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High-Strength Mats from Electrospun Poly(*p*-Phenylene Biphenyltetracarboximide) Nanofibers**

By *Chaobo Huang, Shuiliang Chen, Darrell H. Reneker,* *Chuilin Lai,* and *Haoqing Hou**

Electrospinning has proven to be a very effective method for producing polymer nanofibers.[1] However, the mechanical properties of electrospun polymer nanofibers can be quite different from textile fibers made from the same polymer since the polymer molecules are not optimally aligned in electrospun nanofibers. Many reports have shown that the tensile strength of electrospun mats of non-aligned nanofibers is lower than 40 MPa.[2] Stretching can be an effective method for making high-performance conventional fibers with high degrees of molecular orientation within the fibers. However, stretching is not a practical process for making high-strength nanofibers by electrospinning due to 1) the very small diameters of electrospun fibers and 2) the complicated coiled path of the jet during the electrospinning process. These factors make it very difficult to stretch the electrospun nanofibers enough to produce high degrees of molecular orientation in the fiber.

Multiwalled carbon nanotubes (MCNTs) are commercially available at a competitive price and possess a very high tensile strength of 150 GPa with an elastic modulus of about 1.8 TPa.[3] MCNTs are ideal materials for use in high-performance polymer nanocomposites.[4] There have been several reports on using carbon nanotubes (CNTs) to reinforce fibers or nanofibers.[5] However, the expected degree of reinforcement has not yet been achieved. Many factors, such as adhesion between the polymer matrix and the fillers, and purity and dispersion of CNTs, may be responsible for the observed results; additionally, the geometry of the MCNTs is important for nanofibers reinforced by MCNTs. The MCNTs used to make high-strength nanofibers should be totally straight, since bent, coiled, or spiral-shaped MCNTs cannot be embedded uniformly inside a 300 nm diameter nanofiber, as we have shown previously.[5d] In order to make high-strength composite nanofibers, pure, straight MCNTs with no bent, coiled, or spiral-shaped impurities are desired.

Although pure rod-like MCNTs are difficult to obtain and quite expensive, rod-like macromolecules can be oriented along the fiber axis to make high-strength electrospun polymer nanofibers. Poly(*p*-phenylene biphenyltetracarboximide) (BPDA/PDA) is a rigid-rod-like polyimide (PI) formed from its precursor poly(*p*-phenylene biphenyl tetracarboxamide acid) (BP-PAA), which is flexible and soluble in common organic solvents. The tensile strength of BPDA-PDA PI has been reported to be as high as 1.25 GPa[6] for conventional fibers and 600 MPa for films.[7] X-ray diffraction (XRD) has shown that, in high-temperature-cured BPDA/PDA PI films, the molecular chains are highly ordered and parallel to each other, even in an unstretched film.[8] The high-temperature heat treatment tends to align the rigid-rod-like molecules, which is expected to be useful for making high-performance electrospun nanofibers containing highly oriented polymer molecules.

Here, we present a new strategy for using rod-like macromolecules like BPDA-PDA PI to make high-strength electrospun nanofibers. Non-woven fabric mats composed of these nanofibers show a tensile strength of more than 650 MPa and a tensile modulus of more than 15 GPa. These are the first results demonstrating that mats of electrospun polymer nanofibers can possess such high values of tensile strength and tensile modulus, which are much higher than previously reported values.[1e,f,5c,d] Figure 1 illustrates the chemical and physical conversion of flexible BP-PAA into rigid-rod-like BPDA-PDA PI inside a small diameter nanofiber.

BPDA-PDA PI is insoluble in all organic and inorganic solvents except for sulfuric acid. The BPDA-PDA PI nanofibers have been made by electrospinning a solution of the PI precursor, BP-PAA, in dimethyl acetamide (DMAc). The BP-PAA precursor used in this experiment was synthesized by a three-day-long condensation of highly pure monomers at a temperature of –5 °C. The inherent viscosity of the as-synthesized BP-PAA is 5.17 dL g^{-1} in DMAc at 25 °C, and the absolute viscosity of a 7.77 wt.-% solution in DMAc is 1170 poise (No. 4 rotor (3.20 mm diameter) at 3 rpm), much higher than the viscosity of commercially available BP-PAA (1 poise = 0.1 Pa s). The inherent viscosity of commercially available BP-PAA (Aldrich) is 1.43 dL g^{-1} in DMAc at 25 °C, and the absolute viscosity is 30 poise (No. 4 rotor at 60 rpm), measured using a commercially available solution

