

Alumina Nanofibers Obtained from Poly(Vinyl Alcohol)/Boehmite Nanocomposites

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ABSTRACT: Poly(vinyl alcohol) (PVA)/boehmite nanocomposite (precursor) nanofibers were formed by electrospinning using a PVA aqueous solution of dispersed boehmite nanoparticles as the spinning solution. The alumina nanofibers were obtained by calcination of the precursor nanofibers between 500 and 1200°C. The specific surface area of the precursor nanofibers was around 6 m²/g, and that of the γ -alumina nanofibers calcined at 500°C was around 300 m²/g. The specific surface areas and the fiber diameters were not affected by the alumina contents in the precursors. Also, the di-

ameter of the alumina nanofibers was not affected by the calcination temperature of the precursor nanofibers. The pore characteristics of the alumina nanofibers decreased with increased calcination temperature due to the sintering, and nonporous α -alumina nanofibers were obtained by calcination of the precursor nanofibers at 1200°C. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 1774–1779, 2011

Key words: electrospinning; boehmite; alumina; poly(vinyl alcohol); precursor; nanofiber

INTRODUCTION

Progress in electrospinning (ES) techniques, which form polymeric nanofibers easily,^{1–3} has made it possible to form many inorganic nanofibers. The inorganic nanofibers are mainly obtained by thermal decomposition of the organic–inorganic precursor nanofibers formed by ES.^{4,5} Various nanofibers, such as silica,⁶ titanium oxide,⁷ zirconium oxide,⁸ nickel cobaltite,⁹ and so on, have been formed from precursor nanofibers. The authors have reported the formation of titanium oxide nanofibers and nanotubes from poly(vinyl alcohol) (PVA)-titanium compounds as hybrid precursor nanofibers.^{10,11} The development of high-performance catalysts, fillers and filters can be expected from the fabrication of nanofibers from inorganic materials.

Alumina (Al₂O₃), which exists in large amounts in the earth's crust, has excellent heat resistance, corrosion resistance, and electric insulation, and thus is widely used in the industrial world. The formation of alumina nanofibers has been also reported by several research groups. Larsen et al. formed alumina nanofibers from a precursor obtained by ES of an aluminum alkoxide-ethanol solution.¹² Tuttle et al. obtained alumina nanofibers by calcination of alumi-

num acetate-poly(vinyl pyrrolidone) (PVP) hybrid precursor nanofibers.¹³ However, the aspect ratio of α -alumina nanofibers decreased by calcination at 1200°C. Ethanol was used as a solvent to form the precursor nanofibers by ES in both reports. Also, aluminum alkoxide and aluminum acetate are easily hydrolyzed with humidity and thus require careful handling. Panda and Ramakrishna formed precursor nanofibers by ES of aluminum acetate-PVA or -poly(ethylene oxide) aqueous solution, and alumina nanofibers were formed from these precursors.¹⁴ Alumina nanofibers calcined at 900°C had a patterned indented surface and the one calcined at 1300°C had large fiber-size distribution (20–500 nm).

In this study, boehmite (AlO(OH)·H₂O), which has high stability, was used as the alumina source, and the precursor nanofibers (PVA/boehmite nanocomposites) were formed by ES of a PVA/boehmite nanoparticle/water system. The structure of the alumina nanofibers obtained by calcination of the precursor nanofibers was investigated. Also, the pore characteristics of alumina nanofibers have not been reported. Thus, we investigated the effect of calcination temperature on the pore characteristics of the alumina nanofibers obtained.

