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Preparation and Characterization of Poly (vinyl alcohol)/ Antimony-Doped Tin Oxide Nanocomposites

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Nanocomposites of poly (vinyl alcohol) and antimony-doped tin oxide (ATO) were prepared by solution blending. The PVA composites were characterized by FTIR, TGA, DSC, WXR and stress-strain testing. It has been found that adding ATO to the matrix has great influence on the crystallization behavior and glass transition temperature of PVA. The mechanical properties of PVA changed with the filler content, exhibiting an initial increase in these properties due to polymer-filler interactions. After a maximum value, at about 5 wt%, the mechanical properties decreased. Thermal stability of the nanocomposites was found to be remarkably enhanced by the incorporation of ATO.

Keywords Antimony-doped tin oxide, nanocomposites, PVA, structure and properties

INTRODUCTION

Polymers can be compounded with a variety of common and special fillers, reinforcements, and modifiers to yield specific properties in a wide range of applications. Among these additives are electrically and thermally conductive modifiers that can provide protection against static accumulation, electrostatic discharge and molding cycle reduction. Various fillers, some of them metallic, are used to produce the modification of conductive properties of the neat

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polymer [1,2]. However, high concentrations of filler (e.g., 30% carbon black) are needed that can take a toll on the physical and aesthetic properties of the polymer [3]. The selection of conductive material has often involved compromises to the preparation of polymer composites by the dispersion of small loadings of nanosized fillers in a polymeric matrix, and has lately attracted much attention in academia and industry for its potential in improving the performance of macromolecular materials [4]. A particularly interesting conductive filler is antimony-doped tin oxide (ATO), as it combines good electrical conductivity with optical transparency [5]. The combination of optical transparency and high electrical conductivity is important for applications in solar cells, light-emitting diodes, and permanent anti-static coatings. ATO has been used to increase the electrical conductivity of polyvinyl acetate–acrylate copolymer coatings [6], gelatine and acrylate films [7], and polyacrylonitrile [8].

Poly(vinyl alcohol) (PVA) is an important commercial plastic that finds application in many sectors such as in aircraft glazing, signs, lighting, architecture, transportation and merchandising. Modification of PVA with inorganic fillers was common to improve its film performance such as mechanical strength, thermal resistance and permeability properties [9–11]. The surface characteristics of the filler which determine the interactions between the filler and the PVA are of primary importance in the selection of the filler for PVA composites. To our knowledge there exists no report on the preparation of PVA/ATO composites. In our study, conducting nanocomposites of PVA and ATO were prepared by solution blending. The influences of ATO content on the electrical conductivity, thermal stability, and mechanical properties of the nanocomposites were investigated.

EXPERIMENTAL

Materials

The PVA (1799) employed in this study was purchased from Shanghai Petroleum Chemical Co., Ltd. (Shanghai, China). The nano-ATO particles (specific surface area: $80 \text{ m}^2/\text{g}$, antimony doping level: 15%, average particles size: 40 nm) were purchased from Shanghai Huzheng Technology Co., Ltd. (Shanghai, China).

Preparation of PVA/ATO Composites

PVA composite films with different nano-ATO loadings were fabricated by using the wet-casting method. In a typical procedure, solution of PVA (100 g L^{-1}) was made by stirring appropriate quantities of polymer and distilled water at 95° continuously for 3 h. A stock nano-ATO solution was

prepared by adding a mass fraction of 4 wt% nano-ATO to the water. The solution was sonicated for 2 h in a sonic bath. An exact amount of ATO solution was added dropwise to the PVA solution whilst stirring continually. A range of mass fractions can thus be fabricated by blending this stock solution with the 100 g L⁻¹ PVA solution in the required concentration. After careful mixing of aqueous PVA solution with nano-ATO dispersions followed by subsequently casting, and controlled water evaporation, PAV/ATO composite films were obtained by peeling off from the Teflon disk substrates, and were kept in vacuum desiccators before measurement.

