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Electrospun Polyvinyl Borate/Poly(methyl methacrylate) (PVB/PMMA) Blend Nanofibers

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The aim of this study was to prepare polyvinyl borate (PVB)/poly(methyl methacrylate) (PMMA) blend nanofibers by electrospinning process. Polyvinyl borate was synthesized by the condensation reaction of polyvinyl alcohol and boric acid. FTIR analyses showed that boron atoms were found to be integrated into the polymer network. Blending PMMA with PVB decreased the fiber diameter and enhanced the surface roughness of PVB/PMMA blend nanofiber mats. The water wetting property of the nanofiber mats was influenced by the surface roughness. The blend composition with the highest polyvinyl borate content was found to be suitable for thermally stable nanofiber formation.

Keywords: Contact angle, electrospinning, nanofiber, polymer blends, polyvinyl borate

1. Introduction

Synthetic fibers are mostly polymer-based and they are produced by a spinning process, which involves extrusion of a polymeric liquid through fine holes. Following the extrusion process, the spun fibers are oriented by stretching or drawing, increasing the polymeric chain orientation and the degree of crystallinity [1]. Synthetic fibers drawn from polymeric materials illustrate very promising properties such as ultraviolet resistance, electrical conductivity, and biodegradability, as compared to 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 [2].

Fiber production is classified according to the type of spinning that the molten polymer or the polymer solution undergoes. Melt spinning, dry spinning and wet spinning are among well known fiber manufacturing processes [1]. As an alternative to these commercial techniques, 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 [3].

The water wetting property or hydrophobicity, depending on both chemical composition and surface morphology of a surface, is important and has attracted much interest owing to scientific purposes [4]. The hydrophobicity of a surface can be enhanced by being textured with different length scales of roughness. Electrospinning process takes advantage of this by using a hierarchy of micro- and nanostructures on nanofiber coated surfaces to provide sufficient roughness for hydrophobicity. More specifically, the surface morphology of electrospun nanofiber coated surfaces possesses a randomly rough surface and the water droplet is not able to wet the micro- and nanostructure spaces among nanofibers, which allows air to remain inside these spaces and causes a heterogeneous surface composed of both air and solid [5]. The air fraction between the liquid and the solid interface is the key factor to create hydrophobicity [6].

Boron containing polymers and ceramics are important non-metallic materials with useful physical and chemical
properties. They play specialized roles as high-strength lightweight structural and refractory materials. As an example, 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, and outstanding thermal and electrical properties, which make them strong candidates for high technology applications [7–11]. 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 [12–17]. Polyvinyl borate (PVB), a borate ester of polyvinyl alcohol, has been studied as promising precursor of boron carbide powders [12,13,18–20]. Although it is quite easy to form borate esters from polyvinyl alcohol (PVA) [12,13,18–20], the preparation of polyvinyl borate nanofibers using the electrospinning technique has not been reported in the literature. In our previous study, PVB/PVA blend nanofibers were prepared using the electrospinning process [21]. PVB could not be electrospun alone owing to poor spinning character. Hence, it was blended with a spinnable polymer, polyvinyl alcohol [21]. In spite of superior spinning character, PVA has poor water resistance and insufficient mechanical strength, limiting its application [21–23]. To overcome this limitation, polyvinyl borate/poly(methyl methacrylate) (PMMA) blend nanofibers are prepared in this study by the electrospinning process.

2. Experimental

Raw materials, used to synthesize polyvinyl borate and PVB/PMMA blend nanofiber, were polyvinyl alcohol, boric acid, and poly(methyl methacrylate). Polyvinyl alcohol (Mw, 84000–89000 g/mol; hydrolysis 86–89%) was obtained from Inovenso Ltd., Turkey, and boric acid (H3BO3) was purchased from Merck. In addition, poly(methyl methacrylate) (product # AB211664) was purchased ABCR, Germany. Polyvinyl borate, polymeric precursor of boron carbide, was prepared through the condensation reaction of polyvinyl alcohol 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.

PVB/PMMA solution, utilized to prepare blend nanofibers by electrospinning, was prepared by mixing polyvinyl borate-dimethylformamide (DMF) solution having a concentration of 1.5 wt% and PMMA-DMF solution with a concentration of 5 wt% to obtain 1:3, 1:5, 1:7.5 and 1:10 weight ratios of PVB to PMMA. Laboratory scale electrospinning unit (NE-100, Inovenso) was used to prepare polyvinyl borate/poly(methyl methacrylate) 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 borate, poly(methyl methacrylate) and PVB/PMMA blends were recorded with a Nicolet 380 (Thermo Scientific) spectrometer. For this purpose, polyvinyl borate, poly(methyl methacrylate) and PVB/PMMA 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 to 400 cm⁻¹ with a resolution of 2.0 cm⁻¹. The surface microstructure of the electrospun poly(methyl methacrylate) nanofiber mat and the electrospun PVB/PMMA blend nanofiber mats were analyzed by using a scanning electron microscope (SEM; EVO LS10 ZEISS). The average diameter PMMA nanofibers and PVB/PMMA 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 25 different fibers were analyzed for each blend composition. Results were reported as mean ± standard deviation.