EXPERIMENTAL

Formation of PVA/boehmite precursor nanofibers and alumina nanofibers

Poly(vinyl alcohol) (PVA, degree of polymerization: 1500, Wako Pure Chemicals Ind., Ltd., Japan) 10 wt %

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aqueous solution was prepared. Boehmite nanoparticles were dispersed into the PVA solution (spinning solution). Boehmite nanoparticles [Disperal P2, dispersed particle size, 25 nm (from product information of Sasol)] were kindly gifted from Sasol Japan KK. The spinning solution was loaded into a plastic syringe (2 mL) equipped with a needle. The solution extrusion rate was 0.015 mL/min. A voltage of 15.0 kV was applied to the needle, and then the PVA/boehmite nanocomposite nanofibers were deposited on a collector as a nonwoven fabric. The collector (copper plate) was grounded, and the distance between the tip of the needle and the collector was 10 cm. The PVA/boehmite nanocomposite nanofibers were used as the precursor for the alumina nanofibers.

The precursor nanofibers obtained were calcined up to a given temperature in an electric furnace at 500–1200°C for 5 h (in air, heating speed: 10°C/min), and alumina nanofibers were formed.

Apparatus and procedure

The structure of the nanofibers was observed with a scanning electron microscope (SEM) (Keyence VE-9800, Japan) and transmission electron microscope (TEM) (JEOL JEM-2100, Japan). Using a digitizer on the enlarged SEM images, we estimated the fiber diameter and its standard deviations at each nanofiber. Thermogravimetric (TG) analysis was performed in air at a heating rate of 10°C/min (Shimadzu DTG-60, Japan). X-ray diffraction (XRD) measurements were taken using a $\text{CuK}\alpha$ with a Ni filter (40 kV, 30 mA) (Shimadzu XRD-6100, Japan). The nitrogen adsorption isotherms (-196°C) of the nanofibers were measured with Micromeritics TriStar 3000. The average pore diameters (d_p), with pores assumed to be cylindrical in shape, were calculated from the specific surface area (S) and pore volume (V : determined from the nitrogen adsorption amount at $P/P_0 = 0.98$) for each alumina nanofiber: $d_p = 4V/S$.

RESULTS AND DISCUSSION

Effect of alumina content in the precursors

Figure 1 shows SEM images of the as-spun nanofibers. The shape of the nanofibers is not affected by the addition of boehmite nanoparticles to the PVA matrix. The productivity of the nanofibers decreased when the alumina content was above 50 wt %. This would be due to the increase in the viscosity of the spinning solution (the productivity was improved by diluting the spinning solution with water).

Figure 2 shows the relationship between the average fiber diameter and the alumina content for the as-spun precursor nanofibers. We assumed that all boeh-

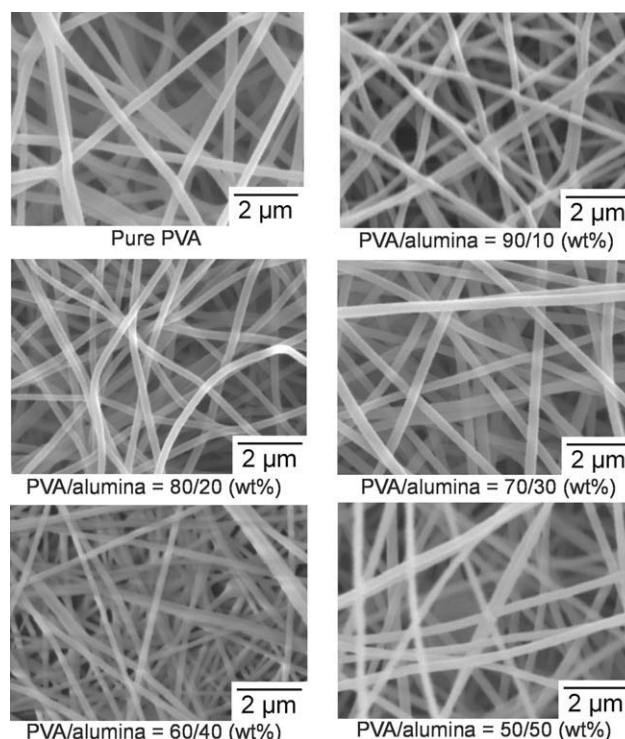


Figure 1 SEM images of as-spun nanofibers.

mite in the precursors is changed to alumina by calcination, and the alumina contents in the precursors were calculated. The average fiber diameters are distributed from 200 to 300 nm, and do not depend on the alumina contents.

