Electrospun Magnetic Fibrillar Polyarylene Ether Nitriles Nanocomposites Reinforced with Fe-phthalocyanine/Fe$_3$O$_4$ Hybrid Microspheres

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ABSTRACT: The electrospinning method has been employed to fabricate ultrafine nanofibers of high-performance polyarylene ether nitriles (PEN) and PEN/Fe-phthalocyanine/Fe$_3$O$_4$ nanocomposite fibers for the first time. Through optimizing the operational conditions, such as polymer concentration, applied electric voltage, federate, and distance between needle tip and collector, bead-free and uniform fibers with smooth surfaces and certain diameters were obtained. The morphology of the PEN nanofibers is correlated to the corresponding rheological behaviors of the polymer solutions. The nanocomposite fibers showed a beads-in-string structures without agglomeration after introducing the Fe-phthalocyanine/Fe$_3$O$_4$ hybrid microspheres in the polymer fibers. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) reveal an enhanced thermal stability of the nanocomposite fibers after introducing the hybrids. The glass transition temperature (T_g) of the nanocomposite fibers increases by 10°C with 30 wt % hybrid microspheres, compared with those of the pure PEN fibers. The magnetic properties of the PEN/Fe-phthalocyanine/Fe$_3$O$_4$ nanocomposite fibers are different from those of the hybrid microspheres. The hybrid microspheres in the composite nanofibers become magnetically harder with a much larger coercivity than that of the fillers. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 1732–1739, 2012

Key words: nanofiber; electrospinning; nanocomposites; polyarylene ether nitriles (PEN); morphology; magnetic properties

INTRODUCTION

Polymer nanocomposites (PNCs) or organic–inorganic hybrids have been extensively investigated for their potential wide applications because of their easy processability, light weight, good adhesion to substrates,[1] and introduce the propensity of the inorganic materials such as high mechanical strength and excellent electrical, magnetic, and optical properties. Furthermore, PNCs even possess unique physicochemical properties or biological properties, which are essentially different from those of the components taken separately or physically combined properties of each component. These PNCs have attracted wide interest in both academic and industrial fields for their diverse potential applications in energy storage devices,[2] electronics,[3,4] and microwave absorbers.[5,6]

Electrospinning, first reported in 1934 by Formhals et al., has attracted much attention in both scientific and industry areas, because it is a very convenient and effective method to produce ultra fine fibers or fibrous structures of various polymers with diameter ranging from a few nanometers to several micrometers.[7–9] Electrospun fibers, especially in the nanoscale size, have found wide applications in various fields. For example, electrospun nanofibers possessing high porosity and large surface-to-volume ratio have been used as membranes for gas separation, protein purification, and wastewater treatment.[10–12] In recent years, much progress has been made using electrospinning to fabricate different types of hybrid nanofibers by incorporating nanomaterials into various polymer matrices. Compared with nanocomposites in other morphologies, electrospun nanocomposite fibers, which possess one dimensional (1-day) nm-or mm-structure, have unique characteristics ranging from specific surface area and high porosity, to excellent structural mechanical properties and high axial strength,[13] which are ideal for certain applications.[8,14,15]

Polyarylene ether nitriles (PEN), as a kind of high-performance engineering material, is well known for its outstanding properties such as radiation resistance, high thermal and thermo-oxidative stability, good mechanical properties and chemical inertness. Therefore, PEN composites are very attractive in
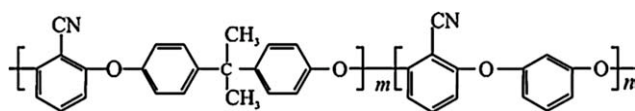
Figure 1 Molecular Structure of polyarylene ether nitriles.

aerospace, industrial and automotive area where elevated temperature and aggressive chemical environment is often encountered.[16–18] So far, PEN has been widely investigated by materials scientists at the millimeter scale. Cao Li et al.[19] studied the new PEN blends PEN (HQ/PP)/PEN (HQ/RS) with improved its compatibility and processability. Zhan[20] prepared the PEN nanocomposites with graphite nanosheets, which possessed good electrical, thermal, and mechanical properties. Various other nanoparticles, such as BaTiO$_3$,[21] TiO$_2$,[18] and multi-walled carbon nanotube[22] were also introduced in PEN matrix to obtain versatile unique properties. But many unique properties have not been explored, especially those on the nanometer scale. The fabrication of PEN nanocomposites with the electrospinning method is rarely reported, even less for the PEN nanocomposites filled with magnetic microspheres.

Fe-phthalocyanine/Fe$_3$O$_4$ hybrid microspheres were chosen due to their high stability in air over that of the pure Fe$_3$O$_4$ nanoparticles, maintaining ferromagnetism and novel electromagnetic properties.[23] Together with the thermal stability of PEN and magnetic properties of Fe-phthalocyanine/Fe$_3$O$_4$ microspheres are expected for high-temperature magnetic sensing and microwave absorption applications.