The water contact angles of the electrospun PMMA nanofiber mat and the electrospun PVB/PMMA blend nanofiber mats were measured with a drop shape analysis system (Krüss, easydrop model) in the sessile mode at room temperature. Five different contact angle measurements were performed for each blend composition and average of these five test results are given with their standard deviations. The thermogravimetric analyses (TGA) of PVB, PMMA and PVB/PMMA blends were performed on a thermogravimetric analyzer (Setaram Labsys TGA/DTA) operating at a heating rate of 5°C/min. up to 450°C under nitrogen atmosphere.

3. Results and Discussion

3.1 FTIR Analysis

The prominence of FTIR analysis is to characterize the chain structure of the synthesized borate ester, polyvinyl borate. The FTIR spectra obtained for polyvinyl borate and poly(methyl methacrylate) are shown in Figure 1 and the assignments of the main absorption bands are illustrated on the same figure. The absorption band at around 3200 cm⁻¹ is attributed to the stretching bond of O-H, which is a sign for unreacted OH groups on polyvinyl borate [12]. The absorption at 2948 cm⁻¹ and 1738 cm⁻¹ in PVB are ascribed to the stretching bonds of C-H and C=O, respectively [12]. The spectrum of PVB also shows B-O stretching vibration at 1433 cm⁻¹ [12]. The peaks at 1287 cm⁻¹, 1197 cm⁻¹, and 1129 cm⁻¹ are attributed to characteristic stretching vibrations of B-O-C bonds, providing strong evidence for the reaction between PVA and boric acid to form polyvinyl borate [12]. FTIR spectrum of PVB is in agreement with the literature [12,13,20]. The characteristic absorption of the PVA main chain at 1027 cm⁻¹, corresponding to the stretching vibration of C-O-C, disappear in the spectrum of PVB, which
Electrospun Blend Nanofibers

is another evidence for the condensation reaction of polyvinyl alcohol and boric acid to form PVB [12]. The characteristic absorptions of the PMMA main chain at 2954, 1732, 1452, 1193, and 1151 cm\(^{-1}\), corresponding to the stretching vibrations of C-H, C=O, CH\(_3\), OCH\(_3\), and C-O, respectively, are also shown in Figure 1 [24–27].

The FTIR spectra of PVB/PMMA blend samples with varying the concentration of polyvinyl borate are shown in Figure 2. The spectrum of PVB matches with that of the blend systems. Characteristic B-O-C stretching vibrations of PVB main chain appear also at 1274 cm\(^{-1}\) and 1195 cm\(^{-1}\) in PVB/PMMA blends [12,13]. The peak for polyvinyl borate at 1433 cm\(^{-1}\), corresponding to the B-O stretching vibration, shifts to 1456 cm\(^{-1}\) and combines with the peak for poly(methyl methacrylate) at 1452 cm\(^{-1}\) [12,25]. On the other hand, the spectrum of PMMA is also in agreement with that of the blend systems. Characteristic C-H, C=O, and C-O stretching vibrations of PMMA appear at 2954 cm\(^{-1}\), 1731 cm\(^{-1}\), and 1153 cm\(^{-1}\), respectively, in PVB/PMMA blends [24,25].

### 3.2 Electrospinning and Morphological Analysis

In order to carry out electrospinning, the polymer must be dissolved in a solvent. Polyvinyl borate is almost insoluble in general solvents, which leads to too low solution viscosity to be stretched by electric field strength [3,28,29]. Since only polyvinyl borate solution is 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.

Apart from our previous study [21]; to date, electrospun blend nanofibers, including boron-containing polymer and polyvinyl borate, have not been fabricated. In our previous study, PVB/PVA blend nanofibers were prepared using the electrospinning technique [21]. Although polyvinyl alcohol possesses superior spinning character and good mechanical properties in the dry state, its applications are limited due to its high hydrophilicity [21–23]. In this study, polyvinyl borate was blended with another spinnable polymer, poly(methyl methacrylate), which is more durable against hydrophilic ambient conditions, and electrospun nanofibers were prepared from their blend solutions.

To observe the effect of varying blend composition on the electrospinning process and the resulting polymer fiber morphology, four different samples have been prepared changing the concentration of PVB to PMMA with 1:3, 1:5, 1:7.5, and 1:10 weight ratios of PVB to PMMA. Solutions including more than 25 wt% PVB in blend composition is inefficient to execute electrospinning. In Figure 3, the SEM image of electrospun poly(methyl methacrylate) nanofibers is illustrated. 5 wt% PMMA-DMF solution yields only fiber structures with an average fiber diameter of 218 ± 19 nm. In Figures 4–7, the SEM images of the electrospun PVB/PMMA blend nanofibers are reported. All of the images illustrate the presence of nanofibers and nano-sized droplets, known as the bead structure.