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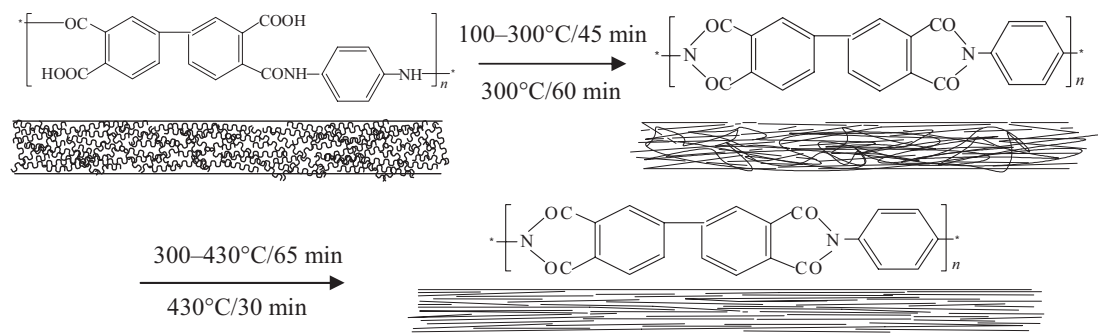E-mail: dhr@polmer.uakron.edu

Figure 1. Schematic depiction of the chemical and physical conversion of an electrospun BP-PAA nanofiber into a BPDA-PDA PI nanofiber with a high degree of molecular orientation in the direction of the nanofiber axis.

of 10.5 wt.-% BP-PAA in 1-methyl-2-pyrrolidinone (NMP, Aldrich).

The electrospinning process was performed using a 5 wt.-% solution of BP-PAA in DMAc. The electric fields used for electrospinning are on the order of 200 kV m^{-1}; a 50 kV electrical potential is applied across a 25 cm gap between the spinneret and the cylindrical collector, which is 0.28 m in diameter. The collector is rotated at a controlled speed. The PI precursor nanofiber sheets are collected on the rotating cylinder, which is turned at surface speeds of 0.59 m s^{-1} and 23.45 m s^{-1}. The low-speed process leads to non-woven mats of non-aligned nanofibers, while non-woven mats composed of aligned nanofibers are formed at high speeds. These as-collected PI precursor nanofiber mats are dried at 100 °C in vacuum for 2 h to remove any residual solvent, and are then converted into BPDA-PDA PI nanofiber mats by curing at high temperature. Scanning electron microscopy (SEM) observations of the resulting nanofibers (Fig. 2) shows that there is no significant morphological or size difference between the PI precursor and the PI nanofibers. The precursor and PI nanofibers have diameters ranging from 50 to 300 nm with the average diameter estimated to be about 180 nm. The surfaces of the precursor PI and nanofibers also seem to be very similar.

Mechanical testing results indicate that the mechanical properties of the aligned, non-aligned, cured, and non-cured nanofiber mats are quite different, as shown in Table 1. The

stress–strain curves in Figure 3 show that the tensile strength of the PI mats depends on both the alignment of the nanofibers in the mats as well as on the curing temperature. The highest tensile strength observed in our experiments is more than 650 MPa, measured for aligned PI nanofiber mats cured at 430 °C. As a comparison, the highest tensile strength previously reported for a nanofiber mat or sheet is 80 MPa, as measured for aligned CNT-reinforced polyacrylonitrile (PAN) nanofiber sheets,[5d] and 370 MPa, measured for heavily compressed CNT-reinforced PAN nanofiber sheets.[5c] The remarkably high tensile strength of 650 MPa, although inferior to conventional BPDA-PDA PI fibers,[6] is of the same order of magnitude as the tensile strength of commercially available BPDA-PDA PI films.[7] It is worth noting that this high tensile strength has been obtained using a pure PI polymer nanofiber mat, which, unlike a polymer film, has many interstices between the nanofibers in the mat, resulting in a lower number of closely adjacent molecules in the mat sample per unit weight than in a regular polymer film. Since strong "sticky" interactions between adjacent molecules make a major contribution to the strength and modulus of the sample, the presence of interstices in nanofiber mats has an adverse effect on the tensile stress of the measured sample.

