

Generation of Polymer Ultrafine Fibers Through Solution (Air-) Blowing

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Received 21 March 2009; accepted 22 May 2009

DOI 10.1002/app.30938

Published online 12 August 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Solution (air-) blowing, an innovative technique for generation of ultrafine polymer fibers from solutions, was developed by feeding polymer solutions (instead of melts) to a die assembly similar to that used in the conventional melt (air-) blowing process. Micro- to nano-scaled polyvinylpyrrolidone (PVP) fibers were produced using PVP solutions with water, ethanol, and/or their mixtures as the solvents; and the morphologies of the fibers were examined by scanning electron microscopy. The processing variables, including PVP concentration, air-blowing pres-

sure, solution-feeding pressure, and the volatility of the solvent system (the ratio of ethanol to water), were systematically investigated. The results indicated that solution (air-) blowing was a viable technique to produce nonwoven fabrics consisting of ultrafine polymer fibers with diameters ranging from micrometers to nanometers. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 3479–3486, 2009

Key words: solution (air-) blowing; ultrafine fibers; nonwoven fabrics; polyvinylpyrrolidone

INTRODUCTION

Melt (air-) blowing is a technique for producing nonwoven fabrics directly from polymer melts using heated and pressured air with high velocity to attenuate the filaments.^{1–5} The melt (air-) blowing technique is notable because of its unique capability to produce microfibers (generally a few micrometers in diameters) that are an order of magnitude thinner than other textile fibers. The products have numerous applications as filtration media, medical fabrics, oil adsorbents, and thermal insulation. In the conventional melt (air-) blowing process, a polymer melt is extruded from the orifices of a die assembly to form filament strands, which are then drawn into fine fibers using hot, compressed air flow. The fibers are generally highly entangled due to the turbulence in the air flow, and a randomly overlaid nonwoven fabric is formed on a collector. The collector can be a roller or a moving belt. Although making nonwoven products using the melt (air-) blowing technique has been considered in recent years as one of the most

rapidly growing techniques in the textile industry, its limitations are also evident. It is well known that some polymers cannot be melted (such as polyacrylonitrile, which decomposes before the melting starts). Included are other polymers (such as polytetrafluoroethylene) which have extremely high melt viscosities (even though they are able to melt) due to their high crystallinity and the associated high melting points. Additionally, the operating windows for successfully melt (air-) blowing polymers are usually quite narrow; and the processing conditions vary significantly with different polymers. Furthermore, the processing technique utilizes polymer melts which also raise a critical concern about degradation, particularly for polyesters (such as polyethylene terephthalate) and polyamides (such as nylon 6,6). The process is also energy-intensive because of the high temperature and the hot, compressed air associated with the process. These reasons limit the use of the melt (air-) blowing technique; currently, most of the commercially available products such as diapers are made of polyolefins, particularly polypropylene.

In this study, we explored the feasibility of the solution (air-) blowing technique; we also carried out preliminary investigations concerning the morphological properties of the products made from several polymer solutions. Our hypothesis was that the significantly lower viscosity of polymer solutions (as compared with that of polymer melts) might result in the reduction of fiber diameters. Additionally, the solution blowing process applied compressed air at

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Contract grant sponsor: The US Army Research Laboratory (Advanced Materials and Processes for Future Combat Systems); contract grant number: DAAD19-02-2-0011.

Contract grant sponsor: The "Center for Accelerated Applications at the Nanoscale (CAAN)" (the South Dakota School of Mines and Technology [SDSM&T]).

