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Electrospun Polyvinyl Alcohol/Waterborne Polyurethane Composite Nanofibers Involving Cellulose Nanofibers

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ABSTRACT: TEMPO-oxidized cellulose nanofibers (TOCNs) were used as nanofillers in this work. Composite nanofibers of polyvinyl alcohol (PVA)/waterborne polyurethane (WPU) reinforced with TOCNs were produced by electrospinning. The reinforcing capability of TOCNs was investigated by tensile tests. Scanning electron microscopy (SEM), X-ray diffraction, and thermogravimetry analyses were also carried out in order to characterize the appearance, crystallinity, and reinforcing effect of the cellulose nanofibers. SEM results showed that PVA/WPU/TOCNs composite nanofibers presented a highly homogeneous dispersion of TOCNs. The reinforced composites had about 44% increase in their mechanical properties with addition of only 5 wt % of TOCNs while about 42% decrease in elongation at break. The TOCNs reinforced composite nanofibers were more thermally stable than pure PVA/WPU nanofibers. The development of crystalline structure in the composite fibers was observed by XRD. Since PVA, WPU, and TOCNs are hydrophilic, non-toxic, and biocompatible, and therefore, these nanocomposite nanofibers could be used for tissue scaffolding, filtration materials, and medical industries as wound dressing materials. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 41051.

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INTRODUCTION

Electrospinning has been extensively explored as a simple and versatile technique to produce nanofibers from a remarkable range of organic and inorganic materials,[1–3] since it provides a potential way to fabricate continuous nanofibers with different structural designs.[4,5] Many polymer systems have been successfully electrospun into ultrafine fibers in recent years mostly in solvent solution and some in melt form.[6,7] The technique has attracted significant attention since the 1990s, on account of its versatility and economic competitiveness at the laboratory scale for producing nanofibers and composite nano-structures with tuneable properties for a broad range of applications such as separation filters, wound dressing materials, tissue scaffold, sensors, and so on.[5,8–10] However, it has been reported in the literature that electrospun fibrous mats of many polymers and biopolymers possess relatively low dimensional stability and mechanical strength, which limits their use in some of the abovementioned applications.[4]

Polyvinyl alcohol (PVA) is water-soluble, semicrystalline, non-toxic, fully biodegradable, and biocompatible, and therefore, it finds use in a broad spectrum of applications.[11,12] Furthermore, PVA-based fibers have been considered as an attractive choice in tissue scaffolding, filtration materials, membranes, optics, protective clothing, enzyme immobilization, drug release, etc.[12] PVA has been used as an important electrospinning auxiliary for those water-soluble but hard-electrospun materials.[11,13,14] Waterborne polyurethane (WPU) are non-toxic, non-flammable, and do not generate polluted air or wastewater.[15–17] The main technological aspects and advantages of WPU are their solvent free and environmental friendly nature, the low temperature for the drying.[18,19] The thermal stability and mechanical properties of the WPU, however, are still lower than those of the organic solvent-borne PU and need to be improved.[20] Nowadays, great interest in the research and development of WPU has been arising in almost all industrial sectors.[21] PVA/WPU nanofiber mats were firstly prepared using electrospinning method with aqueous solutions by Yang et al.[22] Thereafter, electrospun PVA/WPU/montmorillonite clay (MMT) nanocomposite nanofibers[23] and PVA/WPU/Silver Composite Nanofiber Mats[21] have been also fabricated from aqueous solutions. The electrospun PVA/WPU membranes showed higher water uptake and increased elasticity, which could exhibit a better performance than PVA nanofiber mats and would therefore have potential applications in wound dressings.[21,22]

In recent years, the use of natural fibers as reinforcements in polymers and composites has attracted much attention due to the environmental concerns.[1] Polymers reinforced with cellulose nanofibers are interesting because of the high aspect ratio and potentially excellent mechanical properties of cellulose nanofibers (modulus of ca. 150 GPa and tensile strength of ca. 10 GPa).[24] It was reported that cellulose nanowhisker reinforced nanocomposites showed significantly improved mechanical properties for both natural and synthetic polymer matrixes such as starch, cellulose acetate butyrate, ethylene poly(vinyl chloride), and PVA.[1,25] Cellulose nanowhiskers have been used as reinforcing materials for electrospun fibers such as polystyrene,[26] PVA, poly(lactic acid), and so on.[25]

