Amine-functionalized thermoplastic polyurethane electrospun fibers prepared by co-electrospinning with 3-aminopropyltriethoxysilane and preparation of conductive fiber mats

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1. Introduction

TPUs are a widely used class of elastomers. Electrospun TPU fiber mats have good mechanical properties [1–4], suitable for practical applications. However, they only possess limited functionalities, restricting their application fields. Surface modification of TPU fibers with functional compounds is a straightforward way to introduce additional functionalities such as antibacterial activity [5], electrical conductivity and bio-catalysis. Although TPU molecules contain urethane groups, it is difficult to modify TPU fibers through these groups due to their low reactivity and weak interaction with other species. Thus, the search for means to introduce more reactive groups (such as amine groups) onto TPU electrospun fibers is of high interest in view of subsequent surface modification.

Some methods have been reported for introducing reactive groups onto the surface of electrospun polymer fibers including mainly copolymerization, co-electrospinning and post modification. By copolymerizing with a functional monomer, a copolymer bearing reactive groups can be synthesized and electrospun into fibers with reactive groups on the surfaces [6,7]. For example, poly(acrylonitrile-co-maleic acid) [6] and poly(acrylonitrile-co-acrylic acid) [7] have been synthesized and electrospun, and the carboxy groups from maleic acid and acrylic acid monomer units can be used to immobilize respectively lipase and chitosan on the fiber surface through amidation. Co-electrospinning with a polymer or inorganic nanoparticles bearing reactive groups can produce fibers having reactive groups on the surfaces [4,8]. As an example, a mixture of poly(2,6-lactic–co-glycolic acid) (PLGA) and PLGA-b-PEG-NH₂ diblock copolymer has been electrospun to produce fibers with amine groups on the surfaces, and through these reactive groups a cell adhesive peptide has been covalently conjugated to the fibers for enhancing the proliferation of NIH3T3 cells [8]. Post modification of the electrospun fibers is an efficient way to generate reactive groups on fiber surfaces [11–14]. Carboxy groups have been generated on carbon fibers by treatment with nitric acid [12], and both carboxy and hydroxy groups have been generated on poly(l-lactic acid) (PLLA) fibers by partial surface hydrolysis [13]. Plasma treatment is a clean and environmentally friendly way to create reactive groups on the surfaces of electrospun fibers [11,14]. By a proper choice of plasma source, various functional groups such as amine, carboxy, oxide and peroxide groups can be created on the fiber surfaces to allow subsequent...
covalent immobilization of various bio-functional molecules. A large amount of work has been reported on the modification of TPU electrospun fibers, but little involves the introduction of reactive groups onto TPU fiber surfaces for the purpose of further modification and functionalization. In a previous work [4], our research group introduced hydroxy groups onto TPU fiber surfaces by electrospinning with silica nanoparticles, and the fibers showed the ability to adsorb gold nanoparticles after converting the silanol groups into amine groups by treatment with APS. However, the adsorption amount of gold nanoparticles is not significant and their distribution is not uniform because of the limited number and irregular distribution of amine groups.

Alkoxy silanes are known to be able to undergo simultaneous hydrolysis and condensation reactions. This character has been used to prepare poly(vinylidene fluoride) (PVDF)/SiO2 nanofibers by electrospinning blend solutions of PVDF and a precursor of SiO2 (tetraethyl orthosilicate or tetramethyloctrosilicate) [15,16]. By thermal treatment of the as-spun fibers, crosslinked silica network was formed inside the fibers, improving the solvent resistance and mechanical properties of PVDF fibers. APS is a widely used silane coupling agent. It is often used to modify the surfaces of inorganic particles such as silica [17,18]. After setting up a reaction, we often observe that the liquid APS remaining on the surface of the pipette just used to transfer APS had already turned into white solid which is insoluble in toluene, a good solvent of APS. This indicates that APS can easily undergo self-condensation upon exposure to air. Moreover, self-condensation of APS can be accelerated by heating in a ventilated oven. In this work, the self-condensation character of APS is used to prepare amine-functionalized TPU fibers by electrospinning blend solutions of TPU and APS, followed by thermal treatment of the as-spun fibers at 60 °C. The amine-functionalized fibers are fully characterized, including fiber morphology, the distribution of Si, the contents of amine groups, and the contact angles of the fiber mats. To demonstrate the potential applications of the amine-functionalized fibers obtained in this work, gold nanoparticles are adsorbed onto the fibers by spontaneous self-assembly and conductive fiber mats are prepared by electrospraying plating.