room temperature, which eliminated concerns regarding the thermo-degradation of polymers. The recycling of solvent(s) is an issue that does not exist in melt (air-) blowing, but this issue can be readily addressed if the solution blowing is carried out using a production line with a solvent recovery capability. In this exploratory study, we selected the nontoxic solvents of water and ethanol. We believe that the solution blowing technique would save energy, reduce costs, and probably broaden the types and applications of air-blown, nonwoven products. During this investigation, we modified common melt (air-) blowing equipment and fed the polymer solutions from a reservoir through a pump to the die assembly. Compressed air, operating at room temperature of $\sim 25^{\circ}\text{C}$, was used to facilitate solvent evaporation, and more importantly, to attenuate the solution filament strands into ultrafine polymer fibers. Polyvinylpyrrolidone (PVP) is soluble in both ethanol and water, which have different volatilities, and thus was selected as the model polymer. The processing variables, including PVP concentration, air-blowing pressure, solution-feeding pressure, and the volatility of the solvent system (the ratio of ethanol to water), were systematically investigated. The morphologies of the fibers were examined by Scanning Electron Microscopy (SEM). The results indicated that solution (air-) blowing was a viable technique to produce nonwoven fabrics consisting of ultrafine polymer fibers with diameters ranging from micrometers to nanometers. The technique would be particularly useful for creating nonwoven fabrics of ultrafine fibers from polymers that do not melt or have extremely high melt viscosities, but are soluble in relatively nontoxic solvents such as water, ethanol, and others. Additionally, if we simply add an alkoxide precursor (such as tetraethyl orthosilicate, TEOS) of silica (SiO_2) into the spin dope, we could readily make ultrafine hybrid fibers of PVP/TEOS. After placing these fibers under an ambient condition for a time period to allow TEOS to completely hydrolyze, followed by a high temperature pyrolysis to burn/remove the organic component, the ultrafine glass fibers could be prepared.⁶ The ultrafine glass fibers could be potentially useful for many applications, particularly the dental composite application.⁷ Similar approaches could also be utilized to prepare other ceramic materials such as TiO_2 in the ultrafine fiber form; and the ultrafine TiO_2 fibers could be particularly useful for the dye-sensitized solar cell and photo-catalysis applications.⁸

EXPERIMENTAL

Materials

Polyvinylpyrrolidone (PVP, $M_w = 1,300,000$, catalog number 437190) and absolute ethanol (200 proof, cat-

alog number 459828) were purchased from Sigma-Aldrich (St. Louis, MO) and both were used without further purification. Distilled water was supplied by the university facility.

Solution blowing

Several PVP solutions in varying mixtures of water and ethanol were prepared at specific concentrations. All the concentrations used in this article were weight percentages. The solution blowing was conducted using a conventional air blowing equipment manufactured by the Biax-Fiberfilm Corporation (Greenville, WI). Rather than feeding a polymer melt to the die assembly from an extruder, the PVP polymer solutions were fed to the die assembly from a reservoir through a gear pump made by the Cole-Parmer Instrument Company (Vernon Hills, IL). A schematic of the process is provided in Figure 1. Operation was started by adjusting the air pressure delivered to the die assembly. When the air pressure reached the desired value, distilled water was first used to clean and test the die assembly. When the proper operation of the system was verified by a steady water stream through all nozzles in the die assembly, the water was switched out for a polymer solution. As soon as the polymer solution was flowing steadily through the nozzles in the die assembly, the pressure of the polymer solution was regulated to the desired value using the pump's regulator. A mesh-like collector was then inserted into the bottom of the drying chamber and the fiber collection began. When the desired amounts of polymer fibers had been collected, the collector was pulled out and distilled water was again used to clean the die assembly.

Characterization

A Zeiss Supra 40VP field-emission SEM was employed to examine the morphologies of the

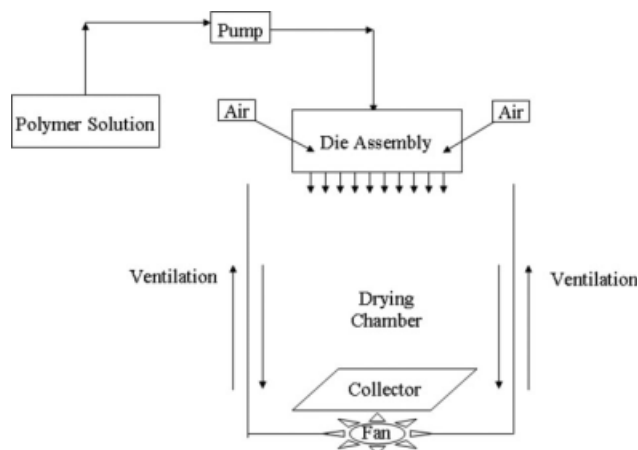


Figure 1 A schematic representation of the solution (air-) blowing process.

