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Characterization of Boron Doped Cobalt/Zinc Acetate Composite Fibers

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Abstract

PVA/cobalt acetate/zinc acetate doped with boron composite fibers were prepared by electrospinning technique. Electrospinning was performed by putting solutions at different applied voltage in a range from 13 to 18 kV.

The fibers were measured and characterized by viscometer, conductiometer (with four-point probe), Fourier transformed infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), and differential scanning calorimetry (DSC).

The viscosity of the Boron doped solution was higher and favoring the formation of thinner and uniform nanofibers. DSC analysis shows that when boron is added to the polymer it increases the crosslinking and amorphous structure of PVA/ cobalt and zinc acetate composite polymer is increased.

INTRODUCTION

Metal oxide ceramic thin films are widely used in the electronics industry and chemical industry as electro catalyst and as selective catalysts for oxidation. In the literature the preparation of metal oxide ceramic films has been accomplished by physical vapor deposition, chemical vapor deposition and chemical solution deposition techniques. Various metal oxide fibers were obtained by high temperature calcinations. Large surface area and high aspect ratio of metal oxide fibers may have significant industrial importance especially for catalysis and filtration applications but conventional metal oxide fiber synthesis techniques of wet, dry, melt, and gel spinning, are capable of producing polymer fibers with diameters down to the micrometer range. Electrospinning is a process capable of producing polymer fibers with nanoscale diameters [1-5] .

Cobalt oxide-based materials are suitable candidates for the construction of solid-state sensors, heterogeneous catalysts, electrochromic devices, and solar energy absorbers [2].

The excellent optical, mechanical, electrical, chemical and photochemical properties of zirconium

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oxide (ZrO_2) made it suitable for different applications such as interferometric filter, coating material, catalyst and sensor [5].

In this article for the preparation of these metal oxides, metal acetates were used because they are very soluble in water, stable chemical solutions, clean decomposition to pure metal oxide ceramics, and, the desired viscosity for electrospinning technology.

In the literature, thin poly(vinylalcohol) (PVA)/cobalt acetate and zinc acetate composite fibers were prepared by using sol–gel processing and electrospinning technique [4]. But to our knowledge, there are few reports about the production of cobalt acetate/zinc acetate composite polymers doped with boron.

In this communication, we obtained the composite polymer fibers of PVA/cobalt acetate and zinc acetate composite doped with boron using electrospinning technique.

EXPERIMENTAL

Materials

PVA had molecular weight of 72000 g/mol, cobalt (II) acetate [$Co(CH_3COO)_2.4H_2O$, 99% purity] and boric acid [H_3BO_3, 99.5-101.0 % purity] supplied by Merck. Zinc acetate dihydrate [$Zn(CH_3COO)_2{\cdot}2H_2O$, 99-102% purity, M_W=219.51 g/mol] was obtained from Sigma Aldrich. Deionized water was used as a solvent.

Preparation of PVA/(cobalt/zinc) acetate doped with boron composite gels

Aqueous PVA solution (about 10 wt.%) was first prepared by dissolving PVA powder in distilled water and heating at 80°C with stirring for 2 h, then cooling to room temperature and stirring for 2 h. Then, 50.0 g of aqueous PVA solution of 10 wt. %, 2.0 g each cobalt(II) acetate and zinc acetate dihydrate were dissolved in 14 g deionized water and added slowly into the PVA solution in drop wise fashion. The reaction proceeded in a water bath at 50°C for 6 h. The same acetate solution was taken and 0.484 g of boric acid is added and the reaction proceeded in a water bath at 50°C for 6 h again for boron doped composite polymer. Thus, a viscous gel of PVA/(cobalt/zinc acetate) composite polymers were obtained. Pure zinc and cobalt acetate solutions were also prepared for comparison of the composite solution.

Preparation of nanofibers

The viscous solution of PVA/(cobalt/zinc) acetate composites was taken in a 10 ml plastic syringe and connected to a high-voltage generator to generate positive DC voltages. The voltage was changed from 13 to 18 kV during the experiments. A grounded iron drum, covered with an aluminum foil, served as the counter electrode. The distance between the capillary tip and the collector was 11–13 cm [6]. The fibers thus formed were dried 12 h at 70°C.

