Preparation and Characterization of Polyvinyl Borate/Polyvinyl Alcohol (PVB/PVA) Blend Nanofibers

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ABSTRACT: In this study, it was aimed to prepare polyvinyl borate/polyvinyl alcohol blend nanofibers by electrospinning process. Polyvinyl borate was synthesized by the condensation reaction of polyvinyl alcohol and boric acid. Polyvinyl borate itself was not suitable for electrospinning process. To improve fiber formation capability, polyvinyl borate was blended with polyvinyl alcohol before electrospinning process. A series of nanofibers with various polyvinyl borate concentrations in polyvinyl alcohol were prepared. Homogeneous and highly porous mat containing 100–250 nm diameter nanofibers were obtained by electrospinning process. According to the FTIR results, boron atoms were found to be integrated into the polymer network. There is not any significant effect of polyvinyl borate content on fiber morphologies according to SEM images. The blend composition with the highest polyvinyl borate content was found to be suitable for thermally stable nanofiber formation according to the TGA results. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 2736–2741, 2012

Key words: polyvinyl borate; electrospinning; polymer blends; spin coating; nanofiber

INTRODUCTION

Fibers drawn from polymers show very promising properties such as ultraviolet resistance, electrical conductivity, and biodegradability, when compared with the material's bulk properties. The current trend in fiber formation processes is to develop submicron scale nanofibers, to achieve a number of desired properties such as increase in surface area to volume ratio, decrease in pore size, a drop in structural defects, and superior mechanical characteristics. The potential target areas of application for these nanofibrous structures are as affinity membranes, scaffolds for tissue engineering, sensors, and protective clothing.[1]

Electrospinning is a unique process that creates nanofibers through an electrically charged jet of polymer solution. The electrospinning process, in its simplest form, consists of two electrodes and a DC voltage supply in the kV range. The polymer drop from the tip of the pipette was drawn into a fiber due to the high voltage. The jet was electrically charged and the charge caused the fibers to bend in such a way that every time the polymer fiber looped, its diameter was reduced. The fiber was collected as a web of fibers on the surface of a grounded target.[2]

Boron containing ceramics are important nonmetallic materials with useful physical and chemical properties. Boron carbides and boron nitrides are the hardest boron containing compounds with high melting point, high modulus of elasticity, large neutron capture section, low density, chemical inertness, outstanding thermal and electrical properties, which make them strong candidates for high technology applications.[3–7] Polymeric precursors have been of interest in the development and utilization of polymer pyrolysis as a low-temperature synthetic route to prepare boron containing ceramic powders.[8–13] Polyvinyl borate, a borate ester of polyvinyl alcohol, has been studied as promising precursor of boron carbide powders.[8,9,14–16] Although it is quite easy to form borate esters from polyvinyl alcohol,[8,9,14–16] the preparation of polyvinyl borate/polyvinyl alcohol blend nanofibers using electrospinning technique has not been reported. In this study, polyvinyl borate, polymeric precursor of boron carbide, is synthesized by the reaction between boric acid and polyvinyl alcohol, and polyvinyl borate/polyvinyl alcohol blend nanofibers are prepared by electrospinning process.

EXPERIMENTAL

Polyvinyl alcohol (PVA), from Inovenso, Turkey, and boric acid (H_3BO_3), from Merck, were used as raw materials. The degree of hydrolysis and the
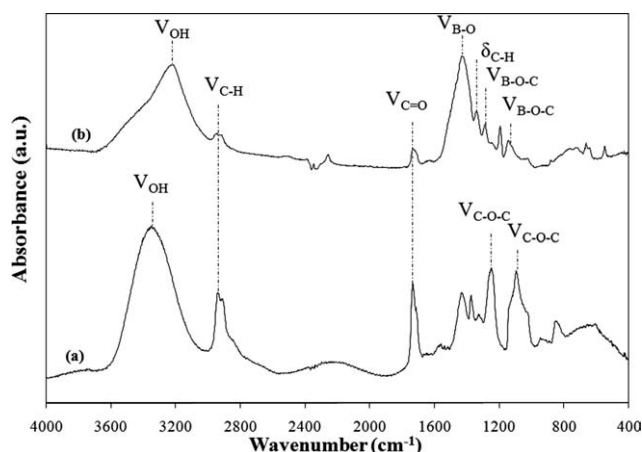
Figure 1 FTIR spectra of (a) PVA and (b) PVB.

degree of polymerization of PVA changes in the range from 86 to 89 mole % and 1700–1800, respectively. Its molecular weight is between 84,000 and 89,000 g/mol. Polyvinyl borate (PVB), polymeric precursor of boron carbide, was prepared through the condensation reaction of PVA and boric acid. PVA (2.0 g) was dissolved in about 50 mL of distilled water by stirring at 800 rpm for 1 h and heating at 80°C. At the same time, boric acid (2.0 g) was dissolved in about 50 mL of distilled water and added into polyvinyl alcohol solution with constant stirring at 800 rpm for half an hour. White powders of polyvinyl borate were obtained after drying the resulting white gel material in an oven at 120°C.

