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Preparation of PVA/Chitosan Doped with Boron Composite Fibers and Their Characterization

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Abstract

In this study, chitosan and poly(vinyl alcohol) were cross-linked with boron in varying concentrations and chitosan and poly(vinyl alcohol) blend fibers were obtained with electrospinning process.

Viscosity and electrical conductivity results revealed that the increase in chitosan and boron content increased the viscosity of the solution and but decreased the electrical conductivity of the fibers. The peaks obtained with FT-IR analyses were in good agreement with literature. SEM micrographs also showed that wavy and curly fibers with relatively small diameters were obtained as the chitosan and boron concentrations were increased. Thermogravimetric data revealed that the formation of a more stable polymer structure as a result of the cross linking with boron.

Key Words: Chitosan, poly vinyl alcohol (PVA), Boron, Boric acid, Electrospin, Nanofibers.

INTRODUCTION

Over the past years, electrospinning has been applied for the fabrication of nanofibrous membranes from both synthetic polymers and natural biomacromolecules, such as collagen, silk and chitosan. Chitosan is generally obtained by alkaline deacetylation from chitin [1] which is promising a biomaterial for tissue engineering as an antimicrobial material, and drug delivery applications [2] because of its biocompatibility, biodegradability, antimicrobial activity, and non-toxicity.

Recently, chitosan-based nanofibers have been successfully electrospun from chitosan solutions blended with poly(ethylene oxide) (PEO), poly(vinyl alcohol) (PVA), or silk fibroin, and electrospinning of homogeneous chitosan nanofibers using various solvents such as acetic acid is also reported [3-6].

Poly(vinyl alcohol) (PVA) is a nontoxic, water soluble, biocompatible, and biodegradable synthetic polymer, which is widely used in biochemical and biomedical applications [7]. PVA has good fiber-forming, highly hydrophilic properties, and its fibers have been commercialized since the 1950s, and used in textiles as a silk substitute [8]. Poly(vinyl alcohol) is a unique type of fiber which is easily spun, coagulated, oriented, and cross-linked [9].

In the present work, chitosan and poly(vinyl alcohol)

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blend fiber can be obtained through electrospinning process. The addition of boric acid into spinning solution may have also an important influence on the spinning performance. The introduction of boric acid into PVA/chitosan composite fiber can improve the tensile strength properties of the blend fiber compared to pure PVA fiber due to crosslinking with boron. Also the strong intermolecular interaction between chitosan and PVA molecule chain results in good miscibility due to the interaction between the hydroxyl groups in PVA and primary amino groups in chitosan through hydrogen bonding [10].

The effect of solution concentration on the diameters and morphology of the fibers has been studied.

EXPERIMENTAL

PVA (MW: 72000 g/mol, %98 hydrolyzed), chitosan (MW: 400 000 g/mol), boric acid and acetic acid were obtained from Merck. All polymer solutions were prepared using deionized water. Aqueous acetic acid (2% [v/v]) was used as a solvent because chitosan is only soluble in acetic acid solutions. The PVA/chitosan solutions were prepared by dissolving PVA in aqueous chitosan solutions at 80ºC. 1, 3 and 5 wt % chitosan in PVA were dissolved in aqueous acetic acid solution (2% [v/v]) by stirring overnight at room temperature.

In this study, boric acid was added to PVA solutions for cross-linking reaction. The ratio of cross-linking was calculated based on tri functionality of boric acid. Boric acid were dissolved in water and added slowly in a drop wise fashion to PVA/chitosan mixtures. These solutions were mixed with magnetic stirrer for two hours at 60ºC in order the reaction between PVA and boric acid to occur.

The blend solution (4 ml) was placed in a 10 ml syringe. The electrode, connected with a high-voltage supply was capable to generate positive DC voltages and the voltage was changed from 15 to 22 kV during the experiments. Grounded aluminum foil was used to collect the electrospun material. The distance between the capillary tip and the collector was 11–13 cm [11].

RESULTS AND DISCUSSION

Viscosity and Electrical Conductivity

The viscosity and conductivity of the electrospun fibers were measured with A&D (SV-10) viscometer (given in Table 1) and the four-point probe method (given in Table 2). During the measurement the thickness of the non-woven fibers was measured using a Mitutoyo brand digital micrometer with a resolution of 1 mm. It should be noted that the four-point probe method measures the volumetric resistivity from which the total conductivity can be calculated and not that of an individual fiber. Accurate measurement of the thickness of the highly compressible fiber mat using a micrometer was highly difficult.