The blend solution (4 ml) was placed in a syringe. Grounded aluminum foil was used to collect the electrospun material.

Measurement and Characterization

The viscosity and conductivity of the electrospun fibers were measured with A&D (SV-10) viscometer, and the four-point probe method, respectively. During the measurement the thickness of the non-woven fiber mat was measured using a Mitutoyo brand digital micrometer (Mitutoyo Corp., Aurora, Il, USA) with a resolution of 1 mm.

For scanning electron microscopy (SEM) investigation, JEOL JSM-5410Lv (Jeol Ltd., Tokyo, Japan) microscope was used. FT-IR spectra were

obtained on a Varian FT-IR spectrometer (Varian Inc. Corp., Palo Alto, CA, USA). Differential Scanning Calorimetry (DSC) measurements (Shimadzu DSC-60, Shimadzu Sci. Inst., Columbia, MD, USA) were carried out on a equipment by using nitrogen as the carrying gas. The temperature was raised from room temperature to 200°C then cooled to room temperature and heating again to 500°C with a heating rate of 10°C/min.

RESULTS AND DISCUSSION

Viscocity and Electrical Conductivity Measurements

The viscosity values of the solutions were given in Table 1 and the conductivity of the electrospun fibers measured was given in Table 2. It is obvious from Table 1 and Table 2 that there is a close relation with viscosity of solution and conductivity of the fibers. Increase in boron content increased the viscosity of the solution, but, decreased the electrical conductivity of the fibers.

Table 1. Viscosity values of the solutions.

	Viscosity (Pa.s) at 29.5°C
PVA/Zinc acetate	1.13
PVA/Cobalt acetate	1.01
PVA/(Cobalt/zinc) acetate with boron	2.66

IR spectra

Figure 1 shows the infrared spectrum of the PVA/Cobalt acetate/Zinc acetate doped with boron composite fiber. The peaks at about 3410, 2938, 1599, 1421, 1338, 1095, and 846 cm^{-1}, corresponding to ν_{O-H}, $\nu_{C-H(aliph)}$, $\nu_{C=C}$, ν_{C-O}, and $\delta_{(O-H)}$ respectively [4,6], the peak around 662 cm^{-1} was assigned to ν_{Co-O} of Co_3O_4 [7,8]. A peak observed at 610 cm^{-1} indicates the Zn-O bending.

Table 2. Conductivity of the fibers.

	Conductivity (S cm^{-1})
PVA/Zinc acetate	2.31×10^{-6}
PVA/Cobalt acetate	7.15×10^{-6}
PVA/(Cobalt/zinc) acetate	6.07×10^{-6}
PVA/(Cobalt/zinc) acetate with boron	6.64×10^{-7}