The solution for electrospinning was prepared by mixing polyvinyl borate solution having a concentration of 1.5 wt % and PVA solution with a concentration of 10 wt % to obtain 1.5 : 5, 2 : 5, and 5 : 5 weight ratios of PVB to PVA. Laboratory scale electrospinning unit (NE-100, Inovenso) was used to prepare polyvinyl borate/polyvinyl alcohol blend nanofibers. The solution was fed into a syringe and the feed rate of the polymer blend solution was kept steady as 0.1 mL/h. An electric potential difference of 30 kV was applied between the collector and the syringe tip, and the distance between the collector and the tip was 10 cm.

Fourier transform infrared (FTIR) spectra of polyvinyl alcohol, polyvinyl borate, and polyvinyl borate/polyvinyl alcohol blends were recorded with a Nicolet 380 (Thermo Scientific) spectrometer. For this purpose, polyvinyl alcohol, polyvinyl borate, and blend films were prepared using a Laurell Model (WS-400BZ-6NP/LITE) spin-coater at 2000 rpm. FTIR characterization was done in the frequency range from 4000 cm^{-1} to 400 cm^{-1} with a resolution of 2.0 cm^{-1}. The surface microstructure of the electrospun polyvinyl borate/polyvinyl alcohol blend nanofibers was analyzed by using a scanning electron microscope (SEM: EVO LS10 ZEISS). The

average diameter PVB/PVA blend nanofibers were analyzed from the SEM images of the fibers using the National Institutes of Health ImageJ software. High resolution (1024 × 768 pixels) tif images were used for image analysis. At least 40 different fibers were analyzed for each blend composition. Results were reported as mean ± standard deviation. The thermogravimetric analyses (TGA) of the PVA, PVB, and PVB/PVA blends were performed on a thermogravimetric analyzer (Setaram Labsys TGA/DTA) operating at a heating rate of 5°C/min up to 550°C under nitrogen atmosphere.

RESULTS AND DISCUSSION

FTIR analysis

FTIR is performed to identify and characterize the synthesized borate ester, polyvinyl borate. Figure 1 presents the FTIR spectra of PVA and PVB and the assignments of the main absorption bands are illustrated on the same figure. The peak at 3370 cm^{-1} is attributed to the stretching bond of O—H, which is a sign for unreacted OH groups on polyvinyl borate. The peaks at 1287 cm^{-1} and 1129 cm^{-1} are corroborated to characteristic stretching vibrations of B—O—C bonds, providing strong evidence for the reaction between PVA and boric acid to form polyvinyl borate.[8] The absorption at 2948 cm^{-1} and 1738 cm^{-1} in PVB, related to the stretching bond C—H and C=O, respectively, become less than that of PVA. The absorption band at 1433 cm^{-1} is assigned to B—O stretching vibration.[8] FTIR spectrum of PVB matches with literature data. Similar absorption bands are obtained for PVB sample.[8,9,16] The characteristic absorptions of the PVA main chain at 1250 cm^{-1} and 1027 cm^{-1}, corresponding to the stretching vibration of C—O—C, disappear in PVB.[8]

Figure 2 presents the FTIR spectra of PVB/PVA blend systems. The spectrum of PVB matches with
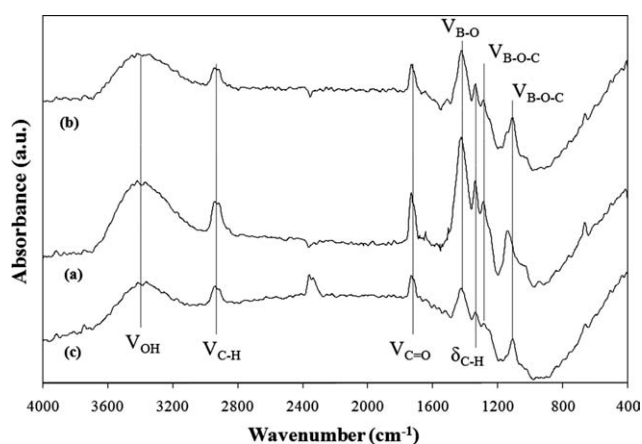