Figure 3 shows TG curves of the pure PVA and the PVA/boehmite nanofibers. The weight residue of pure PVA nanofiber becomes zero at 560°C. From the TG curves of the PVA/boehmite nanofibers, the weight residues at 600°C (the alumina contents in the precursor nanofibers) reflect the boehmite contents in the spinning solutions.

Figure 4 shows the SEM images of the PVA/boehmite nanofibers after calcination at 500°C for 5 h in air. There were no residues after calcination of the pure PVA nanofibers. The fibers retain the shape of the PVA/boehmite (PVA/alumina = 90/10 wt %) precursor nanofibers, but adhesion between the fibers is observed. The reason would be that the amount of the boehmite (alumina) in the precursor was insufficient. On the other hand, well-formed nanofibers are obtained when the alumina content is above 20 wt % in the precursor. Figure 5 shows the relationship between the average fiber diameter of the alumina nanofibers and the alumina content in the precursor nanofibers. The diameters of the alumina nanofibers are distributed from 200 to 300 nm, and do not depend on the alumina contents in the PVA/boehmite precursor nanofibers. This is the same tendency as in Figure 2. From these results, we found that the diameters of the PVA/boehmite nanofibers were not

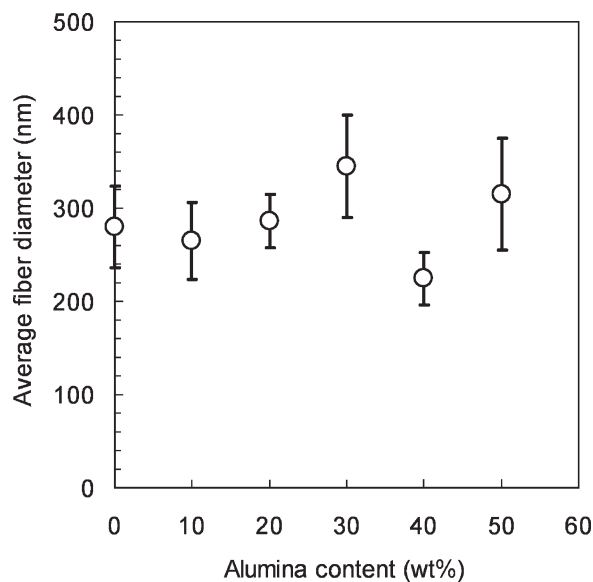


Figure 2 Effect of alumina content upon average fiber diameter for as-spun precursor nanofibers.

changed before and after calcination at 500°C. Compared with the alumina nanofibers reported by other group,¹⁴ alumina nanofibers with a narrower diameter distribution can be obtained by our method although the average fiber diameter was almost the same.

Figure 6 shows TEM images of a pure PVA nanofiber and a PVA/boehmite (PVA/alumina = 70/30 wt %) precursor nanofiber before calcination. The pure PVA nanofiber has a smooth surface [Fig. 6 (a)]. For the precursor nanofiber, it is likely that the boehmite nanoparticles are dispersed homogeneously in the PVA matrix because a dark contrast is observed

