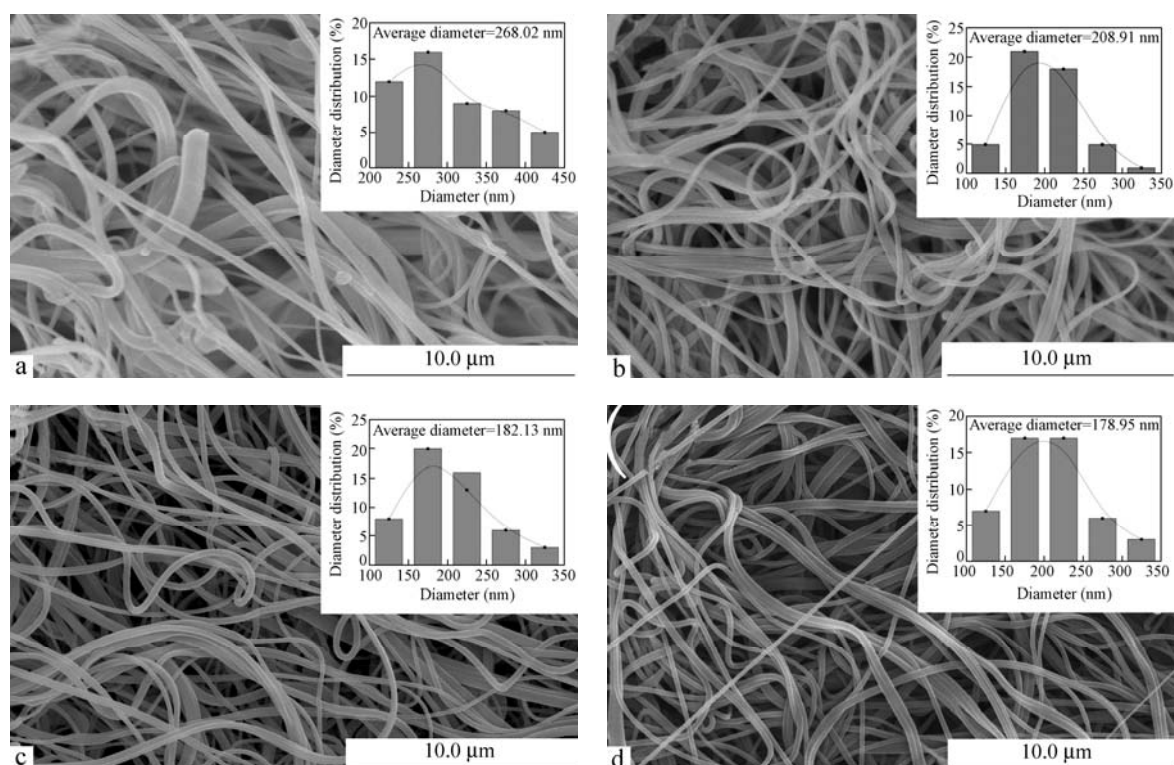


Fig. 2 SEM images of solution blown nanofiber mats: (a) pure nylon 6, (b) 1% PDMS/nylon 6, (c) 2% PDMS/nylon 6 and (d) 3% PDMS/nylon 6

Table 1. Viscosity and surface tension of PDMS prepolymer/nylon 6 blend solutions

Samples	Viscosity value (mPa·S)	Surface tension (mN/m)
16% Nylon6/Formic acid	930	35.6
1%PDMS/nylon 6	780	27.9
2%PDMS/nylon 6	670	26.3
3%PDMS/nylon 6	630	24.8

Superhydrophobic Property of Solution Blown Nanofiber Mats

In the present work, PDMS prepolymer was added into the spinning solutions to fabricate hydrophobic PDMS/nylon 6 nanofibers after the followed curing treatment. Figure 3 shows the water contact angle (CA) of nylon 6 nanofiber mats and PDMS/nylon 6 nanofiber mats. From the figures, the water droplet did not spread out, but formed at equilibrium a spherical cap resting on the nanofiber mats. Nylon 6 nanofiber mats exhibited a water CA of 102.881° . With increasing the PDMS content, the water CA increased to 132.918° , 150.046° and 160.95° for the three PDMS/nylon 6 nanofiber mats, respectively, indicating that the hydrophobicity was greatly improved with the addition of PDMS and showing non-wetting property. The organic portion in PDMS is the methyl group (non-polar), which has almost the weakest intermolecular forces^[29]. The inorganic siloxane backbone, one of the most flexible polymer backbone, allows the methyl groups to be arranged such that PDMS has almost the lowest surface energies known^[29]. So the results were attributed to the low surface energy reduced by PDMS.

