Flame Resistant Electrospun Polymer Nanofibers from Deoxybenzoin-based Polymers

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ABSTRACT: Electrospinning of 4,4′-bishydroxydeoxybenzoin (BHDB)-polyphosphonate was performed by varying polymer concentration, flow rate, and the distance between the charged electrode and the grounded target. High flame-resistant nanofibers with diameters of ∼ 100 nm were obtained by spinning from 65 wt % DMF solution. The nanofibers were unimodal in distribution and uniaxially aligned. The heat release capacity and char yield of the BHDB-polyphosphonate nanofibers were 70 ± 3 J/g K, and 53%, respectively, in close agreement with the values obtained from the bulk materials. Electrospun nanofiber mats of BHDB-polyphosphonate with high flame-retarding properties had good mechanical strength (∼ 95 MPa) and modulus (∼ 3.9 GPa). © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 301–307, 2009

Key words: electrospun; nanofiber; high flame-retarded polymer; deoxybenzoin-based polymer

INTRODUCTION

Electrospinning is a simple and effective method for generating nonwoven polymeric submicron fibers.[1] Materials and applications emerging from electrospun fibers include protective fabrics/membranes,[2,3] nanocomposites,[2] sensors,[4] nanoelectronic/optical devices,[5] tissue engineering scaffolds and drug delivery devices.[6] Flame-resistant or self-extinguishing polymer fibers are extremely important for many applications. Aromatic polyamide fibers such as Nomex® are used in fire-resistant clothing and ballistic protection.[7] Continuous production of uniform polymer fibers with diameters ranging from 10 to 1000 nm is ideal for electrospinning. The high surface-to-volume ratio of such nanofibers provides high efficiency for catalysts[8] and sensors,[9] and in some cases improve mechanical properties.[10] Although flame retardant polymers are widely used in textile and related applications,[11] they are difficult to use in electrospinning.

In electrospinning, the polymer fiber diameter and morphology are found to be influenced by a number of experimental parameters, including solution viscosity,[12] charge density,[13] surface tension,[14] polymer molecular weight,[15] dielectric constant,[16] flow rate,[13] applied voltage,[17] and tip-to-collector distance.[18] Two major strategies have been employed to reduce fiber diameter: (1) the use of very highly diluted polymer solutions in volatile solvents and (2) the use of additives to increase the charge-carrying capacity of the fluid.[19] Recently, uniform fibers have been prepared from two-fluid electrospinning methods.[20,21] In this process, removal of the shell polymers gave fibers with ∼ 100 nm average diameter.[20] Moreover, fiber orientation was achieved by collection of the fibers on a grounded target rotating at high velocity.[22–25] Alternatively, collectors composed of two conductive strips, separated by an insulating gap of variable width, have been used to produce oriented nanofibers.[26] There are no reports in the literature regarding the preparation of electrospun polymer fibers that combine high flame retardancy with good alignment, narrow, nanometer-scale (∼ 100 nm) size distribution.[27,28] More typically, fiber diameters obtained by electrospinning are nonuniform, since the liquid jet generally spreads and splits.[27]

Polymer nanofibers that are both inherently flame resistant and nonhalogenated are potentially useful in applications that require the use of environmentally appropriate polymers. We recently reported the synthesis of novel aromatic polyesters, polyphosphonates, and copolymers of the two that exhibit

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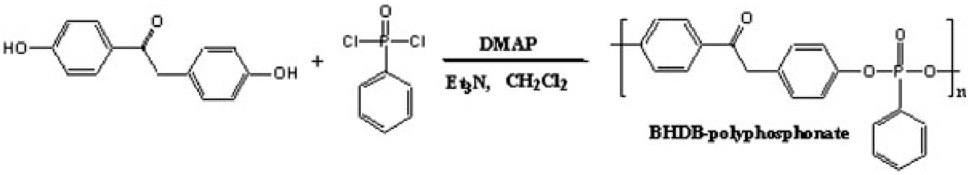

Scheme 1 Synthesis of BHDB-containing polyphosphonates.