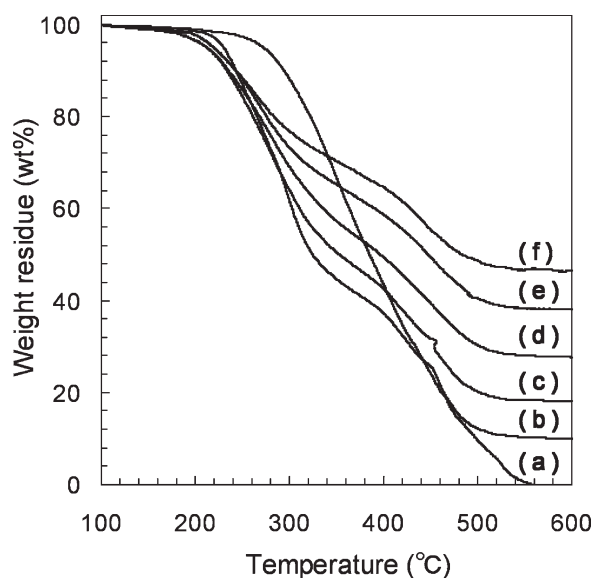


Figure 3 TG curves of (a) pure PVA and (b)–(f) PVA/boehmite nanofibers [(b) PVA/alumina = 90/10 wt %, (c) 80/20 wt %, (d) 70/30 wt %, (e) 60/40 wt %, (f) 50/50 wt %].

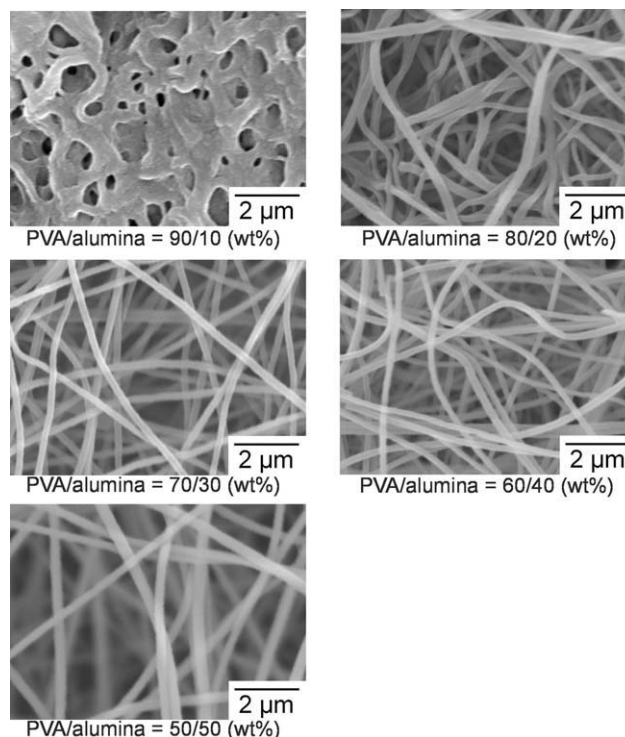


Figure 4 SEM images of PVA/boehmite nanofibers after calcination of 500°C for 5 h in air.

throughout the fiber in Fig. 6(b). Also, the precursor nanofiber has an undulation on its surface. This would be due to the existence of boehmite nanoparticles with ~ 25 nm in diameter in the vicinity of the fiber surface.

The diameters of the precursor nanofibers were not changed by calcination as described above. But their nonwoven fabric shrank by calcination (the fabric of the PVA/boehmite (PVA/alumina = 90/10 wt %)

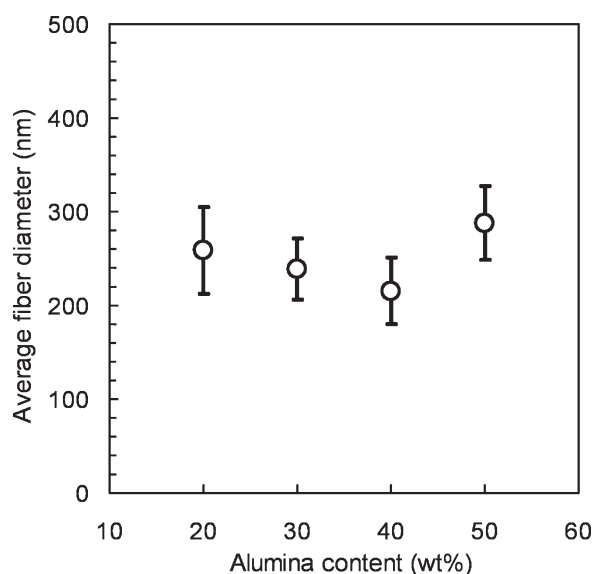


Figure 5 Effect of alumina content in precursor nanofibers upon average fiber diameter of alumina nanofibers.