Characterization and Measurement

The infrared spectra of the PVA/ATO nanocomposites and the neat PVA were recorded in the spectral range from 4000 to 500 cm⁻¹ using a Nicolet 20sx-B Fourier transform infrared (FTIR) spectrometer.

Microphotographs were taken of the surface made by fracturing the specimen in liquid nitrogen and then sputtering with gold. A JSM—5600LV scanning electron microscope was used for morphological observation.

The X-ray diffraction (XRD) measurements of the neat PVA and PVA/ATO nanocomposites were performed on a Bruker-AXC08 X-ray diffractometer.

The thermogravimetric analysis (Perkin-Elmer model TGA-2) of the neat PVA and the PVA/ATO nanocomposites was carried out under a nitrogen atmosphere in the temperature range from 50 to 600°. The heating rate was 10° min⁻¹.

The differential scanning calorimetry (DSC) measurements of the neat PVA and the PVA/ATO nanocomposites were performed under a nitrogen atmosphere on a Perkin-Elmer DSC-2 instrument in the temperature range from 35 to 250°. The heating rate was 20° min⁻¹. In order to insure the same thermal history of the samples, prior to measurements they were heated up to 250°C and then cooled down (heating and cooling rates were 20° min⁻¹).

Electrical conductivity of the blends was measured by the usual four-probe method, doing five measurements in three different samples of each composition, the standard deviation being always less than 1%.

Room temperature tensile testing of the composites was conducted on an Instron1122 testing machine at crosshead speeds of 50 mm/min. All presented results of mechanical and thermal measurements are average values obtained from at least five identically prepared samples.

RESULTS AND DISCUSSION

WXR Analysis

The XRD characterizations of nano-ATO, the pure PVA and the PVA/ATO nanocomposites with 5 and 10 wt% of nano-ATO content were conducted

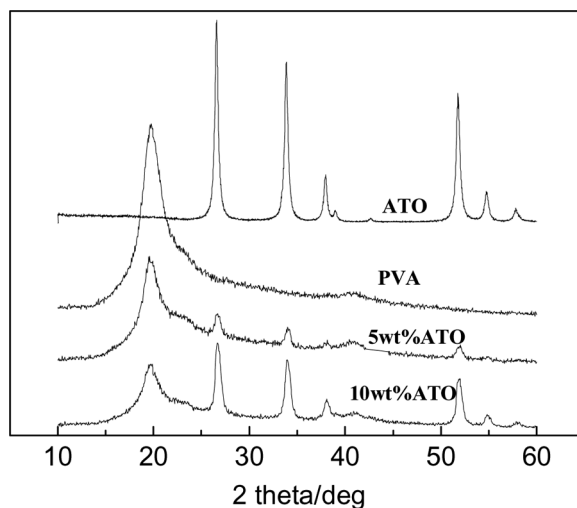


Figure 1: WXR D patterns of ATO, PVA and PVA/ATO nanocomposites.

(see Figure 1). The X-ray patterns of the nano-ATO displayed the presence of five peaks at $2\theta = 26.5^\circ$, 33.7° , 37.7° , 51.7° and 54.7° corresponding to the reflection of (110) (101) (200) (220) and (211). PVA shows only a scattering peak at $2\theta = 19^\circ$. The XRD patterns of the PVA/ATO nanocomposites appear at both the characteristic peaks of the pure PVA and nano-ATO. It is known that the crystalline nature of PVA results from the strong intermolecular interaction between PVA chains through the intermolecular hydrogen bonding [12]. From Figure 1, after being complexed with ATO, the intensity of the PVA diffraction peak weakens with the increasing amount of ATO. It should be the reason that the interactions between PVA chains and ATO particles led to the decrease of intermolecular interaction of PVA chains, which would result in decreasing the crystalline degree of PVA.