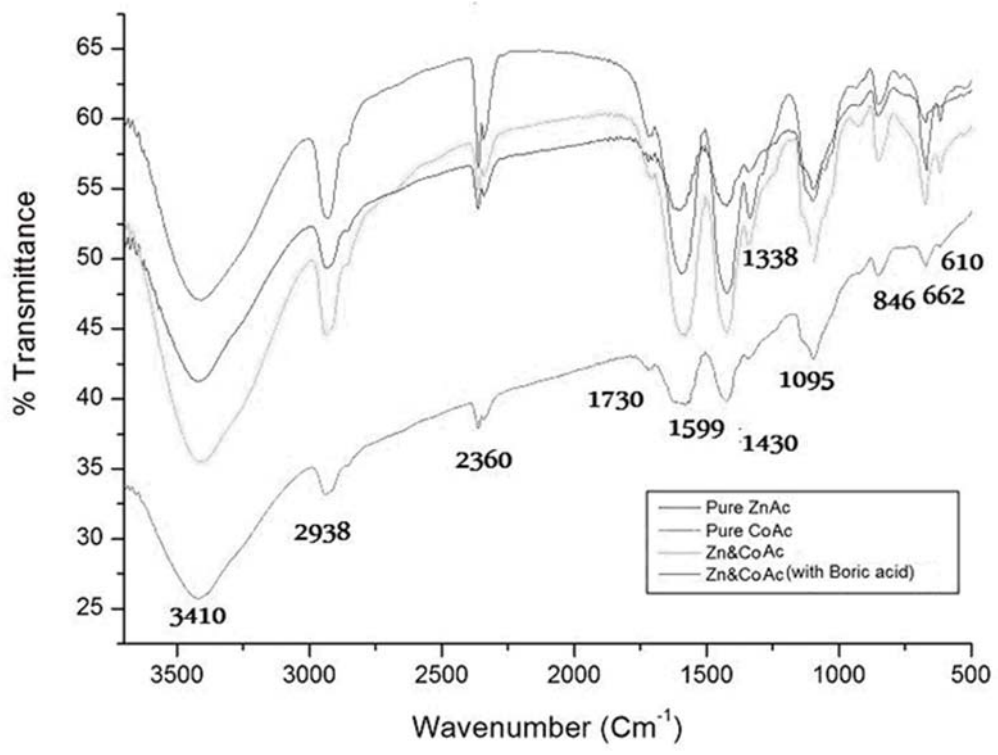

Figure 1. FT-IR spectra of the PVA/cobalt acetate/zinc acetate composite fibers.

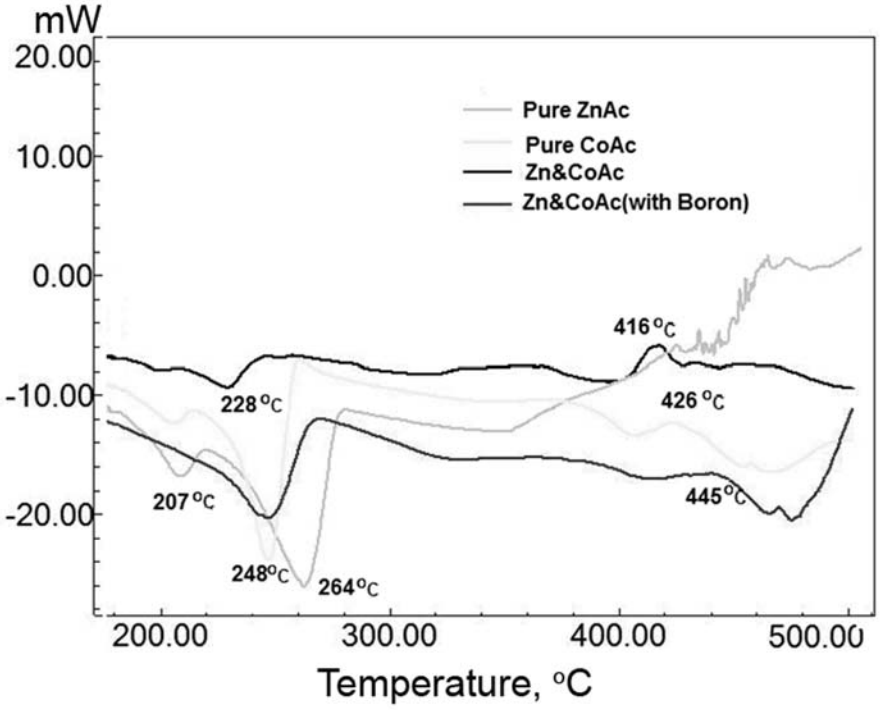

Figure 2. DSC thermograms of the PVA/cobalt acetate composite fibers.

The absorption peak observed at around 1430 cm^{-1} can be ascribed to the B-O stretching vibration. Also, there may be some ester formation in the product due to the presence of C=O peak at 1730 cm^{-1}.

DSC Results

Figure 2 shows DSC thermograms taken between 180°C and 500°C for PVA/zinc acetate, PVA/cobalt acetate, PVA/cobalt acetate/zinc acetate, and PVA/cobalt acetate/zinc acetate (with boron). For PVA/zinc acetate fiber, the melting temperatures are 207°C and 264°C and the degradation temperature is about 416°C, respectively. As seen from Figure 2, there are no melting peaks when boron was added to PVA/cobalt acetate/zinc acetate composite polymers, because, PVA was efficiently crosslinked with boron forming an amorphous structure. It should also be concluded that the degradation peak was broadened for boron cross-linked PVA/metal acetate blend fiber.

SEM results

SEM micrographs of the PVA/cobalt acetate/zinc acetate composite fibers were shown in Figure 3a-d. The surface of as-spun PVA/cobalt acetate/zinc acetate composite fibers has smooth uniform surfaces with varying diameters. There is no beading tendency in either boron doped or undoped fibers.