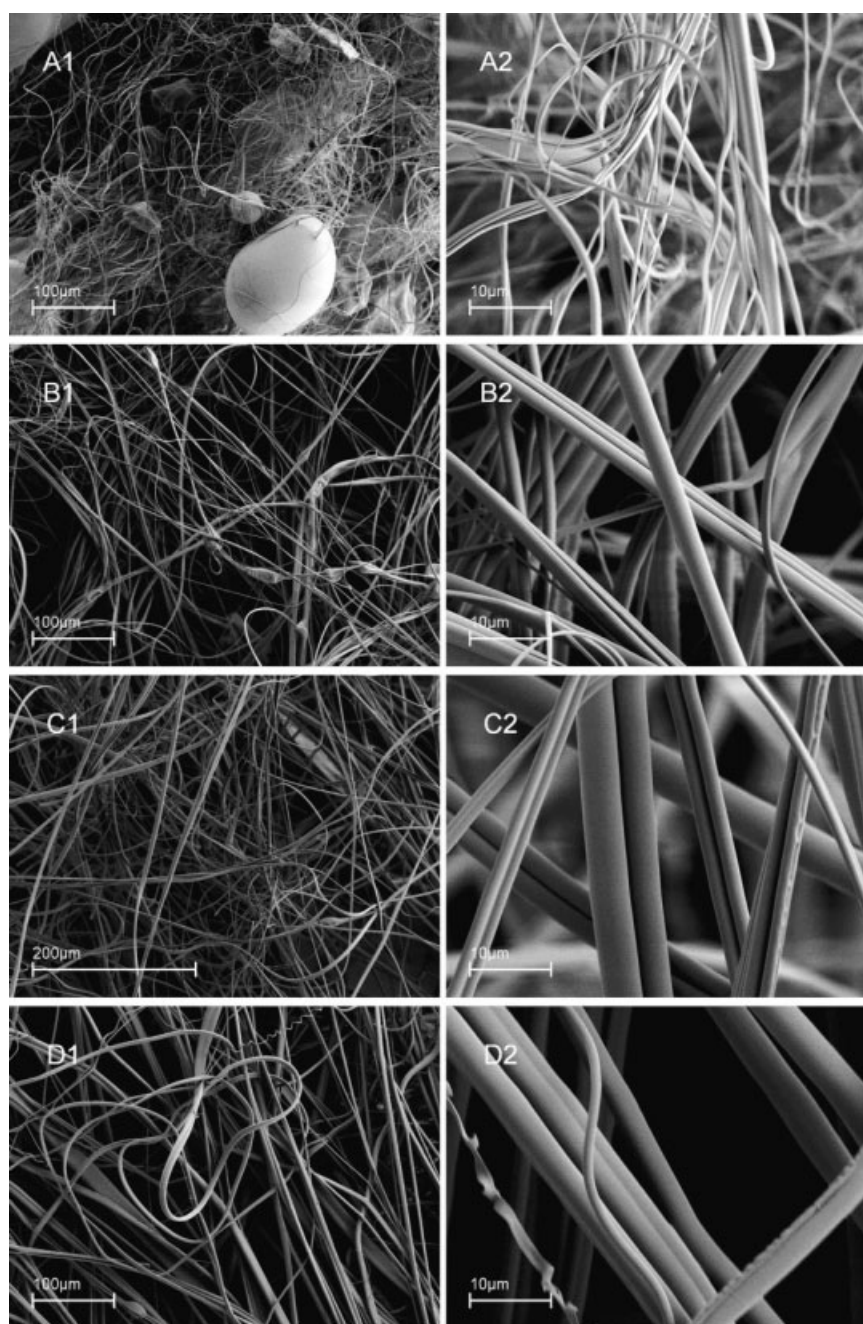


Figure 2 Representative SEM images showing PVP fibers made from 50/50 (wt/wt) ethanol/water solutions at the PVP concentrations of (A) 8%, (B) 10%, (C) 12%, and (D) 14%. The air pressure and solution pressure were fixed at 15 and 70 psi, respectively.

prepared samples. Before SEM examination, the specimens were sputter-coated with gold to avoid charge accumulation.