extremely low flammability.[29–31] Key to the properties of these new polymers is the integration of the monomer 4,4′-bishydroxydeoxybenzoin (BHDB) into the backbone (Scheme 1).[29–31] Pyrolysis combustion flow calorimetry (PCFC),[32,33] a technique for measuring heat release rate and heat release capacity (HRC), revealed exceptionally low HRC values (60 ∼ 80 J/g K) for these BHDB-containing polymers. Such low HRC values are comparable with commercial polymers already in the low flammable category, such as poly(*p*-phenylene sulfide) (165 J/g K), poly (ether imide) (121 J/g K), poly(ether sulfone) (115 J/g K), poly (*m*-phenylene isophthalamide) (52 J/g K), polybenzimidazole (36 J/g K), and polyimide (25 J/g K).[32]

In this study, highly flame-retarded electrospun nanofibers with good alignment and narrow diameter distribution were prepared using BHDB-polyphosphonate polymer.

EXPERIMENTAL

Material and electrospinning

The BHDB was prepared by demethylation of deoxyanisoin.[29] BHDB-polyphosphonate (yield: 90%) was synthesized as described previously (Scheme 1).[30] The molecular weight (M_w) and PDI of BHDB-polyphosphonate used for electrospinning were 44,700, and 3.3, respectively. We chose to electrospin nanofibers using BHDB polyphosphonate,[29,30] as these polymers exhibit solubility well suited for electrospinning (∼ 700 mg/mL in DMF).

The electrospinning apparatus included a high voltage power supply (AU-120P0.5, Matsusada Precision Inc., Kusatsu, Shiga, Japan), a syringe pump (KDS 101, KD Scientific Inc., Holliston, MA), and a grounded cylinder target, as shown in Figure 1. Polymer solution was loaded into the syringe and an electrode was clipped onto the needle. The needle, electrode, and grounded target were all enclosed to reduce the effect of air currents on the trajectory of the electrospun jet.[25] The flow rate of the solution to the needle tip was maintained so that a pendant drop remained during electrospinning. All air bubbles are purged prior to electrospinning and the solution was electrospun between 8 ∼ 16 kV horizontally towards the target. The grounded target was between 5 and 12 cm from the charged capillary tip and may be either stationary or rotating.[25] The 4 in. diameter grounded wheel, ∼ 12 cm from the charged capillary tip, was rotated from 1500 to 2000 rpm and was enclosed.

Characterization

Morphologies such as diameter, surface, and shape of the electrospun nanofibers of BHDB-polyphosphonate and bisphenol A (BPA)-polyphosphonate[30] were observed by field emission scanning electron microscopy (FESEM). Samples were mounted onto SEM plates, sputter coated with gold, and examined using a JOEL JSM 6320FXV electron microscope to determine fiber diameters. Measured fiber diameters included a 5% random error.[25]

Flammability of all the polymers was measured with a PCFC.[32,33] Samples of 1 to 3 mg were pyrolyzed in a commercial device (CDS Pyroprobe 2000) to 900°C at 1°C/s under N_2. The volatiles were swept out continuously by a N_2 flow, mixed with a metered flow of O_2, and completely combusted at 900°C. Consumption rate of O_2 was measured continuously. The heat release results were taken as the average of five measurements for each sample.

The mechanical behavior of the BHDB-polyphosphonate electrospun yarn (average diameter

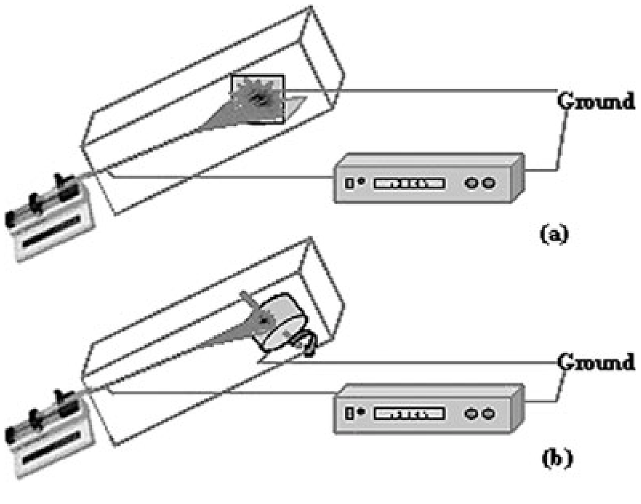

Figure 1 Schematic representation of the electrospinning apparatus with a stationary grounded target (a) and a rotating grounded target (b).

