

# EFFECT OF VISCOSITY ON THE PRODUCTION OF ALUMINA BORATE NANOFIBERS VIA ELECTROSPINNING

## VPLIV VISKOZNOSTI NA IZDELAVO ALUMINIJEVOOKSIDNOBORATNIH NANOVLAKEN Z ELEKTROSPININGOM

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Alumina borate ( $\text{Al}_{18}\text{B}_4\text{O}_{33}$ ) nanofibers have been successfully fabricated with the electrospinning method using a solution that contains polyvinyl alcohol (PVA) and aluminium acetate stabilized with boric acid. The effect of the viscosity on the production of alumina borate nanofibers was investigated and the optimum parameters were determined to obtain the best fibers. DTA/TG analyses were performed to determine the heat-treatment regime. The morphology of the fibers was evaluated by SEM analyses, the phase structure of the fibers was obtained using XRD and the chemical bonding structure was determined by FTIR. On the whole, the results indicated that the viscosity of a solution is an important parameter for producing a homogeneous and thin fiber, while the calcination temperature has a significant effect on the phase structure of the fibers.

Keywords: nanomaterials, nanofiber, electrospinning,  $\text{Al}_{18}\text{B}_4\text{O}_{33}$

Aluminijevoooksidnoboratna ( $\text{Al}_{18}\text{B}_4\text{O}_{33}$ ) nanovlakna so bila uspešno izdelana z elektrospining metodo z uporabo raztopine, ki vsebuje polivinil alkohol (PVA) in aluminijev acetat, stabiliziran z borovo kislino. Preiskovan je bil vpliv viskoznosti na izdelavo aluminijevoooksidnoboratnih nanovlaken in določeni so bili optimalni parametri za pridobivanje najboljših vlaken. Za določitev režima toplotne obdelave so bile izvršene DTA/TG-analize. Morfologija vlaken je bila ocenjena s SEM-analizo, fazna struktura vlaken je bila dobljena z rentgensko difrakcijo (XRD), strukture kemijskih vezav pa so bile ugotovljene s FTIR. Rezultati so pokazali, da je viskoznost raztopine pomemben parameter za proizvodnjo homogenih in tankih vlaken, medtem ko ima temperatura kalcinacije pomemben vpliv na strukturo faz vlaken.

Ključne besede: nanomateriali, nanovlakna, elektrospining,  $\text{Al}_{18}\text{B}_4\text{O}_{33}$

## 1 INTRODUCTION

One-dimensional materials, such as nanowires, nanorods, nanowhiskers and nanofibers, have stimulated great interest due to their importance in basic scientific research and their potential in technological applications. They are expected to play an important role as both interconnector and functional components in the fabrication of nanoscale devices. Many unique properties have already been proposed or demonstrated for this class of materials, such as a high elastic modulus and tensile strength, chemical inertness, excellent resistance to oxidation/corrosion, a low thermal expansion coefficient, a high thermal conductivity, a good stability at high temperature and low-cost production.<sup>1-5</sup> Of these properties, aluminium borate is a famous material as it can be used in a variety of applications, such as high-temperature structural components, nonlinear optical and tribological materials, electronic ceramics and reinforced composite materials.<sup>2,6</sup>

Due to the superior properties of alumina borates, nanostructures such as filaments, powders, fibers, whiskers and wires, they have been synthesized using various techniques. These are vapor-solid reaction,<sup>7</sup> powder

technology,<sup>8</sup> the electrospinning technique,<sup>3,9</sup> the flux method with microwaves,<sup>10</sup> calcination techniques.<sup>1,6,11-14</sup> Dai et al.<sup>3</sup> and Tuttle et al.<sup>9</sup> have produced approximately alumina borate nanofibers 550 nm using the electrospinning technique. Because it is difficult to fabricate the extremely fine nanofibers using electrospinning, we have investigated the effect of viscosity on the process to produce thin nanofibers.

Electrospinning is the most preferred technique to produce nanofibers with a diameter ranging from 20 nm to 1000 nm. The diameter of the fibers depends on the process parameters, such as the viscosity of the solution, the applied electric field, the distance between the collector and the needle, and the feeding rate of the solution.<sup>15</sup> The viscosity of the solution and its electrical properties determine the extent of the elongation of the solution that affects the diameter of the resultant electrospun fibers.<sup>16</sup> Moreover, the viscosity of the solution is very important for its spinability. When the viscosity is too high, pumping of the solution through the syringe needle becomes difficult, which may result in drying of the solution at the tip of the needle before the electrospinning initiates. Additionally, the applied electric field affects the morphology of the fibers that are obtained. Generally, a

higher voltage leads to greater stretching of the solution due to the greater coulombic forces in the jet as well as the stronger electric field. These have the effect of reducing the fiber diameter.<sup>16</sup> On the other hand, the distance between the tip and the collector plate must be high for thin fibers. The feed rate determines the amount of solution available for electrospinning. When the feed rate is increased, the fiber diameter increases.<sup>16</sup>

In this study we attempt to form alumina borate nanofibers and investigate the effect of viscosity during the electrospinning process on the nanofiber morphology and spinability, and the effect of temperature on the phase structure.

