Electrospinning of Waterborne Polyurethanes

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ABSTRACT: Polyurethane (PU) fibers were obtained by electrospinning of waterborne PU dispersions. As dispersion cannot be electrospun, a water-soluble polymer (poly (ethylene oxide) (PEO)) was dissolved in the PU dispersion and fibers were obtained from electrospinning the resulting mixture. Pure PU fibers were obtained after removing PEO with water extraction. Continuous PU fibers were obtained using a PU/PEO weight ratio higher than 2.5. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 1176–1179, 2010

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INTRODUCTION

The electrospinning[1,2] process uses an electrostatic potential to form uniform fibers with diameters of the order of 100 nm to 10 μm. The resulting fibrous mats with high-specific surface area and submicron degree of porosity have a wide range of potential applications, such as, filtration devices, membranes, vascular grafts, protective clothing, molecular templates, and tissue scaffolds. Electrospinning occurs when a charged polymer solution or melt, emits a charged fluid jet in the presence of an electric field.[3,4] The jet follows a chaotic trajectory of stretching and splaying until it reaches a ground target, thereby completing the circuit. A polymer solution with sufficient chain overlapping[5] and entanglements undergoes a bending instability that causes a whip-like motion between the capillary tip and the grounded target, which results in thinning of the jet and formation of submicron scale diameter fibers.

Using this technique, fibers of different morphologies can be generated but the conventional process suffers from the inability to mix ingredients "*in situ*." A recent method that combines electrospinning with the twin-screw extrusion process offers some significant advantages.[6,7]

In the majority of the cases the electrospinning process is carried out using organic solvents.[8–10] Nevertheless, from an environmental and safety point of view, organic solvents are not considered good candidates and water is the preferred solvent. Unfortunately, polyurethanes (PU), and the majority of the polymers, are not water-soluble.

According to literature, a water-soluble polymer can be used to integrate water-insoluble objects into electrospun fibres.[11] Recently, this strategy has been used to electrospin a polystyrene latex using a small amount of poly(vinyl alcohol) and its subsequent extraction by water.[12] Using a similar methodology, in this article, PU fibers were obtained from a waterborne PU dispersion. To the best of our knowledge, this is the first time that PU fibers have been obtained from aqueous media. The use of aqueous dispersions for the preparation of water-insoluble PU fibers by electrospinning offers new perspectives for the preparation of polymer micro and nanofibres.

EXPERIMENTAL

Materials

Isophorone diisocyanate (IPDI), 2,2-bis(hydroxymethyl)propionic acid (DMPA), 1,4-butanediol (BD), Poly(1,4-butylene adipate)diol end-capped (M_n ≈1000) (PBAD), triethylamine (TEA), dibutyltin diacetate (DBTDA), Poly(ethylene oxide) Mv ≈900,000 (PEO), and acetone were purchased from Aldrich Chemical Corporation. All chemicals were used as received.

Preparation of waterborne polyurethanes

Waterborne polyurethanes were synthesized in a 250 mL jacket-glass reactor equipped with a mechanical

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TABLE I
Composition of the Dispersions for Electrospinning

Water (g)	PEO (g)	PU (g)	PEO/water (wt %)	PEO/PU (w/w)
9.5	0.5	0.5	5.3	50/50
9.5	0.5	1.2	5.3	30/70
9.5	0.5	2.0	5.3	20/80
12.5	0.5	2.0	4.0	20/80
16.7	0.5	2.0	3.0	20/80
9.5	0.5	2.8	5.3	15/85
12.5	0.5	2.8	4.0	15/85

stirrer, a nitrogen inlet, and a condenser. A water bath was used for controlling the reaction temperature.

The polyol (PBAD (22.5 g)) and an internal emulsifier (DMPA (1.5 g)) were fed into the flask reactor together with DBTDA (700 ppm). The system was heated at 60°C and once PBAD was totally melted, acetone (40 g) and the required amount of TEA (1.5 g), in order to completely neutralize DMPA acidic groups, were added. When the reaction temperature reached 60°C, IPDI (12.5 g) was added dropwise to the reactor at a rate of 1 mL/min. The reaction was carried out for 4 h under nitrogen atmosphere and mechanical stirring (200 rpm), and afterward the chain extender (BD (2 g)) was added.

The reaction was periodically monitored by FTIR, and was considered complete when the infrared absorbance of NCO groups (around 2260 cm^{-1}) was negligible.

After that, 40 g of the polymeric solution (50% of solids) were introduced into another reactor at 25°C and the mechanical stirring was raised to 400 rpm. Water (65 g) was added dropwise to the reactor at a low-flow rate, continuing the stirring for 30 min. Finally, acetone was removed using a distillation equipment. The resulting dispersion had 22.3 wt % of solids, particle sizes of 80 nm (measured by light scattering), and a weight-average molecular weight (M_w) of 18,000 (calculated by gel permeation chromatography and referred to polystyrene standards).

