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Main-chain polybenzoxazine nanofibers *via* electrospinning

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ABSTRACT

Here we report the successful production of nanofibers from main-chain polybenzoxazines (MCPBz) *via* electrospinning without using any other carrier polymer matrix. Two different types of MCPBz (PBA-ad6 and PBA-ad12) were synthesized by using two types of difunctional amine (1,6-diaminohexane and 1,12-diaminododecane), bisphenol-A, and paraformaldehyde as starting materials through a Mannich reaction. ^{1}H NMR and FTIR spectroscopy studies have confirmed the chemical structures of the two MCPBz. We were able to obtain highly concentrated homogeneous solutions of the two MCPBz in chloroform/N,N-dimethylformamide (DMF) (4:1, v/v) solvent system. The electrospinning conditions were optimized in order to produce bead-free, uniform and continuous nanofibers from these two MCPBz by varying the concentrations of PBA-ad6 (30–45%, w/v) and PBA-ad12 (15–20%, w/v) in chloroform/DMF (4:1, v/v). The bead-free fiber morphology was evidenced under SEM imaging when PBA-ad6 and PBA-ad12 were electrospun at solution concentration of 40% and 18% (w/v), respectively. The nanofibrous mats of MCPBz were obtained as free-standing material, yet, PBA-ad12 mat was more flexible than and PBA-ad6 mat. Furthermore, the curing studies of these MCPBz nanofibrous mats were performed to obtain cross-linked materials.

1. Introduction

Polybenzoxazine is a newly developing phenolic type thermoset resin, which has attracted much interest in recent years because of its fascinating properties, such as near-zero volumetric change upon curing, low water absorption, high glass transition temperature, high char yield and no by-products without any catalysts during curing [1]. In addition, the molecular structure of polybenzoxazines facilitates immense design flexibility which enables tailoring the properties of the cured material for a wide range of applications [1–3]. Conventionally, benzoxazine monomers are synthesized from a phenolic derivative, a primary amine, and formaldehyde by solution or solventless method [1]. The polymerization of benzoxazines can be accomplished by means of thermally induced ring-opening reaction with or without initiator and/or catalyst. In recent years, a new type of benzoxazine has been developed in which oxazine rings are the main component of the polymer chain; main-chain polybenzoxazine (MCPBz) [1,4–20]. The MCPBz can be obtained by using difunctional amines and phenolic derivative, and they can also be synthesized as repeating unit of a polymer chain, block copolymer or as a side chain as well [1,4–20]. The thermal and mechanical performance of polybenzoxazine thermosets obtained from MCPBz are affirmed to be excellent than those obtained from the benzoxazine monomers [12]. In other words, some of the characteristics; for instance easy processibility, flexibility, high density of crosslink after curing and lower fragility for cured end-structures were achieved for polybenzoxazines. In one respect, MCPBz have potentials as an easy processable and crosslinkable thermoplastic, which become thermosets at ~200 °C *via* ring opening of oxazine ring by thermal activation [21,22].

Electrospinning is quite versatile and cost effective technique which facilitates the production of nanofibers from variety of polymers, polymer blends, sol–gels, composites and ceramics, etc [23,24]. In principle, a continuous filament is formed from polymer solution or polymer melt under high electric field which resulted in fibers with diameter ranging from tens of nanometers to a few microns [23]. The morphological characteristics and the diameter of the electrospun nanofibers are governed by process parameters such as applied voltage, tip-to-collector distance, flow rate of the polymer solution and nozzle diameter. On the other hand, intrinsic properties such as polymer type, molecular weight, solvent, concentration, surface tension and conductivity of the polymer solution and fluid elasticity have shown a great influence [23,24]. Notably, environmental conditions such as humidity and temperature also play a crucial role [23,24]. Nanofibers produced by electrospinning have several appreciable features such as a very large surface area to volume ratio and nanoscale pores. In addition,

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materials having nanofibrous structure exhibit distinctive chemical, physical and mechanical properties when compared to their bulk or film forms. The unique properties and multifunctionality of such nanofibrous structures are suitable in variety of application areas including healthcare, filtration, textiles, environmental, energy, electronics, sensors, etc [23–29].

Although a large number of studies on polybenzoxazines are appeared in the literature, only a very few reports are found in the literature on electrospinning of polybenzoxazines [30–34]. Si et al. reported on the synthesis of 1D mesoporous polybenzoxazine (PBZ)-based Fe_3O_4@carbon nanofibers (CNFs) which exhibit an extremely high surface area as well as efficient adsorption for organic dyes and facilely magnetic separation property [30]. Further, the same group reported on the fabrication of 1D PBZ-based magnetic CNFs with hierarchical porous structure by a combination of electrospinning and *in situ* polymerization [31]. In addition, Ren et al. reported on the fabrication of hierarchical porous magnetic CNFs which comprised graphitic fibers and Fe_3O_4 nanocrystals where electrospun polyacrylonitrile/polybenzoxazine (PAN/PBZ) fibers are employed as a composite carbon source [32]. Kao et al. prepared a blend of the poly(3-phenyl-3,4-dihydro-2H-1,3-benzoxazine) and PAN to produce low-surface-free-energy fibers for biononfouling membrane without fluorine and silicon elements [33]. Li and Liu reported polyelectrolyte composite membranes of polybenzimidazole and cross-linked polybenzimidazole/polybenzoxazine electrospun nanofibers for proton exchange membrane fuel cells [34]. The aforementioned studies always used additional polymers as a carrier matrix or main polymeric matrix for the electrospinning of nanofibers incorporating polybenzoxazine. However, to the best of our knowledge, this will be the first report on electrospinning of nanofiber from polybenzoxazine resins without blending with any other polymeric matrix.