In general, the tensile stress in polymer films, conventional fibers, and electrospun nanofibers is related to 1) the chemical structure of the polymer molecule, 2) the molecular weight of the polymer, and 3) the molecular orientation of the polymer
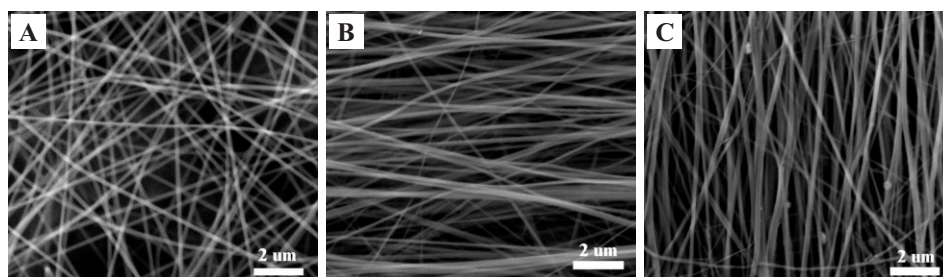

Figure 2. SEM images of the electrospun BP-PAA and BPDA-PDA nanofibers. A) Non-aligned and B) aligned BP-PAA nanofiber mats collected using a rotating cylinder turning with a surface speed of 0.59 m s^{-1} and 23.45 m s^{-1}, respectively. C) Aligned BPDA-PDA PI nanofiber mat collected at a surface speed of 23.45 m s^{-1} and cured at 400 °C.

Table 1. Mechanical properties of BP-PAA and BPDA-PDA PI electrospun nanofiber mats. E-modulus: elastic modulus.

Sample No.	S-1	S-2	S-3	S-4	S-5
Curing temperature [°C]/Time [min]	100/120 [a]	100/120 [a]	430/30 [b]	430/30 [b]	300/60 [b]
Surface speed of collector [m s⁻¹ ([rpm])]	0.59 (40)	23.45 (1600)	0.59 (40)	23.45 (1600)	23.45 (1600)
Alignment state of nanofibers	Misaligned	~80 % Aligned	Misaligned	~80 % Aligned	~80 % Aligned
Thickness of mat [μm]	11.3	8.2	12.5	8.2	8.5
Strain [%]	9.24	10.3	5.22	4.97	4.68
Tensile strength [MPa]	40	187	240.6	663.7	367.3
Statistical distribution of tensile strength [MPa]	41.1/ 44.3/ 35.3/ 37.5/ 39.7/ 42.0/	177.6/196.4/ 192.7/188.9/ 178.9/185.6/	245.6/227.9/ 236.3/250.3/ 242.9/	652.0/598.0/ 655.7/667.9/ 720.2/688.5/	375.1/360.0/ 371.6/342.5/ 387.6/
E-modulus [GPa]	0.7	2.1	5.8	15.3	9.1
Statistical distribution of E-modulus [GPa]	0.69/0.59/ 0.91/0.74/ 0.72/0.56/	1.3/3.0/2.8 1.7/1.5/2.3	5.6/6.7/5.0/ 5.7/6.0/	12.1/13.4/ 16.5/16.5/ 13.8/15.3/	12.5/7.9/ 7.6/9.4/ 8.1/

[a] Heating time in vacuum for removing residual solvent. [b] Heating time at the last curing temperature.
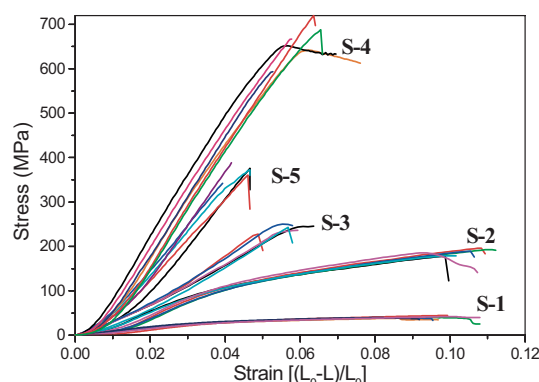