Figure 2 FTIR spectra of PVB/PVA blends; (a) 5 : 5 weight ratios of PVB to PVA, (b) 2 : 5 weight ratios of PVB to PVA, and (c) 1.5 : 5 weight ratios of PVB to PVA.
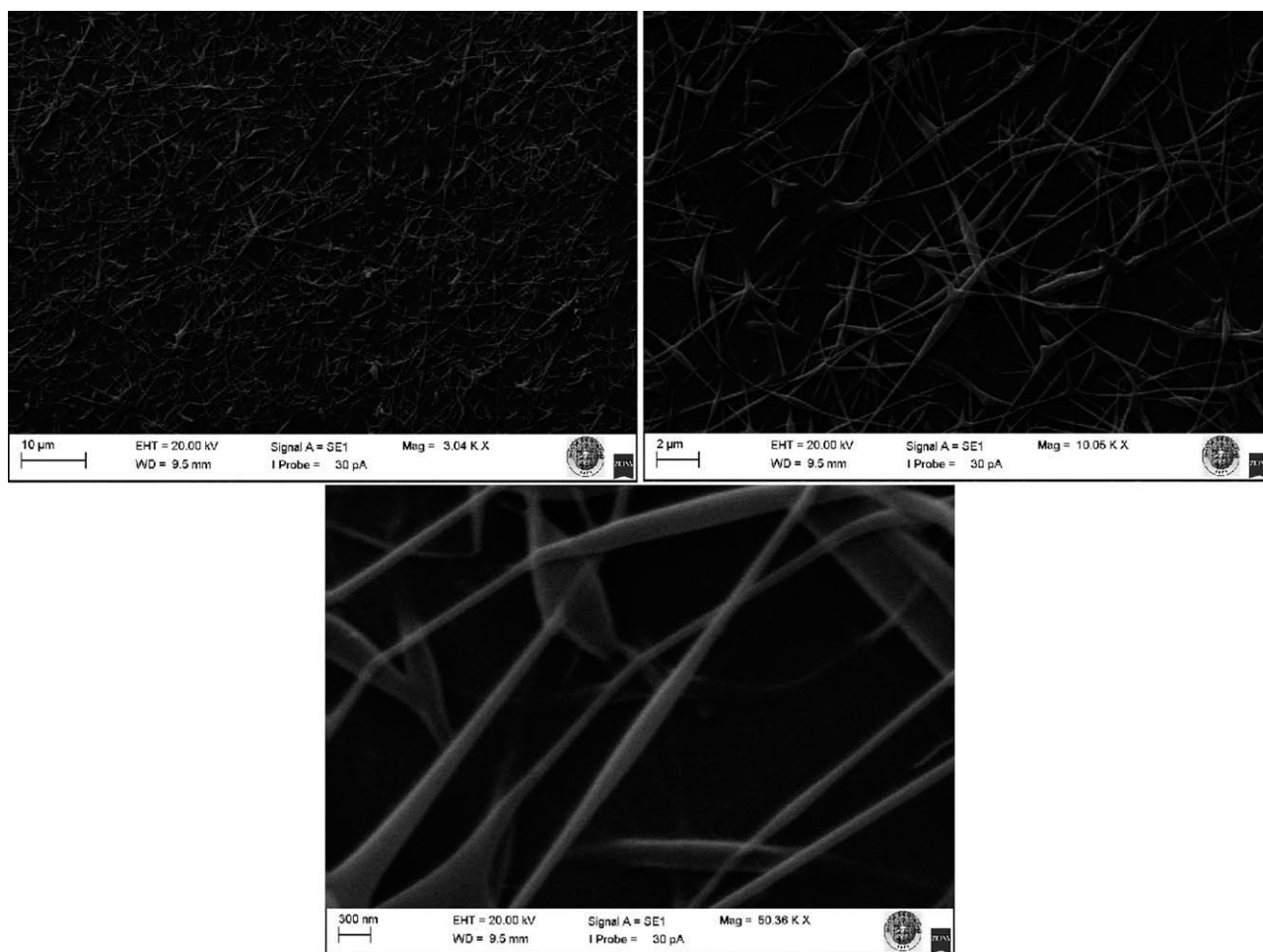
Figure 3 SEM images of the blend sample; 1.5 : 5 weight ratios of PVB to PVA.

that of the blend systems. Characteristic B—O and B—O—C stretching vibrations of PVB main chain appear also at 1433 cm^{-1}, 1287 cm^{-1}, and 1129 cm^{-1} in PVB/PVA blends. An increase in PVB composition of PVB/PVA systems result in following increase in the intensity of the characteristic absorption bands relating to PVB (Fig. 2).