In this work, pure PEN and PEN/Fe-phthalocyanine/Fe$_3$O$_4$ nanocomposite fibers with different Fe-phthalocyanine/Fe$_3$O$_4$ loadings are prepared by electrospinning. The effects of polymer concentration, applied electric voltage, federate, and distance between needle tip and collector on the morphology of the fibers are studied to obtain uniform fibers. The morphology, thermal stability and magnetic properties of the nanocomposite fibers are investigated in this work.

EXPERIMENTAL

Materials

PEN were provided by Union Laboratory of Special Polymers of UESTC-FEIYA, Chengdu, China. It is a copolymer derived from 2, 6-difluorobenzonitrile with bisphenol A(BP-A)and resorcinol (RS) with the inherent viscosity of 0.86 dL/g (in N-methylpyrrolidone, 0.005 g/mL). Figure 1 shows the molecular structure of PEN. N,N′-Dimethylformanide (DMF, 99%), was purchased from TianJin BODI Chemical

Company. Fe-phthalocyanine/Fe$_3$O$_4$ microspheres with an average size of 400 nm were prepared in our lab.[23]

Preparation of Pure PEN Fibers

The PEN/DMF solutions with PEN loading of 9, 12, 15, and 17 wt % were first prepared and then the solutions were used for nanofibers manufacture by electrospinning technique. The viscous polymer solutions were loaded in a 5 mL syringe equipped with a 0.60 mm (inner diameter) stainless steel gauge needle which was connected to a high-voltage power supply. The grounded counter electrode was a flat aluminum foil. The solution was constantly and controllably supplied by a syringe pump and the feedrate was controlled at 1 mL/h, 2 mL/h, and 3 mL/h, respectively. An external electric field with a high voltage (controlled at 15 kV, 20 kV, and 25 kV, respectively) applied to the PEN solution through the positive electrode can overcome the surface tension of the viscous polymer solution and form a polymer jet, which is accelerated toward the collector and forms the PEN fibers. The fibers were accumulated on the aluminum surface after evaporating the solvent. The obtained fibers were then dried completely at 45°C for further SEM observation.

Preparation of nanocomposite fibers

Nanocomposite solutions are prepared from 17 wt % PEN/DMF solution. Fe-phthalocyanine/Fe$_3$O$_4$ (5, 10, 30 wt %, with regard to the weight of PEN) were dispersed in the PEN/DMF solution by ultrasonication at room temperature for 90 min. The freshly prepared solutions were electrospun to nanocomposite fibers by the same method described above.

Characterization

The morphology (shape and diameter) of the pure PEN and PEN/Fe-phthalocyanine/Fe$_3$O$_4$ nanofibers were evaluated by a JEOL JSM-5900LV scanning electron microscopy at 20 kV. The rheological behavior of the polymer solution was investigated with an AR-G2 Rheometer (TA Instrumental Company) at a shear rate of 0.1 to 1200 rad/s at 25°C. A series of measurements were performed in a cone-and-plate geometry with a diameter of 40 mm and a truncation of 64 microns. The glass transition temperature (T_g) was investigated by differential scanning calorimetry (DSC TA Instruments DSC Q-100) with a heating rate of 10°C/min under a N$_2$ atmosphere. The thermal stability of PEN and its nanocomposite fibers with different loadings was studied with a thermogravimetric analysis (TGA, TA Instruments
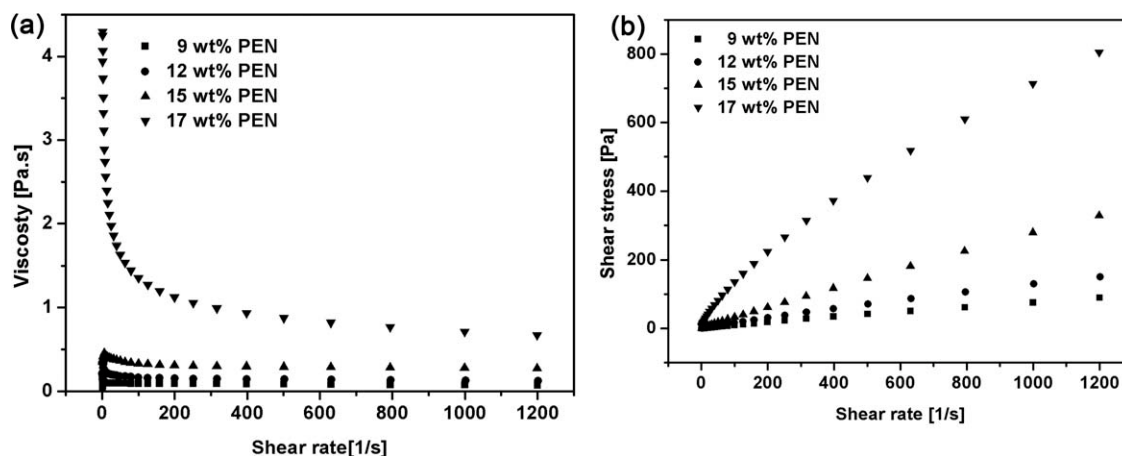
Figure 2 (a) Viscosity of 9 wt % PEN/DMF (■), 12 wt % PEN/DMF (●), 15 wt % PEN/DMF (▲), and 17 wt % PEN/DMF (▼), respectively. (b) Shear stress versus shear rate of the solutions.