In this work, we focus on cellulose nanofibers obtained using 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)-mediated oxidation. Novel nanofiber systems were produced by electrospinning aqueous dispersions of PVA, WPU, and TEMPO-oxidized cellulose nanofibers (TOCNs). As expected, the TOCNs showed significant reinforcing effects on PVA/WPU electrospun composite nanofibers. The effects of TOCNs on PVA/WPU composite nanofiber formation and the properties were characterized with scanning electron microscope (SEM), tensile property measurements, X-ray diffraction (XRD), and thermogravimetric analysis (TGA).

EXPERIMENTAL

Materials

WPU (PUD-2019) was purchased from Shanghai Sisheng Polymer Materials Co., Ltd. (SiwoChem, China). PVA (AH-26) and all other chemicals were analytically pure (Sinopharm Chemical Reagent Co., Ltd., China) and used without further purification. All solutions were prepared with de-ionized water.

Preparation of Cellulose Nanofibers

TEMPO-oxidized cellulose was prepared from a commercial softwood bleached kraft pulp using a TEMPO/NaBr/NaClO system at pH 10, in accordance with a previously reported method.[27] A 0.5 wt % TEMPO-oxidized cellulose/water slurry was mechanically homogenized for 2 h at 20,000 rpm with an IKA T25 digital ULTRA-TURRAX® (IKA® Works, Guangzhou). The resulting gel-like dispersion was further transferred into a lyophilizer at −55°C and kept under a 20 Pa vacuum for 24 h. The nanofibers thus obtained had a good individualization with widths of 3–7 nm and lengths of 300–400 nm.

Preparation of PVA/WPU/TOCNs Blend Solutions

PVA (10 wt %) was dissolved in de-ionized water under magnetic stirring at 80°C followed by cooling to room temperature. After dissolution, the required amount of WPU was added. The PVA/WPU blend solution was prepared by mixing PVA/WPU (7/3) solutions at 13.2 wt % total solution concentration, which was the optimum fabrication condition according to the previous study by Yang et al.[22]. If the WPU mass ratio in the blend solution was higher than 3/7, the viscosity of the solution was too low to be electrospun.[21] TOCNs were added to PVA/WPU blend solution to produce a 5 wt % suspension of TOCNs in solution on a dry basis. The dispersion was kept under vigorous mechanical agitation for 2 min.

Electrospinning

For electrospinning, the suspensions were loaded into a 20 mL plastic, disposable syringe with a stainless steel needle (i.d.: 0.84 mm). The needle was connected to the positive terminal of a voltage generator designed to produce a voltage up to 50 kV DC. A thin aluminum foil covering a 15 cm diameter copper plate was used as a collector. The plate was grounded and set at a working distance of 25 cm. An operating voltage of 20 kV was used and polymer solution was fed into the needle at a rate of 0.5 mL/h by a syringe pump. Electrospinning was performed at room temperature and at 35%−45% relative humidity. After electrospinning, the fiber mats were carefully detached from the aluminum foil for characterization.

SEM

The morphology of electrospun PVA/WPU/TOCNs nanofibers was observed with a SEM (HITACHI SU1510, Japan) at an accelerating voltage of 5 kV after gold coating, and the fiber diameter was measured from the SEM images.

Tensile Tests

Tensile strength was determined by a KDII-0.05 testing machine (SHENZHEN KAIQIANGLI TESTING INSTRUMENTS Co., Ltd, China) at ambient conditions. Tensile properties (tensile strength and elongation at break) were determined using samples cut from electrospun mats, 50 mm in length, 5 mm in width and about 0.03–0.04 mm in thickness, at a crosshead speed of 5 mm/min. At least 10 samples were tested for both PVA/WPU and PVA/WPU/TOCNs composite nanofibers.