Electrospinning

PEO was dissolved in distilled water by gentle stirring with a magnetic bar at 50°C and atmospheric pressure. Once dissolved, the required amount of the PU dispersion was added. Different dispersions were prepared changing the PEO/PU weight ratio from 15/85 to 50/50. Three different PEO/water weight percentages were used 3, 4, and 5.3 wt %. Table I summarizes the composition of the prepared dispersions.

For the electrospinning process, polymer dispersions were placed into a syringe with an 18-gage blunt-end needle that was mounted on a syringe pump (Cole-Parmer). Randomly oriented fibers were electrospun by applying a voltage of 9–10 kV to the needle using a Spellman CZE1000R high voltage supply (0–30 kV, CZE1000R; Spellman High Voltage Electronics Corp.), with a low current output (limited to a few microampere). The ground plate (stainless steel sheet on a screen) was placed at 30 cm from the needle tip. The syringe pump delivered the polymer dispersion at a controlled flow rate of 0.01 mL/h. The resulting fibers were collected on the screen in order to produce a sheet of nonwoven fabric. All the experiments were performed twice.

Removal of PEO

The template polymer (PEO) was removed from electrospun fibers by water extraction. The standard procedure was as follows: fibers were put into distilled water for at least 24 h at room temperature. After this treatment fibers were dried in air for 24 h before characterization.

Instrumentation

Dynamic light scattering (DLS) was used to determine the diameter of the particles, Dp, using a Malvern Nanosizer (Malvern Instruments). The position of the detector was at 173° relative to the laser source (back-scattered detection). All the samples were measured in distilled water thrice and the final

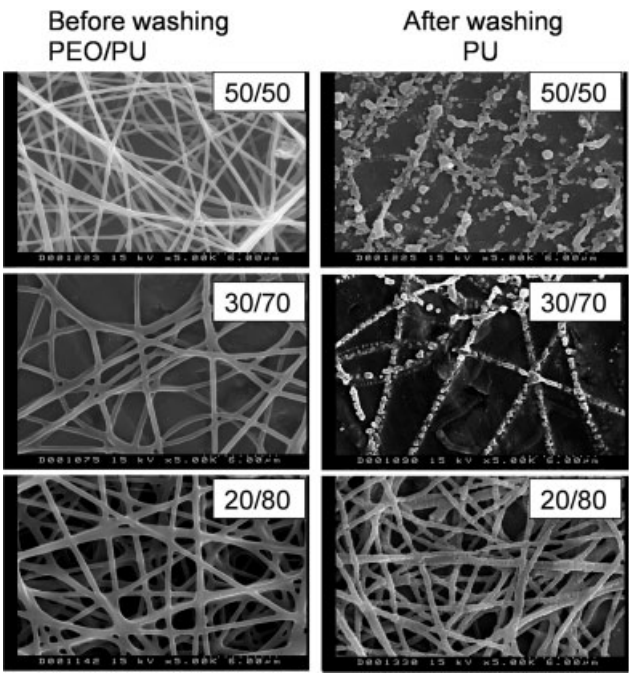

Figure 1 SEM images of fibers obtained by electrospinning from different PEO/PU ratios before and after water treatment (5.3 wt % PEO/water).

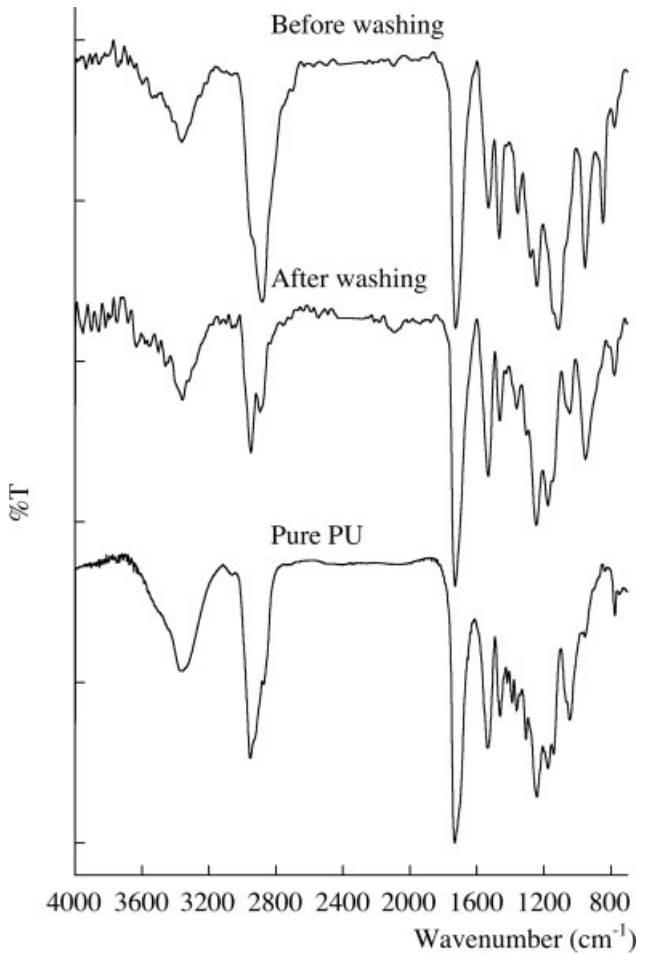

Figure 2 Infrared spectra of the pure polyurethane and PEO/PU 50/50 fibers before and after washing.

value was an average of all of them. The samples were diluted before measuring to avoid multiple light scattering.