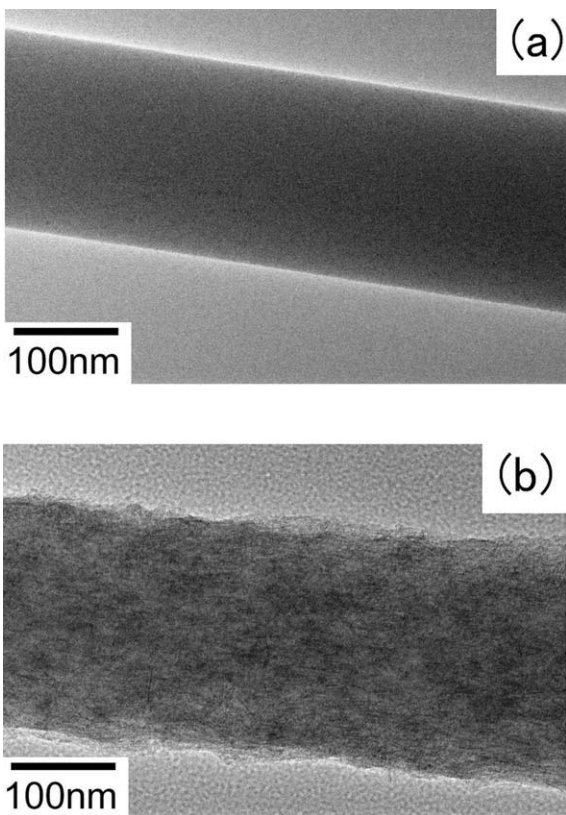


Figure 6 TEM images of (a) pure PVA nanofiber and (b) PVA/boehmite (PVA/alumina = 70/30 wt %) precursor nanofiber before calcination.

nanofibers was reduced to particles by calcination). Figure 7 shows the relationship between the shrinkage ratio of the nonwoven fabric and the alumina content in the precursors. The shrinkage ratio was calculated as follows: (the apparent area of fabric after calcina-

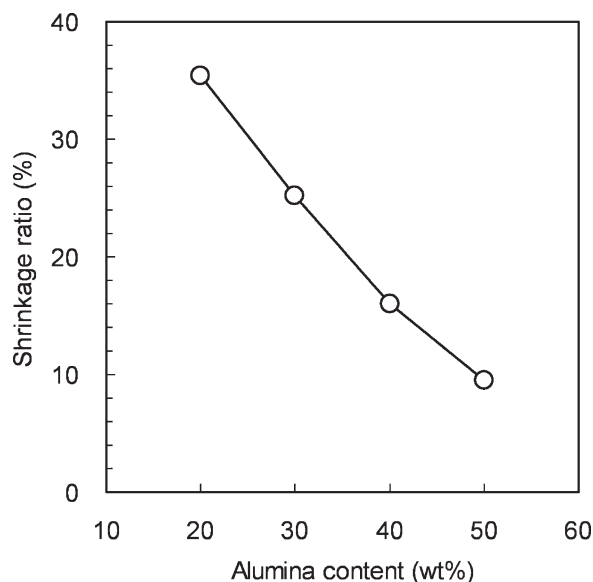


Figure 7 Effect of alumina content in precursors upon shrinkage ratio of nonwoven fabric by calcination (500°C, 5 h).