Figure 3. Typical stress–strain curves of BP-PAA and PBDA-PDA PI electrospun nanofiber mats. The numbering corresponds to the sample numbers in Table 1. *L*: strained sample length; L_0: original sample length.

along the stretching direction. The electrospun BPDA-PDA PI nanofiber mat should have a high tensile stress since 1) the molecular weight of the PI precursor, BP-PAA, from which the BPDA-PDA PI is made, is very high (the inherent viscosity is more than 5.0 dL g⁻¹) and 2) the PI polymer molecules are highly oriented along the nanofiber axes, and the nanofibers are about 80 % aligned along the stretching direction of the nanofiber mat. However, the presence of interstices between the nanofibers adversely affects the mechanical properties of the nanofiber mat, as mentioned above. The net result of these positive and negative contributions is that the tensile strength of the PI nanofiber mat is of the same order of magnitude as previously reported for films made from the same PI. However, in comparison to conventional PI fibers, the tensile strength of the electrospun BPDA-PDA PI nanofiber mat is substantially lower.[6] Apart from the negative contribution from the interstices between the nanofibers in the mat as discussed above, the alignment of the polymer molecules along the stretching direction is better optimized in a conventional fiber than in a nanofiber since 1) the mechanical stretching process (during fabrication of the fiber) highly aligns the poly-

mer molecules along the fiber axis in conventional fibers, and 2) the misaligned nanofibers in a mat reduce the polymer molecular orientation along the stretching direction, as compared to a conventional fiber.

The alignment process permits each nanofiber to share the stretching force and thereby strengthens the nanofiber mats. The heat treatment chemically transforms the BP-PAA nanofibers into BPDA-PDA PI nanofibers and orders the PI molecular chains along the nanofiber axes, as confirmed by XRD. The alignment of the molecules along the nanofiber axis strengthens the PI nanofibers, as illustrated in Figure 1. The diffraction peaks (Fig. 4) have been indexed as previously reported.[8b] Because of the alignment of the molecular chains along the nanofiber axis, the (200) peak of orthorhombic BPDA-PDA PI almost disappears in the aligned nanofibers, the (210) peak is weakened, and the (110) peak is strengthened relative to the intensity of these peaks in a BPDA-PDA
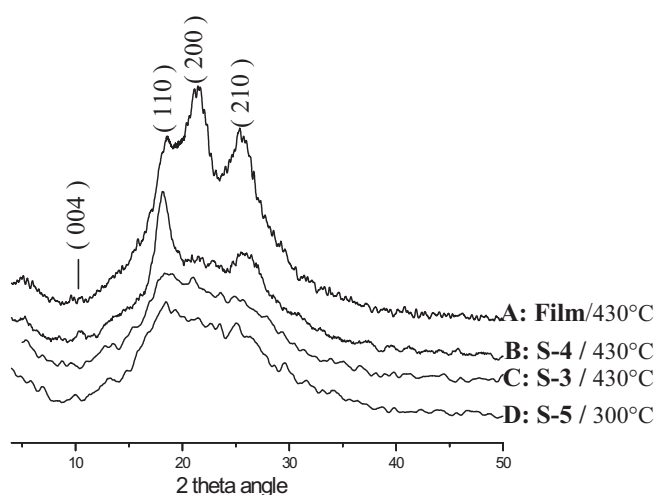

Figure 4. Wide-angle X-ray diffraction patterns of the PBDA-PDA PI film and electrospun nanofiber mats: A) PI film (15 μm thick) cured at 430 °C; B) aligned PI nanofiber mat sample S-4 in Table 1; C) non-aligned PI nanofiber mat sample S-3; D) aligned PI nanofiber mat sample S-5.

