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Photophysical and surface characteristics of electrospun polysulfone/nickel fibers

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ABSTRACT

One-dimensional polysulfone/nickel fibers with different content of nickel nanoparticles were prepared by electrospinning method. The contact angles and wettability of the resulting fibers were determined by static water contact angle method. The experimental results revealed that values of contact angle of the fibers were affected by composition of the fibers. In the photoluminescence spectra of the PSU/Ni nanocomposites an emission band located in the range 346–362 nm was observed, which was progressively shifted toward the shorter wavelengths, as the nickel content increased. Two average lifetimes with a short decay time, τ_1 (contributions of this component is 56.01–87.15%) and a long decay time, τ_2 (with the slow decay contribution 12.85–40.28%) were obtained. The content of Ni from polysulfone fibers determine the photophysical and surface characteristics.

1. Introduction

In recent years, a large amount of publications are dedicated to the development of new organic–inorganic nanocomposites based on combining the advantages of the two components: polymer and inorganic part (metal nanoparticles). Polymer nanocomposites consisting of inorganic particles and polymer matrices represent a new class of materials that have improved performances but also afford new advanced characteristics which differ those of bulk materials [1]. By modifying or improving the properties of the two components new materials with special properties can be obtained, which make these nanocomposites to be used in various applications such as electronic, optical, mechanical devices, magnetic recording media, catalysis, superconductors, ferrofluids and magnetic refrigeration systems [2–5]. When inorganic nanoparticles and polymers are encountered, the resulting hybrid materials possess the superior characteristics of both components such as the high electron mobility of inorganic part and the good optoelectronic properties of polymers. In this context the optical, magnetic or electrical properties of polymer nanocomposites depend on the type, size, shape and concentration of inorganic component as well as the interactions of the nanoparticles incorporated in the polymer matrix [6–8]. These materials provide a large variety of systems such as one-dimensional, two-dimensional, three-dimensional and amorphous materials, by mixing different components at the nanometer scale [3]. Nanocomposite materials can be classified, according to their matrix component, in three different categories: ceramic matrix nanocomposites, metal matrix nanocomposites and polymer matrix nanocomposites [3,4,9,10].

Nickel nanoparticles have attracted extensive interests because of their applications as magnetic storage materials, gas sensors, magnetic inks, catalysts or in biomedical fields [11–14]. The main reason determining their uses is given by high surface–volume ratio which results from their very small sizes. The incorporation of the ferromagnetic metals (especially, Ni nanoparticles) in a polymer matrix used electrospinning method is still rarely reported to date. Recently, the morphology and thermal stability of some electrospun magnetic fibrillar polystyrene/Ni nanocomposites was reported by Chen et al. [15].

Among polymers, polysulfone (PSU) is considered a good matrix because of its low price and good solubility. Polysulfone is an amorphous thermoplastic polymer having excellent mechanical properties even at higher temperatures due to its high glass transition temperature (T_g = 185 °C), good heat resistance and dimensional stability as well as easy processing [16–18].

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Polymer nanofibers attracted a lot of attention due to the high surface area to volume ratio characteristic, along with adjustable morphology and superior mechanical performance making them good candidates for nanodevices and nanomembranes [2,19]. The incorporation of metal nanoparticles into polymer nanofibers can be achieved using either electrospinning of the polymer solutions containing metal nanoparticles or by reducing the metal salts or complexes in the electrospun polymer nanofibers. Electrospinning has been found to be a very facile and feasible method for fabricating nanofibers [20]. In addition, due to its simplicity and low-cost, this method is suitable to control the surface properties of the nanostructures and the supramolecular assembly of the polymer molecules within the nanofibers [21]. In a typical electrospinning process, electrostatically driven polymer jet is ejected from polymer solution, which undergoes bending instability wherein the solvent evaporates and ultra fine stretched fibers are formed on a metal collector plate [22,23].

In the present work, we reported about the fabrication of some composite fibers from an electrospun PSU solution, by incorporating different amounts of Ni nanoparticles. The electrospun solution was analyzed by viscometric and oscillatory measurements. Photophysical characteristics of polysulfone/nickel fibers were investigated using steady-state and time-resolved emission measurements. Morphological, surface characteristics of obtained fibers were evaluated and correlated with photophysical changes in the presence of different Ni nanoparticle contents. Fluorescence decays and quantum yield values can afford a better understanding of the excited state properties of these polysulfone/nickel fibers.

2. Experimental

2.1. Materials

Polysulfone (M_w = 35,000) and dimethylformamide (DMF) (ACS spectrophotometric grade) were obtained from Sigma–Aldrich and were utilized without further purification. Nickel nanoparticles were prepared by chemical reduction method as described previously [24].

