The effect of various electrospinning parameter on preparation of alumina nanofibers

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Abstract. Alumina nanobers were successfully prepared via an electrospinning technique with combination of aluminum oxyhydroxide (AlOOH) as alumina precursor and Polyvinylpyrrolidone (PVP) as the polymer precursor. To produced alumina precursor, Aluminum Isopropoxide (AIP) was dissolved in distilled water under the constant stirring process at 80°C. Electrospinning solution was prepared by mixing Aluminum Oxyhydroxide (AlOOH) and Polyvinylpyrrolidone (PVP) aqueous solution for 2 hours under room temperature. Different concentrations of polymer precursor and various electrospinning parameters such as applied voltage, distance tip to collector, and flowrate of sol-gel were studied. The as-spun fibers were calcined at 1200°C and characterized by SEM. Results showed that the average fiber diameter decreases with decreasing of Polyvinylpyrrolidone (PVP) concentration, increasing of applied voltages and decreasing of electrospinning flow rate. At 10%wt Polyvinylpyrrolidone (PVP) concentration with 17.5v of applied voltages and 0.03 ml/min of flow rates, calcined fibers showed an average diameter of 100-200nm.

1. Introduction
Over the past decade, the fabrication of ceramic metal oxide composites has gained much attention due to their unique properties and wide range applications such as high-temperature insulation, supercapacitor, optical, and as brake-disc in automotive brake system[1]. Alumina which also calls as Aluminum Oxide (Al2O3) is ceramic metal oxide where its superiority has opened up opportunities for the discovery of outstanding materials and applications[2]. Due to its high temperature capacity, alumina is widely used in high-temperature applications such as blast furnace slag component[3]. Moreover, good abrasion resistance of alumina making it useful for abrasive material[4]. Solid alumina has been used in manufacturing of orthopedic implant and electrical insulator while alumina fiber is widely used in manufacturing of fire retardation components[5]. For future applications of alumina, Bacciarini[6] reported that metal matrix composite reinforced alumina powder shows promising features for airframe applications in the aerospace industry[6].
Electrospinning is a process of producing nanofibers and microfibers by which involves an electrohydrodynamic process. It is a unique method used to produces long and short ultrafine fibers with a simple setup[7]. The basic apparatus of electrospinning includes a high voltage power supply, pump, syringe, and wire grounded collector. Around the beginning of the electrospinning process, high voltage power is connected to the syringe before the sol-gel is injected. Due to the voltage applied, an electrical field is generated from syringe tip to the collector. As the sol-gel is injected from the syringe, an electrical repulsive force directs the fiber in form of jet onto the collector. The fibers then are calcined at high temperatures to remove the polymer precursor and the desired ceramic phase is obtained. The ultrafine fibers prepared by this process demonstrate a brilliant performance and tremendous mechanical properties[8].

Enhancement of mechanical properties of fibers has resulted in a major interest in nanomaterials. In nanofiber composite, the mechanical properties of fiber-reinforced composite depend extensively on the quality of bonding between fiber and matrix[9]. Sethuramalingam[10] in his study revealed that increasing the area of the contacted surface between fibers and matrix enhanced mechanical properties of the composites[10]. This can be achieved by various approaches includes reduction of diameter sizes of the fibers. Through an electrospinning process, fiber diameter can be minimized by different parameters setting such as increasing the voltage applied and increasing the distance of an electric field traveled by the polymer[11]. Reducing polymer concentration also resulted in smaller fiber diameters. The effect of different parameter settings on the preparation of alumina nanofibers through an electrospinning process has been reported. Despite that, most of the previous researches on the fabrication of alumina nanofibers are focused on the preparation of fibers in form of continuous strand [12].

In some applications, short fibers demonstrate better performance above the continuous fibers by offering high level of stiffness to weight ratio[13]. Moreover, short fibers much more versatile in term of processibility which it can be used in most extrusion techniques with thermoplastics[14]. However, the preparation of short fibers through the electrospinning process usually required a post-spinning process. Most of the previous researches utilized the conventional method to shortening the fibers such as grinding and milling[15]. One of the major limitations of these post-processing methods is the fiber must be reasonably brittle to fracture. Therefore, the nonconventional method to fabricate short fibers by which may eradicate the need for post-processing process is studied.

In this study, attempts have been made to prepare short alumina nanofibers by electrospinning technique by studying the effect of different precursors concentration and other processing parameters on morphology of nanofibers. Initially, aluminum isopropoxide (AIP) which could be easily dissolved in ethanol was selected as the alumina precursor. Meantime, high molecular weight Polyvinylpyrrolidone (average Mw 1,300,000) was used as the polymer precursor.

2. Experiment

2.1. Materials
Aluminum isopropoxide (AIP) with a reagent grade of 99 % from Sigma Aldrich was used as the source of alumina precursor. For polymer precursor, high molecular weight Polyvinylpyrrolidone (Mw 1300000) was purchased from Sigma Aldrich alongside nitric acid (HNO3) and Ethyl Acetoacetate which also obtained from Sigma Aldrich.