The existence of PDMS in the resultant PDMS/nylon 6 nanofiber was confirmed by XPS. As shown in Fig. 4, survey scan of PDMS/nylon 6 showed a characteristic Si_{2p} peak at 102 eV^[30], which proved that PDMS was present at the surface of blend nanofiber mats. Table 2 shows the EDX analysis of 2% PDMS/nylon 6 nanofiber mat. The calculated and measured atomic concentration (atom %) agreed well for PDMS/nylon 6 for C, N, O, and Si, which verified the XPS data and also revealed the presence of PDMS. The existence of PDMS had built up a low surface energy at mat surface, which improved the hydrophobic property of mats.

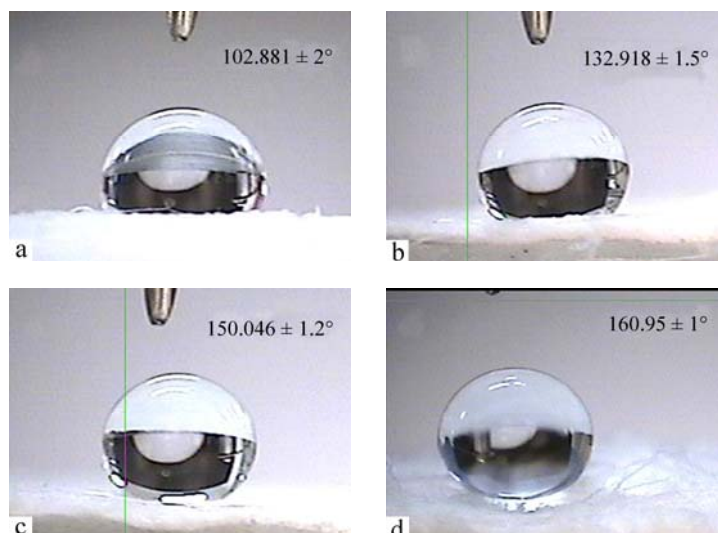


Fig. 3 Images and water contact angle of different content PDMS/nylon 6 nanofiber mats: (a) pure nylon 6, (b) 1% PDMS/nylon 6, (c) 2% PDMS/nylon 6 and (d) 3% PDMS/nylon 6

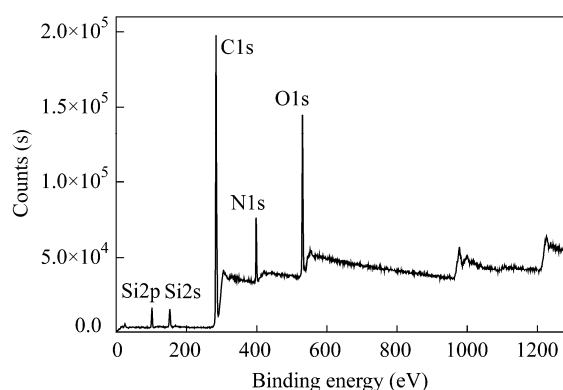


Fig. 4 XPS of solution blown 2% PDMS/nylon 6 nanofibers confirming the incorporation of PDMS into the nanofibers

Table 2. EDX analysis of 2% PDMS/nylon 6 nanofiber mat

Element	Atom content (%) ^a	
	Calculated	Measured
CK	74.75	74.19
NK	12.37	12.41
OK	12.63	13.09
SiK	0.25	0.31

^a Atom content was calculated using (C₆NO) and (C₂SiO) as the repeat unit for nylon 6 and PDMS, respectively. The ratio of PDMS: nylon 6 was 2:98.

Protection Performance and Transport Properties of Solution Blown Nanofiber Mats

To evaluate their protection performance and transport properties as protective cloth materials, nylon 6 and 2% PDMS/nylon 6 nanofiber mats were chosen to evaluate the effect of area density on their filtration and transport properties. They were fabricated with different area densities (5 g/m², 10 g/m² and 15 g/m²). The samples were labeled as Nylon-5, Nylon-10 and Nylon-15 for nylon 6 nanofiber mats, and PDMS/Nylon-5, PDMS/Nylon-10 and PDMS/Nylon-15 for 2% PDMS/nylon 6 ones with different area densities. Their protection performance and transport properties are tabulated in Table 3.

