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Preparation and Characterization of PVA/Boron Polymer Produced by an Electrospinning Technique.

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***Abstract**:* In this study, poly(vinyl alcohol) were cross-linked with boron in varying concentrations and blend fibers were obtained with diameters ranging from 0.3 µ to 4.0 µm with the use of electrospinning process. The resulting product was characterized by SEM, DSC, and FT-IR techniques. There is no beading tendency in either boron doped or undoped fibers. When the amount of boric acid in PVA solutions was increased the conductivity of the polymer decreased. The data indicated the existence of boron oxide in the polymeric structure and the formation of B-O-C bond. SEM micrographs reveal that higher viscosity favors the formation of thicker fibers. Boron addition seems to disturb the easy detachment of the fibers from the tip of the Taylor Cone

Introduction

Polyvinyl alcohol (PVA) as an important water-soluble polymer is widely used in synthetic fiber, paper, textile, coating, and binder industries due to its excellent chemical and physical properties, non toxicity, processability, good chemical resistance, wide range of crystallinity, good film formation capacity, complete biodegrability and high crystal modulus etc. [1]. PVA is used in fully hydrolyzed form with degree of hydrolysis 98-99%, and partially hydrolyzed form, with a degree of hydrolysis of approximately 85%. Fully hydrolyzed PVA is generally used in fiber production. The fully hydrolyzed form has been used in this study. The molecular weight and distribution of polyvinyl chains strongly affect the chemical and physical properties of PVA [2-3].

Although PVA has good mechanical properties in the dry state, its applications are limited in wet state. Chemical and mechanical properties of PVA can be drastically changed by cross-linking. For example the increase in the degree of cross-linking can result in the disappearance of the melting point, decrease in the solubility, and increase in the tensile strength of the resulting polymer. PVA can be cross-linked using physical techniques such as heat treatment and radiation or chemical agents such as haxamethylene or hexaetylene diisocynate, glyoxal, boric acid etc. Boron is used as a cross-linking agent in this study since boron improves the strength, flame retardant characteristics and flexibility of the resulting electrospun fibers. The crystallinity of the crystal structure is reduced with cross-linking. The melting point disappears when PVA fiber aggregates are fully cross-linked [5-9].

This paper will present PVA and PVA/Boron fibers prepared by electrospinning technique. It should be noted that the melting temperature of electrospun PVA fibers showed an increase because the molecular orientation in the fiber aggregate was higher than that in the PVA powder [5-6].

Electrospinning process utilizes electrical force to produce polymer fibers. Electrospinning setup consists of four major components: The high-voltage power supply, the spinneret, the syringe pump and the electrically conductive collector. Syringe pump is one of the important components of the process to achieve a constant and adjustable feeding rate of the polymeric solution [7].

Results and Discussion

Conductivity measurements

The conductivity of the polymer fibers was measured using four point probe technique (ENTEK Company). When the amount of boric acid in PVA solutions is increased the conductivity of the polymer is observed to decrease as given in Table 1.

Tab. 1. Fiber Conductivity Values of the Samples.

	Fiber conductivity (S cm^{-1}) electrospun from the solutions				
	Pure PVA Fiber	PVA/BA ratio			
		1:0.2	1: 0.4	1: 0.6	1: 0.8
Abbrevation	P1	P2	P3	P4	P5
Conductivity	7.61×10^{-5}	2.40×10^{-6}	1.79×10^{-6}	1.45×10^{-6}	1.41×10^{-6}

Infrared Spectroscopy (FT-IR)