Electrospinning

To carry out electrospinning, the polymer must first be in a liquid form, either as molten polymer or as polymer solution. For electrospinning, polyvinyl borate solution having a concentration of 1.5 wt % is prepared since higher concentrations of this solution cannot be dissolved in water. In electrospinning, a high voltage is applied to a polymer fluid such that charges are induced within the fluid. When charges within the fluid reached a critical amount, a fluid jet will erupt from the droplet at the tip of the needle resulting in the formation of a Taylor cone.[2] Dilute solutions of polyvinyl borate having concentrations less than 1.25 wt % does not yield Taylor cone for-

mation, which is a prerequisite for electrospinning. Hence, polyvinyl borate solution of 1.5 wt % composition is selected for electrospinning experiments. However, only polyvinyl borate solution was inadequate to carry out electrospinning and also to form polymer nanofibers. It needs to be blended with an electrospinnable polymer to prepare the nanofiber structures, because polyvinyl borate is almost insoluble in general solvents, which leads to too low solution viscosity to be stretched by electric field strength.[2,17,18] Another electrospinnable polymer, polyvinyl alcohol, was introduced to obtain blend nanofibers. Till date, polyvinyl borate/polyvinyl alcohol blend nanofibers have not been fabricated using the electrospinning technique.

Morphological analysis

To observe the effect of polyvinyl alcohol on the electrospinning process and the resulting polymer fiber morphology, three different samples have been prepared changing the concentration of PVB to PVA with 1.5 : 5, 2 : 5, and 5 : 5 weight ratios of PVB to
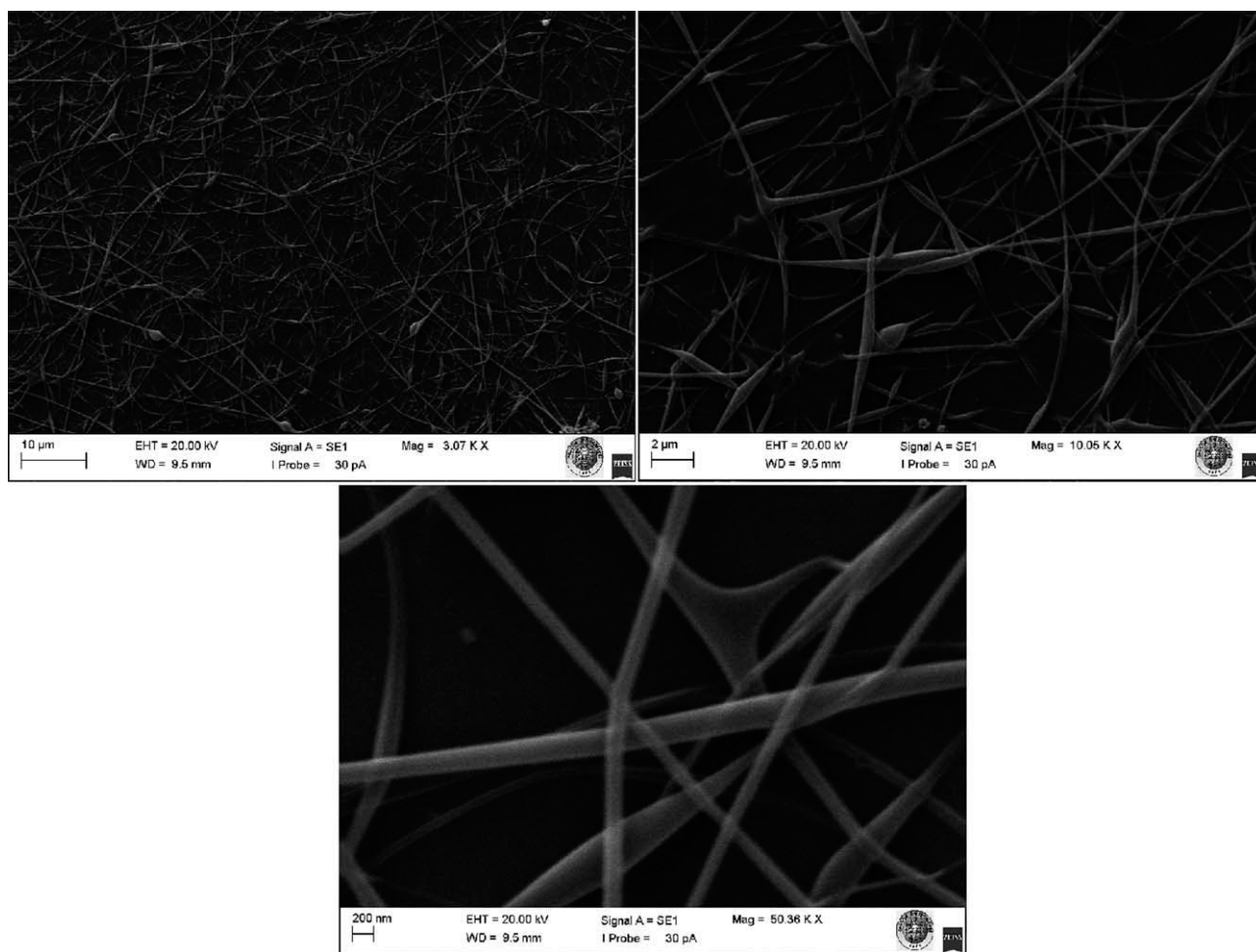
Figure 4 SEM images of the blend sample; 2 : 5 weight ratios of PVB to PVA.