2.2. Preparation of sol-gel
To simplify the condition for analysis, a typical procedure was selected, different concentration of polymer solutions was prepared by adding Polyvinylpyrrolidone (PVP) into ethanol with stirring for 2hours at 50°C. As preparation of alumina precursor, initially a number of grams of Aluminum isopropoxide (AIP) was added into 10ml of deionize water under stirring process. Then, a few drops of Ethyl Acetoacetate were added and the stirring process was continued for 16hours. Both solutions then were transferred onto glass beaker for mixing process of 2hours at 50°C. A numbers of different concentration were studied includes 6%, 8%, 10% and 12%.
2.3. Electrospinning process
The solution was transferred into a plastic syringe equipped with a 23-gauge needle. The needle was connected to a voltage supply which is capable of generating DC voltage as high as 25kV. In a typical procedure the distance between the needle and collection screen was fixed at 16cm. The relative humidity was controlled between 50% and 60% at room temperature. Throughout the electrospinning process, the voltage was kept constant at 17.5kV. 0.01ml/min of flowrate is used during electrospinning of different polymer concentrations. After optimum concentration of polymer was selected, A set of different flowrates was studied includes 0.03ml/min, 0.04ml/min and 0.05ml/min.

2.4. Characterization
The morphology of fibers was examined by scanning electron microscopy (SEM).

3. Result and discussion

3.1. Effect of solution concentration
From the SEM micrographs, solution concentration had considerable influence on the morphology of the nanofibers. From the morphology images illustrated in Figure 1, it can be observed that there is formation of bead on electrospun fibers. The formation of beads is related to the instability of the jet of polymer solution which is due to the insufficient amount of viscoelastic force to overcome the repulsive forces of charge. As can be observe from the figures, beads and beaded fibers are less likely to be formed for the more viscous solutions. The diameter of the beads become bigger and the average distance between beads on the fibers longer as the viscosity increases. Meanwhile, the shape of the beads gradually changes from spherical to spindle-like. At higher concentration of polymer (12%wt), the stack fibers are formed. Due to its large diameter size, the concentration is not suitable for fabrication of nanofibers. Based on the morphological result, 10%wt polymer concentration was selected.

3.2. Effect of different flowrates setting
From the SEM micrographs illustrated in Figure 2 until Figure 4, the influence of flowrates on the morphology of the nanofibers can be observed. At flow rate of 0.03 ml/min (Figure 2), 0.04ml/min (Figure 3) and 0.05ml/min (Figure 4), the bead formation on fibers were reduced due to the feeding rate was proportional to the electrospinning speed. In this case, electrospinning process was accomplished under stable condition, lesser probability of instability and lesser falling droplets of the unspun polymer jet. Even though no bead found at the flowrates of 0.04ml/min and 0.05ml/min of fibers, the fibers have bigger diameters. The distribution of fiber diameters was affected by flow rate variations. Obviously, when the flow rate is increased, fiber diameter distribution became wider which also resulted in the selection of 0.03ml/min of flowrate as the most optimum for fabrication of short alumina nanofibers.
Figure 1. SEM micrographs of electrospun fibers.

(a) Fibers from 6%wt polymer concentration
(b) Fibers from 8%wt polymer concentration
(c) Fibers from 10%wt polymer concentration
(d) Fibers from 12%wt polymer concentration
Figure 2. Fibers from 0.03ml/min of flowrate.

Figure 3. Fibers from 0.04ml/min of flowrate.

Figure 4. Fibers from 0.05ml/min of flowrate.
Figure 5. Short alumina nanofibers with an average diameter of 100-200 nm.

4. Conclusion
In this study, the effect of flow rate and polymer concentration on the morphology of electrospun nanofibers was investigated. It was found that the fiber diameter distribution and the morphology of the produced nanofibers were all influenced by the flow rate and concentration of the polymer solution. Moreover, beaded fibers are less likely to be formed for the more viscous solutions. However, at higher concentration of polymer (12%wt), the stack fibers are formed. Due to its large diameter size, the concentration is not suitable for fabrication of nanofibers. Reduction of beaded fibers has been achieved from all set of flowrates studied (0.03 ml/min, 0.04ml/min, and 0.05ml/min). However, the fibers of 0.04ml/min, and 0.05ml/min of flowrates have bigger diameters. Obviously, when the flow rate was increased, fiber diameter distribution became wider which also resulted in the selection of 0.03ml/min of flowrate as the most optimum for fabrication of short alumina nanofibers. In a nutshell, alumina short nanofibers have been successfully fabricated as shown in Figure 4. At 10%wt Polyvinylpyrrolidone (PVP) concentration with 17.5V of applied voltages and 0.03 ml/min of flow rates, calcined fibers showed an average diameter of 100-200 nm.

5. References
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