Polyurethane/Multiwalled Carbon Nanotube Nanowebs Prepared by an Electrospinning Process

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ABSTRACT: Polyurethane (PU) and PU/multiwalled carbon nanotube (MWCNT) nanocomposite nanofibers, both with diameters of 350 nm, were prepared by an electrospinning process from PU dimethylformamide solutions. The appearance of nanowebs in PU/MWCNT nanofiber structures containing PU fibers with diameters of 20–40 nm was observed. The existence of these structures could have been based on the occurrence of strong secondary electric fields, which were created between individual conducting MWCNTs (distributed in the PU/MWCNT nanocomposites), which started to behave as the local moving nanoelectrodes promoting the creation of additional very fine nanowebs during the electrospinning processes. To our knowledge, this is the first report describing nanowebs from synthetic polymers prepared by an electrospinning process.
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INTRODUCTION

Electrospinning is a unique and attractive methodology for nanoscale fiber production from both synthetic[1,2] and natural sources[3] through the use of an external electric field imposed on a polymer solution[4] or melt.[5] Fibers prepared by electrospinning technology may have almost circular cross sections, smooth surfaces, and diameters ranging from a few nanometers to several micrometers.[6] These fibers have great applicability for drug-delivery media, medical implants, nanocomposites for dental restoration, preservation of bioactive agents, biosensors, molecular separation, filters, tissue engineering, wound dressing, and protective clothing.[6–8] The main weakness of these structures seems to be their poor mechanical properties caused by relaxation processes occurring immediately after fiber formation, at which a certain degree of molecular orientation is lost.[9–12] With the aim to overcome this problem, nanocomposite fibers can be combined with single-walled carbon nanotubes (SWCNTs) or multiwalled carbon nanotubes (MWCNTs) to achieve a significantly enhanced Young's modulus.[12]

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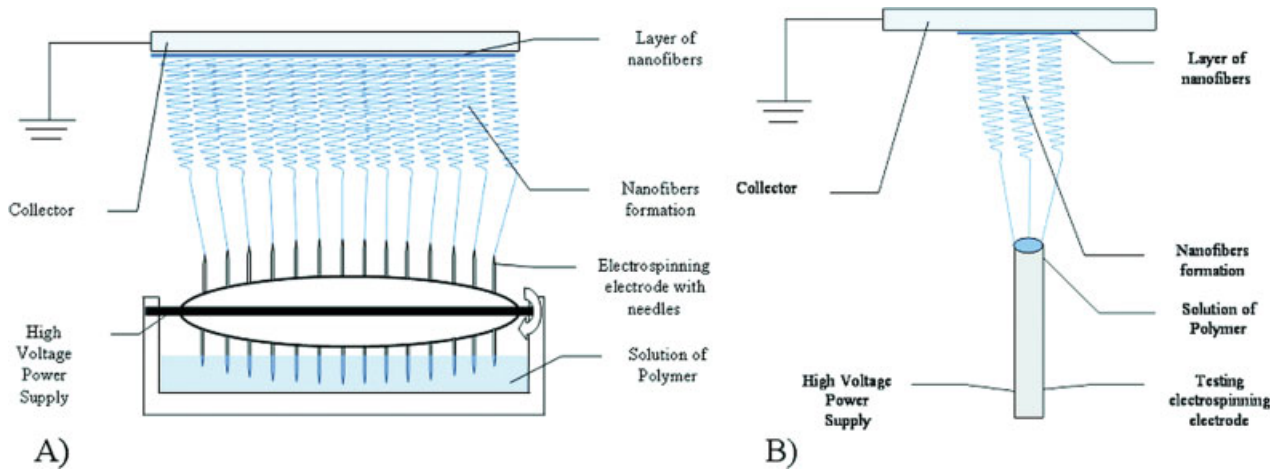
Recently, weblike structures (containing very fine fibers 5–15 nm in diameter) occurring together with aligned fibers with much higher diameters (100–150 nm) have been identified in natural biopolymers, such as collagen spider silk, denatured collagen, and Bombyx mori silk, reinforced by SWCNTs (produced by electrospinning technology[12–14]). As these structures mimic natural tissue structure, they can be used as scaffolds for biomedical tissue engineering.[6] Such nanowebs structure can also lead to enhanced mechanical properties in fibers prepared via electrospinning.[12,13] Lam[13] explained weblike structure formation during silk electrospinning by the creation of small SWCNT ropes (created from SWCNT cluster breakdown during the dispersion of the SWCNTs by sonication), which were consequently reagglomerated in the silk solution to form a large bundle (with a diameter exceeding that of the nanofiber) and expelled during electrospinning from the polymer jet under extremely high force and velocity, which caused the bundles to open and form nanowebs.