XRD

XRD was carried out on a Bruker-AXS D8 DISCOVER X-ray diffractometer. The instrument was equipped with a Cu tube. The samples were examined over the angular range of 10°–40° with a step size of 0.02° and a scanning rate of 2.0°/min. The crystallinity index CI (XD) was determined by the method reported.[28,29]

$$\mathrm{CI\,(XD\,)} = \frac{\Sigma A_{\mathrm{Crystal}}}{A_{\mathrm{Total}}} \times 100$$

where A_{Total} is the sum of the areas under all the diffraction peaks and $\Sigma A_{\mathrm{Crystal}}$ is the sum of the areas corresponding to crystalline peaks.

Thermogravimetry

Thermogravimetric (TG) curves were recorded with a TG Instruments model TGA/SDTA 851^e (METTLER TOLEDO). The samples were heated from 25°C to 600°C at a heating rate of 10°C/min under nitrogen atmosphere.

RESULTS AND DISCUSSION

Morphology

Figure 1 shows the TEM images of the TOCNs. And it can be seen from the picture that the nanofibers thus obtained had a good individualization with widths of 3–7 nm and lengths of 300–400 nm. The morphology of composite nanofibers produced by electrospinning, under the conditions previously presented, was studied by SEM. Figure 2 shows typical SEM micrographs for fibers electrospun from PVA/WPU and also from PVA/WPU with TOCNs (5 wt %). The SEM images in

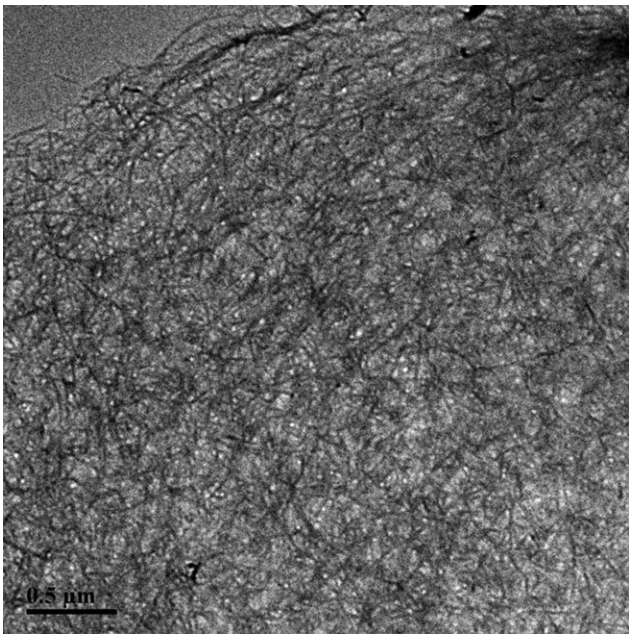

Figure 1. TEM image of dispersions of the TOCNs.

Figure 2(c,d) show that surface of the composite fibers is smooth and has no cracks, therefore, it indicates that the TOCNs elements are well dispersed in the solid PVA/WPU matrix without significant aggregation. A homogeneous distribution of the nanocellulose in the WPU or PVA matrix were observed and proofed by many researchers before.[12,30,31] And it should be attributed to the hydrophilicity of all components and the hydrogen-bonding interactions existing among filler/filler and filler/matrix.[12,30] It is found that nanocomposite nanofibers with average diameters of around 400–700 nm were obtained. The average diameter of PVA/WPU/TOCNs nanofibers depended only on the PVA/WPU ratios.[21] There was almost no change in the fiber diameter as the addition of TOCNs and the surfaces of the fibers were also very smooth.

Tensile Properties

The tensile strength of PVA nanofiber mats was lowered when incorporating WPU into it.[22] Nevertheless, previous studies have demonstrated that nanocellulose has a positive effect on improving mechanical properties for polymer matrixes.[1,25,26] The TOCNs were firstly applied to reinforce the PVA/WPU electrospun nanofibers in this research. To evaluate the tensile properties of composite nanofibers obtained from electrospinning of PVA/WPU and the corresponding nanocomposites with TOCNs, longer electrospinning collection times were used to produce thicker mats suitable for analyses. Stress–strain analysis was carried out using standard procedures at an extension rate of 5 mm/min. The mechanical properties of the electrospun nanofibers of PVA/WPU/TOCNs were compared with nanofibers of PVA/WPU electrospun in the same experimental conditions. Typical stress–strain curves of electrospun nanofibers of PVA/WPU and PVA/WPU reinforced with cellulose nanofibers were illustrated in Figure 3. The composite nanofibers showed a