PVA. Solutions including more than 50 wt % PVB in blend composition is inefficient to execute electrospinning. In Figures 3–5, the SEM images of the three electrospun samples are reported. All of the images illustrate the presence of nanofibers. The images also illustrate that changing the PVA concentration does not significantly influence the size of nanofibers. The diameter values range from 100 to 250 nm for all the three samples. The average fiber diameter for 1.5 : 5, 2 : 5, and 5 : 5 weight ratios of PVB/PVA blend systems range from 114 ± 103, 102 ± 68, and 152 ± 94 nm, respectively.

According to the SEM images (Figs. 3–5), nanofibers contain rare bead structures which usually result from low solution viscosities. The initiation of electrospinning requires the charged solution to overcome its surface tension. As the jet travels toward the collection plate, the surface tension may cause the formation of beads along the jet. Surface tension has the effect of decreasing the surface area per unit mass of a fluid. In this case, when there is a high concentration of free solvent molecules, there is a greater tendency for the solvent molecules to congregate and adopt a spherical shape due to surface tension. In our study, distilled water was used to dissolve PVB and PVA molecules and the surface tension of water is quite higher than those of various solvents, which may be the reason for the rare bead structures shown on the SEM images of the three samples. In addition, the concentration of the solutions prepared for electrospinning was quite dilute, resulting low solution viscosities, and this may be another potential reason for the rare bead structures.