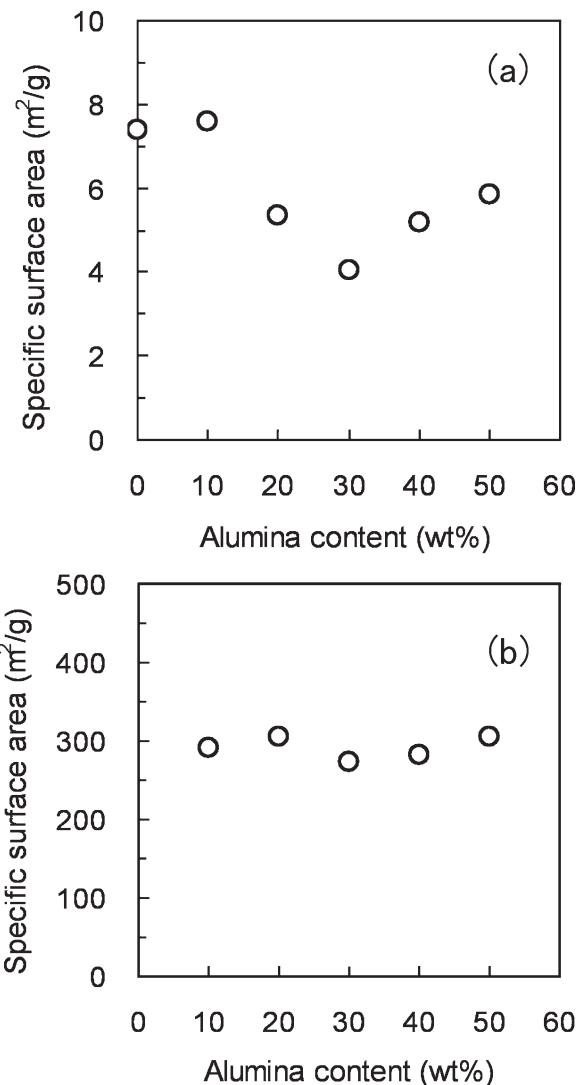


Figure 8 Effect of alumina content in precursors upon specific surface area of nanofibers (a) before and (b) after calcination (500°C, 5 h).

tion (500°C, 5 h)/the apparent area of fabric before calcination) $\times 100$ (%) (the thickness of the fabric was unconsidered). The fabric before calcination was square in shape and ~ 3 cm in height and width. As can be seen from Figure 7, the shrinkage decreases as the alumina content in the precursors increases. The shrinkage of the fabric by calcination was caused by the following two factors: (1) The space between the nanofibers constituting the nonwoven fabric became denser; and (2) the fiber length of the nanofibers becomes shorter by the thermal decomposition of the PVA matrix.

Figure 8 shows the relationship between the specific surface area of the nanofibers (a) before and (b) after calcination at 500°C for 5 h and the alumina content in the precursors. The specific surface area of the precursor nanofibers is around 6 m²/g, and that of the alumina nanofibers is around 300 m²/g.

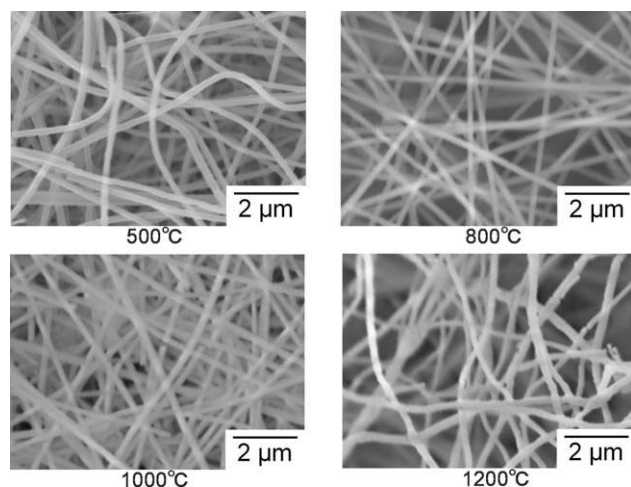


Figure 9 SEM images of alumina nanofibers obtained by calcination at prescribed temperatures.

Thus, it is likely that the surface areas of the nanofibers are not affected by the alumina contents in the precursors in each case [the specific surface area of boehmite nanoparticles (Disperal P2, Sasol) after calcination at 500°C for 5 h was 271.3 m²/g].