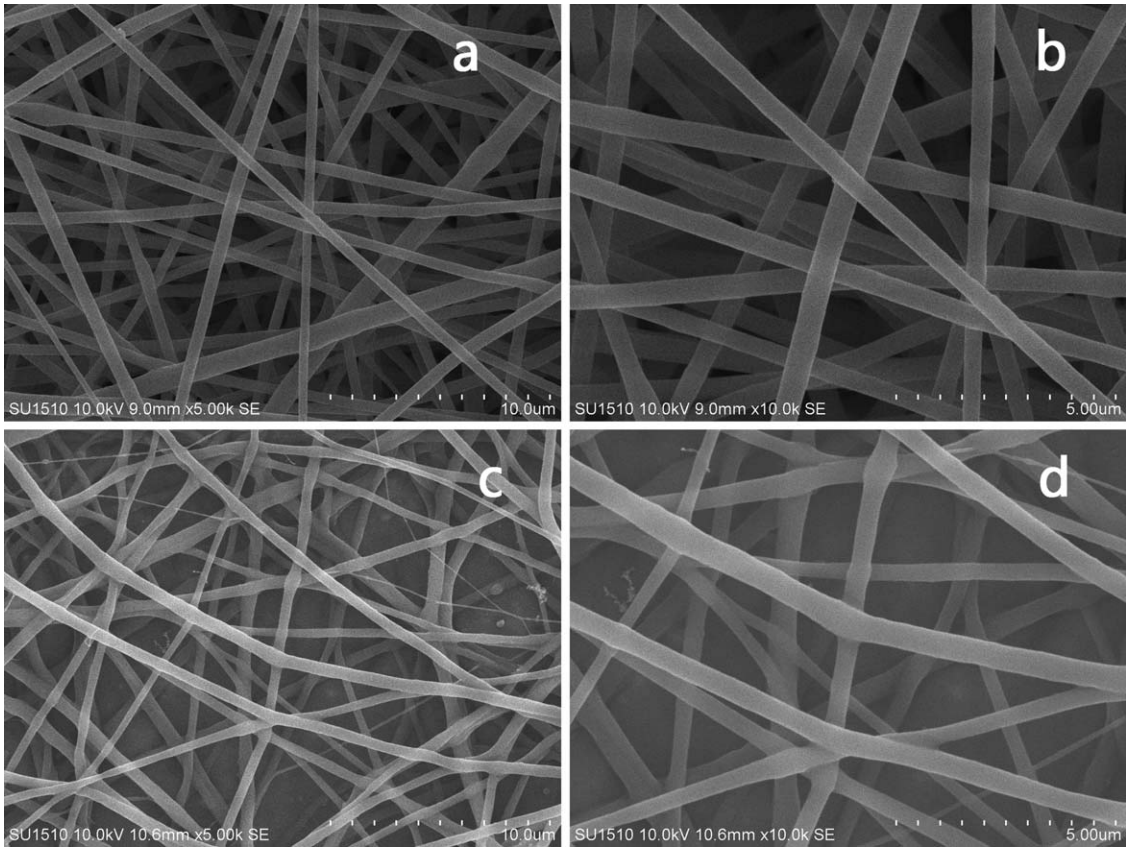

Figure 2. SEM images of pure PVA/WPU nanofibers (**a, b**) and PVA/WPU/TOCNs nanofibers prepared with TOCNs (5 wt %) (**c, d**).

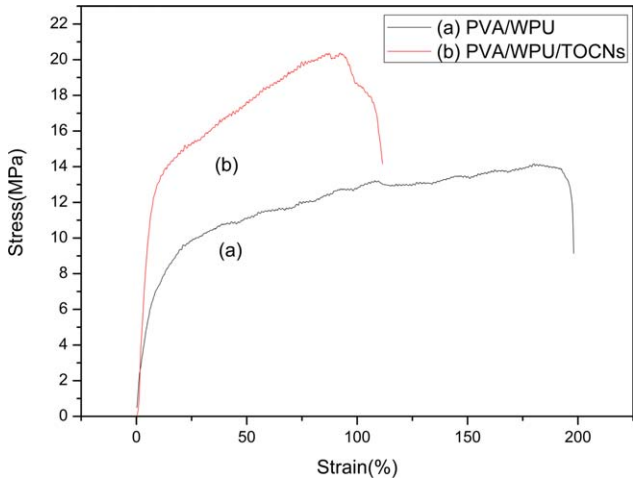

Figure 3. Typical stress–strain curves of electrospun composite nanofibers of PVA/WPU (**a**) and PVA/WPU/TOCNs (**b**). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