RESULTS AND DISCUSSION

Concentration

Four solutions with the PVP concentrations of 8, 10, 12, and 14% in 50/50 (wt/wt) ethanol/water were blown at a fixed air pressure of 15 psi and a poly-

mer solution pressure of 70 psi to study the concentration/viscosity effect on the fibers' formation and morphology. At the PVP concentration of 8%, large beads with dimensions ranging from a few 10s of micrometers to over a 100 μm were embedded within the PVP fibers; and the fibers were curved and/or coiled in bundles [Fig. 2(A1)]. This confirmed the observation made during the process of solution blowing that the fiber collector was covered with solution droplets as well as with fibers. The SEM image at a higher magnification [Fig. 2(A2)]

showed that the fibers were randomly packed and varied in sizes from ~ 300 nm to ~ 2 μm , but the majority of the fibers were in the submicron range. At the PVP concentration of 10%, beads were also observed with dimensions in the ~ 15 μm scale [Fig. 2(B1)]. The fibers were slightly larger but less curved than those made from the 8% PVP solution. Some of the fibers were as small as ~ 400 nm but the majority of the fibers were in the range of 1–3 μm [Fig. 2(B2)]. Further increases in PVP concentrations resulted in even larger fibers [Figs. 2(C,D)]. At the PVP concentrations of 12 and 14%, much improved and more uniform fibers were observed in the range of 1–5 μm with scattered beads having dimensions of ~ 12 μm . Some ribbon-shaped fibers with dimensions of ~ 18 μm were also observed at the 14% PVP concentration. It was noteworthy that the solution feeding pump could barely drive the 14% PVP solution, and the cleaning of the nozzles became difficult due to the high viscosity of the polymer solution. The optimal concentration for blowing PVP solutions in this study was therefore determined at 12%. Solutions at a lower PVP concentration had a low viscosity and droplets falling from the nozzles were observed during the process. Solutions at the higher concentrations did not improve fiber morphology and were difficult to process. The 12% PVP solution was selected for the studies that followed. In all instances, some interfiber adherence/conglutination was observed, probably due to the contact by the solution jets before the solvent was completely evaporated.

Air pressure

In our solution blowing process, high velocity air pressure, streaming from the top and bottom of the die nose-piece, evaporated the solvent, attenuated the polymer solution jets, and solidified them into ultrafine fibers. Five different solution air processing pressures including 5, 10, 15, 20, and 25 psi were investigated. A standard 12% PVP solution in 50/50 (wt/wt) ethanol/water mixture and a fixed polymer solution pressure of 70 psi was adopted. PVP solution dripped from the nozzles during the solution blowing process at the 5 psi air pressure. It was determined, therefore, that the 5 psi air pressure was too low to effectively evaporate the solvent. The other four air pressures resulted in acceptable fibers with similar sizes. The majority of the fibers were observed in the range of 1–5 μm , whereas a small quantity of larger fibers (15–30 μm) were also present (Fig. 3). It was noted that the presence of solution dripping from the nozzles was still evident at 10 psi air pressure and more curled and/or coiled fibers were observed at the high end of the air pressure (25 psi). Additionally, the turbulent air flow at 25 psi air pressure made some of the fibers fly out

of the drying chamber and many others were deposited on the internal side walls of the drying chamber instead of on the collector at the bottom of the chamber. The optimal air processing pressure in this study was determined to be 15 psi. Air pressures (<10 psi) could not effectively evaporate the solvent and led to liquid droplets, forming large beads on the collector. High air pressures (>20 psi) resulted in excessive turbulence, causing twisted loop fibers in the product, reduced fiber collection efficiency, and also caused an amount of short, fine fibers to be dispersed into the ambient air out of the chamber.

