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Improvement of hydrophilic properties of electrospun polyamideimide fibrous mats by atmospheric-pressure plasma treatment



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1. Introduction

Fibrous mats are porous permeable materials composed of individual nonwoven polymer nanofibers oriented randomly on a mat plane. These mats are widely used because of their high surface area, small fiber diameter, ability to incorporate active functional groups, filtration properties, thinness, high permeability, and low basis weight [1–3]. In recent years, fibrous mats have attracted considerable attention for biological applications, such as drug delivery, tissue engineering, and wound healing, owing to their very large surface area-to-volume ratio, flexible surface functionality, and superior mechanical performance [4–7].

Over the past two decades, electrospinning has been used to fabricate polymeric fibrous mats from continuous fibers with diameters ranging from tens of nanometers to less than ten micrometers. This process has two major advantages for the production of advanced polymer fibers that lead to its broad application in traditional markets [8–10]: firstly, compared to conventional fiber spinning, electrospinning can be used to manufacture large quantities of nanofibers relatively inexpensively and is applicable to a wide range of polymers, including those used in conventional spinning, e.g., polyolefins, polyamides, polyesters,

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ABSTRACT

Polyamide-imide (PAI) fibrous mats were fabricated through electrospinning and further treated with atmospheric-pressure plasma. The surface characteristics of the PAI fibrous mats were examined to determine the effect of plasma treatment on the hydrophilic properties. FT-IR, X-ray photoelectron spectroscopy, and contact-angle analysis indicated that the hydrophilicity of the PAI fibrous mats increased upon the introduction of hydrophilic groups by plasma treatment. The concentration of functional groups, including oxygen, and the surface roughness of the PAI fibrous mats increased with increasing treatment time. The optimum plasma treatment time for surface modification of the PAI fibrous mats under atmospheric pressure was 120 s.

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aramids, and acrylics [10]. Secondly, electrospinning enables easy control of the fiber diameter, surface-to-volume ratio, aspect ratio, and pore sizes of non-woven fabrics [10–12]. Recently, electrospun fibers have been extensively studied and used as scaffolding sub-strates for biomedical engineering, catalyst supports, sensors, and filters [5,13].

The initial work on this topic focused on engineering polymers, such as polyacrylonitrile, which were used as polymer precursors for electrospinning. Later, Schueren et al. examined electrospinning using more flexible, temperature-resistant organic polymers, such as polyamide [14,15]. Polyamide-imide (PAI), which is a class of high-performance engineering plastic, is widely used in electronic materials, adhesives, composite materials, fibers, and coatings, as well as other engineering materials; this is because of the excellent characteristics of the polyamide and polyimide groups present in the polymer backbone, which impart dimensional stability and beneficial thermal and mechanical properties [16,17]; in particular, PAI is easier to process and has better heat resistance than polyimide and polyamide. Many studies have examined the applicability of PAI in filtration media, electrical insulating wires, and reinforcements [18].

A range of techniques have been developed to improve the surface properties of fibrous mats. Surface treatment with atmospheric-pressure plasma is often used to chemically modify polymeric materials owing to its low cost, environmental

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Fig. 1. Chemical structure of PAI.



Fig. 2. (a) FTIR spectra of PAI fibrous mats and (b) magnified FTIR spectra of OH vibrational bands.

sustainability, high efficiency, and low energy consumption [19]. In addition, this method can be used to improve the wetting, adhesion, and filtration properties at the interface between nanofibers [20]. Therefore, atmospheric-pressure plasma treatment is suitable for controlling the surface properties of fibrous mats for a wide range of applications.

This study examines the effect of the plasma treatment time on the surface characteristics of PAI fibrous mats to determine the optimum conditions for developing hydrophilic functionalities. The effects of the duration of atmospheric-pressure plasma treatment on the chemical composition, surface functionality, and surface morphology of the PAI fibrous mats were investigated



Fig. 3. XPS spectra of PAI fibrous mats as a function of plasma treatment time: (a) 60 s, (b) 120 s, (c) 180 s, and (d) 240 s.

using X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM), respectively. The changes in the surface hydrophilicity of the PAI fibrous mats were determined via water contact-angle analysis.

2. Experimental procedure

2.1. General remarks

2,2-Bis[4-(4-aminophenoxy)phenyl]propane (BAPP), terephthalic acid (TPA), thionyl chloride (TC), N-methyl-2-pyrrolidone (NMP), and dimethyl formamide (DMF) were purchased from Aldrich Chemicals and used as received without further purification. PAI was prepared using the method reported by Hong et al.; following their method, thionyl chloride (13.08 g, 0.11 mol) was added to NMP (200 mL) in an ice-water bath and stirred for 10 min. TPA (8.31 g, 0.05 mmol) in NMP (200 mL) was then added in one portion, and the resulting mixture was stirred at room temperature for 40 min. Subsequently, BAPP (35.09 g, 0.05 mmol) in 200 mL of NMP was added. An exothermic reaction occurred, but the reaction temperature was maintained at room temperature for 4 h. The HCl by-product was removed by adding propylene oxide (11.02 g, 0.22 mmol), and the reaction was allowed to proceed at room temperature for 2 h. The resulting viscous mixture was poured rapidly into methanol with constant stirring in a Waring blender. The final products were washed with water and methanol, collected by filtration, and dried at 120 °C under reduced pressure for 24 h [21]. Fig. 1 shows the chemical structure of PAI.

2.2. Preparation

First, 25 wt% of PAI was dissolved in DMF, and the solution was stirred at 60 $^{\circ}$ C for 3 h. This polymer solution was spun into a fiber

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