FTIR Analysis

Infrared spectroscopy has been proven to be a highly effective means of investigating specific interactions between polymers. The interaction between nano-ATO and PVA was studied by FTIR spectra, and representative FTIR spectra of the pure PVA and PVA/ATO nanocomposites with different ATO content are shown in Figure 2. Two characteristic bands at 3400 and 1090 cm^{-1} were observed. The absorption band at 3400 cm^{-1} in all spectra was attributed to the O-H stretching vibration band. And another absorption band at 1092 cm^{-1} was attributed to the hydroxy C-O stretching band. Notably, compared with pure PVA, the absorption band at 3400 cm^{-1} became wide and the intensity of the absorption bands at 3400 and 1090 cm^{-1} weaken with an

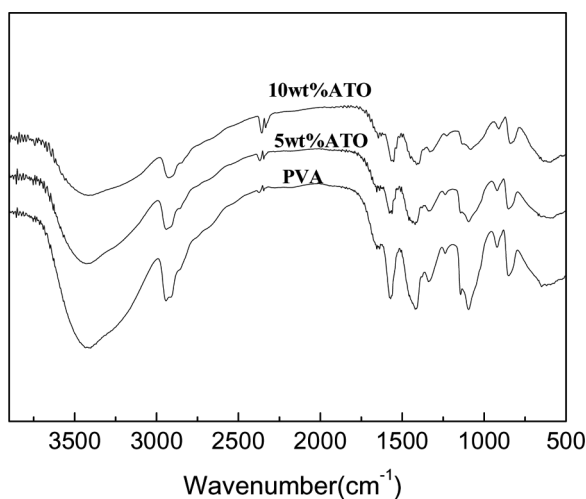


Figure 2: FTIR spectra of PVA and PVA/ATO nanocomposites.

increase nano-ATO content. This is indicative of a new hydrogen bond being formed between PVA and nano-ATO. The intensity of the band at 1090 cm^{-1} was also a measure of the degree of crystallinity of PVA [13]. Thus, this result clearly supported the suggestion that the introduction of nano-ATO decreased the degree of crystallinity of PVA, which was consistent with the XRD results.

SEM Analysis

The homogeneous dispersion of nanoparticles in the polymer matrix is one of the challenges for obtaining a composite with good mechanical properties. To further characterize the internal structure of the PVA/ATO composites, SEM observations of fracture surfaces are shown in Figures 3 and 4. The dark regions are related to the PVA phase and the bright regions to the conductive nano-ATO phase. Figure 3 gives the fracture surface of a PVA film containing 5 wt% ATO. The image clearly shows that ATO disperses well through the PVA. With further increase of nanoparticle loading to 10 wt%, ATO in the PVA is apt to aggregate into a network structure.

Conductivity Analysis

The variation of the electrical conductivity of composites vs. the content of nano-ATO was shown in Figure 5. PVA is electrically nonconductive and has conductivity of about 10^{-12} S/cm in a dry state at room temperature. It can be seen that the electrical conductivity of the PVA/ATO nanocomposite increases with increasing nanocomposites content. The incorporation of very

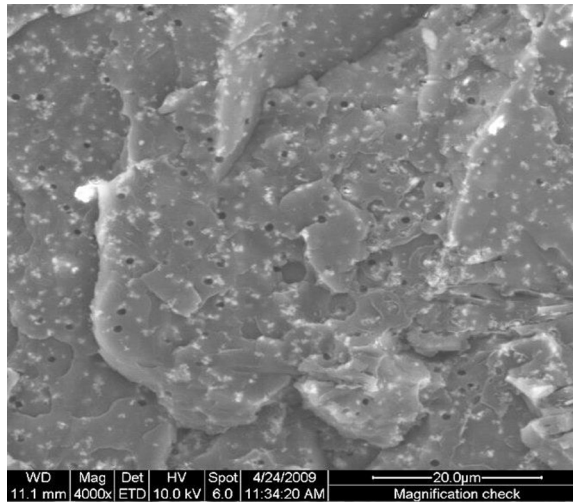


Figure 3: SEM micrograph of PVA/ATO nanocomposites with 5 wt% of nano-ATO content.

small amounts of nano-ATO into the PVA matrix had dramatically increased the conductivity of composites with a sharp transition from an electrical insulator to an electrical semiconductor. After the nano-ATO content reached 5 wt%, the electrical conductivity of the nanocomposites tended to level off with further increasing nano-ATO content. This demonstrates the very low percolation threshold value for a conducting nanocomposite prepared with nano-ATO, which is much smaller than that of conventional conducting macrocomposites [14].