2. Experimental section

2.1. Materials

TPU (T1180PC) was obtained from Yantai Wanhua (China). It is a polyester type with Mn of 107,800 and Mw/Mn of 1.76, as determined by GPC using tetrahydrofuran (THF) as the eluent. APS was obtained from Aladdin Chemistry Co. Ltd. Hydrogen tetrafluoride (HAuCl4 $\cdot$HCl) was obtained from Aladdin Chemistry Co. Ltd. Hydrogen tetrabromide (NH2OH$\cdot$HCl) were analytical grade and used without further purification.

2.2. Electrospinning

The TPU/APS electrospinning solutions were prepared as follows: TPU was dissolved in DMF/THF (4:6 v/v) by stirring at room temperature for 12 h, then APS was added and the solution was further stirred for 6 h. The concentration of TPU was fixed at 23 wt%. APS contents were 0, 3, 8 and 13 wt% to TPU. Electrospinning was conducted at ambient conditions. The solution was placed into a 10 mL glass syringe capped with a 9-gauge blunt end needle. The positive lead from a high voltage supply was connected via an alligator clip to the external surface of the needle. A grounded metal drum (diameter 6 cm, length 17 cm), wrapped with a layer of aluminum foil and a layer of filter paper, was used as rotating collector. The collector was placed 15 cm from the tip of the needle. The voltage was kept at 15 kV, and the solution flow rate was 1 mL/125 min. After electrospinning, the fiber mats were placed at ambient conditions for 48 h and then heated in a ventilated oven at 60 °C for 24 h.

2.3. Preparation and adsorption of gold nanoparticles

The gold sol containing gold nanoparticles of 16 nm was prepared by the aqueous reduction method [19] and used for adsorption. The electrospun fiber mat together with the filter paper was cut into rounds of 4.0 cm diameter and placed in a vacuum funnel. A certain amount of gold sol was filtered through the mat. Then the mat was rinsed five times with deionized water by filtration.

2.4. Preparation of conductive electrospun mats

Before plating, all glassware was soaked in aqua regia for 1 h and then cleaned with deionized water. The plating solution, containing 0.1 mg/mL HAuCl4 $\cdot$H2O and 0.02 mg/mL NH2OH$\cdot$HCl, was filtered through the mat [20]. Then, the mat was washed five times with deionized water by filtration and then dried at 60 °C for 24 h in a vacuum oven.

2.5. Characterization

The morphology of the fibers was examined using a JSM-7401 FESEM at an accelerating voltage of 1 kV. The average fiber diameters were determined by measuring and averaging the diameter of 50 fibers using JEOL software (SMILEVIEW). In order to investigate the distribution of silicon on the fiber surfaces, the spectrum of EDX was applied on a JSM7001FESEM. The TGA (TA 2050) measurements were carried out at a heating rate of 20 °C/min from ambient temperature to 800 °C under nitrogen atmosphere. XPS data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W AlKα radiation. The base pressure was about 3 × 10$^{-9}$ mbar. The binding energies were referenced to the C1s line at 284.8 eV. The water contact angles were measured with a sessile drop method using a Dataphysics OCA-20 contact angle system, the droplet volume was 4 μL. The solution viscosity was measured with a rotating viscometer (Model NDJ-8S, Shanghai Rex Instruments). The solution conductivity was tested with a conductivity instrument (Model DDSNDSJ-307, Shanghai Rex Instruments). The solution surface tension was measured with Dataphysics DCAT 21 tensionmeter. The contents of amine groups were measured by chemical titration method. The TPU/APS fiber mat was cut into 1 cm × 1 cm squares and immersed in standardized aq. HCl for 2 h and ultrasonic treatment was applied once per 0.5 h to allow the formation of quaternary ammonium salts. After filtration, the filtrate was titrated with standardized aq. NaOH. The content of amine group equaled the reacted HCl during immersing. Because TPU is not swollen in aq. HCl, only the NH2 groups on the fiber surfaces can react and transfer into ammonium salts, therefore, the content of NH2 groups measured by this method represents the NH2 groups on the fiber surfaces. The surface resistivities of the conductive electrospun mats were measured by the four-point probe method.