nonlinear elastic behavior in the low-stress region and plastic deformation at higher stress. In the case of PVA/WPU/TOCNs nanofibers, their tensile strength and elongation at break were dramatically changed compared with the pure PVA/WPU nanofibers. It can be observed in Figure 3 that tensile strength of reinforced composites increased by about 44% by addition of only 5 wt % of TOCNs. Meanwhile, elongation at break was decreased by about 42%. A similar behavior was found by Lee and Deng[25] with isotropic PVA electrospun fiber reinforced with cellulose nanowhiskers in which tensile strength is almost doubled by adding 15% cellulose nanowhiskers. As we know that the addition of stiff reinforcements can reduce the elongation of break of the matrix since the reinforcements will cause stress concentrations.[32]

It is obviously to see the improvement in the tensile strength of the PVA/WPU nanocomposites with the addition of TOCNs at only a 5 wt % concentration to the matrix. This was attributable partly to the homogeneous distribution of cellulose nanofibers in the polymer, and the high level of compatibility between the nanofibers and polymer matrix, which was aided by the high interfacial surface area.[24,33] The synergistic interaction between fillers and between the filler and polymer matrix played an important role in reinforcing the nanocomposites.[34] Additionally, the inherent stiffness of the TOCNs was also very important. Wu et al.[35] found that the original TOCNs film had a Young's modulus and a tensile strength of 11.6 GPa and 210 MPa, respectively. Furthermore, the hydrogen bonding between the cellulose nanofibers and PVA/WPU matrix resulted in the formation of a rigid network, yielding improved mechanical properties.[24] Since Yang et al.[22] has proofed that the water uptake of the electrospun PVA/WBPU membranes is high. And moreover, the mechanical properties of the electrospun PVA/WBPU nanofiber mats could be improved by incorporating a small amount of TOCNs. So the electrospun PVA/WBPU/TOCNs nanofiber mats would have better potential applications in wound dressings than PVA or PVA/WPU mats.

XRD Data

The XRD pattern of PVA/WPU electrospun nanofibers shows diffraction peaks at 2θ of about 13.9°, 27.4°, and 31.6°, respectively [Figure 4(a)]. It is readily to find a different diffraction peaks at 2θ of about 19.7° in the XRD pattern [Figure 4(b)] of PVA/WPU/TOCNs composite nanofibers. This was obviously due to the contribution of the TOCNs included in the composite. Zhou et al.[33] studied the XRD of the TOCNs and pointed out that peaks were observed at $2\theta = 14.8°$, 16.6°, and 22.9°, corresponding to a cellulose I structure. However, the peak of $2\theta = 14.8°$, 16.6° of TOCNs disappeared with incorporation of PVA and WPU. And it indicated that strong interaction occurred among TOCN, PVA, and WPU molecules in the composite nanofibers.[36] Crystallinity indexes were determined from the XRD data. And as expected, the incorporation of TOCNs produced an increase of 2% in the crystallinity index of composite nanofibers. TOCN elements were likely dispersed individually in the solid PVA/WPU matrix without significant aggregation, and played a significant role in enhancing degree of PVA/WPU chain orientation of the amorphous PVA/WPU molecules. Endo et al.[37] said that such "nano-effects" arising from the addition of only 1 wt % TOCN clearly manifest on the composite fiber and the crystallinity increased by adding 1% TOCNs.

