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Preparation of elastomeric tree-like nanofiber membranes using thermoplastic polyurethane by one-step electrospinning

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ABSTRACT

Recently, the multi-level structure materials with some superior performances has attracted broad attentions. In this study, the elastomeric tree-like thermoplastic polyurethane (TPU) nanofiber membranes with multilevel structure were prepared by introducing tetrabutylammonium chloride (TBAC) via one-step electrospinning. The coverage rate and average diameter of the TPU tree-like nanofibers could be controlled by varying the solution concentrations and electrospun parameters. The special multilevel structure with trunk fibers (diameter 300–500 nm) and branch fibers (diameter 20–80 nm) significantly improved crystallinity, hydrophilicity and flexibility performances comparing with pristine TPU nanofibers, and the novel hierarchical elastomeric tree-like nanofiber membrane had a bright future in various potential applications, such as medical, filtration and protective field, etc.

1. Introduction

With rapid rising of nanotechnology for multi-disciplinary research, electrospinning as a very powerful method for creating diverse kinds of microstructures has caused extensive concern [1]. There has been an increased interest in electrospinning of multi-level structured functional micro-/nano-fibers with large specific area and additional heterogeneous interface [2], such as spider-net structure [3], porous structures [4], tubular structure [5], peapod structure [6], etc. Such materials can be more applicable to sensors [7], adsorption [4], catalysis [8–11], bio-field [12–13] and other fields.

Inspired by tree trunks and tree branches, some groups have successfully prepared hierarchical tree-like nanofibers with unique structures, enhance specific areas and ample internal cavities [14]. Cedar-like hierarchical TiO_2 and secondary ZnO film had been prepared via a combination of electrospinning and hydrothermal [15,16]. Bai [17] reported hierarchical corn-like ZnO/Cu material via facile low temperature hydrothermal and photo-deposition methods. Shi [18] reported branch-like carboxylated (f-MWCNTs)/Chitosan nanofibrous membranes based on the simultaneous electrospinning and spraying. All of these materials had enhanced application performances. However, these tree-like materials were fabricated by multi-step or post-treatment processes and complicated in actual production.

Thermoplastic polyurethane (TPU) is a class of polymer boasting excellent properties of toughness, elastomeric and durability, making it have widespread uses [19–22]. While previous works demonstrated the feasibility of preparing TPU nanofibers by electrospinning, considerable attention have been focused on the decreasing diameter and designing special structures of TPU nanofibers by controlling the electrospun process [23]. Ding [24] reported the polyurethane (PU) nano-fiber/net membranes with spider-like structures via an electro-spinning/netting process. However, the TPU tree-like nanofiber membrane, especially elastomeric tree-like nanofiber membrane, had never been put forward before.

Herein, the elastomeric tree-like nanofiber membrane was presented which was prepared using TPU/tetrabutylammon-ium chloride (TBAC) mixing spinning solution by one-step electrospinning. Different parameters were discussed to obtain optimal parameters. The nanofibers in membrane showed tree-like morphology composed of main fibers acting as trunk fibers (diameter 300–500 nm) and minimal fibers acting as branch fibers (diameter 20–80 nm), and such kind of structure significantly improved properties in terms of crystallinity and hydrophilicity comparing with pristine TPU nanofibers. Moreover, the elastomeric tree-like nanofibers membrane with good shielding property could be used as promising materials for a variety of potential applications in liquid separation and protection field.

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2. Materials and methods

N,N-dimethylformamide (DMF) and TBAC were purchased from Kemiou Chemical Reagent Co., Ltd (Tianjin, China). TPU (Mw = 88,1084) were purchased from the Lubrizol Corporation (Wickliffe, Ohio USA). Spinning solutions were prepared by dissolving TPU (7 wt.%) and TBAC (0.5, 1 and 2 wt.%) in DMF with vigorous stirring over 10 h. To reduce solution viscosity and increase TPU solubility, a slight amount of LiCl was introduced into the solution [25], and then the mixed spinning solutions were transferred into a syringe. The voltages (35, 40, 45 kV) were applied with a high voltage power supply. The outer diameter of needle was 0.8 mm, and a syringe pump was used to control the feed rates (0.5, 1, 1.5 ml/h). The elastomeric TPU/TBAC tree-like nanofiber membranes (TPU/TBAC-TLNMs) were received on the aluminum foil-covered rotating receptor at selected distances of 10, 15 and 20 cm (Fig. 1).

The surface morphologies were characterized by field-emission scanning electron microscopy (FE-SEM, Hitachi S-7400, Japan) after 2 min gold coating (E1045, Hitachi ion sputter, Japan). The diameters were measured by an image analyzer (IPPwin32, Soft Imaging System). The elements at the fibers surface were analyzed by energy disperse spectroscopy (EDS) connected to the FE-SEM. The degree of crystallinity was characterized by X-ray diffraction (XRD) (Rigaku D/MAX-2500, Japan). Thermal stability was evaluated using thermogravimetric analysis (STA 449 F3 JupiterR, NETZSCH, Germany), and samples were heated from 50 to 600 °C at a rate of 10 °C/min under air. Water contact angles (WCA) were analyzed by JYSP-180 (Jinshengxin Detection Instrument Co., Ltd., China) equipped, and the diameter of the water drop was controlled at 1.2 mm. The mechanical properties and flexural rigidity were measured by monofilament tensile testing machine (YG005E, Wenzhou Fangyuan Co., Ltd., China) and automatic fabric stiffness tester (YG022D, Quanzhou Meibang Co., Ltd., China), respectively.