3. Results and discussion

3.1. Co-electrospinning of TPU and APS

Solutions of TPU/APS containing different amounts of APS (0%, 3%, 8%, and 13%) in DMF/THF 4:6 were electrospun under the same conditions as described in the Experimental section. The fiber morphology was observed by FESEM and shown in Fig. 1. Smooth
fibers without beads were observed for all the four samples. The average fiber diameter decreases significantly when the amount of APS increases, from 1.90 μm (0% APS) to 0.59 μm (13% APS) (Fig. 2). In general, the fiber diameter is related to the properties of the electrospinning solutions when the environmental and equipment conditions are kept constant. As shown in Table 1, the solution viscosity increases significantly with 3% addition of APS, indicating that strong intermolecular interaction exists between TPU and APS, presumably through hydrogen bonding between the urethane groups of TPU and the amine group of APS. With more addition of APS (8% and 13%), the solution viscosity decreases, because the excess APS, as low molar mass liquid having very low viscosity, plays a role of diluting agent. Anyway, the viscosities of all the solutions containing APS are higher than that of neat TPU solution. The solution conductivity increases significantly when the amount of APS increases. Generally speaking, the increase in solution viscosity increases the fiber diameter and the increase in solution conductivity shows opposite effect. In this case, the effect of conductivity is more pronounced than that of viscosity, leading to a decrease in fiber diameter with increasing incorporation of APS.

Fig. 3 shows the EDX Si-mapping micrograph of TPU/13% APS fiber mat. The bright spots representing the silicon element indicate a homogeneous distribution of silicon (thus amine groups) on the fiber mat. The results of the quantitative analysis of silicon element by XPS for the three fiber mats containing different amounts of APS are listed in Table 2. The atomic concentration of Si increases with increasing APS content. Taking TPU/13% APS fiber mat as an example, the Si content in the surface layer of the mat is 1.72 mmol/g, much more than the initial incorporated APS level (0.5 mmol/g), indicating an enrichment of APS on the fiber surface. This can be explained by the different mobility of TPU and APS molecules during electrospinning. Small APS molecules move much faster than TPU macromolecules, and tend to migrate to the surface layer of the fibers.

Fig. 1. FESEM micrographs of TPU/APS fibers containing different amounts of APS: (a) 0%, (b) 3%, (c) 8% and (d) 13%.

Fig. 2. Average fiber diameter as a function of APS content.

The contents of amine groups on the surfaces of TPU/APS fibers were determined by chemical titration method, and the results are listed in Table 2. The number of surface amine groups per gram of fibers increases with increasing incorporation of APS, indicating that the number of surface amine groups can be controlled by the feed. The percentage of the amine groups detectable by chemical titration to the feeding is in the range of 25–39%, further confirming the enrichment of APS condensate on the fiber surfaces. The fact that not all the APS molecules come to the surface layer can be interpreted by the strong interaction between TPU and APS as revealed earlier by the huge increase in the viscosity of the electrospinning solution after the incorporation of APS. The percentage of the amine groups detectable by chemical titration to the feeding
increases when more APS is incorporated, because of the decrease in fiber diameter which increases the specific surface area.

The contact angle measurements further confirm the existence of amine groups on the fiber surfaces. As listed in Table 2, TPU fiber mat is hydrophobic with a water contact angle of 120.5°. After the incorporation of APS, the contact angle decreases. When water was dropped onto the surface of TPU/13% APS fiber mat during contact angle measurements, it penetrated into the mat almost immediately, indicating that the mat has a superhydrophilic surface because of the presence of a significant number of amine groups on the fiber surfaces.

### 3.2. Adsorption of gold nanoparticles on the TPU/APS fiber mats

It is well-known that amine groups have good affinity for gold [21]. To demonstrate the potential applications of the TPU/APS fiber mats as functional materials, the adsorption of gold nanoparticles was investigated. Fig. 4a–d shows the micrographs of the fibers made with different amounts of APS (0–13%) after treating with 10 mL of gold sol. Clearly, no gold nanoparticles were observed on neat TPU fibers, but they were observed on all the fibers containing APS with almost uniform distribution. The presence of gold nanoparticles on TPU/APS fiber surfaces is confirmed by XPS analyses which give an Au atomic concentration of 2.1% for the sample in Fig. 4d. The color of the fiber surfaces change from white into purple, the color of gold nanoparticles. Most gold nanoparticles are monodisperse in an average size of 16 nm, although some slight agglomerates were also observed somewhere on the fiber surfaces. The average particle distance decreases when APS content increases, implying that the ability to adsorb gold nanoparticles is related to the content of amine groups. A significant number of amine groups are needed for high level adsorption of gold nanoparticles. Fig. 4d–f shows the micrographs of the fibers made with 13% APS after treating with different amounts of gold sol (10 mL, 20 mL and 40 mL). The average interparticle distance decreases when more gold sol is used, indicating more adsorption of gold nanoparticles, which can also be visually observed by the change in fiber color from light purple to dark purple. Although the gold nanoparticles seem to pack closely to each other when 40 mL of gold sol is used, the fiber mat is not conductive, indicating that the interparticle distance is still beyond 10 nm, the maximum distance to allow tunneling effect to happen [22].