Solution pressure

The solution pressure was adjusted by a liquid feeding pump and was measured by a gauge before the solution entered the die assembly. The effects of the solution pressure on the fiber formation were examined at five different solution pressures including 35, 70, 105, 140, and 175 psi, using the standard 12% PVP solution in 50/50 (wt/wt) ethanol/water and a fixed air pressure of 15 psi. At solution feeding pressures of 35 and 70 psi, the fiber sizes were predominantly in the range of 1–5 μm with random larger fibers of ~ 18 μm in size [Figs. 3(B) and 4(A)]. Some submicron scaled fibers were observed at 35 psi. At a solution pressure of 105 psi, the fiber sizes increased, with the majority in the range of 2–8 μm . Large fibers (~ 20 μm) and beads (~ 50 μm) appeared more frequently [Fig. 4(B)]. During the solution blowing process, significant liquid (the polymer solution) dripping occurred and the productivity was increased, compared with the lower solution pressures. At solution pressures of 140 and 175 psi, the fiber sizes became widely distributed [Fig. 4(C), (D)]. The proportion of large fibers (>10 μm) and beads (>40 μm) increased, whereas other fibers sizes were in the range of 1–10 μm . The productivity increased at the higher solution pressures but the solution dripping from the nozzles also increased. The optimal solution pressure in our solution blowing experiments was determined to be 70 psi. Lower pressures resulted in less fiber productivity. Although higher pressures produced higher fiber productivity, the solution dripping at the nozzles ruined the product. Higher solution pressure meant higher polymer solution flow rate, and the air flow was not able to completely dry all the solution jets. This caused more dripping at the nozzles during the solution blowing process and correspondingly large beads were formed in the final fiber product.

Solvent variation

Five different solvent systems, including 100% ethanol, 75/25 (wt/wt) ethanol/water, 50/50 (wt/wt) ethanol/water, 25/75 (wt/wt) ethanol/water, and