TABLE I
Average Diameters of Electrospun Fibers of BHDB-Polyphosphonate at Different Concentrations in DMF

Grounded target	Applied voltage (kV)	Distance between needle and target (cm)	Flow rate (mL/s)	Diameter (nm) of 55 wt %	Diameter (nm) of 60 wt %	Diameter (nm) of 65 wt %	Diameter (nm) of 70 wt %
Stationary	10	5	0.06	–	–	–	–
	10	12	0.06	118 ± 63	136 ± 27	149 ± 21	162 ± 31
	10	12	0.18	–	126 ± 43	140 ± 29	154 ± 34
Rotating (9.8 m/s)	10	12	0.06	–	115 ± 12	100 ± 10	145 ± 28

588 ± 87 nm) from a solution concentration of 65 wt % (0.65 g/mL) prepared using a rotating target was examined using an Instron 5564 with a crosshead speed of 2 mm/min (10% strain rate) in tension at room temperature. And also, the mechanical behavior of the 65% BPA-polyphosphonate electrospun yarn with average diameter of 345 ± 85 nm and moderate flammability (HRC ~ 350 ~ 500 J/g K) was examined to compare with BHDB-polyphosphonate electrospun yarn that has ultra low HRC (HRC ~ 70 J/g K). The molecular weight (M_w) of BHDB-polyphosphonate and BPA-polyphosphonate used for electrospinning were 69,500 and 67,700, respectively. Samples for tensile testing were mounted by bonding to paper tabs and had a 20 mm gauge length, as described elsewhere.[25] The cross-sectional area of the tensile test samples was calculated from the measured denier and the density (0.95 g/cm^3 and 0.98 g/cm^3, respectively) of BHDB-polyphosphonate and BPA-polyphosphonate polymers. The initial modulus, ultimate strength, and elongation at ultimate strength were measured.

RESULTS AND DISCUSSION

As the solubility and processibility of low flammability materials is usually very low, the BHDB-polyarylates and polyphosphonates appeared to have good potential for the preparation of novel nanofibers using thermal processing or nonaggressive solvents. As described below, with BHDB polyphosphonates, highly flame-resistant nanofibers with diameters of ~ 100 nm were obtained by spinning from 65 wt % DMF solution. The nanofibers