As explained above, the alumina content in the precursors did not have an influence on the fiber diameter and the specific surface area of the precursor and alumina nanofibers, and only had an influence on the shrinkage ratio of the nonwoven fabric composed of the nanofibers.

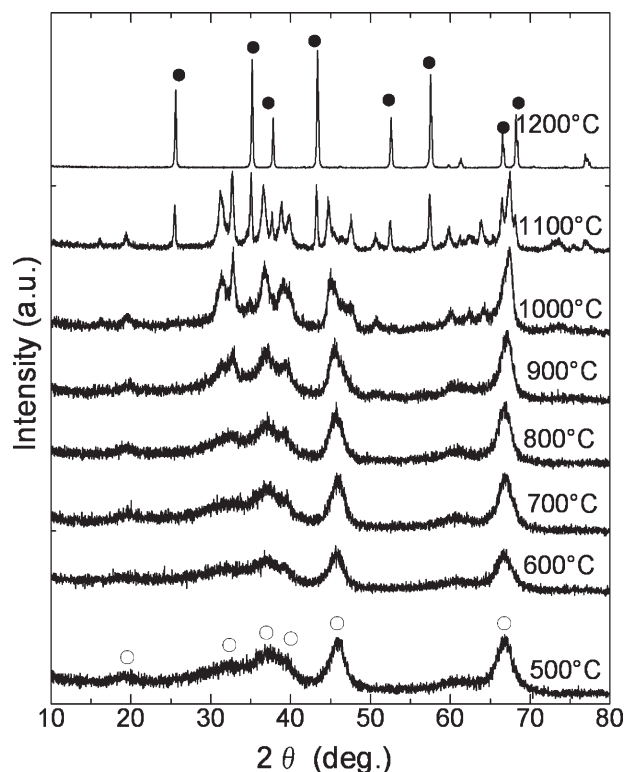


Figure 10 XRD curves of alumina nanofibers obtained (○: γ -alumina, ●: α -alumina).

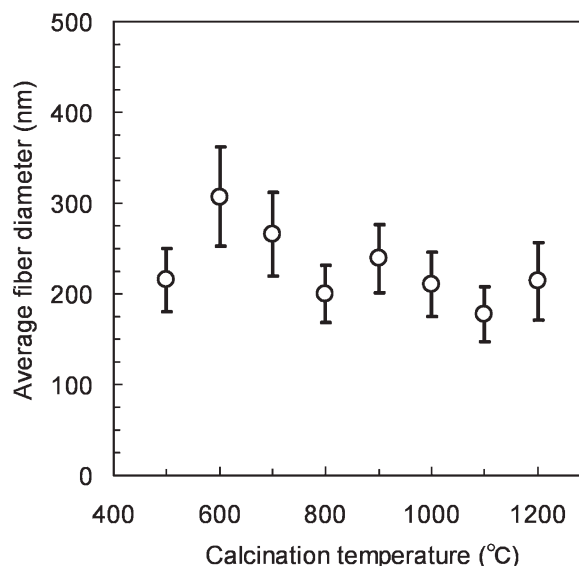


Figure 11 Effect of calcination temperature upon average diameter of alumina nanofibers obtained.

Effect of calcination temperature of the precursor nanofibers

Alumina nanofibers were formed from the PVA/boehmite (PVA/alumina = 60/40 wt %) precursors at various calcination temperatures between 500 and 1200°C. Figure 9 shows SEM images of the alumina nanofibers obtained by calcination at the prescribed temperatures. Alumina nanofibers are obtained at all calcination temperatures. Figure 10 shows the XRD curves of the alumina nanofibers obtained. γ -Alumina is formed by calcination at temperatures from 500 to 900°C, and the peak becomes sharp with increase in the calcination temperature. Moreover α -alumina is formed at 1200°C (δ - or θ -alumina is