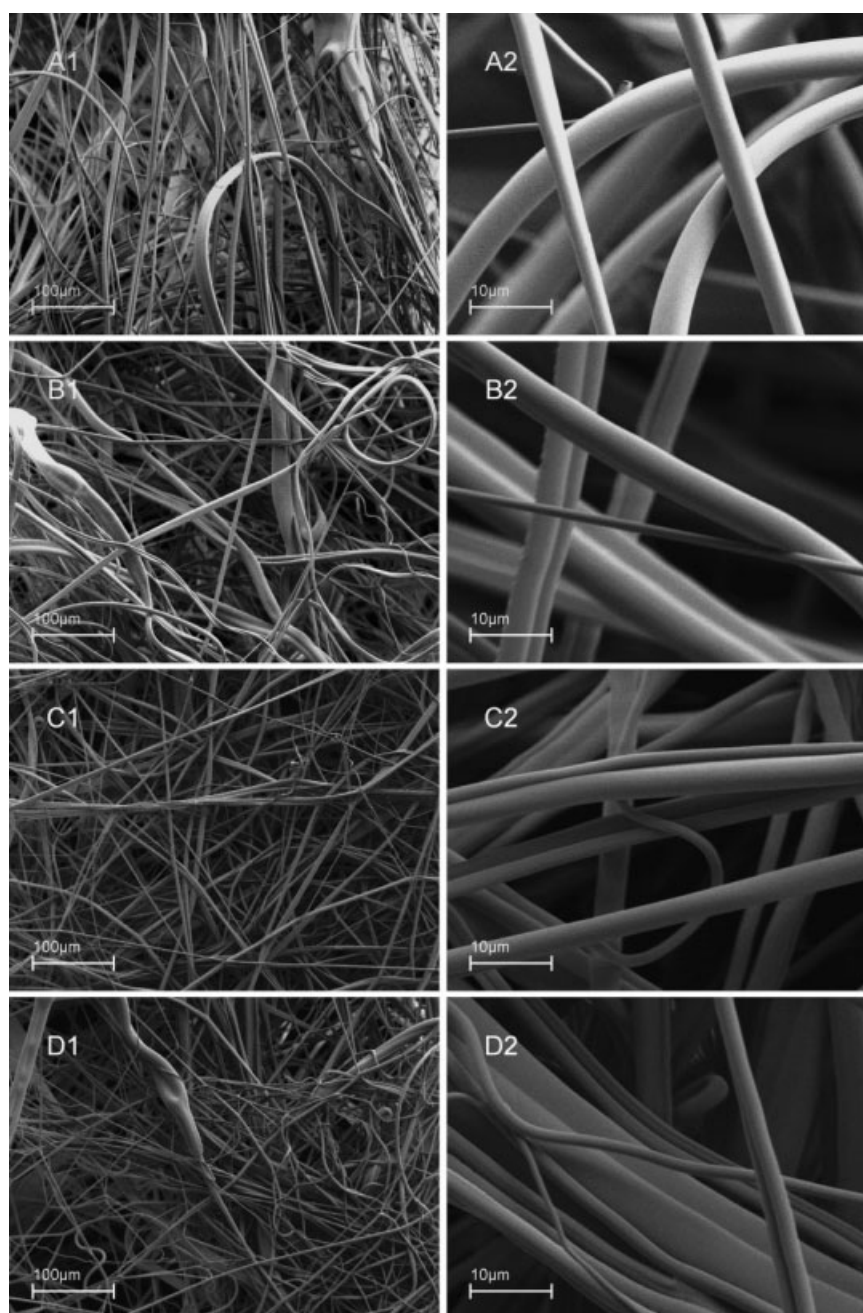


Figure 3 Representative SEM images showing PVP fibers made from 50/50 (wt/wt) ethanol/water solutions at the air pressures of (A) 10 psi, (B) 15 psi, (C) 20 psi, and (D) 25 psi. The PVP concentration and solution pressure were fixed at 12% and 70 psi, respectively.

100% water, were investigated with the PVP concentration of 12%. The air pressure and the solution pressure were fixed at 15 and 70 psi, respectively. The solution system consisting of 100% water as the solvent could not effectively produce fibers. Severe dripping made it difficult, if not impossible, to collect fibers. The 25/75 ethanol/water mixture reduced the solution dripping, but the fiber productivity was rather low, and only a small amount of fiber was deposited on the collector. In spite of many large beads (ranging from ~ 20 to ~ 300 μm), the fiber sizes

appeared to be small [Fig. 5(A)]. The majority fell into submicron range (some as fine as ~ 200 nm), whereas large fibers (1–2 μm) were also visible. Increases in the ethanol percentages caused improved fiber formation. At 75% ethanol, much less solution dripping was observed during the solution blowing process and higher fiber productivity was observed when compared with the solutions containing less ethanol and more water. Most of fibers were in the range of 1–3 μm , including some submicron fibers and some ~ 20 μm fibers [Fig. 5(B)]. At 100% ethanol,