TGA Q-50) at a heating rate of 20°C/min from room temperature to 700°C under a N_2 atmosphere. The magnetic properties of the PEN/Fe-phthalocyanine/Fe_3O_4 nanocomposites at room temperature were performed by a vibrating sample magnetometer (VSM, Riken Denshi, BHV-525).

RESULTS AND DISCUSSION

Microstructure of PEN nanofibers

In electrospinning process, beads are observed widely and are considered as the main shortcoming of the electrospun fibers.[24] Many factors can affect the occurrence of beads, such as applied voltage, charge density, viscoelasticity of the solution, and surface tension of the solution. To obtain uniform, bead-free nanofibers, the effects of experimental parameters (solution concentration, applied electric voltage, federate, and distance between needle tip and collector) on the morphology of electrospun PEN fibers are systemically investigated, and the optimal parameters are obtained.

PEN concentration effect

It has been reported that solution concentration has a significant effect on the morphology of the fiber produced by electrospinning process because it is strongly related to the viscosity of the solution.[24] A low solution concentration can usually generate a mixture of fibers and beads; while a high
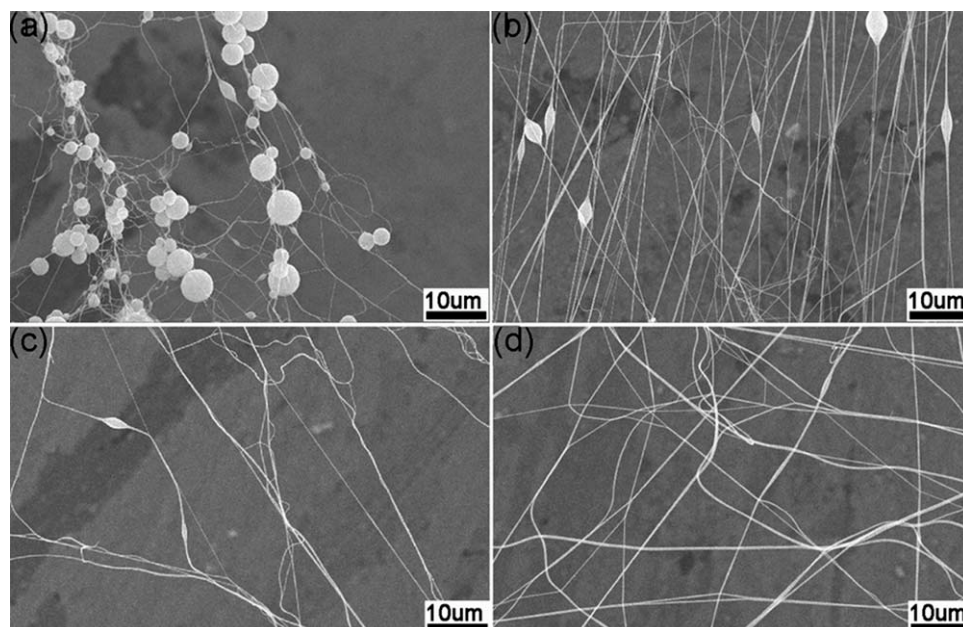