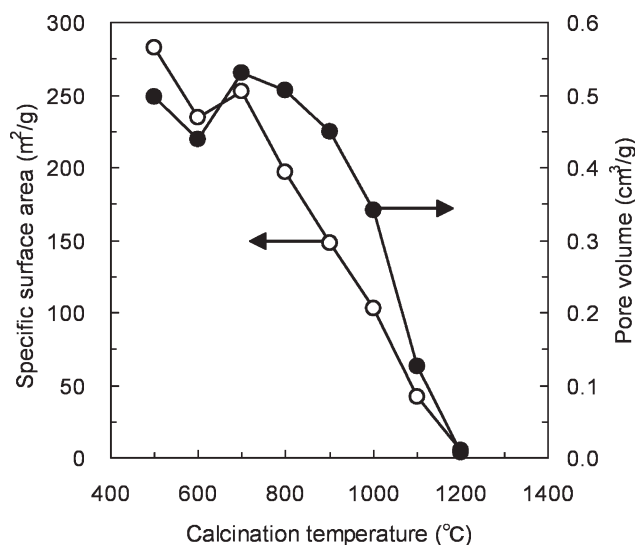


Figure 12 Effect of calcination temperature upon pore characteristics (specific surface area and pore volume) of alumina nanofibers obtained.

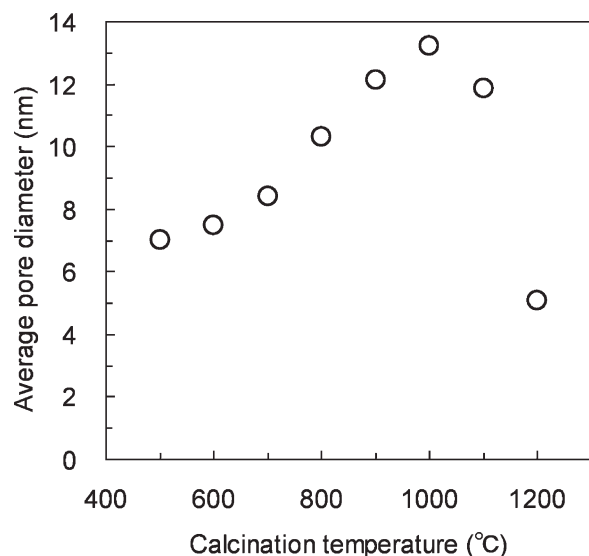


Figure 13 Effect of calcination temperature upon average pore diameter of alumina nanofibers obtained.

formed at around 1000°C). From these results, compared with those of Tuttle et al.,¹³ α -alumina with a higher aspect ratio could be obtained by our precursor nanofibers. Figure 11 shows the relationship between the average diameter of the alumina nanofibers obtained and the calcination temperature of the precursors. The diameter does not depend on the calcination temperature, and the values are distributed from 200 to 300 nm.

Figure 12 shows the relationship between the pore characteristics (the specific surface area and the pore volume) of the alumina nanofibers obtained and the calcination temperature of the precursors. The pore dimensions decrease with increasing the calcination temperature due to sintering. The specific surface area of the alumina nanofiber calcined at 1200°C (5.38 m²/g) is equivalent to that of the pure PVA nanofiber (7.38 m²/g). Thus, it is likely that nonporous α -alumina nanofibers can be obtained by calcination of the PVA/boehmite precursor nanofibers at 1200°C. Figure 13 shows the relationship between the average pore diameter of the alumina nanofibers and the calcination temperature. The pore size

increases with the calcination temperature up to 1000°C but it begins to decrease at 1100°C due to the sintering. From Figure 13, the alumina nanofibers obtained in this study (calcination temperature: below 1100°C) are classified as a mesoporous material.

CONCLUSIONS

The alumina nanofibers were obtained by calcination of the PVA/boehmite nanoparticles precursors. The alumina content in the precursors did not influence the fiber diameter and the specific surface areas of the precursor and alumina nanofibers, and only had an influence on the shrinkage ratio of the nonwoven fabric composed of the nanofibers. Also, the diameter of the alumina nanofibers obtained was not affected by the calcination temperature of the precursor nanofibers.

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