Thermal analysis

According to the TGA analysis (Fig. 6), boron containing polymer, PVB, and PVB/PVA blend systems present better thermal stability than PVA. The good thermal resistance of B—O—C compared with the purely organic bonds is the reason behind the enhancement in the thermal properties.[19] In addition, the blend system with high PVB composition
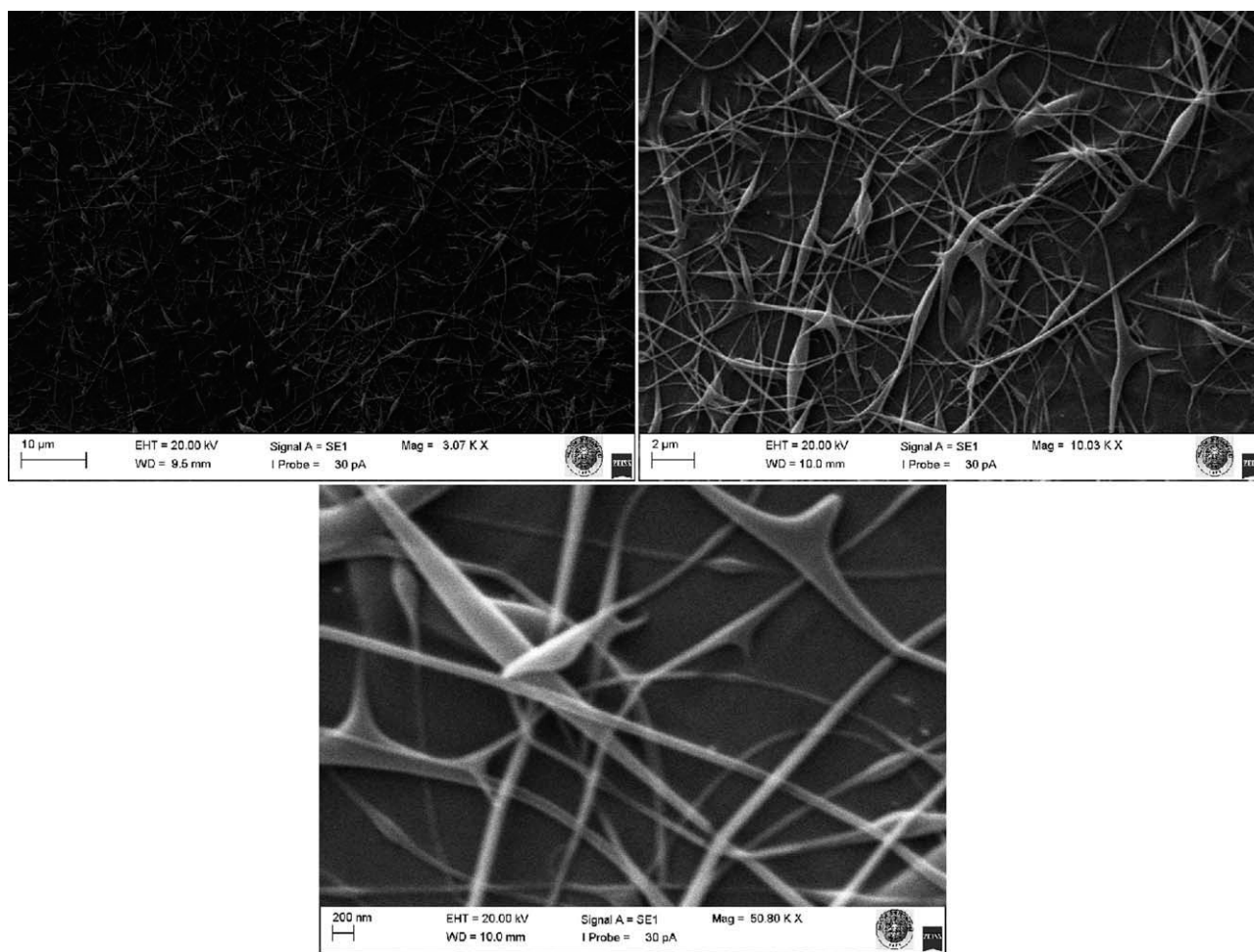
Figure 5 SEM images of the blend sample; 5 : 5 weight ratios of PVB to PVA.

presents a better thermal stability than the blend system with low PVB composition.

CONCLUSIONS

Polyvinyl borate/polyvinyl alcohol blend nanofibers have been prepared using electrospinning technique.
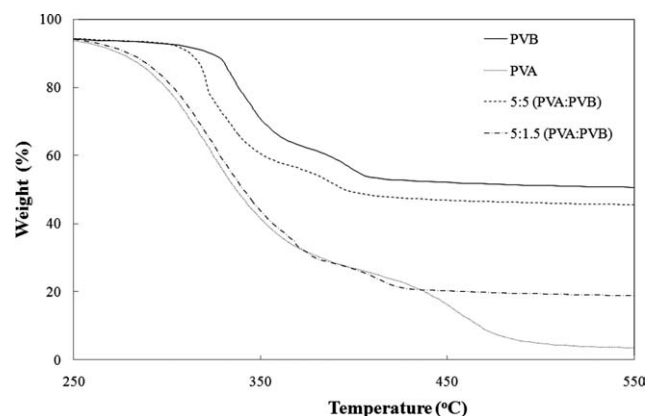

Figure 6 TGA curves of PVB, PVA, and PVB/PVA blends.

Their diameters range from 100 to 250 nm. The morphology of the nanofibers was independent of the composition of PVA to PVB. Rare bead structures appear on the elecrospun nanofibers, which may result from the high surface tension and low viscosity of prepared solutions used for electrospinning. The incorporation of boron chemistry into the polymer matrix enhanced thermal properties of the polymer. The potential usage of the as prepared nanofibers in the form of thin mat is under investigation.

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