Figure 3 SEM of PEN nanofibers with a PEN loading (a) 9 wt % (b) 12 wt %, (c) 15 wt %, and (d) 17 wt %. Electrospinning operational parameters: 20 kV, 1 mL/h, and 12 cm.
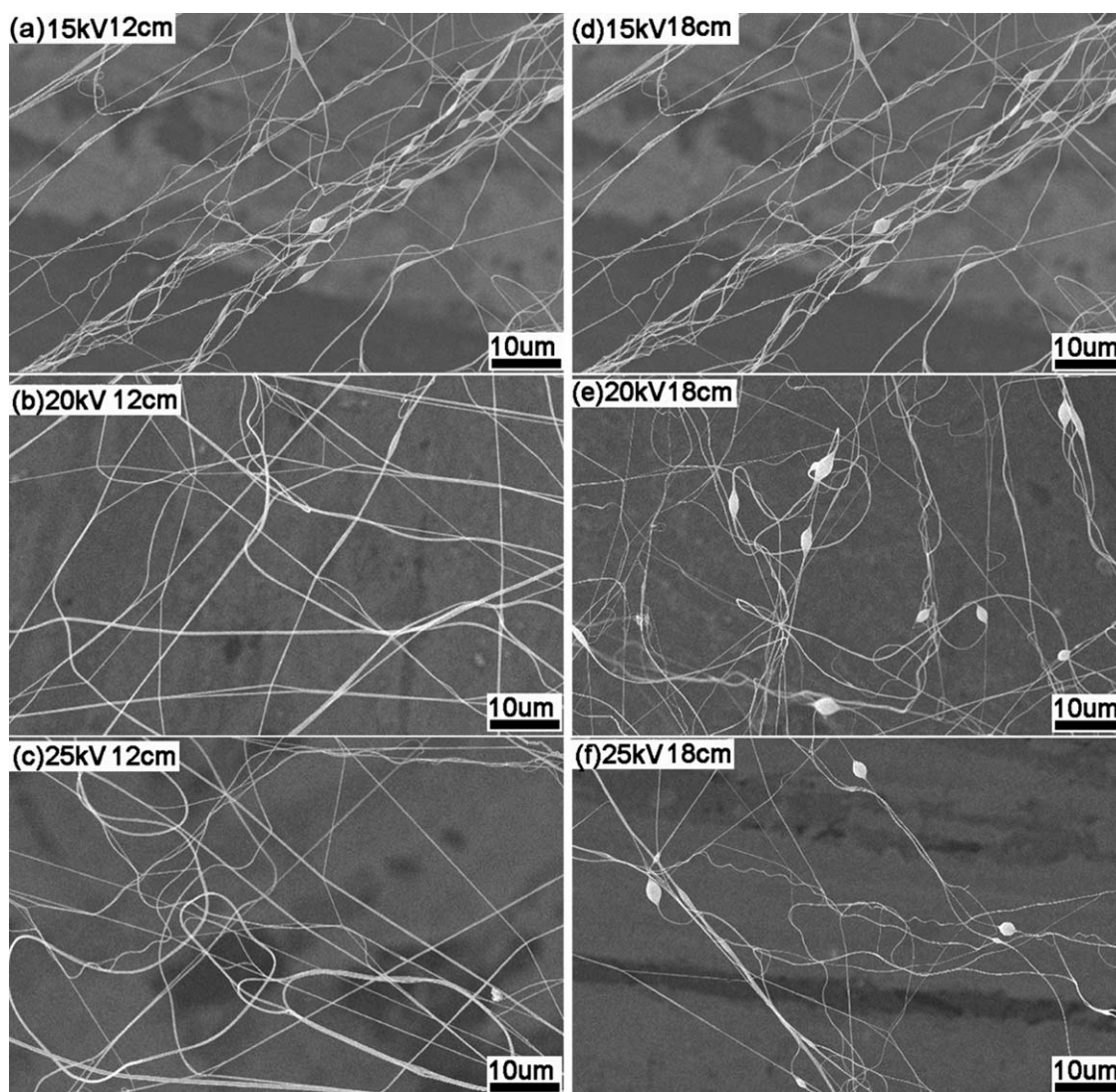
Figure 4 SEM images of 17 wt % PEN nanofibers under an applifed voltage of (a) 15 kV 12 cm, (b) 20 kV 12 cm, and (c) 25 kV 12 cm; (d) 15 kV 18 cm, (e) 20 kV 18 cm, and (f) 25 kV 18 cm. Electrospinning operational parameter: feedrate: 1 mL/h.

concentration may result in high viscosity, thus hampering the formation of fibers.[25] The jets in the electrospinning process will break up into droplets and form beads if the solution viscosity is extremely low, such as the 9 wt % PEN/DMF solution, which only shows an average viscosity of 0.09 Pa·s within the shear rate range from 1 to 1200 L/s, as shown in Figure 2(a). The viscosity sharply increases to 2.10 Pa·s when the polymer concentration increases to 17 wt %. Figure 2(b) shows the corresponding shear stress (Pa) as a function of shear rate (l/s) for the polymer solutions. The shear stress is observed to increase almost linearly with the increase of the shear rate, indicating a Newtonian fluid behavior. The low viscous solution (9 wt % PEN/DMF) is observed to form beads under the electrical field, Figure 3(a). One can clearly observe large numbers of beads in Figure 3(a), indicating that the polymer solution concentration with 9 wt % PEN is too low

to obtain bead-free fibers. From Figure 3(b, c), it can be seen that the number of beads obviously decreases with the polymer solution concentration increasing to 12 wt % [0.190 Pa·s, Fig. 2(a)] and 15 wt % [0.355 Pa·s, Fig. 2(a)]. However, one can observe uniform and straight PEN nanofibers without any beads when the polymer solution concentration increases to 17 wt %, as shown in Figure 3 days. This indicates that the jet without breaking up due to the cohesive nature of the high viscosity, travels to and finally forms the fibers on the collecting grounded electrode.