## 2 EXPERIMENTAL

PVA solutions were prepared in different concentrations in mass fractions, i.e., 6 %, 8 %, and 10 %, by dissolving the PVA in 80 °C distilled water and cooling down to room temperature while stirring for 24 h. Next, 1 g of aluminium acetate stabilized with boric acid ( $\text{CH}_3\text{CO}_2\text{Al}(\text{OH})_2 \cdot 1/3\text{H}_3\text{BO}_3$ ) was added to the PVA solution and the stirring was continued until a transparent and homogeneous solution was obtained. The viscosities of solutions were determined by CVO 100 Digital Rheometer (Bohlin Instrument).

In order to produce the nanofibers, transparent solutions were immediately loaded into a plastic syringe. A 22-gauge stainless-steel needle was used as a nozzle. The emitting electrode from a power supply was attached to the needle. The grounding electrode from the same power supply was attached to a piece of 316L stainless steel, which was used as the collector plate and was placed approximately 10 cm below the tip of the needle. A high voltage ranging between 20 kV and 30 kV was applied across the needle and a non-woven mat of fine fibers were fabricated. The alumina borate/PVA fibers were heat treated at 800–1200 °C for 2 h in air using an electrical tube furnace to obtain the alumina borate fibers.

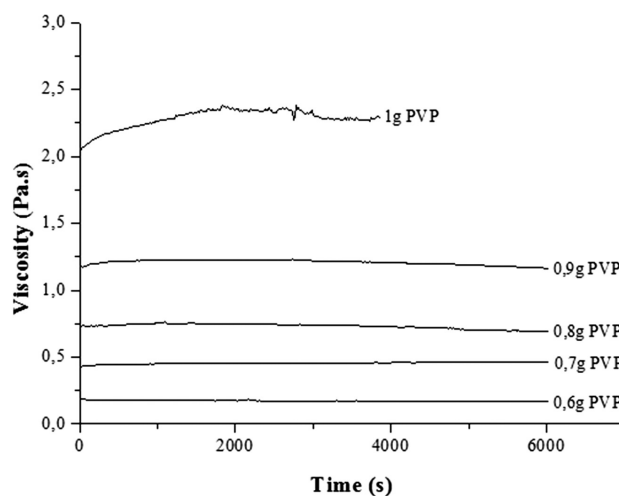
The prepared solution used in the electrospinning was dried at 100 °C for 1 h and the obtained powder was subjected to thermogravimetric differential thermal analysis (DTA/TG) (Shimadzu DTG-60H) to define the reaction type of the intermediate temperature products and to use a suitable process regime. The chemical bonding structures of the fibers before and after the heat treatment were determined with Fourier Transform Infrared Spectroscopy (FTIR) (Perkin Elmer Spectrum BX). The X-ray diffraction (XRD) measurements were performed for the crystal-phase identification (Rigaku D/Max-2200/PC) with  $\text{CuK}_\alpha$  radiation. The morphology and the average fiber diameter of the nanofibers were characterized using a scanning electron microscope (JSM-6060 JEOL).

## 3 RESULTS AND DISCUSSION

The solution viscosity plays a major role in producing a uniform nanofiber. For a low viscosity it is common to find beads along the fibers. As the viscosity increases, a gradual change in the shape of the fibers takes place until smooth fibers are obtained.<sup>16</sup> For spinability the viscosity must be neither very high nor very low. The viscosity of the prepared solutions at various concentrations are determined in the range 0.17–2.34 Pa s (**Figure 1**). In the **Figure 1** it is clear that as the concentration of the solution increases, the viscosity of the solution increases. Furthermore, the viscosity does not change with time, indicating the stability of the solution, which is an important property for obtaining uniform fibers. While the viscosity of the solution prepared by dissolving 6 % PVA is very low for spinability, it is very high for the solution prepared by dissolving 10 % PVA. However, the viscosity of the solution prepared by dissolving 8 % PVA is convenient for spinability.