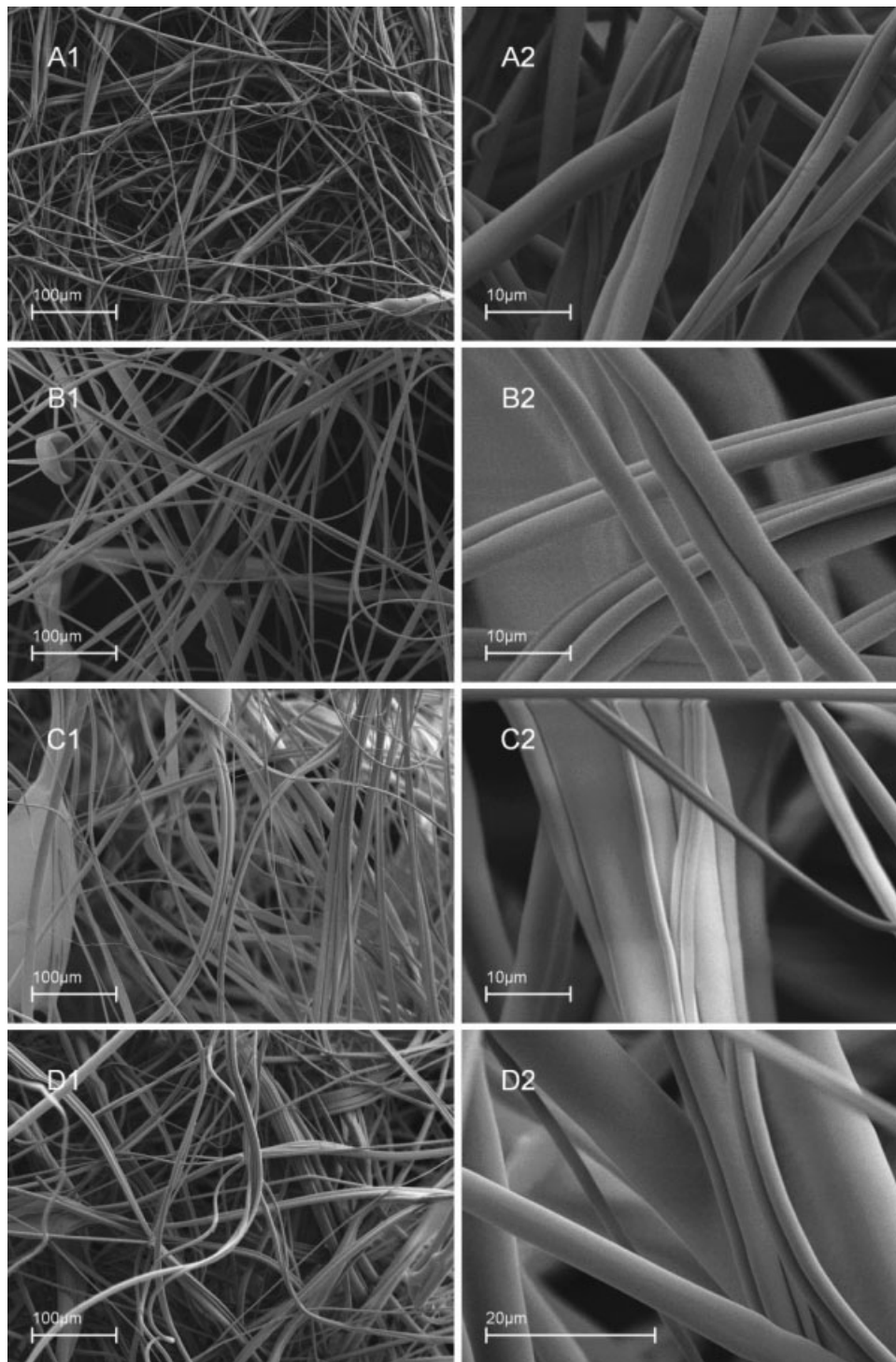


Figure 4 Representative SEM images showing PVP fibers made from 50/50 (wt/wt) ethanol/water solutions at the solution pressures of (A) 35 psi, (B) 105 psi, (C) 140 psi, and (D) 175 psi. The PVP concentration and air pressure were fixed at 12% and 15 psi, respectively.

no solution dripping occurred and the solution delivered the highest fiber productivity. The fibers were relatively uniform with sizes of 1–3 μm , although a few large fibers ($\sim 8 \mu\text{m}$) were also present [Fig. 5(C)]. The above results indicated that ethanol is bet-

ter than water for solution blowing of PVP. The high volatility and the associated fast evaporation rate of ethanol facilitated fiber formation; the solution dripping from the nozzles was eliminated, and the fiber product was of the best quality we observed.