In addition, with the increase of polymer concentration, the diameters of the fibers increase from about ∼ 130 nm to ∼ 300 nm. This may be due to the reduction of mass loss during solvent evaporation or due to the higher resistance of the more viscous solution being stretched by the electric charges.[26,27]

face and can fully stretch the solution jet, thus can produce more uniform and smooth nanofibers.[28] In addition, many loops can be observed in the resultant sample, when the voltage is increased to a high value (25 kV), as shown in Figure 4(c), due to the excessively increased voltage. The reason may be that when the applied voltage is beyond a critical
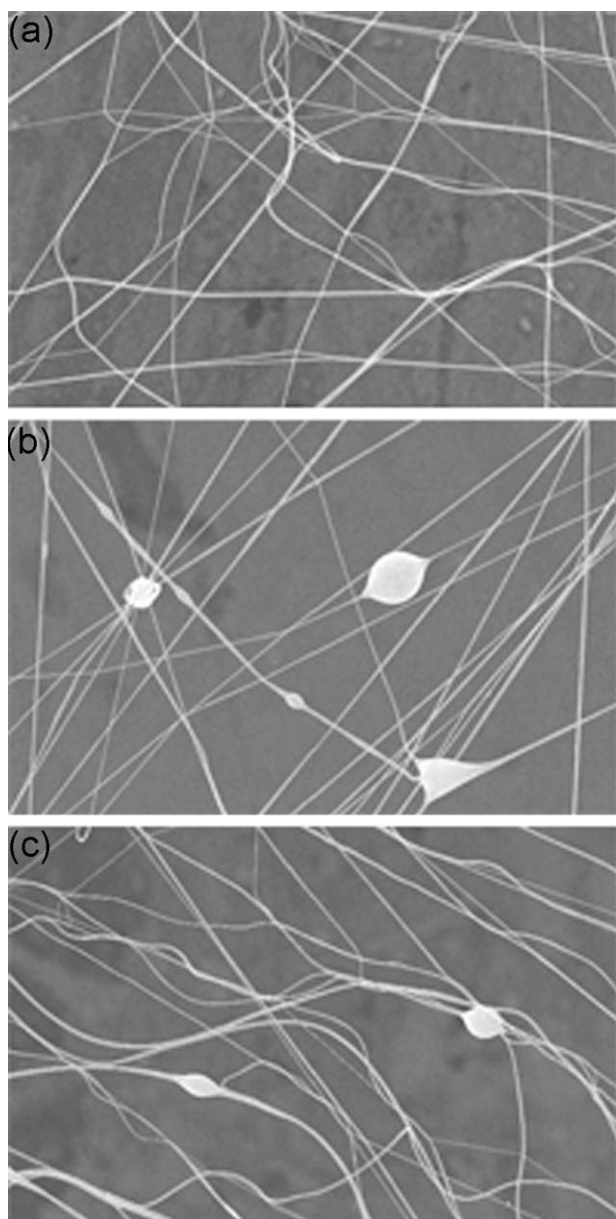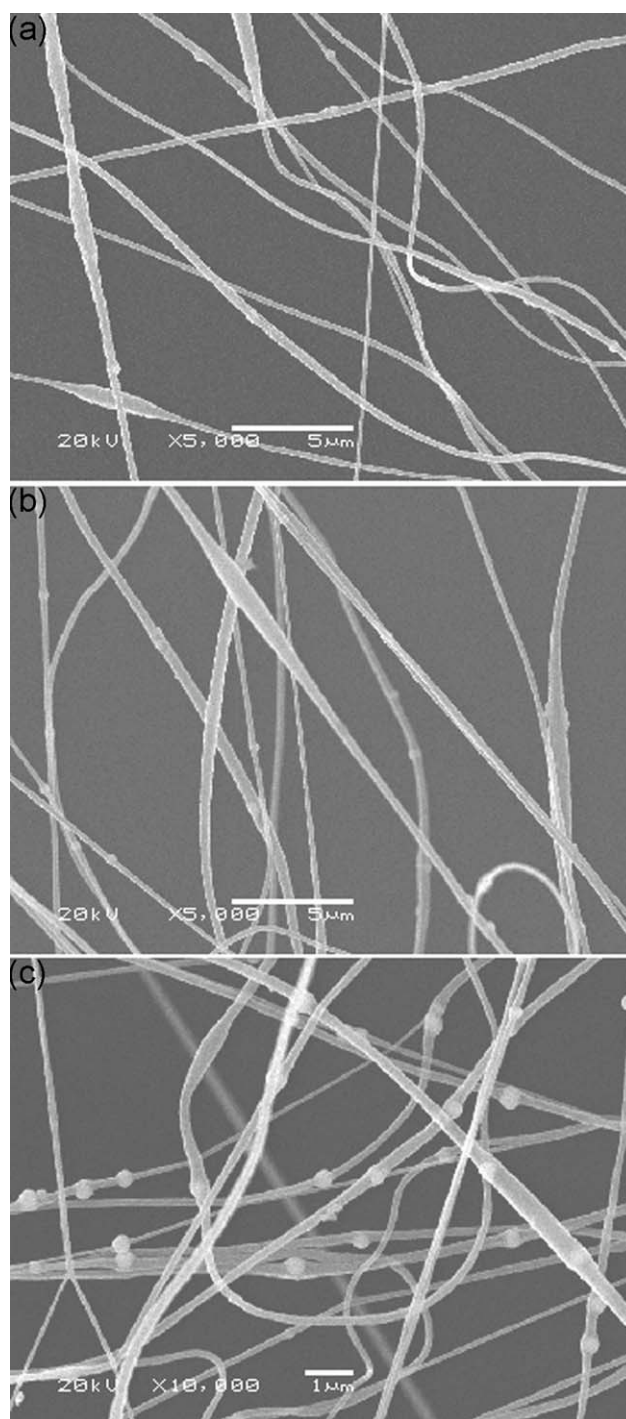