Table 1. Viscosity of the solutions.

	Viscosity (Pa.s) at 29^{o}C	
	Without Boron	PVA/BA (30% ratio of rxn)
1% Chitosan	1.33	1.40
3% Chitosan	2.39	3.60
5% Chitosan	5.87	6.70

It is obvious from Table 1 and 2 that there is a close relation with viscosity of solution and conductivity of the fibers. Increase in chitosan and boron content increased the viscosity of the solution, but decreased the electrical conductivity of the fibers.

Table 2. Fiber conductivity values of the samples.

	Fiber conductivity (S cm^{-1}) electrospun from the solutions		
	Without Boron	PVA/BA (extend of rxn)	
		10%	30%
1% Chitosan	2.30×10^{-7}	9.82×10^{-6}	5.98×10^{-6}
3% Chitosan	1.89×10^{-5}	1.25×10^{-5}	1.06×10^{-5}
5% Chitosan	1.53×10^{-5}	1.00×10^{-5}	9.98×10^{-6}

FTIR Analysis

The absorption peaks at 1440 (cm^{-1}) (CH_2 bending) and 858 (cm^{-1}) (CH_2 rocking) characteristic to PVA were seen in all of the spectra. But the peak heights are different.

In addition characteristic absorptions of the PVA main chain were observed at 3400 cm^{-1}, 2860 cm^{-1}, 1285 cm^{-1}, corresponding to *v*O-H, *v*C-H, *v*C=O and *v*O-C-C, respectively.

The absorption peaks at 1650 cm^{-1} and 1325 cm^{-1}, which are characteristic of chitin and chitosan and reported as amide I and III peaks, respectively [3, 11] were apparent in spectra (b), (c), and (d). The broad peak at 1096 cm^{-1} indicates the C-O stretching vibration. Peak at 2932 cm^{-1} are the typical C-H stretch vibrations. Formation of the 1561 cm^{-1} peak is the symmetric deformation of $-NH_3^+$ and the peak at 1417 cm^{-1} indicates the presence of carboxylic acid in the polymers. The peaks at 1710 cm^{-1} are characteristic of the carboxylic acid dimer due to the acetic acid used for dissolving the chitosan [11].

Broad peak at 3400 cm^{-1} is caused by amine N-H symmetrical vibration sharpened gradually for samples from (a) to (d) respectively.