The amounts of gold adsorption are quantitatively measured by TGA. As shown in Fig. 5, the gold contents are estimated to be 4.5%, 5.7%, 7.5% and 9.7% from the residues at 800 °C after deducting the contribution of TPU/13% APS, when 10 mL, 20 mL, 30 mL and 40 mL of gold sol were used, respectively.

In the literature, there are two methods to prepare polymer/gold nanoparticle composite fibers [4,9,23–32]. The first method is co-electrospinning with gold nanoparticles or their precursor (HAuCl4) [23–28]. The second is the adsorption of gold nanoparticles or their precursor (HAuCl4) on the electrospun fibers bearing functional groups such as amine, thiol and pyridyl groups, which have affinity for gold or HAuCl4 [4,9,28–32]. The main shortage of the first method is that a large proportion of gold nanoparticles is embedded inside the fibers, and the gold nanoparticles on the fiber surfaces are limited. In the second method, the gold nanoparticles are all adsorbed on the fiber surfaces, facilitating the use of the resulting functional fibers. However, this method relies on the use of polymers bearing functional groups or other types of substances such as aminated silica [32], and such polymers or substances suitable for a particular case are limited. The method of introducing amine groups on the fibers reported in this paper is simple and versatile, because it uses low molar mass APS, which is soluble in a wide range of organic solvents, for co-electrospinning with a polymer, and the network structure of APS condensate is formed after electrospinning. Other methods for the immobilization of gold nanoparticles onto electrospun fibers could be developed by referencing the reported work on silver nanoparticles such as the cation-exchange method [33].

### 3.3. Formation of conductive fiber mats

Conductive fiber mats were prepared using the gold nanoparticles adsorbed on the fibers as the seeds, and aqueous solution of HAuCl4·4H2O/NH2OH·HCl as the plating solution. As shown in
Fig. 6, when increasing amounts of the plating solution (100 mL, 200 mL and 400 mL) were filtered through the TPU/13% APS fiber mat treated with 10 mL of gold sol, gold particles grew from 16 nm to 27 nm, 49 nm and 101 nm respectively. With 400 mL of the plating solution the gold particles become big enough to pack closely to each other and form a continuous gold-colored conductive film having a surface resistivity of 1.3 Ω/sq (Table 3). When more plating solution (500 mL) is used, the gold particles can still grow, resulting in a conductive fiber mat with even lower surface resistivity (0.3 Ω/sq). The growth of gold nanoparticles can also be revealed by observing the cryo-fractured cross-sections of the mats (Fig. 6e, f). Gold nanoparticles are also observed inside the mats, but their sizes are smaller than those on the mat surfaces and they are not connected to each other, indicating that the conductive mats obtained in this work can only be used in applications where a conductive surface is needed.

The gold particles have good adhesion to TPU/APS fiber mats. They are not moved after immersing the conductive mats in water for 3 h. Bending the mats manually does not delaminate the gold layer. The morphology and surface resistance of the conductive
mats have almost not changed after bending. Several methods [20,21,34–38] have been reported in the literature for the preparation of conductive composite films, including solution casting polymer/carbon nanotube solutions [34], electroless plating [20,21], deposition of metal nanoparticles on a polymer substrate [35,36], co-sputtering polymer and metal nanoparticles [37], formation of a conducting polymer such as polypyrrole on flexible fabrics [38], etc. The procedure reported in this work, which uses TPU/APS electrospun fibrous mat bearing NH2 groups as the flexible substrate and electroless plating after the adsorption of gold nanoparticles for forming a conductive gold layer, could be a good alternative to the existing methods for making films bearing a conductive surface.

4. Conclusion

Co-electrospinning of TPU and APS in combination with thermal treatment is a simple and efficient method to obtain amine-functionalized TPU electrospun fibers. The amine groups are enriched on the fiber surfaces because of the higher mobility of low molar mass APS during electrospinning compared to high molar mass TPU. Up to 39% of the amine groups are found on the fiber surfaces with homogeneous distribution when 13% APS to TPU is used. The content of surface amine groups can be controlled by the amount of APS feeding. Because APS is soluble in various types of organic solvents, the method could be easily applicable to other types of polymers. The adsorption of gold nanoparticles and formation of conductive gold layer on the amine-functionalized TPU fiber mat demonstrate that the amine groups can be used to bring additional functionalities to the fibers, increasing their application fields.

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<th>Plating solution (mL)</th>
<th>Diameter (nm)</th>
<th>Surface resistivity (Ω/sq)</th>
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<tr>
<td>100</td>
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<td>400</td>
<td>101 ± 7</td>
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Acknowledgments

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References