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Development and optimization of alumina fine fibers utilizing a centrifugal spinning process

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ABSTRACT

Aluminum isopropoxide and poly(vinylalcohol) fine fibers were successfully fabricated and optimized utilizing the response surface methodology. The optimized composite fibers showed mean fiber diameter of 304 nm. The fiber samples were calcined at different temperatures to attain both gamma and alpha phases of alumina. Various characterization methods including scanning electron microscopy, thermogravimetric analysis, x-ray diffraction and nitrogen adsorption/desorption analysis were conducted. The BET analysis revealed a surface area of 261 m^2g^{-1} for the mesoporous gamma alumina structure. Statistical analysis of electron microscopy micrographs showed a mean fiber diameter of 272 nm for the crystalline alpha alumina fine fibers, calcined at 1200 °C.

1. Introduction

Fiber systems (e.g. organic and inorganic), have generated growing interest because of their wide applications, for example in biomedical, filtration, and electronic applications [1,2]. In general, composite fibers possess the benefits of organic polymers coupled to the intrinsic electrical, thermal and mechanical properties of inorganic materials [2–4]. Aluminum oxide has been extensively investigated due to its promising applications in many areas such as catalyst and supports, adsorbents, coatings, etc. [5–7]. Nanoparticles, nanorods and nanofibers systems are typical structures for alumina materials [8,9]. Most of these systems are prepared utilizing polymer composites as precursors. Polyvinyl alcohol (PVA), polyethylene oxide (PEO), polyvinylpyrrolidone (PVP), and polyacrylonitrile (PAN) have been the polymers of choice and are combined with different alumina precursors such as aluminum acetate, aluminum nitrate, aluminum chloride, aluminum isopropoxide or aluminum 2,4-pentanedionate [1,10]. These nanofibers are mostly prepared by electrospinning [6,7,11–16], sol-gel methods [17–21], mercury mediated technique [22], solvothermal [23,24], hydrothermal [25–28], and a variety of other methods [29–33].

The sol-gel technique has been extensively applied for the preparation of porous alumina structures which involves hydrolysis of a metal oxide such as aluminum isopropoxide [5,21]. Electrospinning has been the most commonly used method. For example, Azad showed successful fabrication of alpha alumina nanofibers by electrospinning a solution of PVP and aluminum 2,4-pentanedionate followed by calcination at 1500 °C [11]. Yu et al., prepared composite nanofibers by electrospinning a solution of PAN-DMF/aluminum 2,4-pentanedionate. Alpha alumina nanofibers were attained at a temperature of 1200 °C with fiber diameter ranging between 150 and 500 nm [15]. Panda and Ramakrishna reported alpha alumina nanofiber formation at a temperature of 1300 °C using solutions of aluminum acetate and PVA and PEO [12]. Mahapatra et al., prepared alpha alumina nanofibers (diameter in a range of 100–500 nm) using a solution of PVP–Aluminum acetate [7]. Shen et al. reported on gamma alumina nanofibers obtained from a solution of PVP/Aluminum nitrate-PAMAM-G1 (as structural agent) and calcined at 700 °C [8]. Nakan et al. also reported on nanofibers made by the electrospinning method. They used a solution of PVA/boehmite, alpha alumina nanofibers with surface area of 5.32 m^2g^{-1} were obtained at a temperature of 1200 °C [34].

The forcespinning® technique, which uses centrifugal force to make fibers, has been successfully applied for the fabrication and mass production of fine fibers made from different polymeric systems (PP, PS, PLA, PVP, PAN, etc), metal oxides, and various polymer composites, to name a few. The main advantage of utilizing forcespinning relies on the much higher yield and simplicity of the procedure. In forcespinning and electrospinning the viscoelastic properties of the melt or solution are important parameters to be considered along with fabrication related parameters. For example, in forcespinning the angular velocity has to be considered to produce fibers while in electrospinning many other

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parameters need to be considered such as solution or melt conductivity, electrostatics, electric field strength, surface charge, ionization field, etc. [35–37]. This study reports on the optimization and production of alumina fine fibers utilizing a combination of sol-gel technique and centrifugal spinning process. To the authors' knowledge, this is the first paper that presents the fiber diameter optimization of the aluminum isopropoxide (AIP)/PVA composite fine fibers, using response surface methodology (RSM)-Box-Behnken design. RSM comprises a set of mathematical methods for process/product optimization and improvement [38,39]. Compared to the other optimization techniques, RSM is largely applied and consolidated because of the possibilities of gathering useful information from a few number of tests along with detecting the interaction effects of the parameters on the response [39].

2. Materials and methods

2.1. Preparation method

High purity aluminum isopropoxide (AIP) and nitric acid were purchased from Sigma-Aldrich. Granular poly(vinylalcohol), 96% hydrolyzed with viscosity of 27 cps was obtained from Kuraray. Distilled water was used as the solvent.