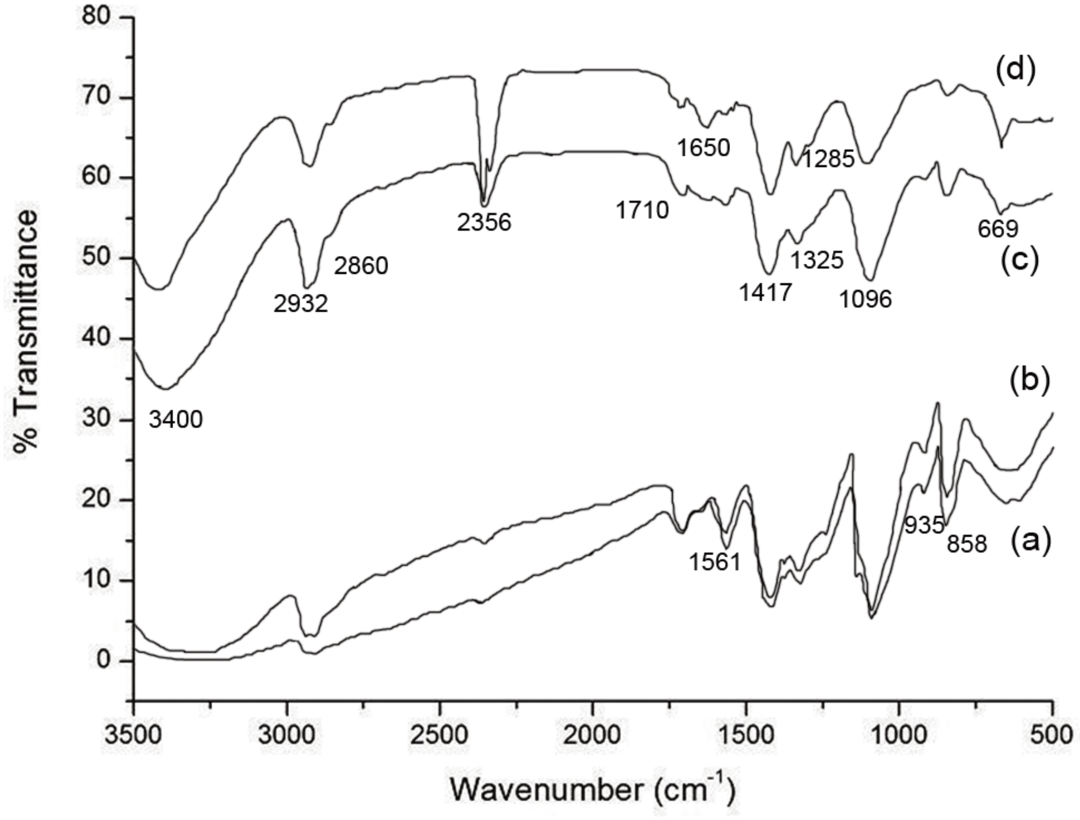

Figure 1. FT-IR spectra of (a) pure PVA, (b) 1% Chitosan added to PVA (c) 3% Chitosan added to PVA with 10% of rxn Boron, (d) %5 Chitosan added to PVA with 30 % of rxn Boron.

DSC Analysis of Chitosan/PVA Nanofibres

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 heating again to 500^{o}C with a heating rate of 10^{o}C/min.

Figure 2 is DSC thermogram results of 1% chitosan added to PVA and 3% chitosan added to PVA with 10% of rxn Boron. It was found that the thermal degradation behavior of these two fiber structures are quite different. The DSC thermogram of fibers electrospun from 1% chitosan added to PVA aqueous solution showed a melting endotherma at about 109^{o}C, 210^{o}C and 300^{o}C and a decomposition peaks at 420^{o}C and 450^{o}C.

As seen from Figure 2, there are no melting peaks when boron added to PVA/chitosan blend polymer showing that boron was efficiently cross-linked with the polymer forming an amorphous structures. The melting point disappears when PVA fiber aggregates are properly cross-linked. There are two degradation peak of PVA/chitosan fiber. The degradation peak was broadened for boron cross-linked PVA/chitosan fiber.

In a summary, DSC analysis shows that when boron is added to the polymer it increases the crosslinking and the crystallinity of the PVA/chitosan hybrid polymer is reduced.

SEM Analysis

The morphology of the PVA/chitosan doped with 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.

Figure 3 shows the SEM images of pure PVA fibres. There are very long and straight electrospun nanofibers with relatively homogeneous diameters ranging from 500 to 800 nm.