From Table 3, the two kinds of nanofiber mats showed similar trend in filtration efficiency which increased with the area density increasing, *i.e.* the filtration efficiency of nylon 6 nanofiber mat was increased from 46.39% to 93.45% and the value was raised from 59.77% to 95.61% for PDMS/nylon 6 nanofiber mat. At same area density, the filtration efficiency of PDMS/nylon 6 blend nanofiber mats was higher than that of nylon 6 nanofiber mats. It might be reasoned that the smaller diameter of PDMS/nylon 6 nanofiber was acquired, which benefitted for the filtration efficiency. The effect of area density on pressure drop is listed in Table 3, and the results show the samples with higher area density get higher pressure drop. However, all the values of the nanofiber mats were below 35 Pa. While a 10.75 g/m² electrospun mat had about 150 mmH₂O (equivalent to 1471 Pa) pressure drop at the same face velocity^[1]. Herein, the protection performance was suggested providing an acceptable level of high purifying efficiency and low pressure loss for filtration applications.

Transport properties were investigated by measuring the air permeability and moisture vapor transmission rate (MVTR). Table 3 shows the effects of area density on air permeability and MVTR of solution blown nanofiber mats. As shown in Table 3, the nanofiber mats exhibited the high air permeability of 416.46 cm³/s/cm² for Nylon-5 and 329.80 cm³/s/cm² for PDMS/Nylon-5. With the area density increasing, the air permeability was reduced by more than half with respect to the original mats, going to 180.2 cm³/s/cm² and 107 cm³/s/cm², respectively. The results showed that air permeability was strongly dependent on the area density of the nanofiber mats (which was inversely proportional to nanofiber area density) as predicted by other authors^[31]. However, the air permeability of nanofiber mats was above 100 cm³/s/cm², which was higher than most protective clothing materials currently in use^[32].

The moisture vapor transmission rate (MVTR) represents the ability of a material to allow the transfer of moisture vapor through the material. It becomes extremely important in determining wear comfort, especially in hot environments. As shown in Table 3, the nylon 6 nanofiber mats and PDMS/nylon 6 blend nanofiber mats had similar vapor transmission rates, even though the air permeability of nylon 6 mats was much higher than that of PDMS/nylon 6 blend nanofiber mats. The MVTR of the solution blown nanofiber mats were in a range comparable to typical woven work clothing fabrics^[32]. Thus, it could be concluded that the solution blown nanofiber mats are in an acceptable range in terms of air and moisture vapor transport.

Table 3. Protection performance and transport properties of solution blown nanofiber mats

Samples	Filtration efficiency (%)	Pressure drop (Pa)	Air permeability (cm ³ /s/cm ²)	MVTR (g/m ² /h)
Nylon-5	46.39	6.20	416.46	22.1
Nylon-10	82.00	20.0	344.10	22.0
Nylon-15	93.45	30.4	180.20	19.1
PDMS/Nylon-5	59.77	12.7	329.80	23.1
PDMS/Nylon-10	89.54	28.3	210.57	22.6
PDMS/Nylon-15	95.61	34.9	107.00	21.6

CONCLUSIONS

Solution blowing process is an effective method for manufacturing nanofibers directly and continuously. In this study, superhydrophobic PDMS/nylon 6 nanofiber mats were spun *via* solution blowing of the blend solutions of nylon 6 and polydimethylsiloxane prepolymer and the followed curing treatment. SEM images showed the addition of PDMS prepolymer improved the spinnability of the blend solutions and resulted in PDMS/nylon 6 nanofibers with smooth surface and 100–350 nm in diameter. Hydrophobic test indicated that the PDMS/nylon 6 nanofiber mats exhibited superhydrophobicity with high water contact angle (CA). The existence of PDMS built up a low surface energy at mats surface, which improved the hydrophobic property of mats.

Protection performance and transport properties of nanofiber mats were evaluated. The PDMS/nylon 6 nanofiber mats showed satisfactory filtration efficiencies over 90% for aerosol particles (size: 0.3 μm) and pressure drops below 35 Pa at an area density of 15 g/m². The air permeability and the MVTR also were in a

range comparable to typical woven work clothing fabrics. Solution blowing nanofiber mats with PDMS is a simple and effective method to develop non-wetting breathable materials for protective clothing systems.

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