Polymer 54 (2013) 2364–2372

Contents lists available at SciVerse ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Further improvement of air filtration efficiency of cellulose filters coated with nanofibers via inclusion of electrostatically active nanoparticles

Daehwan Cho [a,b], Alexander Naydich [a], Margaret W. Frey [b], Yong Lak Joo [a,*]

[a] School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY 14853, USA
[b] Department of Fiber Science & Apparel Design, Cornell University, Ithaca, NY 14853, USA

ARTICLE INFO

Article history:
Received 6 November 2012
Received in revised form
6 February 2013
Accepted 18 February 2013
Available online 26 February 2013

Keywords:
Filter media
TiO_2 nanoparticles
Pressure drop

ABSTRACT

Air filtration efficiency and pressure drop of nanofibrous filter media based on polyacrylonitrile (PAN) nanofibers with and without TiO_2 nanoparticles were evaluated. The nanofibrous filter media were fabricated by covering a cellulose substrate with varying masses of PAN fiber or PAN/TiO_2 hybrid nanofiber. Capillary flow porometry tests revealed that the hybrid nanofibrous filter media showed larger pore size and broader pore size distribution than their counterpart pure PAN nanofibrous filter media. The pressure drop of the filter media covered with the PAN/TiO_2 hybrid nanofibers (0.5 g/ft^2) was 4 times less than that of the counterpart filter media at an air velocity of 80 cm/s. Despite less fiber coverage density on the cellulose substrate and a greatly reduced pressure drop, the filtration efficiency of the nanofibrous filter media made with PAN/TiO_2 hybrid fibers was found to be much greater than that of those made with just pure PAN fibers, especially for smaller particles in the range 0.1–0.5 μm. These results might be influenced by the added electric charge caused by the insertion of TiO_2 nanoparticles in the fibers. Therefore, the improvement of two important features, enhanced filtration efficiency and reduced pressure drop can be simultaneously achieved through the use of polymer/TiO_2 hybrid nanofibrous filter media. This holds promise for facile development of energy-saving, high performance filters.

1. Introduction

Nonwoven filter media are composed of randomly oriented fibers with diameters of about a few dozen micrometers [1]. Although nonwoven filter media can achieve high filtration efficiency (removing approximately 90% of micron-sized particles), they are limited to use in pre-filters and are not used further downstream as high performance filters [2]. Particularly, the most penetrating particle size, between 0.1 and 0.5 μm, cannot be removed by the present nonwoven filter media because the size of pores formed with micron-scale fibers is considerably larger [3]. To enhance the filtration efficiency of the filter media, it is necessary to make much thicker media for smaller pore sizes. However, thicker filter media can be difficult to use due to increased pressure drop, and thus higher energy cost.

In the last 20 years, there has been considerable development of nanotechnology for filtration applications, and it is now possible to fabricate polymeric nanofibers and produce nanofibrous filter media [4,5]. It is expected that nanofibrous filter media can overcome or reduce the shortcomings of nonwoven filter media. Filter media coated with polymeric nanofibers have been used in a number of commercial air filtration applications, including filters for mining vehicle cabins, turbine-powered military tanks, and automobile air intakes [5]. The many potential uses of nanofibrous filters and the high yield and ease of production of nanofibers provide motivation for the investigation of possible methods to further improve nanofiber filtration efficiency. Almost all companies now have a nanofiber product in their filter media such as Donaldson Company Inc. (Ultra-Web) (refer to Ref. [6] in more detail).

Electrospinning is a key technology for the fabrication of nonwoven mats with sub-micron to nano-size fibers [7,8]. Electrospinning involves applying an electrical potential between a metal plate and a needle, through which a polymer solution is fed. The potential difference draws the solution into a jet in the direction of the plate. The jet then undergoes a whipping motion due to electrostatic repulsion between its own surfaces, drawing it out to sub-micron scale diameters. As the solution jet travels toward the plate, the solvent evaporates, producing a mat of nonwoven polymer nanofibers. These nanofibrous mats are characterized by a large surface area-to-volume ratio, small pore size, and high porosity compared to non-woven fabrics. As such, they are good

* Corresponding author. Tel.: +1 607 257 8556; fax: +1 607 255 9166.
E-mail address: ylj2@cornell.edu (Y.L. Joo).

0032-3861/$ – see front matter
http://dx.doi.org/10.1016/j.polymer.2013.02.034

candidates for filtration of particulate matter from air, and when spun onto a substrate made of relatively thick fibers, they have been shown to increase filtration dramatically especially in capturing and holding particles of sub-micron size. In fact, nanofibers with diameters in the sub-micron range are known to provide filtration efficiencies superior to non-woven filter media with larger, micron-scale fibers [9–11].

Both the physical structures and chemical properties of nanofibrous filter media are important to improving filtration performance. Functional or affinity membranes have recently become an interesting research area. Up to the present, some studies have been performed to modify the surface of nanofibers in order to endow the fibers with a specific functionality, as most polymeric nanofibers are chemically inert [12–15]. Ma et al. studied the feasibility of applying cellulose acetate nanofibers as an affinity membrane [13]. Zhang et al. used modified electrospun polyacrylonitrile (PAN) nanofibers as a novel affinity membrane, using bromelain as a research model. Their work demonstrated that the electrospun PAN nanofiber membrane has potential for affinity membrane applications in wastewater treatment systems [15]. Desai et al. have reported on chitosan-based nanofibrous filter media and their applicability for air and water filtration [12]. They fabricated nanofibrous filter media by electrospinning of chitosan/polyethylene oxide (PEO) blend solution onto a spunbonded non-woven polypropylene substrate. Their results showed that filtration efficiency of the nanofibrous mats was strongly related to the size of the fibers and their surface chitosan content. Recently, there have been a few reports about the loading of nanoparticles (Al_2O_3, TiO_2, Ag) in as-spun nanofibers to improve membrane efficiency [16,17].