In this study, we mainly focus on the optimization of electrospinning conditions in order to produce uniform and bead-free nanofibers from polybenzoxazines by itself without blending with a polymeric matrix. For this purpose, two different MCPBz were synthesized by using two different difunctional amine (1,6-diaminohexane and 1,12-diaminododecane), bisphenol-A and paraformaldehyde as starting materials through a Mannich reaction. Afterwards, electrospinning was performed for different MCPBz concentrations in chloroform/DMF (4:1, v/v) solvent system in order to produce uniform and bead-free nanofibers from these two MCPBz. Furthermore, curing studies were performed to obtain thermoset polybenzoxazine nanofibers, yet, MCPBz nanofibers could not retained their fibrous structure due to their low melting point.

2. Experimental

2.1. Materials

Paraformaldehyde (Sigma–Aldrich, 95%), bisphenol-A (Sigma–Aldrich, 97%), 1,6-diaminohexane (Aldrich, 98%) and 1,12-diaminododecane (Aldrich, 98%) were used without further purification. Chloroform (Sigma–Aldrich, 99%), N,N-dimethylformamide (DMF, Fluka, 98%), methanol (Sigma–Aldrich, 99.7%) and tetrahydrofuran (Merck, 99.7%) were used as received. FTIR grade potassium bromide (Sigma–Aldrich, 99%) and deuterated chloroform (Merck, 99.8%) were used for FTIR and NMR spectroscopies, respectively.

2.2. Synthesis of main-chain polybenzoxazines (MCPBz); PBA-ad6 and PBA-ad12

Two different types of MCPBz were synthesized from two different difunctional amines (1,6-diaminohexane and 1,12-diaminododecane), bisphenol-A and paraformaldehyde as starting materials by using solvent method. The MCPBz named as PBA-ad6 was synthesized from 1,6-diaminohexane (25 mmol), bisphenol-A (25 mmol) and paraformaldehyde (100 mmol) in a 1:1:4 M ratios. Reactants were taken in a 500-mL round-bottom flask and 250 mL of chloroform was added to the reaction mixture. Then, the solution mixture was refluxed for 7 h at 60 °C. Afterwards, chloroform was evaporated completely from the solution by using rotary-evaporator system and the product were dried under vacuum at 45 °C for 24 h. In order to remove any residual reactants, PBA-ad6 was purified by washing through with cold methanol several times and then dried under vacuum at 45 °C for 24 h. Overall yield of the synthesized PBA-ad6 was 83%. According to the GPC measurements, weight average molecular weight (M_w) and polydispersity index of this sample was calculated as ~11,500 and 4.7, respectively. Similar procedure was followed for the synthesis of PBA-ad12; 1,12-diaminododecane (25 mmol), bisphenol-A (25 mmol) and paraformaldehyde (100 mmol) were put in a 500-mL round-bottom flask and 250 mL of chloroform was added to the reaction mixture. In this case, the solution was refluxed for 10 h at 60 °C. For PBA-ad12, the drying and purification steps were same as PBA-ad6. Overall yield of the synthesized PBA-ad12 was 71%. According to the GPC measurements, weight average molecular weight (M_w) and polydispersity index of this sample was calculated as ~17,000 and 5.3, respectively.

2.3. Electrospinning of PBA-ad6 and PBA-ad12 nanofibers

The homogenous solutions of MCPBz (PBA-ad6 and PBA-ad12) were prepared in different concentration in chloroform/DMF mixture solvent system (chloroform:DMF; 4:1, v/v). For the electrospinning of PBA-ad6 nanofibers, solution concentration was varied from 30% to 45% (w/v) and the clear and light yellow color solutions were obtained after stirring for 3 h at room temperature. For the electrospinning of PBA-ad12 nanofibers, 15%, 18% and 20% (w/v) solution concentrations were prepared and solutions were stirred for 6 h to obtain a clear and homogenous solutions. The solutions were taken in 1 mL syringes with metallic needle of 0.6 mm outer diameter. The syringe was positioned horizontally on the syringe pump (KD Scientific, KDS 101) and the positive electrode of the high voltage power supply (Matsusada Precision, AU Series) was clamped to the metal needle (Fig. 1). In order to optimize the electrospinning parameters, flow rate of the polymer solution (0.5–1.5 mL/h), applied voltage (10–20 kV) and tip-to-collector distance (10–20 cm) were varied within the ranges given in the parenthesis. The most favorable results were obtained when the electrospinning parameters are 0.5 mL/h, 12.5 kV, 10 cm for the electrospinning of PAB-ad6 nanofibers and 1 mL/h, 15 kV, 15 cm for the electrospinning of PAB-ad12 nanofibers. In all cases, the electrospinning was carried out in a horizontal position at 24 °C and 18% relative humidity in a completely enclosed plexiglas box. Electrospun nanofibers were collected on a grounded stationary cylindrical metal collector covered by a piece of aluminum foil. After the electrospinning, the collected nanofibrous mats were dried over night at 25 °C under vacuum in order to remove any residual solvent.

2.4. Measurements and characterization

The structure of the synthesized PBA-ad6 and PBA-ad12 were confirmed by proton nuclear magnetic resonance (^{1}H NMR, Bruker Advance III 400 MHz) spectrometer. Samples were prepared by dissolving about 20 mg/mL polybenzoxazines in deuterated chloroform ($CDCl_3$). ^{1}H NMR spectra of the samples were measured with 16 scans in the range of 0–10 ppm. Fourier transform infrared (FTIR, Bruker-VERTEX70) spectrometer was employed to verify the