Figure 5 SEM images of 17 wt % PEN nanofibers under different feedrate conditions. (a) 3 mL/h, (b) 2 mL/h, and (c) 1 mL/h. Electrospinning operational parameter: 20 kV, 12 cm.

Voltages effect and distance effect

Figure 4 shows the SEM micrographs of PEN nanofibers fabricated at different applied electric voltages and different tip-to-collector distance, respectively, with 17 wt % polymer solution and a feedrate of 1 mL/h. One can observe that the obtained fibers are not uniform when using a relative low electric voltage (15 kV), as shown in Figure 4(a). However, a very uniform and smooth nanofiber can be seen in Figure 4(b) by using 20 kV. This indicates that the applied electric voltage have a significant effect on the fiber morphology. As is well known that a high voltage can induce more charges on the solution sur-

Figure 6 SEM images of PEN/Fe-phthalocyanine/Fe_3O_4 nanocomposite fibers with different Fe-phthalocyanine/Fe_3O_4 loadings (a) 5 wt %, 20 kV, 15 cm, 1 mL/h; (b) 10 wt %, 25 kV, 15 cm, 1 mL/h; (c) 30 wt %, 30 kV, 15 cm, 1 mL/h.
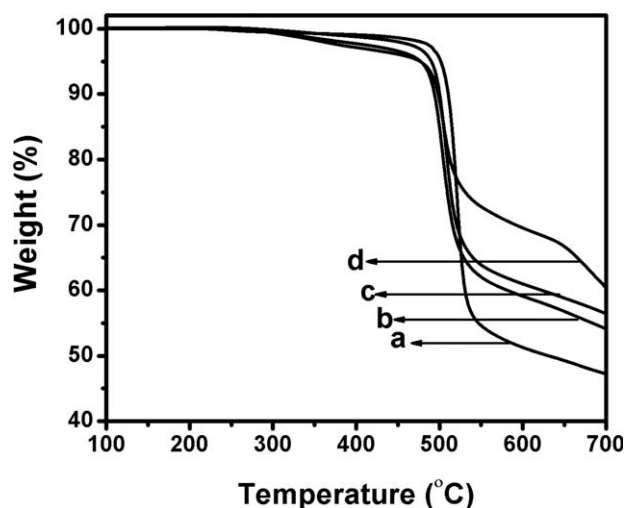
Figure 7 TGA curves of PEN/Fe-phthalocyanine/Fe$_3$O$_4$ nanocomposite fibers with different Fe-phthalocyanine/Fe$_3$O$_4$ loadings (a) 0 wt %, (b) 5 wt %, (c) 10 wt %, and (d) 30 wt %.

value, the resulting higher electrical force will break the ideal balloon, and the jet will be unstable during the electrospinning process.[29] Figure 4 also shows the effect of tip-to-collector distance on the morphology and diameter of the fibers. It can be seen that the obtained PEN fiber is not uniform and some beads even appear on the fiber [Fig. 4(d–f)]. On the other hand, when the distance is too long (18 cm), the jet has enough time to dry, but the reduced electric field strength results in the nonuniform fiber morphology with some beads, as can be observed in Figure 4(f). This is similar to the case of high feedrate.[29]