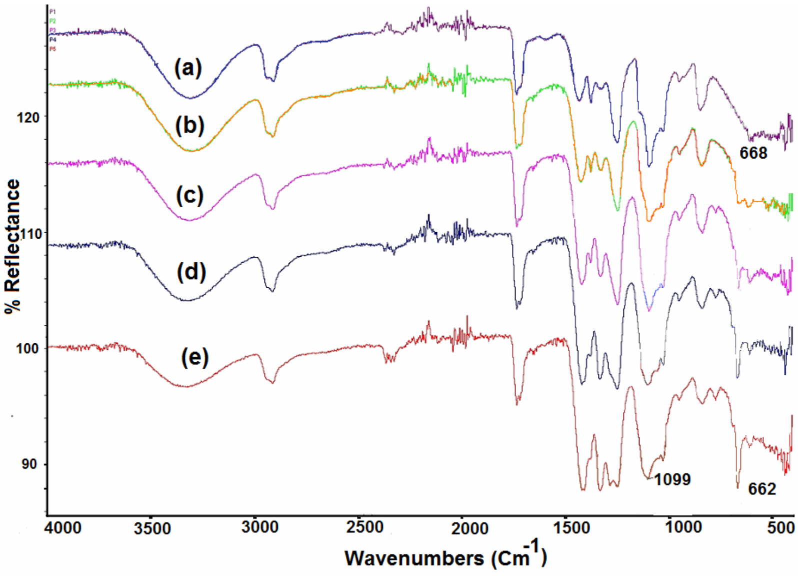

Fig. 1. Arranged in order (from above to below) a) pure PVA (P1) b) PVA/BA ratio 1:0.2 (P2) c) PVA/BA ratio 1:0.4 (P3), d) PVA/BA ratio 1:0.6 (P4), e) PVA/BA ratio (P5) 1:0.8.

FT-IR results were obtained using Thermo Nicolette 6700 spectrometer. Figure 1 and 2 shows the infrared spectra of the polymer fibers. When the amount of BA used for the synthesis of the hybrid polymer is increased, both the peaks at 670 cm^{-1} O-B-O bending and the peak at 760 cm^{-1} corresponding to B-OH stretching modes are observed to increase.

The band at 1030 cm^{-1} assigned to the stretching of B-O-C bond was observed to be unchanged. Deformation δ (CH) peaks at 1376 cm^{-1} is increased when the amount of boric acid in solution is increased.

The peak at 1410 cm^{-1} is caused by asymmetric B-O stretching ($\nu3$). The increase in boric acid sharpened the peak at 1410 cm^{-1} corresponding to B-O stretching. These results prove the formation of boron oxide in the hybrid polymer structure.

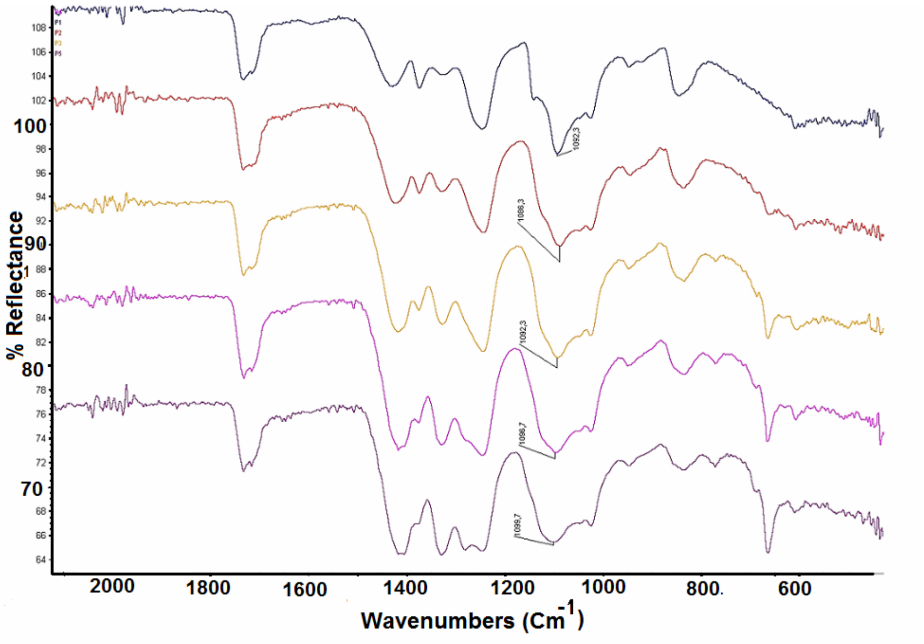

Fig. 2. The part of 400-2100 cm^{-1} of Figure 3.