The precursor solutions were fabricated by dissolving PVA (12 wt %-16 wt %) in water, this solution was stirred at a temperature of 70 °C for 1 h. Aluminum solutions were prepared using AIP (PVA/AIP a range between 0.75 and 2.25 based on the experimental design), water (molar ratio of water/AIP = 30) and nitric acid (molar ratio of HNO_3/AIP = 0.06). The AIP solution was retained under vigorous magnetic stirring at a temperature of 85 °C for 2 h. The two solutions were then mixed together at room temperature and aged for at least 3 h until a white opaque AIP/PVA homogeneous solution was obtained.

The solutions were then spun in the Cyclone system manufactured by Fiberio Technology Inc. A solution based cylindrical spinneret was used equipped with 30 gauge needles, 2 mL of the homogenous AIP/PVA solution were injected into the spinneret. The temperature and humidity level of the area were fixed within 70–75 °C and 40–45%, respectively. The angular velocity of the spinneret was varied from 7000 to 9000 rpm to study the effect of ultimate fiber size and homogeneity. A metallic frame was used to collect the produced AIP/PVA composite fine fibers. The obtained mats were dried at a temperature of 250 °C for 1 h with a rate of 3 °C/min and calcined under air atmosphere at 650 °C and 1200 °C for 3 h at 3 °C/min. Different calcination temperatures were used to obtain different crystalline structures of the resultant alumina fine fibers. Fig. 1 shows the fabrication process of the AIP/PVA composite fibers and resultant alumina fibers.

2.2. Characterization methods

Scanning electron microscopy (SEM) was used to analyze the morphology of the fibers and measure its diameter, a Carl Zeiss SIGMA VP. SEM analysis was conducted at low voltage, 3 kV for all the prepared samples. Fiber diameters were measured using Image J software. For each sample, at least ten different SEM micrographs were used to determine the fiber diameters from at least 100 fibers. The mean fiber diameter and the histograms were generated by means of Minitab® 17 Statistical Software. The specific surface area, pore size and pore volume were achieved by Nitrogen adsorption/desorption isotherms from a Micromeritics ASAP 2020 instrument. The Brunauer-Emmett-Teller (BET) technique was applied to determine surface area and pore size distribution, these were calculated by the Barrett- Joyner- Halenda (BJH) method using adsorption and desorption isotherms. A small sample (0.1–0.3 g) was preheated at a temperature of 250 °C for 15 h to certify degassing and subsequently followed by introducing liquid nitrogen (at 77 K). X-ray diffraction (XRD) patterns for the samples were conducted by a Bruker D8 Advanced X-ray Diffractometer, 2θ in a range of 10°–90° with a scan rate of 0.5° C/min. Thermogravimetric experiments (TGA-DTG) were performed under a TA Instrument SDT Q600 TGA, using a heating rate of 10° C/min under a nitrogen atmosphere. Minitab® 17 software was implemented for the statistical and optimization analysis.

Table 1
Three factors with their corresponding levels based on the Box- Behnken experimental design method.

Variables	Levels		
	−1	0	+1
PVA (X1)	12	14	16
PVA/AIP (X2)	0.75	1.5	2.25
Speed (X3)	7000	8000	9000

Table 2
Coded factors levels and samples names with their corresponding fiber diameter as response.

Number of Exp.	Parameters			Sample name	D (nm)
	X1	X2	X3		
1	−1	−1	0	OAP-1	343
2	+1	−1	0	OAP-2	660
3	−1	+1	0	OAP-3	451
4	+1	+1	0	OAP-4	530
5	−1	0	−1	OAP-5	360
6	+1	0	−1	OAP-6	460
7	−1	0	+1	OAP-7	573
8	+1	0	+1	OAP-8	780
9	0	−1	−1	OAP-9	530
10	0	+1	−1	OAP-10	463
11	0	−1	+1	OAP-11	687
12	0	+1	+1	OAP-12	727
13	0	0	0	OAP-13	430
14	0	0	0	OAP-14	415
15	0	0	0	OAP-15	466

D:mean fiber diameter.

3. Design of experiments

Response surface methodology (RSM) provides an optimization tool to evaluate the interaction of parameters, using a minimum number of experiments. Here, RSM was used to investigate the effect of processing variables on the fiber diameter of as-spun AIP/PVA composite fibers. Three major parameters including PVA, PVA/AIP ratio and centrifugal

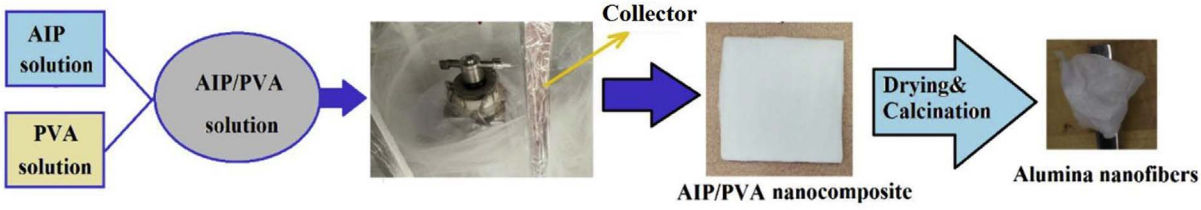

Fig. 1. Schematic of alumina fibers production process.