High efficient particulate air (HEPA) filters show an ability of the extreme filtration efficiency, filtering out 99.97% of particles greater than or equal to 0.3 μm in diameter [6]. In comparison, the filtration efficiency of the nylon 6 nanofibrous filter media (made of 80–200 nm diameter fiber), which have a coverage density of 1.0 g/ft^2, were found to be superior to that of the commercialized HEPA filter [18]. However, with extended operation, the air flow rate across the nanofibrous filter media decreases significantly; adding a high coverage density of nanofibers on top of an existing filter substrate results in considerably increased pressure drop and reduced operating life [19,20]. Therefore, the pressure drop as well as the filtration efficiency needs to be coincidently considered to improve the performance and life of the filter media.

TiO_2 nanoparticles have been widely used in various applications such as photocatalysts, pigments and cosmetics additives, often in media of intermediate polarity [21,22]. However, the effect of the incorporated TiO_2 particles in nanofibers covering a filter substrate on air filtration efficiency has been not studied thoroughly. In the present study, we report the achievement of excellent air filtration efficiency and maintain low pressure drop by covering the substrate with polymeric nanofibers containing metal oxide nanoparticles, which can strongly influence electrostatic interactions between dust particles and nanofibers. Filtration efficiency of filter media covered with pure PAN nanofibers and PAN/TiO_2 hybrid nanofibers was evaluated, taking into account properties affecting filtration efficiency, including the structural properties of filter media (pore diameter, pore size distributions, pressure drop) and the electric charge property of the as-spun fibers. We demonstrate that despite less fiber coverage density on the cellulose substrate, the filtration efficiency of the PAN filter media with TiO_2 nanoparticles added can be much greater than that of those made with just pure PAN fibers, even with reduced pressure drop. Such enhancement is explained by the added electric charge interaction between TiO_2 nanoparticles in nanofibrous filter media and the simulated dust particles, an explanation supported by thermally stimulated current (TSC) results.

2. Experimental section

2.1. Materials

Polyacrylonitrile (PAN) (M_w 150,000) and Dimethylformamide (DMF) were purchased from Sigma–Aldrich Co. The anatase TiO_2 with a particle size ranging 5–10 nm was supplied by Samsung Co. (Korea). The cellulose bare filter media used in the study was provided by Clark Filter Inc. (USA). The fiber diameters of the bare filter ranged between 20 μm and 50 μm.

2.2. Fabrication of nanofibers and nanofibrous filter media

To analyze the effects of different TiO_2 concentrations in the PAN fibers on the electrical charge, pure PAN solution and three PAN/TiO_2 hybrid solutions were prepared as shown in Table 1. First, three different volume percentages of TiO_2 nanoparticles (PAN/TiO_2 = 97:3, 92.5:7.5, 87:13 v/v%) were dispersed in 2 mL of DMF with a vortex. PAN polymers were dissolved in DMF at 100 °C for 4 h and each TiO_2/DMF solution was then added to the PAN/DMF solution to give overall 10 wt% PAN in DMF. A pure 10 wt% PAN/DMF solution was also prepared. Each of the four solutions was then electrospun in three coverage densities (0.1, 0.25, and 0.5 g/ft^2) onto 3″ × 3″ commercial cellulose filters, which were held to a metal plate covered with aluminum foil. This produced a total of 12 nanofibrous filters with varying TiO_2 concentrations and fiber coverage densities. Electrospinning was performed using an 18 gauge needle with a flow rate of 0.025 mL/min. The potential difference applied between the needle and collector plate was 15 kV, and the distance between the plate and the tip of the needle was 13 cm.

2.3. Characterization of nanofibers and nanofibrous filter media

2.3.1. Scanning electron microscopy (SEM)

The morphology of the electrospun fibers and the surface of the nanofibrous membrane before and after filtration testing were examined with a Leica 440 scanning electron microscope (SEM) after being coated with Au–Pd. The diameter of the spun fibers was measured using Image analysis software (ImageJ 1.41).

2.3.2. Electron microprobe analyzer (EMPA)

The presence of TiO_2 nanoparticles in the as-spun fibers was confirmed using an electron microprobe analyzer (EMPA, Jeol Model 8900R) that used the same Au–Pd coated specimens. EMPA was used in the wavelength dispersive spectrometer mode for TiO_2 mapping. As the TiO_2 particles are present in the PAN/TiO_2 hybrid fibers, the TiO_2 map directly indicates the location of the TiO_2 particles in the as-spun fibers.

2.3.3. X-ray diffraction measurement (XRD)

XRD measurements were also performed to confirm the presence of TiO_2 nanoparticles in the as-spun fibers and their influence on PAN crystallization by a Scintag Theta–theta X-ray Diffractometer (nickel-filtered CuKα radiation, $\lambda = 1.54$ Å) operating at 45 kV

Table 1
Spinning dope recipes for the electrospun nanofibers.

Sample name (volume % of TiO_2)	Volume ratio (%)	
	PAN	TiO_2
Pure PAN	100	0
PAN/TiO_2 (3.0 v%)	97.0	3.0
PAN/TiO_2 (7.5 v%)	92.5	7.5
PAN/TiO_2 (13 v%)	87.0	13.0