Differential Scanning Calaromitery (DSC)

Differential Scanning calorimetry (DSC) measurements were carried out with Schimadzu DSC-60 by using nitrogen as the carrier gas. The temperature was raised from room temperature to 200 ^{o}C then cooled to room temperature and heated again to 500 ^{o}C with a heating rate of 10 $^{o}C/min$.

Figure 3 shows DSC thermograms taken between 100 to 500 ^{o}C for PVA and Sample P5 (PVA/BA ratio1:0.8). For pure PVA fiber, the melting (peak) temperature is about 193 ^{o}C and the degradation temperature about 270 ^{o}C, respectively. The melting point disappeared for sample 5, probably PVA is fully cross-linked with boron forming an amorphous structure. This shows that cross-linking decreases the degree of crystallinity which is in good accordance with literature.

For pure PVA, the weight loss at around 424, 435 and 460 ^{o}C was considered to reflect the decomposition of side chain and main chain of PVA, respectively. It is consistent with literature [5-6] that degradation peak was broadened and decreased to 411 °C for boron cross-linked PVA sample (P5).

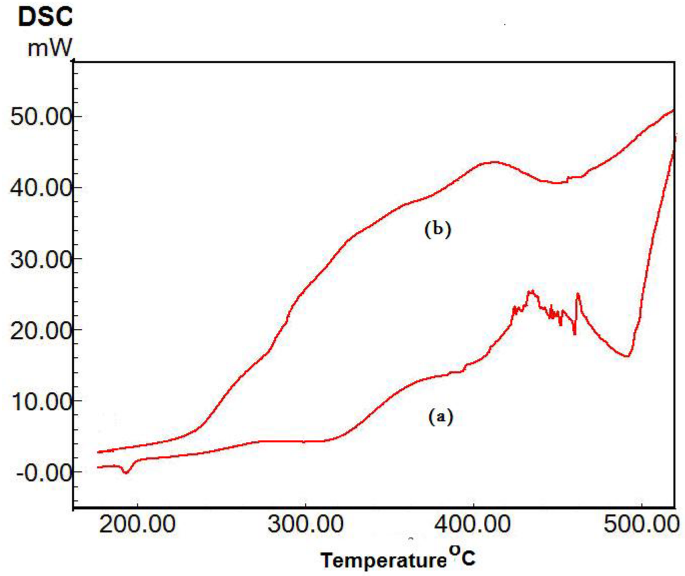

Fig. 3. DSC thermograms from 100 to 500 °C for PVA: a) pure PVA b) PVA/BA ratio (P5) 1:0.8.

Scanning Electron Microscope

The morphology of the PVA doped with different ratio of boron composite electrospun fibers produced were examined using SEM micrographs. The scanning electron microscopy (SEM) measurements were recorded on a Jeol JSM (5410 LV) model microscope.

SEM micrographs of the PVA doped with different ratio of boron composite fibers were shown in Figure 4 a-d. The surface of as-spun composite fibers have varying diameters with smooth uniform surfaces. There is no beading tendency in either boron doped or undoped fibers.

Figure 4a is pure PVA (P1) with fiber diameter range from 0.3 μm to 1.6 μm. In Figure 4b PVA/BA ratio is 1:0.2 (P2) and diameters of the fibers range from 0.5 μm to 2.0 μm. Diameters are a little bit higher in Figure 4.c (range from 0.5 μm to 3 μm) where PVA/BA ratio is ratio 1:0.4 (P3). Finally in Figure 3d PVA/BA ratio is 1:0.8 (P5) and fiber diameters range from 1.0 μm to 4.0 μm.

As expected from the decrease of the conductivity with the addition of boron to PVA with different ratio, the average diameter of PVA fibers was increased. However, the effect of conductivity on the fiber diameter might be limited because the average diameter of electrospun fibers was not directly related to the magnitude of conductivity. For example the viscosity of the boron doped solution was observed to be higher. SEM micrographs reveal that higher viscosity favors the formation of thicker fibers. Boron addition seems to disturb the easy detachment of the fibers from the tip of the Taylor Cone.