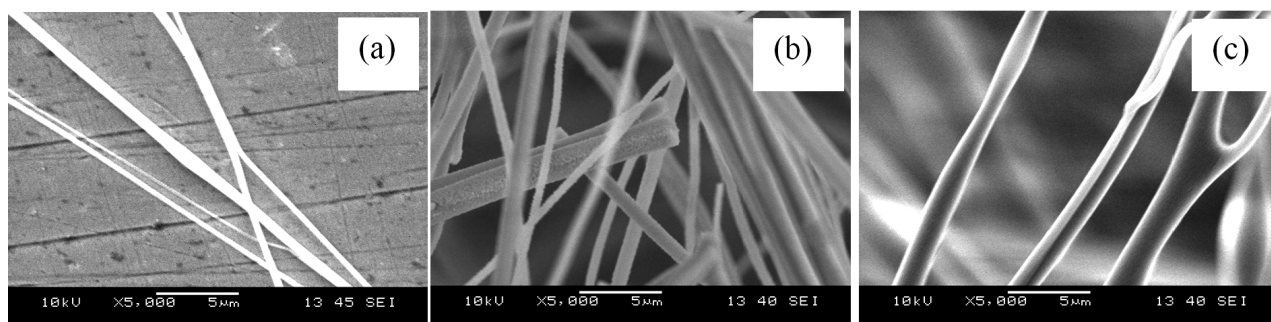
**Figure 2** shows SEM images of heat-treated  $\text{Al}_{18}\text{B}_4\text{O}_{33}$  nanofibers that were prepared with solutions that have different concentrations. It is clear that the fibers that were obtained from the 6 % PVA solutions are very thin, but the amount of them is very small. On the other hand, the diameter of the fibers produced from the 10 % PVA solution is very large. These results were consistent with the viscosity analyses. As a result, the solution prepared with 8 % PVA was determined to be the optimum solution and used in the following process.

The DTA/TG analysis of the prepared alumina-borate/PVA solution is shown in **Figure 3**. The DTA curve shows endothermic peaks between 100 °C and 300 °C that indicates the loss of citric acid, which gets stabilized with boric acid in the aluminium acetate. Degradation of the PVA occurs between 300 °C and 600 °C in four steps. A broad endothermic peak in the range 900 °C to



**Figure 1:** Viscosity of the solutions prepared with mass fractions 6 %, 8 % and 10 % PVA solutions

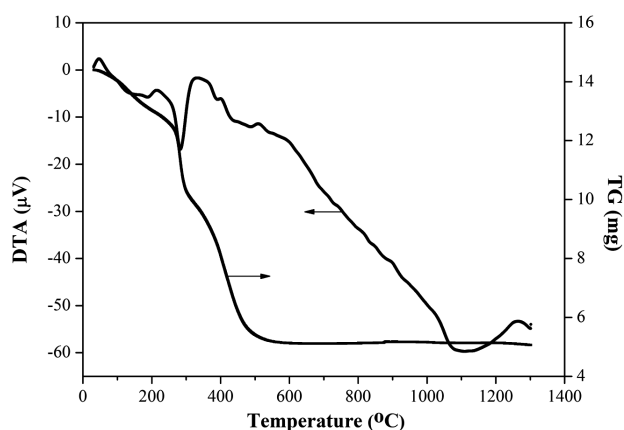
**Slika 1:** Viskoznost raztopine, pripravljene z masnimi deleži 6 %, 8 % in 10 % PVA



**Figure 2:** SEM images of nanofibers prepared at: a) 6 %, b) 8 % and c) 10 % concentrations

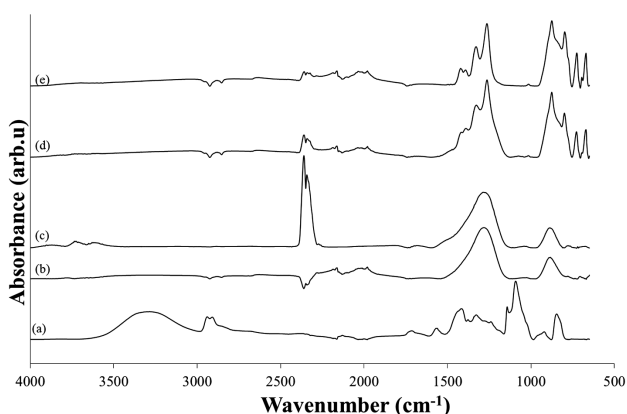
**Slika 2:** SEM-posnetki nanovlaken, pripravljenih s koncentracijo: a) 6 %, b) 8 % in c) 10 %

1200 °C indicates the crystallization of the  $\text{Al}_{18}\text{B}_4\text{O}_{33}$ . According to the studied TG curve, the weight loss of the alumina-borate/PVA solution was determined to be approximately 63 % and it was followed by the removal of the PVA from the sol structure.