Polyurethane (PU) elastomeric materials pose desirable technological and life-cycle properties. Their physical and mechanical properties can be significantly varied in terms of the amount of soft and hard segments during polymer synthesis. They are resistant to microorganisms and abrasion with high hydrolytic stability. Unfortunately, up to now, there has been no research reported about a procedure that can be used to produce nanowebs from any synthetic polymers such as PU. Thus, the main aim of this study was to investigate whether these structures could be obtained by an electrospinning



Scheme 1 (A) Scheme of the electrospinning process with the NanoSpider machine with a rotating electrospinning electrode with needles. (B) Scheme of the electrospinning process with one electrospinning electrode for TEM sample preparation. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

process applied onto a PU solution and to provide a plausible explanation for the mechanism leading to the development of these structures.

EXPERIMENTAL

Materials

PU solution in dimethylformamide (DMF) was synthesized from monomers such as 4,4′-methylenebis(phenyl isocyanate), polyester diol (number-average molecular weight $\sim 2 \times 10^3$), and 1,4-butandiol at a molar ratio of 6: 1 : 5 at 90°C for 5 h. A prepared solution suitable for electrospinning had a total PU concentration of about 13 wt %, a viscosity of 1.4 Pa s, and a conductivity of 140 μS/cm (adjusted by tetraethylamonium bromide). The dispersion of MWCNTs in PU solution was prepared with help of sonication with a Dr. Hielscher GmbH apparatus (ultrasonic horn S7, amplitude = 88 μm, density of power = 300 W/cm^2, frequency = 24 kHz) for 4 h at 65°C. The MWCNTs (acetylene type, purified) were supplied by Sun Nanotech Co., Ltd. (China; diameter = 10–30 nm, length = 1–10 μm, purity > 90%, volume resistance = 0.12 Ω cm, as reported by the supplier). The MWCNT material was used as received or with a surface modification. The modification was done through a two-step oxidation as described in ref. 15; that is, hydrogen peroxide was applied first, and a nitric and sulfuric acids (1 : 3 volume ratio) mixture was used in the second step. Oxidized MWCNTs were washed and dried before reaction with 4,4′-methylenebis(phenyl isocyanate) in DMF to derive carboxylic and hydroxyl groups from isocyanate ones.[16]

Electrospinning process and analysis

In the first step, pure PU and PU/MWCNT nanofibers were prepared from a PU solution in DMF with a commercially available NanoSpider machine (Elmarco s.r.o. Liberec, Czech Republic) (http://www.elmarco.com/) with one rotational electrode with needles [see Scheme 1(A)]. Consequent structure analyses were done by field emission scanning electron microscopy (FESEM; JSM-6700F, Jeol, Tokyo, Japan). With the aim of analyzing the presence of MWCNT material in the prepared PU/MWCNT nanofibers and also of understanding the PU nanoweb structures in more detail, transmission electron microscopy (TEM; JEM 2010, Jeol, Tokyo, Japan) was used. For an effective detailed structure analysis of the certain part of the PU/MWCNT and nanowebs, it was necessary to prepare a sample containing only a small amount of nanofibers/nanowebs by means of an electrospinning process with one static electrode only, as depicted in Scheme 1(B). The experimental conditions of the electrospinning process with both types of electrodes were the same as the following ones: relative humidity ≈ 29%, temperature ≈ 25°C, electric voltage ≈ 75 kV, distance between electrodes = 18 cm, electrode spin = 7 r/min, and speed of antistatic polypropylene nonwoven fabric collecting nanofibers = 0.16 m/min. The square weight of one prepared nanofiber layer was measured to be about 900 mg/m^2 (rotational electrode).

RESULTS AND DISCUSSION

FESEM analysis of the PU and PU/MWCNT nanofibers prepared by the electrospinning process with a rotating electrode are provided in Figure 1(A,B). It