The viscosity of the boron doped solution was higher and higher viscosity favors the formation of thicker fibers as seen in Figure 3c and 3d. Boron addition seems to disturb easy detachment of the fibers from tip of the Taylor Cone. Fibers which are entrapped in the spider-like web envelope between the tip of the syringe and the collector further prevents easy spread of the jet tip. On the contrary, the undoped solutions can form regular fibers mats depositing on the aluminum foil observed in electrospinning processes.

CONCLUSION

PVA/cobalt acetate/zinc acetate doped with boron composite fibers were easily prepared by using sol–gel processing and simple and inexpensive electrospinning technique. The fibers were measured and characterized by viscometer,

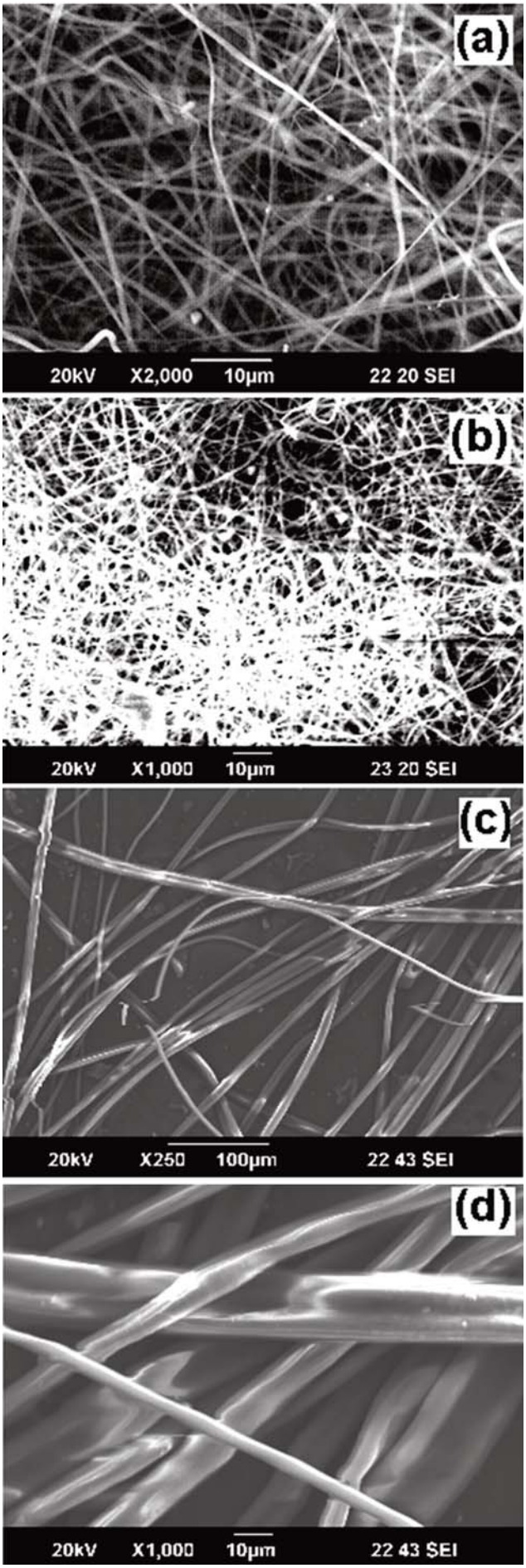

Figure 3. SEM micrographs of (a) PVA/cobalt acetate (b) PVA/cobalt acetate/zinc acetate (c) and (d) PVA/cobalt acetate/zinc acetate doped with boron composite fibers.

conductometer (with four-point probe), FT-IR, scanning electron microscopy, SEM, respectively.

The formation of PVA/cobalt and zinc acetate composite polymer was confirmed by FT-IR spectra. DSC analysis shows that when boron is added to the polymer it increases the crosslinking and amorphous structure of PVA/cobalt and zinc acetate composite polymer is increased. These results suggested that electrospinning is an effective method for the fabrication of PVA/cobalt acetate/zinc acetate doped with boron composite fibers. The viscosity of the boron doped solution was higher and favoring the formation of thinner and uniform nanofibers.

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