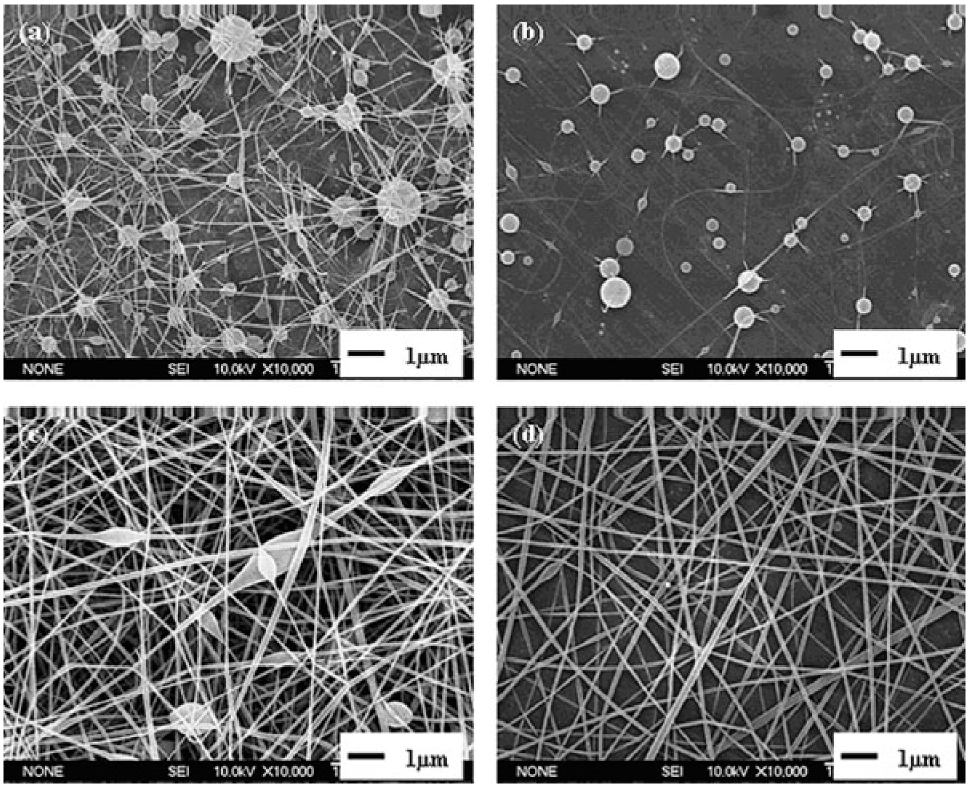

Figure 2 FESEM images of 50 wt % (a,b) and 55 wt % (c,d) of BHDB-polyphosphonate electrospun nanofibers with a distance of needle to target of 5 cm (a,c), 12 cm (b,d) on a stationary target.

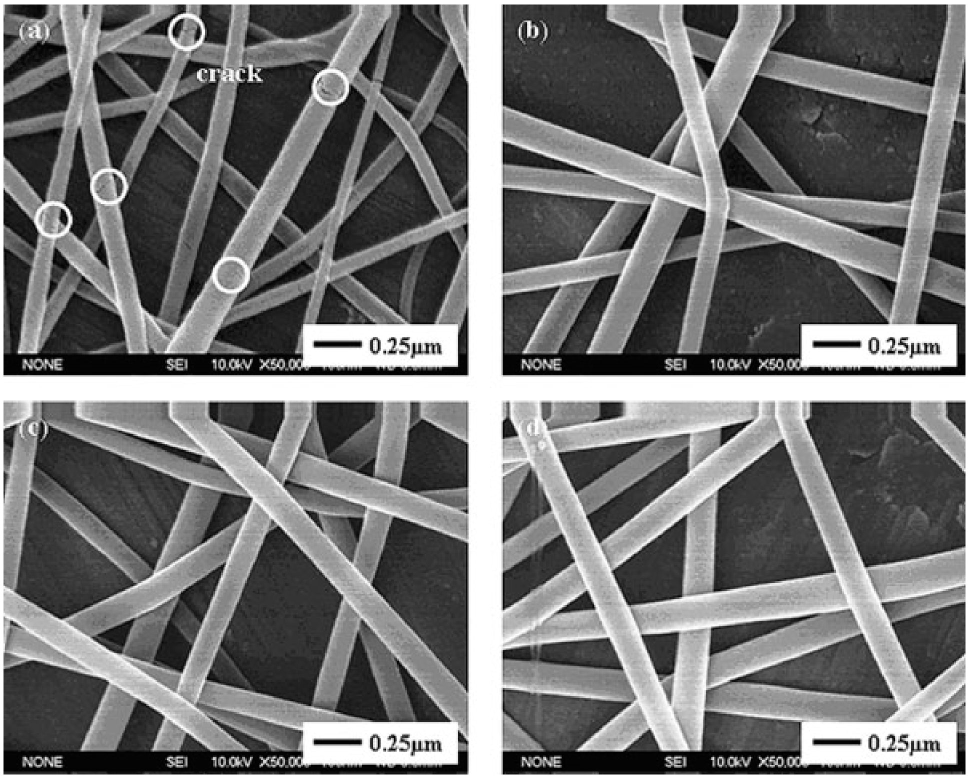

Figure 3 FESEM images of BHDB-polyphosphonate electrospun nanofibers from 55 wt % (a), 60 wt % (b), 65 wt % (c), and 70 wt % (d) BHDB-polyphosphonate solutions in DMF at 10 kV on a stationary target.

were unimodal in distribution and uniaxially aligned. The HRC and char yield of the BHDB-polyphosphonate nanofibers were 70 ± 3 J/g K, and 53%, respectively, in close agreement with the values obtained from the bulk materials.