In order to prepare PVB/PMMA blend solutions, certain amount of polyvinyl borate-DMF solution with a concentration of 1.5 wt% is added to 5 wt% poly(methyl methacrylate)-DMF solution, which reduces the final concentration of the PMMA solution. The property of the polymer solution plays a significant part in the electrospinning process and the resultant fiber morphology [3,30]. Especially, the polymer solution concentration has a significant effect on the final size and the shape of the electrospun particle [3,22]. For electrospinning, if the concentration is too low, the electrospinning process generates a mixture of fibers and droplet [3,22]. This is the reason for the fiber and the bead structures observed on the SEM images of PVB/PMMA blend nanofibers (Figures 4–7). In addition, the
average fiber diameter for 1:10, 1:7.5, 1:5, and 1:3 weight ratios of PVB/PMMA blend systems range from 130±12 nm, 101±16 nm, 91±13 nm, and 93±10 nm, respectively.

Water contact angle measurements of a series of PVB/PMMA blend nanofiber mats including different amounts of the polyvinyl borate, were carried out and their results are shown on Table 1. Figure 8a illustrates a water droplet formed on the electrospun PMMA nanofiber mat. The surface contact angle of the nanofiber mat is 118.1°, in agreement with the pronounced hydrophobicity of PMMA to water. The image in Figure 8b illustrates a significant increase in the contact angle on the PVB/PMMA blend nanofiber mat, which may be ascribed to the enhanced surface roughness. The surface roughness and the porosity have significant effect on the apparent contact angle. Poly(methyl methacrylate) nanofiber mat with enhanced surface roughness and porosity results in higher contact angle when compared with the PMMA nanofiber mat having low surface roughness [31,32]. The surface roughness and the porosity of the electrospun mat can be enhanced by reducing the fiber diameter and/or by modifying the fiber dimension with bead structures [31,32]. Polyvinyl borate/poly(methyl methacrylate) blend nanofiber mats, especially 1:3 and 1:5 weight ratios of PVB to PMMA, exhibit fine-spun nanofibers with bead structures (Figures 6 and 7), contributing to the surface roughness and the porosity, and increasing the contact angle (Table 1).

### 3.3 Thermal Analysis

TGA results of PVB, PMMA, and PVB/PMMA blends are illustrated in Figure 9. TGA plot presents that pure PMMA degradation is completed with two step process, attributed to decrease in the PMMA solution concentration with the PVB solution contribution gives rise to a decrease in the solution viscosity. When the viscosity decreases, there is a gradual change in the shape of the fibers from spindle-like to spherical. A minimum viscosity for each polymer solution is required to yield fibers without beads. With reduced solution viscosity, the diameter of the electropun fiber also decreases [3,30]. The images also illustrate that increasing the PVB concentration reduces the diameter of the blend nanofibers slightly (Figures 4–7). The

<table>
<thead>
<tr>
<th>Weight ratio of PVB to PMMA</th>
<th>Contact angle</th>
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<tr>
<td>Pure PMMA</td>
<td>118.1°±2.9°</td>
</tr>
<tr>
<td>(PVB/PMMA: 1/10)</td>
<td>115.2°±4.8°</td>
</tr>
<tr>
<td>(PVB/PMMA: 1/7.5)</td>
<td>123.7°±4.2°</td>
</tr>
<tr>
<td>(PVB/PMMA: 1/5)</td>
<td>128.2°±3.0°</td>
</tr>
<tr>
<td>(PVB/PMMA: 1/3)</td>
<td>138.3°±2.8°</td>
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Fig. 8. Water contact angle images of (a) the electrospun PMMA nanofiber mat and (b) the blend nanofiber mat; 1:3 weight ratios of PVB to PMMA.
scission at the vinyl terminated end and to random scission of the PMMA backbone, respectively. The degradation profile of pure PMMA is in agreement with the literature [33–36]. PVB has a pronounced effect on the thermal behavior of PVB/PMMA blend degradation. According to the TGA plot (Figure 9), boron containing polymer, PVB, and PVB/PMMA blend systems present better thermal stability than pure PMMA. The good thermal resistance of B-O-C compared to the purely organic bonds is the reason behind the enhancement in the thermal properties [37]. In addition, the blend system with high PVB composition presents a better thermal stability than the blend system with low PVB composition. During PMMA degradation, polymer chains turn into methyl methacrylate monomers, which are transported from bulk of the material to the surface [33,38]. Boron containing residue in PVB/PMMA blends provides a barrier to the transport of methyl methacrylate monomers, which limits the mass loss of PVB/PMMA blends when compared with pure PMMA [33].

4. Conclusions
Boron-containing polymer, polyvinyl borate, was synthesized and mixed with poly(methyl methacrylate) to prepare PVB/PMMA blend nanofibers using the electrospinning process. Blending of the poly(methyl methacrylate) with polyvinyl borate resulted in a change in the fiber diameter from 218 nm to 93 nm and gave rise to the bead structures along the nanofibers depending upon the composition, which improved the hydrophobicity of the electrospun mat owing to the enhanced surface roughness. The incorporation of boron chemistry into the polymer matrix enhanced thermal properties of the polymer, polyvinyl borate, and its blends.

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References