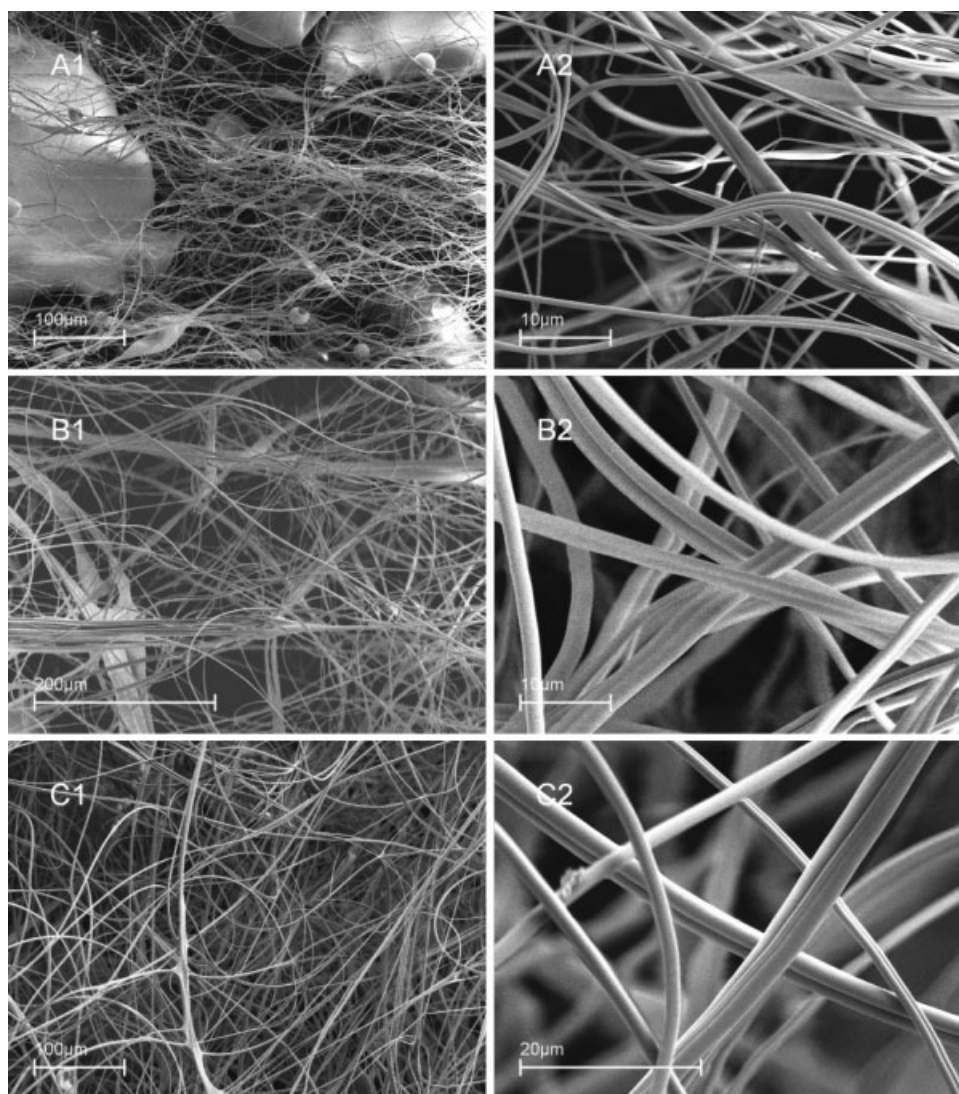


Figure 5 Representative SEM images showing PVP fibers made from the solvent systems of (A) 25/75 (wt/wt) ethanol/water, (B) 75/25 (wt/wt) ethanol/water, and (C) pure ethanol. The PVP concentration, air pressure, and solution pressure were fixed at 12%, 15 and 70 psi, respectively.

SUMMARY

This investigation reported the formation of fibers using the solution (air-) blowing technique. The processing parameters of air pressure and solution feeding pressure, as well as the solution parameters that included the PVP concentration, and the solvent mixture were studied. In general, our solution blowing process worked for PVP solutions and generated PVP ultrafine fibers with diameters primarily in the range of 1–10 μm .

Solutions at low PVP concentrations had low viscosities and led to solution dripping at the nozzle during the solution blowing process. Solutions at high PVP concentrations did not provide improved fiber morphology and the high viscosity degraded the solution blowing process. The solution with the

PVP concentration of 12% was determined to be the optimal.

Low air pressures (<10 psi) could not effectively produce fibers probably due to the poor evaporation of the solvent and the formation of liquid droplets on the collector; on the other hand, high air pressures (>20 psi) reduced the fiber productivity caused by the excessive air turbulence. The air pressure of 15 psi demonstrated desired fiber productivity.

The fiber productivity was significantly reduced at the lowest solution (feeding) pressure of 35 psi. The fiber productivity increased as the solution pressure was increased. Although higher pressures (>105 psi) gave rise to higher fiber productivity, the solution dripping ruined the product due to the formation of beads in the product. It was determined that the

solution pressure of 70 psi resulted in good quality fibers with an acceptable productivity level.

Ethanol was better than water for solution blowing of PVP. As the ethanol content in the ethanol/water mixture was increased, the fiber productivity was much improved and, when using the 100% ethanol, the solution dripping at the nozzles was completely eliminated. The results suggest that a minimum of 50% ethanol in the solvent system with water is necessary to obtain good quality fibers with acceptable fiber productivity.

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