3. Results and discussion

Fig. 2a showed the SEM images of TPU/TBAC-TLNMs with various TBAC concentrations. The pristine TPU nanofibers (TPU-NMs) (Fig. 2a1) had a uniform diameter. After adding TBAC into spinning solutions, the nanofibers exhibited a dramatically decreased average diameter (Fig. 2a2-a4). Among Fig. 2a, the TPU/TBAC-TLNMs (1 wt.%) presented the most obvious tree-like structure. The thicker nanofiber was acted as a support for the multi-level nanofibers like tree trunk, and the thinner fiber formed by splitting was like tree branch. The results might be attributed to the increased conductivity and decreased viscosity (from 2.19 to 1.11 Pa·s at 25 °C and shear rate 10 1/s) of the spinning solution after adding salt [26], and the instability of the Talor cone induced by the high electric-field resulted in splitting. The great influence of salt addition on the electric conductivity of the mixture was revealed in Fig. 2b. It concluded that the morphology of TPU/TBAC-TLNMs strongly based on TBAC contents because increasing conductivity promoted the creation of branch fibers during the electrospinning process.

The morphology and structure of nanofibers are dependent on some electrospinning process parameters [27]. With voltage increasing, the average diameters of branch and trunk fibers decreased (Fig. 2c1-c4). The reason was that the increased voltage brought larger electrostatic forces to the jets, thus leading to the jets fully drawing and splitting into branch fibers, and the fibers with thinner diameters were obtained. However, the process would be unstable when the applied voltage was over 45 kV. It could be concluded that high voltage could lead to the formation of large-scale tree-like nanofibers.

Fig. 2d1-d3 presented SEM images with different injection rates and the average diameters were shown in Fig. 2d4. The solution jets could not keep continuous while the injection rate was lower than 0.3 ml/h, and a large number of branch fibers structure appeared when the injection rate increased to 0.5 ml/h. Further increased the injection rate to 1 ml/h, the branch fibers structure was reduced even disappeared. The results indicated that lower injection attributed to minimizing intermolecular force because of less TPU macromolecules in the body of the jets. The nanofibers were easy to split and form tree-like structure during the process of whipping and stretching of the jet in the electrostatic field. Thus lower injection rate also led to larger-area of tree-like nanofibers. The average diameters of branch and trunk fibers increased with increasing distances (Fig. 2e1-e4). When distances were less than 10 cm, no obvious solution jets were observed. The membranes exhibited large scale tree-like nanofibers at 10 cm. However, the solution jets became unstable and uneasy to be collected when the distance was over 20 cm. The results indicated that the shorter distance was benefit to generate better tree-like structure. It could be explained that high electric intensity around the solution interface attenuated the polymer solution jets.

The EDS patterns (Fig. 3a1-a2) revealed that membrane surface contained C, O and N. Cl peak was appeared on the TPU/TBAC-TLNMs, but no in TPU-NMs, which were attributed to the existence of TBAC. The TPU/TBAC-TLNMs with a large broad diffraction peak around 19.5° indicating an amorphous structure was similar to TPU-NMs (Fig. 3b), but the diffraction peak area was dramatically increased leading to higher crystallinity degree and molecular orientation which was attributed to significant stretching TPU/TBAC

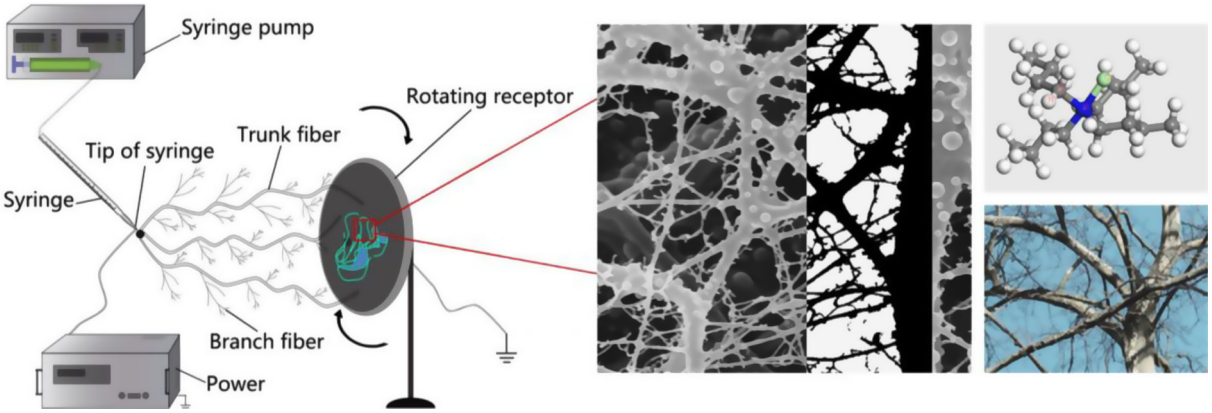

Fig. 1. The schematic of electrospinning.