Electrospun fiber morphology was analyzed before and after water treatment using a Hitachi S-2700 scanning electron microscope (SEM) at 15 kV accelerating voltage, after putting the samples on a SEM disk and sputter-coated with an 8 nm Pt/Au layer to reduce electron charging effects.

The infrared analysis of the electrospun samples was performed in a Nicolet Magna-IR 560 spectrometer with an attenuated total reflectance (ATR) objective equipped with a zinc selenide crystal (Spectra Tech.). The spectra were collected at a spectral resolution of 8 cm^{-1} by accumulating 64 scans.

RESULTS AND DISCUSSION

It is well-known that one of the necessary conditions in order to obtain fibers through the electrospinning technique is the existence of entanglements among polymeric chains. In fact, we were able to do so from acetone solutions of the PUs aforementioned. However, it was not possible to obtain fibers from the aqueous dispersions of the same polymers unless a template water-soluble polymer was used.

To electrospin the PU dispersion, a water-soluble polymer (PEO) was added to the dispersion. According to literature,[5] a minimum concentration of 4 wt % of PEO in water is necessary to obtain fibers by electrospinning, therefore a slightly higher concentration (5.3 wt %) of PEO was selected to prepare the dispersions. Different PEO/PU blends were prepared at this concentration and stable fibers were obtained in all the blends except in the 15/85 composition. In this case, it was not possible to stabilize the electrospinning process because of the high viscosity of the blend. Figure 1 (before washing PEO/PU) shows the SEM photographs of the obtained fibers.

The obtained fibers were washed with water in order to remove PEO and obtain pure PU fibers. The extraction process was monitored using infrared spectroscopy. Figure 2 shows the infrared spectra of one of the investigated systems before and after water extraction.

When comparing the spectra of the fibers shown in Figure 2, a band centered at about 1120 cm^{-1} is clearly seen, attributable to the C—O—C stretching vibration of PEO. This band disappears once the fibers were washed. Moreover, the spectrum of the fibers after water washing shows the same absorptions than the spectrum of pure PU. According to this, it can be concluded that using the described washing methodology PEO was completely removed from the fiber.

The fiber SEM photographs after water extraction are also shown in Figure 1 (after washing PU). After the cleaning process, in the materials obtained using

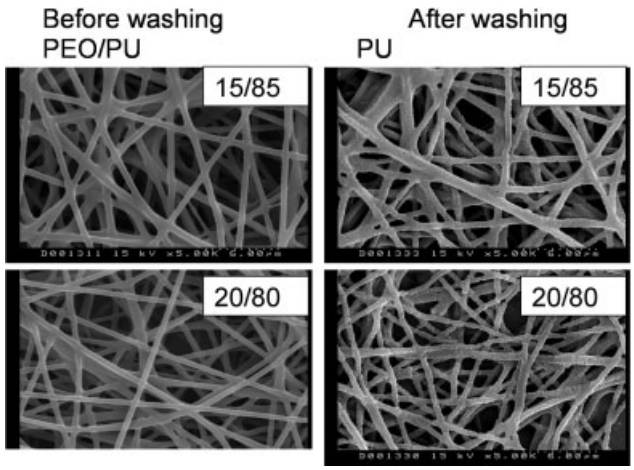

Figure 3 SEM images of fibers obtained by electrospinning from different PEO to PU ratios before and after water treatment (4.0 wt % PEO/water).

50/50 and 30/70 PEO/PU weight ratio the fibers disintegrate after the removal of the template polymer. Using higher PU concentrations, the fibers preserved their shape after the water treatment, indicating their stability. According to literature,[12] polystyrene fibers obtained by electrospinning, using poly(vinyl alcohol) as a template, maintained the spherical particle shapes of the original dispersion, as was easily observed by SEM photographs. On the contrary, in our case, the PU particles were not observed in the obtained fibers. This result can be attributed to the glass transition temperature of the PU used in this work ($\cong -70°C$), which is below room temperature. Therefore, during the electrospinning process, PU particles join together and coalesce due to solvent evaporation and thinning of the jet.

In an attempt to minimize the use of the template polymer, PEO concentration was reduced to 4 wt %. The dispersions (PEO/PU 20/80 and 15/85) were electrospun and the morphology of the obtained fibers is shown in Figure 3.

As shown in Figure 3, after water washing, continuous PU fibers can still be obtained reducing PEO concentration to the minimum concentration suggested in literature.[5]

Finally, we tried to obtain fibers reducing this concentration to a low value (3 wt %) but a combination of beads and fibers was obtained. According to this, in order to obtain fibers, at least 4 wt % of PEO/water concentration must be used.

CONCLUSIONS

Using PEO as template polymer, a waterborne PU dispersion has been successfully electrospun. After water washing, fiber-like morphology was obtained using a minimum of 4 wt % PEO water concentration and PU/PEO weight relations higher than 2.5.

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