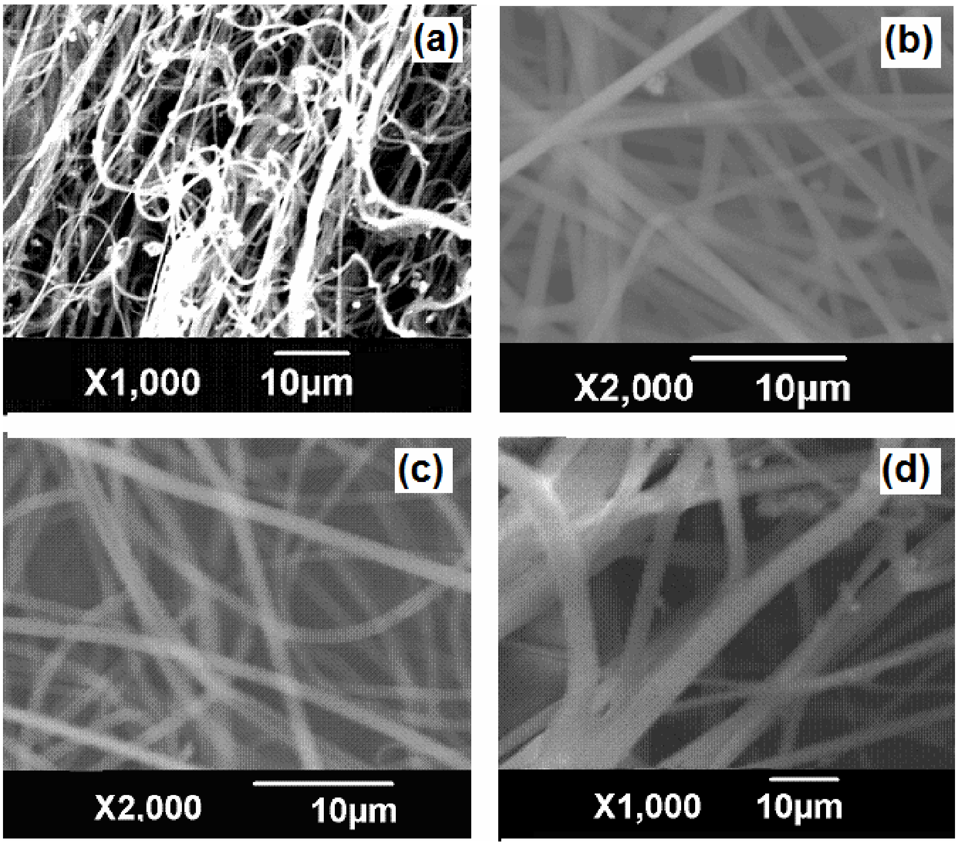

Fig. 4. SEM micrograph of samples for a) pure PVA (P1) b) PVA/BA ratio 1:0.2 (P2) c) PVA/BA ratio 1:0.4 (P3) , d) PVA/BA ratio 1:0.8 (P5)

Conclusions

The experiments revealed that it was possible to obtain composite fibers with the use of electrospinning technique. Addition of boron to PVA increased the fiber diameters probably because the addition of boron decreases the conductivity of the fibers and increases the viscosity of the solution. DSC results showed that increase of boron also increased the stability of the fiber.

Experimental

Fully hydrolyzed (98-99%) granuled PVA (Merck, M_w 72000) was used in the experiments. PVA and Boric acid (BA) (Merck, M_w 61.83 g/mole) were separately dissolved in distilled hot water (80 ^oC) stirring with magnetic stirrer. Then the boric acid solution was added to the PVA solution for cross-linking reaction slowly in drop wise manner in hot conditions (at 60 ^oC) stirring constantly with a glass rod to prevent the formation of fluffy and rubbery material and homogenize the solution. . The ratio of cross-linking was calculated based on trifunctionality of boric acid. Four experimental samples and one pure PVA sample were prepared (pure PVA (P1), PVA/BA ratio 1:0.2 (P2), PVA/BA ratio 1:0.4 (P3), PVA/BA ratio 1:0.6 (P4), and PVA/BA ratio (P5) 1:0.8). Each solution was mixed with magnetic stirrer for two hours at 60 ºC in order for the reaction between PVA and boric acid to occur.

The polymer solutions were electrospun at a positive voltage of 25 kV and a tip to collector distance of 15 cm.

Acknowledgments

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