Electrospinning of BHDB-polyphosphonate was performed by varying polymer concentration from 50 ~ 70 wt %, flow rate of 0.06 ~ 0.18 mL/m, and the distance between the charged electrode and the grounded target of 5 ~ 12 cm (Table I). To obtain aligned nanofibers, the target was rotated at a controlled take-up velocity (9.8 m/s). The electric field was 10 kV. The droplet of solution at the capillary tip elongates from hemispherical to conical (Taylor cone) with increasing electric field. Conventional electrospinning performed on BHDB-polyphosphonates produced isotropic, amorphous entangled polymer (Fig. 2), with an apparent lack of control over fiber orientation.[25] For electrospinning BHDB-polyphosphonate, ~ 60 wt % solutions proved optimum.

The fiber diameter was seen by SEM to increase with solution viscosity (i.e., higher polymer concentration) (Table I, Fig. 3). FESEM images of the fibers spun from 55 wt % solution [Fig. 3(a)] showed surface cracks, a typical result of electrospinning from

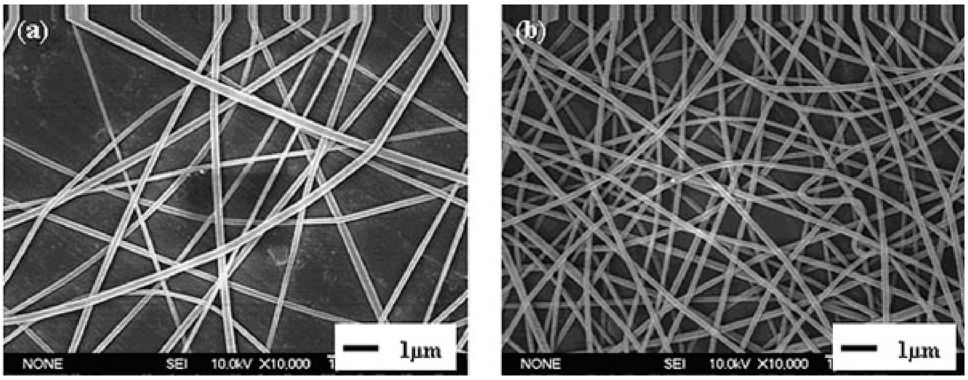

Figure 4 FESEM images of BHDB-polyphosphonate electrospun nanofibers prepared from 65 wt % solutions at a flow rate of 0.060 mL/s (a) and 0.180 mL/s (b) on a stationary target.