PI film. To our surprise, the (110), (200), and (210) peaks almost disappear from the diffraction pattern of the non-aligned BPDA-PDA PI nanofiber mat (sample S-3). The aligned nanofiber mat (sample S-5) cured at 300 °C has almost the same diffraction pattern as the non-aligned nanofiber mat (sample S-3). This result indicates that BPDA-PDA PI nanofibers prepared at temperatures below 300 °C are not well crystallized and do not have a well-developed molecular orientation, although IR analysis shows no difference between samples S-3 and S-5 (Fig. 5).
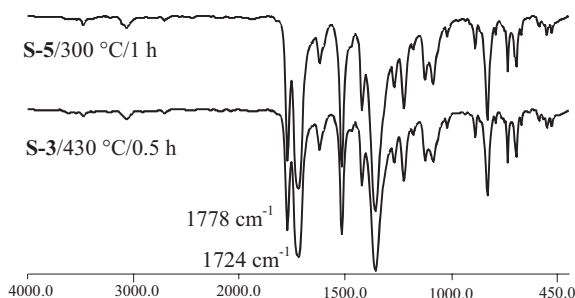

S-5/300 °C/1 h

S-3/430 °C/0.5 h

1778 cm^{-1}

1724 cm^{-1}

4000.0   3000.0   2000.0   1500.0   1000.0   450.0

Figure 5. IR spectra of BPDA-PDA nanofiber mats cured at 300 °C and 430 °C, respectively.

In summary, high-strength mats of electrospun nanofibers have been prepared using rigid-rod-like BPDA-PDA PI created by high-temperature heat treatment of BP-PAA. The high-performance non-woven mats made from aligned electrospun PI nanofibers have a tensile strength of 664 MPa, a tensile modulus of 15.3 GPa, and an elongation to break of 5 %. Non-aligned, non-woven fabric mats have a tensile strength of 241 MPa, a tensile modulus of 5.8 GPa, and an elongation to break of 5.2 %. These high-performance electrospun nanofibers with excellent mechanical properties and heat resistance are expected to be useful for applications such as protective clothing and heat-resistant filters.

Experimental

BPDA (2.9421 g, 0.01 mol) and PDA (1.0814 g, 0.01 mol) were mixed in equimolar amounts in 76.45 g DMAc at –5 °C with intense mechanical stirring for 72 h to give a 5 wt.-% solution of BP-PAA, a precursor to BPDA-PDA PI. This solution was used for 1) measurement of the inherent viscosity, 2) solution casting of BP-PAA films on glass plates, and 3) formation of electrospun nanofibers and non-woven fabric mats.

The above solution of precursor molecules in DMAc was electrospun into nanofibers. Dodecylethyldimethylammonium bromide (0.1 wt.-%) was mixed into the precursor solution to increase the electrical conductivity of the solution. The as-electrospun BP-PAA nanofibers were imidized in a high-temperature furnace using the following protocol: 1) 100 °C in vacuum for 2 h to remove any residual solvent, 2) heating up to 200 °C at a rate of 10 °C min^{-1} in vacuum and annealing for 15 min, 3) heating up to 300 °C at a rate of 5 °C min^{-1} and annealing for 60 min in vacuum to complete the imidization of the precursor nanofibers, and 4) heating up to 430 °C at a rate of 2 °C min^{-1} in vacuum and annealing for 30 min, which allows ordering of the PI molecules in the nanofibers.

IR spectra of the BPDA-PDA PI nanofiber mat samples were recorded on a Perkin–Elmer 781 spectrophotometer. Wide-angle X-ray diffraction (WAXD) measurements were performed using a Siemens D5000 instrument with Cu Kα radiation. The samples were imaged using a Quanta 200 SEM. The tensile strength and modulus of the electrospun BPDA-PDA PI nanofiber mats were measured using a CMT-8102 electromechanical universal testing machine (SANS Company). The mat samples used for tensile testing were 2 mm wide and 60 mm long. The sample was directly mounted on the sample clamps and stretched at a strain rate of 2 mm min^{-1}. The thickness of the sample was calculated from the sample weight and density of the PI or PI precursor. For example, the weight of a 60 mm × 30 mm piece of a PI nanofiber mat was 15.8 mg, and the density of the BPDA-PDA PI is 1.467 g cm^{-3} [7]. Thus, the thickness of the sample was calculated to be 5.98 μm. The PI precursor, BP-PAA, had a density of 1.153 g cm^{-3}, which was determined by weighing a 15 μm thick BP-PAA film.

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