Figure 4 A is the image of 1% chitosan added to PVA

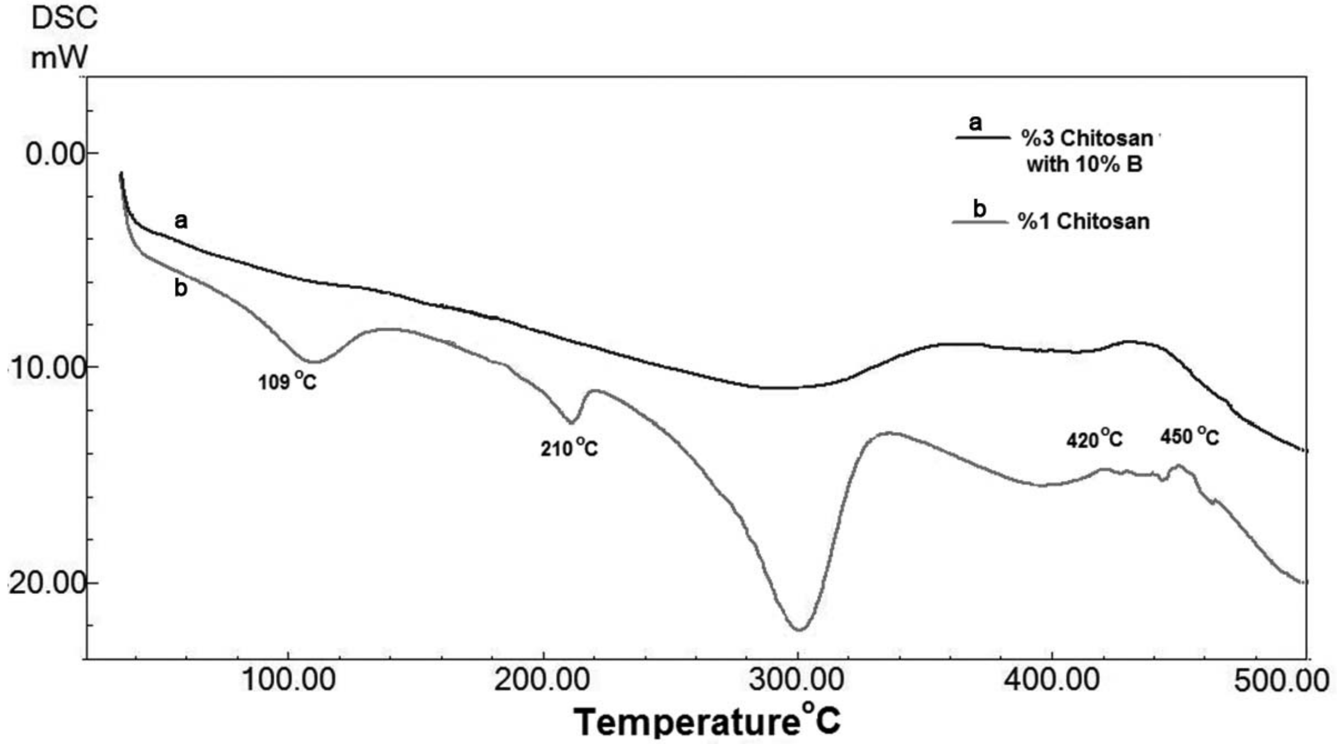

Figure 2. DSC analysis of 1% Chitosan added to PVA and 3% Chitosan added to PVA with 10% of rxn Boron

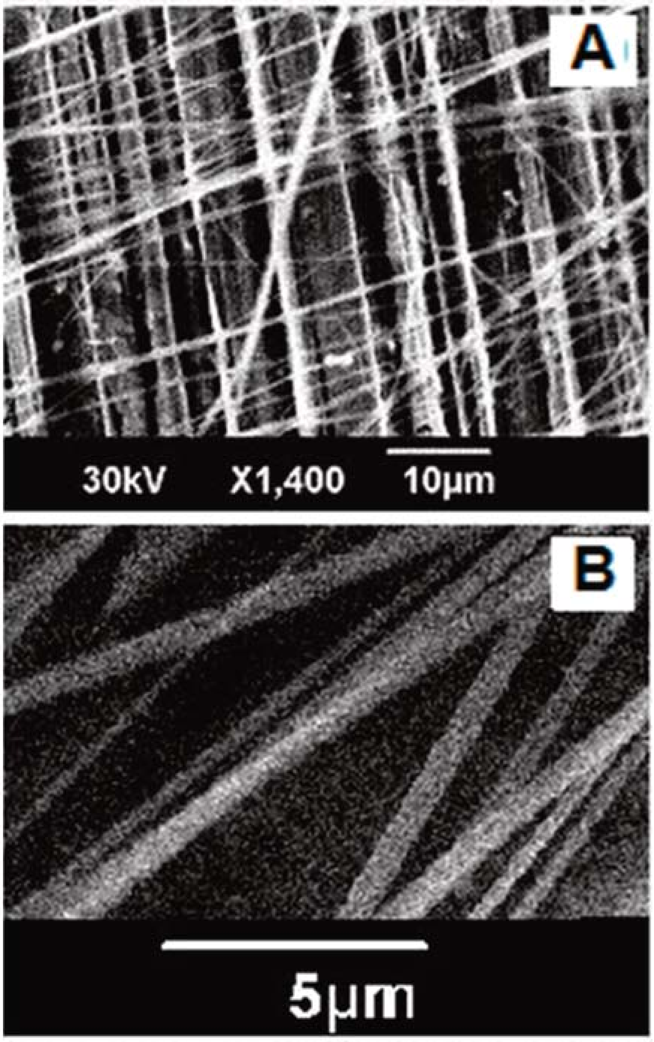

Figure 3. SEM images of pure PVA.

without boron. Fiber diameters range from 300 to 800 nm. The SEM image of 5% chitosan added to PVA with 10% rxn of boron is shown in Figure 4 B where fiber diameters ranged from 600 to 300 nm. Figure 4C is the image of 5% chitosan added to PVA with 30% rxn of boron resulting fibers with diameters ranging from 500 to 200 nm.

Pure PVA electrospun fibers appear to be randomly distributed in the non-woven mat. These fibers generally had a slightly varied thickness without the presence of any beads. As seen from SEM micrographs the increase of the chitosan and boron concentrations, resulted curly and wavy structures. Increase of in chitosan and boron content increased the viscosity of the solution and the electrical conductivity of the fibers. It is given in the literature that conductivity and viscosity are also very important parameters for the electrospinning process.