2.2. Characterization

The rheological behavior of electrospun solutions was studied on a Bohlin rheometer (Malvern Instruments, UK) equipped with a cone (angle 4°, diameter 40 mm) and plane measuring system, at room temperature. The steady shear data were obtained from share rate tests ranged from 2 to 100^{-1}. The oscillatory shear tests were conducted in a frequency range from 0.2 to 100 Hz. The morphology of the electrospun nanofibers was analyzed using an environmental scanning microscope Quanta 200 operating at 20 kV with secondary electrons in low vacuum mode. Transmission electron microscopy (TEM) images were obtained with a Hitachi High-Tech HT7700 instrument at an acceleration voltage of 120 kV.

Fluorescence spectra were collected with an Edinburgh Instrument FLS 980 fluorospectrometer. The excitation and emission slits were set at 0.5 and 10 nm, respectively for all the measurements. The fluorescence quantum yield was determined using integrating sphere, at room temperature. Fluorescence lifetime measurements were obtained using the time-correlated single photon counting method with FLS 980 fluorimeter. The excitation source was a nitrogen nanosecond flash lamp. Samples were excited at 300 nm. Decay time data analysis was made with the method of nonlinear last square iterative reconvolution. The quality of the fit was estimated by the reduced chi-square χ^2 and the autocorrelation function of the residuals.

Contact angle measurements (θ) were carried out on a CAM101 contact angle meter (KSV Instruments) at room temperature, using sessile drop method (1 μL droplet volume). The test liquid was distilled water, with surface tension γ_{lv} = 72.8 mJ m^{-2} [25]. For each sample, five drops were placed at different locations on the surface and the mean value from these determinations was used as the final contact angle value.

2.3. Preparation of nanocomposites

Firstly, 7.5 mg nickel nanoparticles were suspended in 10 mL DMF under stirring (solution A). Then, 3.5 g polysulfone (PSU) were dissolved in 10 mL DMF at 50 °C which were stirred for 24 h. This solution was named as "B". The electrospun solutions consist of 4 mL solution B in which quantified volumes of solution A were added as follows: F9 with 0.4 mL solution A (4%). F10 contains 0.6 mL solution A (6%) and the last sample F11 with 0.8 mL solution A (8%). These electrospun solutions were homogeneously mixed under stirring for 30 min. Each resulting solution was transferred in a medical syringe fitted with a metal needle with an inner diameter of 0.8 mm. The applied voltage was of 20 kV with a needle tip – collector distance of 15 cm and the solution feeding rate corresponds to 0.75 mL/h. An aluminum foil was used as collector for PSU/Ni composite nanofibers.

3. Results and discussion

3.1. Scanning electron microscopy analysis

The morphology of the polysulfone electrospun fibers was examined by SEM, with representative images shown in Fig. 1 for F10. Results suggested that long, uniform and continuous fibers can be obtained without any branch structures. The fibers exhibit a smooth surface with small variations in diameters. The average fiber diameter was about 800 nm. Because small amounts of Ni nanoparticles were added, the shape and size of the fibers were not practically changed (confirmed by SEM measurements). Changes in surface and photophysical characteristics of nanofibers occurred with the increase of Ni content in fibers.

TEM image of Ni nanoparticles obtained by chemical reduction method using poly(vinyl pyrolidone) as a surfactant in non-aqueous medium [24] is displayed in Fig 2b. The Ni nanoparticles were all about spherical size shape with an average size about 10–20 nm as shown in Fig. 2b. Because the size of Ni nanoparticles was so small as compared to the fiber dimension, from SEM images the Ni particles cannot be observed on the surface of composite fibers. In order to see that the Ni nanoparticles are uniform distributed on polysulfone fibers, a small amount of sample F10 was dispersed in ethanol under gentle stirring. This suspension was transferred on a carbon-coated copper grid and it was analyzed by TEM (Fig. 2a). As shown in Fig. 2a, black dots were observed with uniform dispersion in the fiber composite which we assume to be nickel nanoparticles. In Fig. 2c and d TEM images of PSU/Ni (F9 and F11) composite fibers were displayed. The Ni nanoparticles which are present in nanofibers are shown in Fig 2d (inset). Because the size of the nanoparticles is smaller than the diameter of the fibers they can not see as individual nanoparticles. The morphologies obtained from SEM and TEM microscopy of 4 and 8% Ni nanofibers are similar to sample F10. Thus, higher content of Ni does not modify the morphology of nanofibers evidently. The Ni nanoparticles was homogeneously dispersed in the polysulfone matrix without to form aggregates.

3.2. Rheological properties

Fig. 3 shows the steady-state rheological behavior of electrospun solutions based on neat PSU and PSU/Ni nanocomposites. As observed the viscosity level of the PSU/Ni nanofibers decreased when compared with the neat polysulfone.