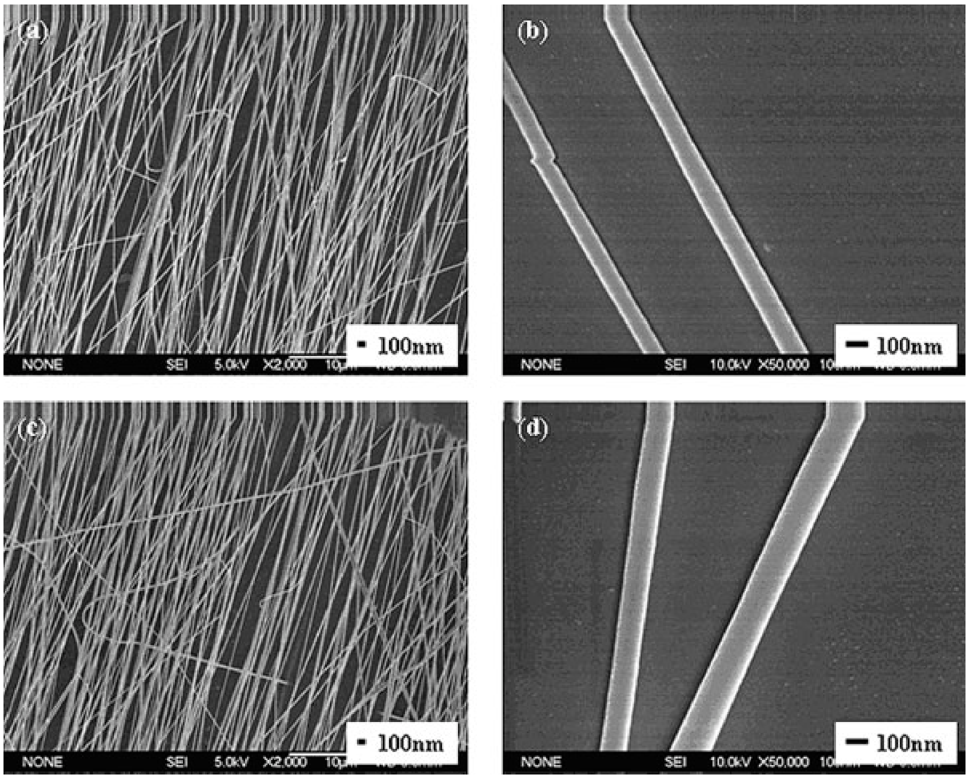

Figure 5 FESEM images of BHDB-polyphosphonate electrospun nanofibers with a solution concentration of 65 wt % (a,b), 70 wt % (c,d) on a rotating target with a take-up velocity of 9.8 m/s.

dilute solution. However, the morphology of the electrospun fibers from polymer solutions of 60 wt % or greater [Fig. 3(b–d)] showed little to none of this undesired cracking.

The effect of the solution flow rate is presented in Figure 4. Controlled fiber diameters with fairly narrow distribution in fiber width were observed at higher flow rate and different concentrations (Table I).

Well-aligned fibers with diameters ~ 100 ± 10 nm were collected on a rotating target with a take-up velocity of 9.8 m/s [Table I, Fig. 5(a)]. The alignment of the collected nanofibers can be improved with increasing take-up velocity. As demonstrated in Figures 3 and 4, stationary targets show nonaligned nanofibers, whereas uniaxially aligned nanofibers were formed at the relatively high take-up velocity of 9.8 m/s. BHDB-polyphosphonate solutions of 65 and 70 wt % were shown to be generally oriented at this take-up velocity (Fig. 5), with very few fibers oriented outside of the aligned texture.

The HRC of all the BHDB-polyphosphonate electrospun nanofibers, measured by PCFC, were under

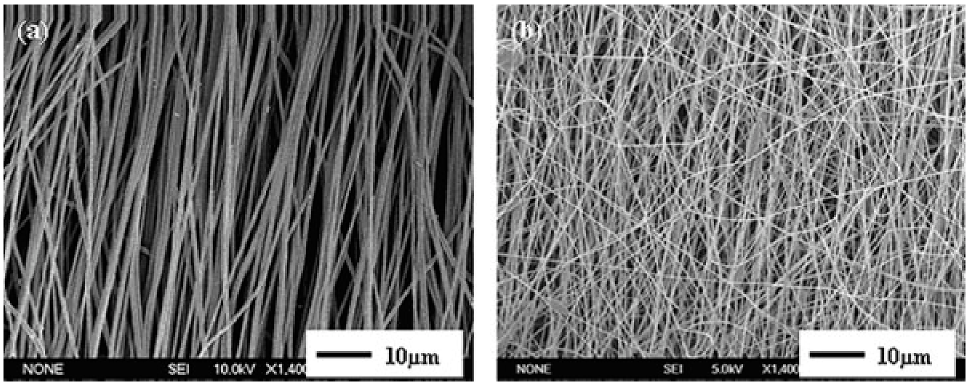

Figure 6 FESEM images of the BHDB-polyphosphonate (a) and BPA-polyphosphonate (b) electrospun nanofibers with a solution concentration of 65 wt % on a rotating target with a take-up velocity of 7.3 m/s.