Feedrate effect

Figure 5 shows the feedrate effect on the morphology and diameter of the fibers. It can be observed from Figure 5(a) that the surface of the fiber is unsmooth and several beads even appear when the federate is as high as 3 mL/h. When decreasing the feedrate to 2 mL/h, little improvement in the fiber quality can be observed, as is shown in Figure 5(b). Nevertheless, the relatively uniform PEN nanofibers without any beads are successfully produced as feedrate decreasing to 1 mL/h, as can be seen in Figure 5(c). This demonstrates that a relatively lower federate is more desirable for bead-free PEN fiber manufacturing. The reason may be that for a given electric voltage, an appropriate feedrate is required to maintain the stable Taylor cone, which is necessary for uniform and bead-free fiber fabrication. The lower feedrate will allow the solvent to have more time to evaporates, and the fibers will have more time to stretch, which will favor the formation of more uniform nanofibers. Therefore, a lower fee-

drate is more desirable for bead-free fiber manufacturing. Furthermore, as the feedrate decreases from 3 mL/h to 1 mL/h, the diameter of PEN fibers decrease from approximately 500–300 nm, which consists well with the other researcher's observation that a higher feeding rate leads to the formation of thicker fibers.[25]

Microstructure of PEN/Fe-phthalocyanine/Fe$_3$O$_4$ nanocomposite fibers

PEN/Fe-phthalocyanine/Fe$_3$O$_4$ nanocomposite fibers with different Fe-phthalocyanine/Fe$_3$O$_4$ loadings were fabricated (Fig. 6). The solutions with higher Fe-phthalocyanine/Fe$_3$O$_4$ loadings were observed to require larger applied electrical voltages to obtain nanocomposite fibers due to the increased viscosity as particle loadings increase, To be specific, high electrical voltage provides larger electrical force between the tip of the needle and the collecting electrode, which is used to overcome the enhanced internal adhesion force and larger surface tension of the polymer solutions introduced by the addition of microspheres. The surface of nanocomposite fibers is relatively rougher as compared with that of the pure PEN fibers. The more viscous nanocomposite solutions retard the solvent evaporation process, which introduces more relaxation time for polymer chains. And the introduced nanoparticles restrict the motion of the polymer chain. Under such circumstances, the polymer chains are less patterned as compared with the pure PEN fibers, thus show a rougher surface.[29,30] Furthermore, with the increase of Fe-phthalocyanine/Fe$_3$O$_4$ loadings, nanocomposite
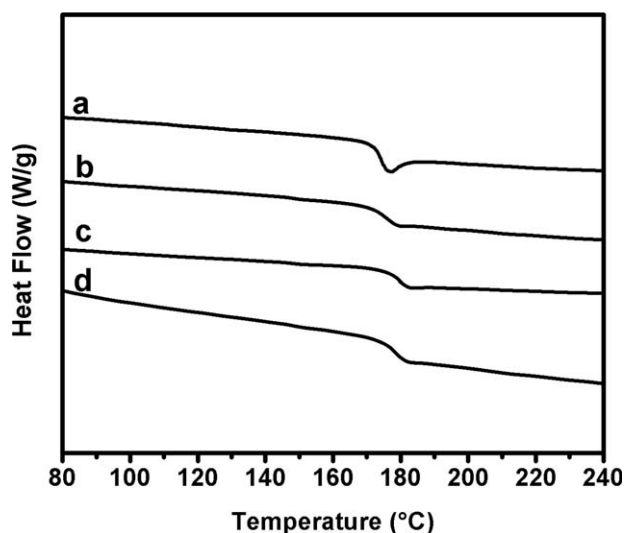

Figure 8 DSC thermograms of PEN/Fe-phthalocyanine/Fe$_3$O$_4$ nanocomposite fibers with different Fe-phthalocyanine/Fe$_3$O$_4$ loadings (a) 0 wt %, (b) 5 wt %, (c) 10 wt %, and (d) 30 wt %.
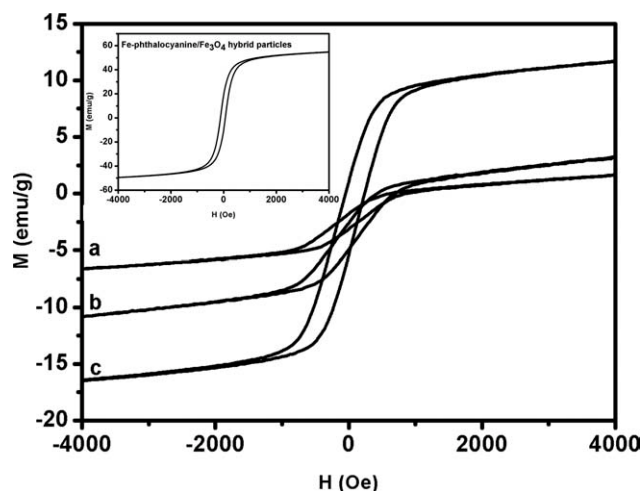
Figure 9 Room temperature hysteresis loops of PEN/Fe-phthalocyanine/Fe$_3$O$_4$ nanocomposite fibers different Fe-phthalocyanine/Fe$_3$O$_4$ loadings (a) 5 wt %, (b) 10 wt % (c) 30 wt %; inset shows Fe-phthalocyanine/Fe$_3$O$_4$ hybrid microspheres.