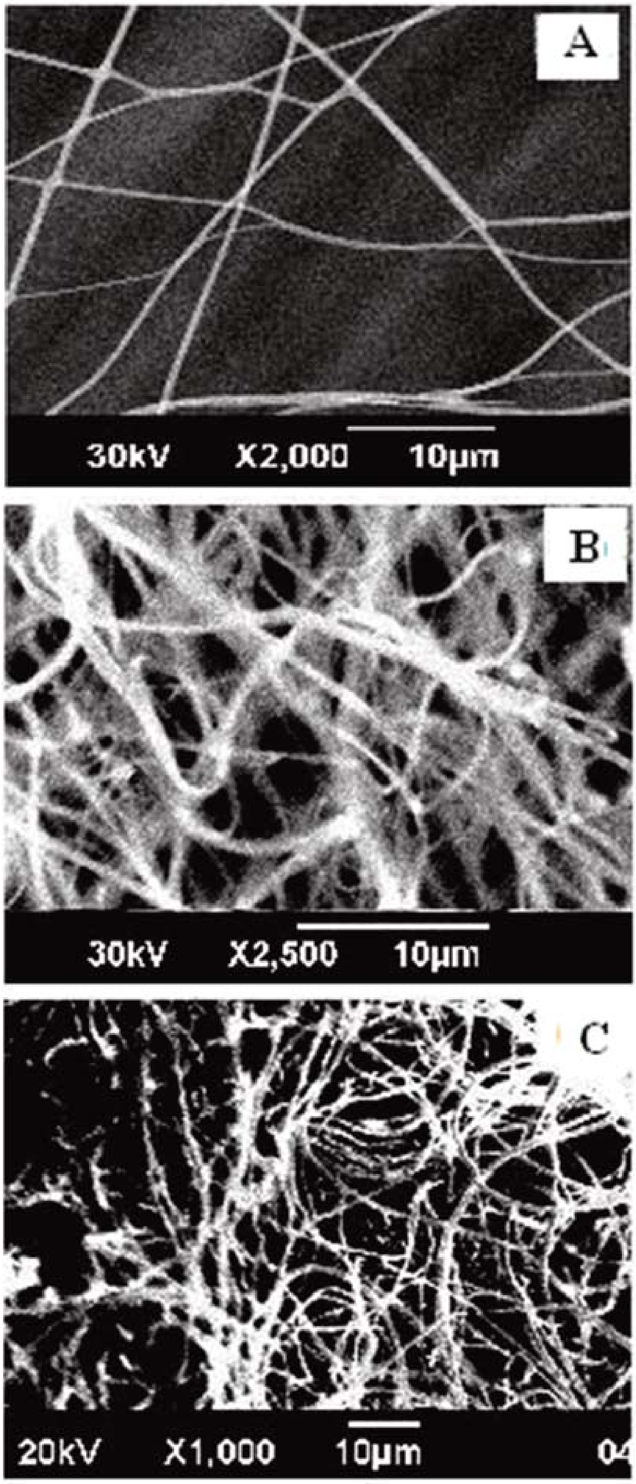

Figure 4. SEM images of 1% chitosan added to PVA (a) 3% chitosan added to PVA with 10% of rxn boron (b) and 5% chitosan added to PVA with 30% rxn boron (c).

Higher viscosity solution favors the formation of thicker fibers. In our results it is not the case because of the increased conductivity of the fibers. The addition of chitosan and boron the medium increased the conductivity of the solution which in turn increased the conductivity of the fibers resulted the diameters of the fibers being relatively smaller than expected [13].

CONCLUSION

The present study, biocompatible fibers were prepared from chitosan and poly(vinyl alcohol), and cross-linked with boric acid in varying concentrations. Addition of boron increased the stability of the polymer.

The increase in boron and chitosan contents resulted in the curly and wavy fiber structures. This was attributed to the increase in the viscosity of the solution and the electrical conductivity of the resulting fibers. Which caused the diameters of the fibers smaller than expected.

The spectroscopic and thermogravimetric data showed the crystalline structure of PVA turned into an amorphous structure by cross linking with boron. It is well known that blending is an effective and convenient method to improve the performance of polymer materials. The morphological structure and miscibility of the blend fibers were studied with the aid of infrared spectra (FT-IR), differential scanning calorimetry (DSC), and scanning electron micrograph (SEM),

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