



Macromolecular Nanotechnology

Solvent-assisted heat treatment for enhanced chemical stability and mechanical strength of *meta*-aramid nanofibers

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ABSTRACT

Meta-aramid exhibits excellent chemical stability and mechanical strength owing to its rigid crystal structure. However, the crystal structure is destroyed when *meta*-aramid nanofibers (mANFs) are fabricated by electrospinning, which results in nanofibers with poor performance characteristics. Here, we present a facile solvent-assisted heat treatment for the efficient crystallization of mANFs. The optimal volume ratio of the co-solvent solution was determined to be 6:5:100 (DMAc:ethylene glycol:water), and the optimal crystallization temperature 120 °C. The crystallinity of the mANFs obtained under these optimized conditions (mANF-6-120) is higher than the crystallinity of mANFs heat-treated at 300 °C (mANF-HT). As a result, mANF-6-120 exhibits superior chemical stability and mechanical strength compared to mANF-HT. After immersion in DMAc for 48 h, the weight of mANF-6-120 is reduced to 28% of its original weight, whereas the relative remaining weight of mANF-HT is less than 8%. The value of Young's modulus of mANF-6-120 is 1.7 times higher than that of mANF-HT. The crystallization process developed in this study requires less energy and is less expensive than the conventional high-temperature heat treatment process. The *meta*-aramid nanofiber mat obtained using the proposed process shows great promise for application to water purification and the treatment of polluted air.

1. Introduction

Poly(m-phenyleneterephthalamide), *meta*-aramid, is an aromatic polyamide possessing superior chemical stability, mechanical strength, and thermal resistance because of its rigid backbone structure and a large number of hydrogen bonds [1–3]. Therefore, *meta*-aramid fibers are used in various applications such as flame-resistant barriers, protective apparel, electrical insulation, and high-temperature filter materials [4–6]. In addition to the bulk *meta*-aramid fibers, the commercial nanofibrous *meta*-aramid is currently used for protective clothing to improve its smoke shielding properties [7]. The nanofibrous *meta*-aramid has also received much attention recently in relation to environmental issues such as water and air purification due to its high hydrophilicity and excellent adsorption performance. Among the various types of nanofibrous polymer, electrospun polymer nanofibers are well suited for the protective clothing and environmental applications because of their high porosity, large specific surface area, small pore size, and ease of manufacture [8–13].

Several studies have demonstrated that electrospun *meta*-aramid nanofiber (mANF) mats are useful as a membrane for water purification, air filtration and flame retardants, etc. [14–21]. However, as-spun

mANF mats typically have low crystallinity, because the rigid chains are difficult to align and form a crystalline structure during electrospinning. Therefore, the as-spun mANF mats have shown a low elastic modulus and a poor chemical resistance to polar solvents such as DMF, DMAc and DMSO. Although the low crystallinity of mANF is a major constraint to its practical usage, only few studies have discussed methods for the regeneration of the crystal structure of mANF. Yao et al. reported that crystallization did not occur even after annealing mANFs at 150, 200, and 250 °C for 2 days [22]. Oh et al. exposed an mANF mat to microwaves at approximately 80 °C after wetting the mat in water [23]. The mat was successfully crystallized by the microwave treatment, due to which the tensile strength of the mat was 2.8 times higher than that of the original. However, the chemical stability of the mANF mat was not confirmed. Furthermore, a large amount of energy was required to apply microwaves continuously over a large area of a nanofiber mat under well-controlled temperatures. In our previous study, we reported that mANF crystallized under heat treatment at 300 °C for 10 min after removing salts in mANF by washing with water [24]. The regeneration of the crystal structure resulted in enhanced chemical stability and mechanical strength. However, heat treatment at high temperature is unsuitable for practical applications. High-temperature heat treatment

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requires high energy consumption, and causes undesirable changes such as decomposition and carbonization of the nanofibers. Furthermore, on the surface of nanofiber mat directly exposed to the heat, the nanofibers deform very rapidly, and this deformation is very difficult to control. Therefore, it is necessary to develop a more efficient and practical method for the crystallization of mANF.

As a facile method for crystallizing the rigid chains in nanofibers, solvent-based treatment has been frequently employed. For instance, electrospun silk and syndiotactic polystyrene nanofibers were successfully crystallized in chambers filled with saturated solvent vapor [25–27]. Plasticization of the local chains occurs when the solvent vapor molecules permeate into the nanofiber matrix, inducing the crystallization of nanofibers. In addition to vapor treatment, crystallization of nanofibers has also been conducted in a wet condition. Ahn et al. reported that glucose polymer chains were crystallized when ionic liquid was extracted from cellulose nanofibers to the coagulant [28]. The crystallinity of cellulose nanofibers increased as the extraction of ionic liquid became slower, because the slower extraction, the more time for crystallization. Kim et al. also suggested that poly(3,4-ethylenedioxythiophene) (PEDOT) chains could be stabilized in highly concentrated H₂SO₄ solution, and a crystalline PEDOT nanofibril structure could be formed by rinsing the H₂SO₄ solution in water [29]. Although these studies have proved that solvent-based treatment is useful for the crystallization of nanofibers, there have been no studies yet on the crystallization of mANF via solvent-based treatment.