fibers showed a beads-in-string structures without agglomeration of microspheres, as shown in Figure 6(e, f).

Thermal stability

Figure 7 shows the TGA curves of the pure PEN and PEN/Fe-phthalocyanine/Fe$_3$O$_4$ nanocomposite fibers up to 700°C. It can be seen that a minor mass loss (about 4%) of nanocomposite fibers takes place between 330°C and 470°C. It is due to the decomposition of organic phthalocyanine introduced into the hybrid microspheres.[23] The thermal stability of nanocomposite fibers is observed to increase significantly with the increase of the Fe-phthalocyanine/Fe$_3$O$_4$ due to the restriction of the nanoparticles on the long-range chain mobility of the PEN phase within the nanocomposites. Many groups have also reported the stability enhancement effect of nanomaterials in polymer hybrid materials.[29–31]

DSC analysis

Figure 8 shows the DSC curves of pure PEN and PEN/Fe-phthalocyanine/Fe$_3$O$_4$ nanocomposite fibers. It is evident that the glass transition temperature (T_g) increase with the increase of the Fe-phthalocyanine/Fe$_3$O$_4$ loading. The T_g for the pure PEN fibers is 173.5°C and increases to 176.1, 179.8, and 181.1°C for the nanocomposite fibers with a particle loading of 5, 10, and 30 wt %, respectively. It is attributed to the interactions between the functional groups which are formed on the hybrid microspheres and PEN matrix[21,24] and the nanoconfinement of microspheres

on the polymer chains, which restrict the segmental motions at the organic–inorganic interface.[32]

Magnetic property

Figure 9 shows the room temperature magnetic hysteresis loops of the prepared nanocomposites and as-received pure Fe-phthalocyanine/Fe$_3$O$_4$ hybrid microspheres. Coercivity and saturation magnetization values for all samples are listed in Table I. It can be seen that the hysteresis loops of the samples are the typical loops of a soft magnet and the saturation magnetization (Ms) is observed to increase with increasing hybrid microspheres loadings. The coercivities of the PEN nanocomposites are 117.1, 131.9, and 143.9 Oe for 5, 10, and 30 wt % loadings, respectively, which are much larger than that of the Fe-phthalocyanine/Fe$_3$O$_4$ hybrid microspheres. Such behavior, however, is typical of magnetic nanocomposites. This indicates that the hybrid microspheres become magnetically harder after being dispersed in the PEN matrix within the nanocomposite fibers. The enhanced coercivity of nanoparticles is due to the decreased interparticle dipolar interaction, which arises from the enlarged nanoparticle spacer distance for the single domain nanoparticles,[30,31,33] as compared with the closer contact of the hybrid microspheres.

CONCLUSIONS

Pure PEN and PEN/Fe-phthalocyanine/Fe$_3$O$_4$ nanocomposite fibers are produced by electrospinning. The effects of polymer concentration, applied electric voltage, federate, and distance between needle tip and collector on the morphology and size distribution of the fibers are systematically studied. The nanocomposite fibers showed a beads-in-string structures without agglomeration after introducing the Fe-phthalocyanine/Fe$_3$O$_4$ hybrid microspheres in the polymer fibers. TGA and DSC results reveal an enhanced thermal stability of the nanocomposite fibers after introducing the hybrids, with an increased glass transition (T_g) temperature of the nanocomposite fibers as compared

TABLE I
Magnetization Data for PEN/Fe-Phthalocyanine/Fe$_3$O$_4$ Nanocomposite Fibers with Different Fe-Phthalocyanine/Fe$_3$O$_4$ Loadings

Sample	H_c (Oe)	Ms (emu g^{-1})
a	117.1	4.2
b	131.9	7.6
c	143.9	14.4
d	93.7	55.7

(a) 5 wt %, (b) 10 wt %, (c) 30 wt %, and (d) Fe-phthalocyanine oligomer/Fe$_3$O$_4$ hybrid microspheres.

with that of the pure PEN fibers. The nanoparticles in the nanocomposite fibers become magnetically harder with a much larger coercivity than that of the hybrid microspheres.

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