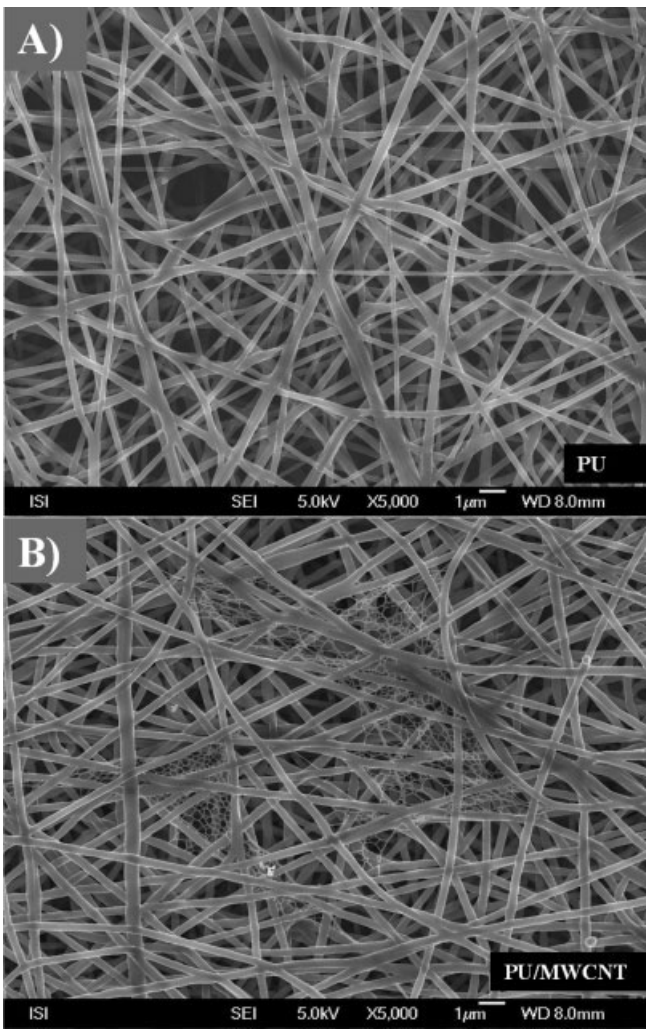


Figure 1 FESEM images of the PU-based nanofibers: (A) without and (B) with MWCNTs (no applied surface modification).

was clearly shown that the presence of the MWCNTs promoted the creation of weblike structures in comparison with the PU nanofibers without MWCNTs. The diameter of the PU nanofibers was about 350 nm, whereas the weblike structures consisted of regularly distributed very fine nanofibers with diameters of just about 20–40 nm, which were strongly embedded in the thicker PU nanofibers [see Fig. 2(A)]. These PU weblike structures were very similar to the Bombyx mori silk nanofibers containing SWCNTs.[12] TEM analysis of the PU/MWCNT nanofibers prepared by the electrospinning process with one static electrode only is provided in Figure 2(B) with the aim of analyzing the creation of the one nanoweb fiber. It was clearly visible that individual and very well aligned MWCNTs (except for a small curvature at the junction point) occurred in the outer surface of the main nanofiber from which nanoweb fiber was created. This observation led us to conclude that the nanoweb formation was based on the occurrence of strong secondary electric fields that were created between individual MWCNTs (or their agglomerated forms) and that started to behave as local moving nanoelectrodes promoting the creation of additional very fine nanowebs during the electrospinning processes.

CONCLUSIONS

PU and PU/MWCNT nanocomposite nanofibers created via an electrospinning process from PU solution were successfully prepared with average diameter around 350 nm. MWCNTs were present inside the PU/MWCNT nanofibers as individual tubes well aligned with nanofibers axes. Finally, so-called nanowebs were observed during the electrospinning process for PU-containing MWCNTs. We suggest that these nanowebs were created because of strong

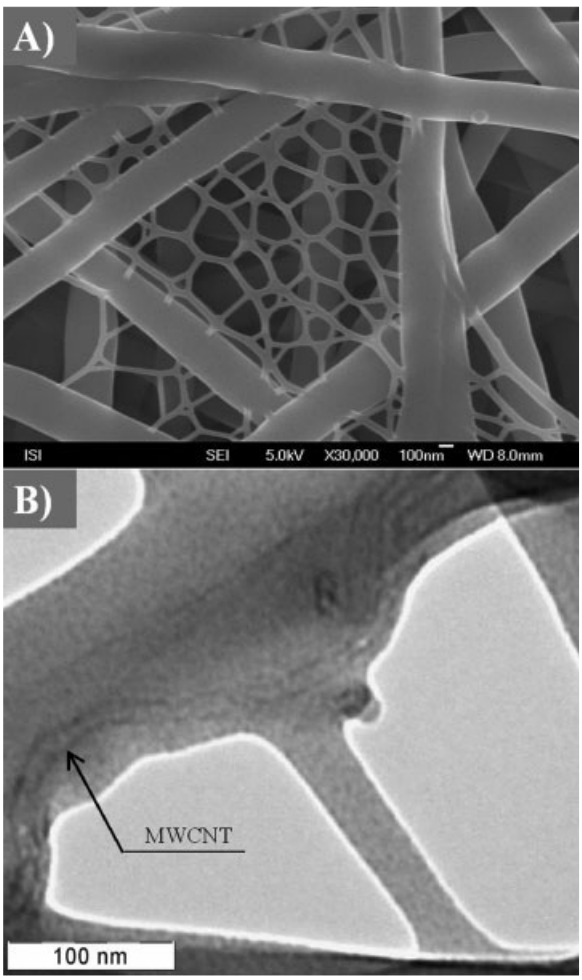


Figure 2 Detailed views of the weblike structures of the PU-based nanofibers with MWCNTs. (A) FESEM image of the weblike structure (MWCNTs with no surface modification). (B) TEM image of the weblike structure (MWCNTs with surface modification); detailed view of the strongly embedded fine fiber of the weblike structure to the thicker PU/MWCNT nanofiber containing an individual MWCNT.

secondary electric fields occurring between MWCNTs during the electrospinning process.

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