**Figure 3:** DTA/TG analyses of the prepared solutions prepared with the mass fraction 8 % PVA solution

**Slika 3:** DTA/TG-analiza pripravljenih raztopin, pripravljenih z masnim deležem PVA raztopine 8 %

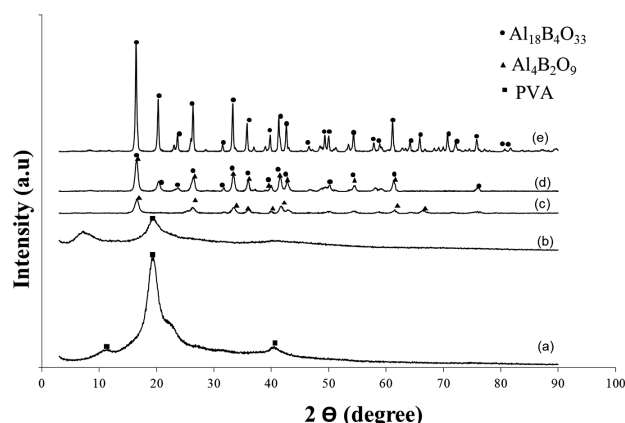


**Figure 4:** FTIR spectra of: a) PVA, b) alumina-borate/PVA composite fibers and alumina borate fibers heat treated at: c) 800 °C, d) 1000 °C and e) 1200 °C

**Slika 4:** FTIR-spektri: a) PVA, b) aluminijevoosidni borat/PVA kompozitna vlakna in aluminijevoosidnoboratna vlakna, toplotno obdelana pri: c) 800 °C, d) 1000 °C in e) 1200 °C

**Figure 4** shows the FTIR absorption peaks of the PVA, the alumina-borate/PVA composite fibers and the alumina borate fibers heat treated at 800 °C, 1000 °C and 1200 °C. A broad peak at about 3400  $\text{cm}^{-1}$  corresponds to the H-OH stretch. The peaks between 1300  $\text{cm}^{-1}$  and 1700  $\text{cm}^{-1}$  correspond to the characteristic PVA peaks in **Figure 4a**.<sup>3</sup> When the PVA is mixed with Al acetate that is stabilized with boric acid the absorption peaks show a change (**Figure 4b**). This indicates that there is an interaction between them. After a heat treatment at 800 °C, there are no PVA peaks because of the degradation of the polymer (**Figure 4c**). When the calcination temperature is increased to 1000 °C and 1200 °C (**Figures 4d** and **4e**), a class of peaks appeared at 650–950  $\text{cm}^{-1}$  and 1200–1500  $\text{cm}^{-1}$ . These peaks can be attributed to the formation of crystalline alumina borate.<sup>3</sup> Furthermore, all the FTIR graphs show a sharp peak at about 2400  $\text{cm}^{-1}$ , which corresponds to the  $\text{CO}_2$  peaks that appear because of the ambient atmosphere during the analyses.

**Figure 5** presents a typical XRD pattern of the products before and after the heat treatment at different temperatures and the pure PVA powder. The characteristic peak of the PVA at  $2\theta = 20^\circ$  is shown in **Figures 5a** and **5b**. When the alumina borate/PVA composite fibers



**Figure 5:** XRD pattern of: a) PVA, b) alumina-borate/PVA composite fibers and alumina borate fibers heat treated at: c) 800 °C, d) 1000 °C, e) 1200 °C

**Slika 5:** XRD-posnetek: a) PVA, b) aluminijevoosidni borat/PVA kompozitna vlakna in aluminijevoosidnoboratna vlakna, toplotno obdelana pri: c) 800 °C, d) 1000 °C, e) 1200 °C

were heat treated at 800 °C, this peak disappeared and the crystalline  $\text{Al}_4\text{B}_2\text{O}_9$  peaks occurred. The peak positions and the relative intensities match well with those of the fiber  $\text{Al}_4\text{B}_2\text{O}_9$  (JCPDS 00-047-0319). Nevertheless, as the intensity of the peaks increased with the increase in the calcination temperature from 800 °C to 1000 °C, the crystalline  $\text{Al}_{18}\text{B}_4\text{O}_{33}$  formed. At a calcination temperature of 1200 °C, all the XRD peaks belong to crystalline  $\text{Al}_{18}\text{B}_4\text{O}_{33}$ , which matches with JCPDS 00-053-1233 and 00-032-0003.

#### 4 CONCLUSION

In summary, this study was structured to use the electrospinning technique to produce alumina borate/PVA composite nanofibers. In addition, the effect of viscosity on the spinability and the morphology of the alumina borate/PVA nanofibers were investigated. After a heat treatment at 1200 °C, alumina borate ( $\text{Al}_{18}\text{B}_4\text{O}_{33}$ ) fibers were produced.

On the whole, we found that the viscosity of the prepared solution affects the fiber morphology. The increase in the viscosity depends on the increase of the concentration of the solution, while the spinability of the solution adopts an opposing relation with the dense solution, which leads to clogging of the needle tip. As a conclusion, the viscosity of the PVA polymer solution has a very important effect on the diameters of the nanofibers. In addition, the phase structure of the aluminium borate depends on the calcination temperature.

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