In this study, solvent-assisted heat treatment was used for the crystallization of mANF. N,N-dimethylacetamide was used as a solvent for the as-spun mANF, whereas ethylene glycol and water were used as non-solvents. After wetting the as-spun mANF in the co-solvent, the solvent molecules were extracted by low-temperature heat treatment. To control the solvent extraction rate, the heat treatment temperature was adjusted (90, 120, and 150 °C). It was found that mANF mat treated in the optimized solvent-assisted heat treatment condition exhibits high crystallinity. The high crystallinity resulted in excellent chemical stability and mechanical strength. To the best of our knowledge, this is the first report which elucidates the mechanisms for the crystallization of mANF via solvent-assisted heat treatment. The facile and cost-effective crystallization process could significantly contribute to the application of mANF to various industrial fields ranging from water purification technology to high-temperature air filtration systems.

2. Experimental section

2.1. Materials

Poly(*meta*-phenylene isophthalamide) (*meta*-aramid, Nomex®) fiber was purchased from DuPont Plant. Ethylene glycol (EG, anhydrous, 99.8%) and lithium chloride (LiCl, ACS reagent, ≥99%) were purchased from Sigma-Aldrich. N,N-Dimethylacetamide (DMAc, ≥99.5%) was purchased from Daejung Chemical & Metals Co. All materials were used as received without further purification. The LiCl and *meta*-aramid were dried at 80 °C for 24 h in a vacuum oven to remove the moisture. Highly deionized water (18 MΩ cm⁻¹) was used throughout the experiments.

2.2. Fabrication of *meta*-aramid nanofibers

The electrospinning solution was prepared by dissolving *meta*-aramid fibers and LiCl in DMAc at 50 °C for 24 h in an oven shaker. The concentration of *meta*-aramid was 12, 14, and 16 w/v%. The *meta*-aramid/LiCl ratio was 5:2 by mass. *Meta*-aramid nanofibers were prepared using an electrospinning apparatus (NanoNC, Korea). The device was composed of syringe pumps, a high DC-voltage supply, and a rotating drum-type collector. The *meta*-aramid solution was placed in a 10-mL syringe equipped with a steel needle with an internal diameter of 0.33 mm. The collector was covered by aluminum foil and placed 15 cm

away from the needle tip. A positive voltage of +15 to 20 kV was applied to the tip of the syringe needle and a negative voltage of –10 kV was applied to the collector. The rotating speed of the collector was 100 RPM and the flow rate of the solution was 0.2 mL/h. The temperature and relative humidity in the electrospinning apparatus were maintained in the ranges 20–25 °C and 40–50%, respectively. Electrospinning was conducted using four syringes for 12 h. The as-spun *meta*-aramid nanofibers were denoted as mANF-As.

2.3. Crystallization of *meta*-aramid nanofibers

A co-solvent was prepared by mixing DMAc and EG in deionized water. The volume ratio of water to EG and DMAc was 100:5:x with x varying from 0 to 12. The *meta*-aramid nanofiber (mANF) mats were fixed to a square-shaped stainless steel frame and immersed in the co-solvent for 30 min. After the immersion, the mANF mats were heat-treated in air for 30 min at 90, 120, and 150 °C, respectively. The mANF mats were washed with deionized water and dried in a vacuum oven at 50 °C for 24 h. The mANF mats obtained via solvent-assisted heat treatment were denoted as mANF-x-y where x indicates the volume percentage of DMAc versus water and y refers to the heat treatment temperature. A control group was prepared for comparison purposes by applying the high-temperature process we developed in the previous study to the mANF-As [24]. The mANF-As were washed with deionized water for 30 min and heat-treated at 300 °C in air for 10 min. The mANF subjected to high-temperature treatment is denoted as mANF-HT.

2.4. Characterization of *meta*-aramid nanofibers

The microstructure of the mANFs was observed by field emission scanning electron microscopy (FE-SEM, JSM-6700F) at an accelerating voltage of 10 kV. The diameter of mANFs was measured using image analysis software (EyeViewAnalyzer, Digiplus Inc.). The average diameter was determined by measuring the diameter of 100 nanofibers from the FE-SEM images at random. The crystal structure was analyzed using X-ray diffraction methods (XRD, New D8 Advance) over the 2θ range of 10–40° using Cu K_α radiation as the X-ray source (λ = 0.154 nm). The chemical structure was observed using attenuated total reflection Fourier transform infrared spectroscopy (ATR FT-IR, Nicolet iS5) at room temperature over the range of 4000–650 cm⁻¹. The thermal properties were studied by thermal gravimetric analysis (TGA, Discovery TGA) and differential scanning calorimetry (DSC, Discovery DSC). The TGA analysis was conducted under a nitrogen condition, and the temperature range for the TGA analysis was 25–700 °C and the heating rate was 10 °C/min. DSC analysis was conducted under a nitrogen condition in the temperature range 25–350 °C. The DSC analysis was carried out in the order of first heating–first cooling–second heating. The heating rate and cooling rate were 10 °C/min. The chemical stability of mANFs was evaluated by soaking the mANF mat in DMAc. The relative weight of the mANF mat was measured by weighing the mat after a specified immersion period (12, 24, 36, and 48 h). The mechanical properties of mANFs were obtained using a universal testing machine (UTM, Instron 3343). Dog bone-shaped specimens were prepared in accordance with the ASTM D638 Type V. The tensile stress was applied in the horizontal and vertical directions in the alignment direction of the nanofibers at a crosshead speed of 1 mm/min.

3. Results and discussion

3.1. Morphology and crystal structure of *meta*-aramid nanofibers

The morphology and diameter of mANF-As were observed by FE-SEM. As shown in Fig. 1 and Table 1, three nanofiber mats with fibers of three different average diameters (120, 170, and 270 nm) were successfully fabricated. The nanofibers tended to be aligned in the rotation direction of the collector. In addition, the nanofibers were gathered into

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