TABLE II
Mechanical and Thermal Properties of BHDB-Polyphosphonate and BPA-Polyphosphonate Electrospun Nanofibers

Sample	M_w (g/mol)	PDI	Density (g/cm^3)	Tensile strength at break (MPa)	Initial modulus (GPa)	Elongation at break (%)	Heat release capacity (HRC, J/g K)	Electrospinning		
								Conditions	Average diameter (nm)	Morphology
Undrawn 65% BHDB-P	69,500	2.29	0.95	60 ± 5	1.2 ± 0.1	113 ± 4	70 ± 3	16 kV, 7.3 m/s, 0.004 mL/m	588 ± 87	Good; no beading
50% drawn 65% BHDB-P	69,500	2.29	0.95	95 ± 3	3.9 ± 0.2	68 ± 5	–	–	–	–
Undrawn 65% BPA-P	67,700	1.40	0.98	19 ± 1	1.7 ± 0.1	21 ± 1	359 ± 5	16 kV, 7.3 m/s, 0.004 mL/m	345 ± 85	Mid; some beads

100 J/g K, in accord with the values reported previously for the bulk materials.[30] In addition, char yields of 50% were measured using PCFC and TGA. The HRC of the BPA-polyphosphonate electrospun nanofiber was 359 ± 5 J/g K. These values were similar to those of the non electrospun polymers (BHDB-polyphosphonate ~ 80 J/g K, BPA-polyphosphonate ~ 365 J/g K). These ultra low HRC values, and high char yields of BHDB-polyphosphonate nanofibers are promising for many applications.

The initial modulus, ultimate strength, and elongation at break of undrawn electrospun yarn of 65% BHDB-polyphosphonate without beads, which was prepared at an applied voltage of 16 kV, take-up velocity of 7.3 m/s, and flow rate of 0.004 mL/m, were 1.2 ± 0.1 GPa, 60 ± 5 MPa, and 113 ± 4%, respectively, [Fig. 6(a); Table II]. In addition, the initial modulus and ultimate strength of 50% drawn, based on initial gauge length, electrospun yarn of BHDB-polyphosphonate were 3.9 ± 0.2 GPa and 95 ± 3 MPa, respectively. Otherwise, the undrawn 65% BPA-polyphosphonate electrospun yarn (HRC 359 ± 5 J/g K) with some beading, which was prepared at same conditions as the BHDB-polyphosphonate yarn, exhibits low mechanical properties (initial modulus 1.7 ± 0.1 GPa, ultimate strength 19 ± 1 MPa, elongation 21 ± 1%) compare to that of BHDB-polyphosphonate electrospun yarn [Table II, Fig. 6(b)] due to their poor morphology such as beading. The 65% BPA-polyphosphonate electrospun yarn with beads was produced and evaluated because better nanofibers could not be produced no matter how the variables of electrospinning were varied [Fig. 6(b)].

CONCLUSIONS

The electrospinning technique is proving useful for obtaining oriented polymer nanofibers of BHDB-polyphosphonate, with diameters in the ~ 100 nm range. Under optimized electrospinning conditions, the nanofibers exhibited good morphologies, free of beads and cracks, with well-controlled diameters and good alignment. The well-aligned nanofibers with diameters of 100 nm were collected from highly concentrated BHDB-polyphosphonate solutions (up to 70 wt %) on a rotating target with a high take-up velocity. The low HRC of these nanofibers (~ 70 J/g K) and high char yields (50%) are in accord with properties of the bulk material. Electrospun nanofiber yarns of BHDB-polyphosphonate with high flame-retarding properties had good mechanical strength (~ 95 MPa) and modulus (~ 3.9 GPa), and could be useful in future preparations of protective textiles, heat-resistant membranes, electronic components, construction and transportation materials.

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