Thermal Stability

Yang et al.[22] said that thermal degradation temperature of WPU is not as high as that of the PVA, therefore, the thermal properties were lower as a higher mass ratio of WPU in the PVA/WPU blend nanofiber mats. Nevertheless, the thermal stability of PVA/WPU nanofibers could be increased by using MMT[23] or Ag[21]. The influence of TOCNs on thermal properties of polymer matrix was explored as well in this work. Thermal stability of electrospun PVA/WPU/TOCNs nanofibers was measured using TGA in nitrogen atmosphere. Figure 5 shows TGA

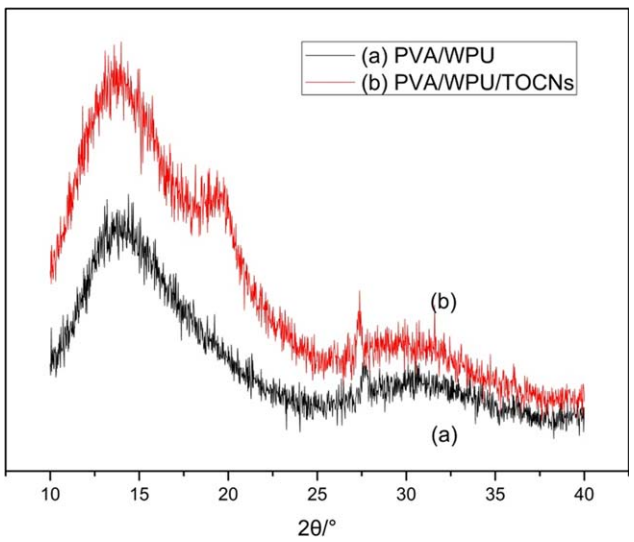

Figure 4. XRD patterns of electrospun nanofibers of PVA/WPU (**a**) and PVA/WPU/TOCNs (**b**). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

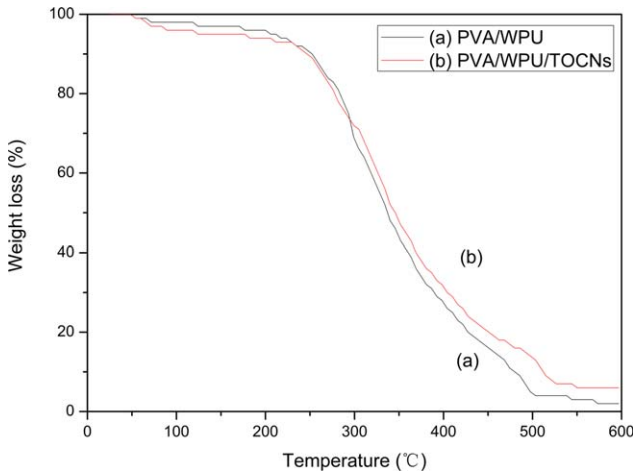

Figure 5. TGA curves of electrospun nanofibers of PVA/WPU and PVA/WPU/TOCNs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

thermograms of PVA/WPU composite nanofibers with and without TOCNs. Both of the curves showed the same trend of thermal stability: three weight loss peaks were observed in Figure 4 and rapid change in mass occurs in the range of 240°C–380°C. All the samples showed an initial weight loss around 75°C resulting from the moisture vaporization in electrospun nanofibers upon heating.[24,38] Up to 300°C, there was an increased thermal stability from the pure PVA/WPU nanofibers to PVA/WPU/TOCNs nanofibers. The increased thermal stability was due to the restriction of the mobility of polymer chains and suppression of the decomposition as a result of the homogeneous distribution of cellulose nanofibers in the polymer.[24]

CONCLUSIONS

Electrospun composite nanofibers of PVA/WPU reinforced with TOCNs were successfully produced. The TOCN elements were well dispersed in the polymer matrix. And it was confirmed that the incorporation of TOCNs into the PVA/WPU electrospun nanofibers increases the physical properties of electrospun composite nanofibers. The reinforced composites had their tensile strength increased by about 44% by addition of only 5 wt % of cellulose nanofibers due to the good interaction between PVA and cellulose nanofibers during the electrospinning process. Nevertheless, the elongation at break was decreased by about 42%. Moreover, in terms of thermal properties, the thermal stability was also improved through incorporating TOCNs. Therefore, these results indicate that addition of TOCNs to electrospinning solution of PVA/WPU is a promising method to improve the mechanical strength and thermal stability of electrospun nanofibers. The electrospun nanofibers could be considered as an attractive choice in tissue scaffolding, filter, wound dressing materials, and so on.

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