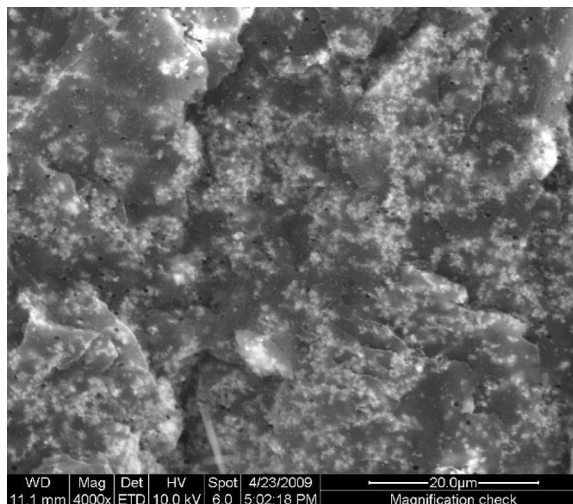


Figure 4: SEM micrograph of PVA/ATO nanocomposites with 10 wt% of nano-ATO content.

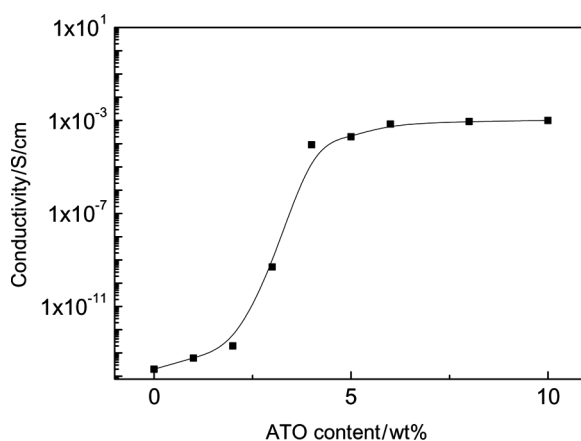


Figure 5: Electrical conductivity of PVA/ATO as a function of ATO.

Mechanical Properties

The tensile strength and elongation at break of the PVA/ATO composites with different ATO contents are shown in Figure 6. The tensile strength of PVA/ATO nanocomposites increased with increasing ATO content up to 5 wt% and then decreased at higher loading. The elongation at break behaves in a similar way. With low adding of ATO, the filler is uniformly dispersed in the PVA matrix. The filler has a high aspect ratio, which tends to improve interfacial bonding and form filler-polymer interaction because of the high specific surface area of the filler. The lower tensile strength of nanocomposites at a higher ATO loading was due to the inevitable aggregation of ATO

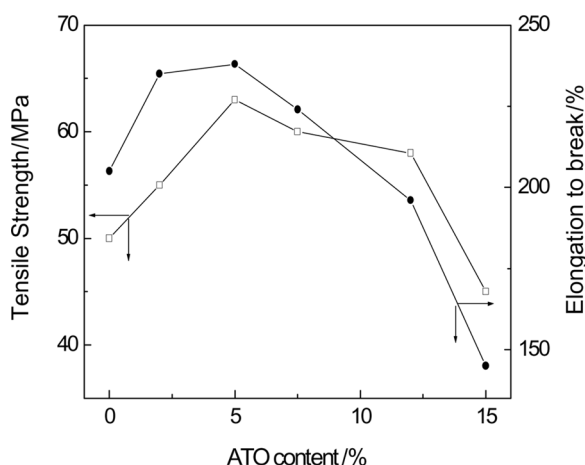


Figure 6: Effect of ATO content on tensile strength and elongation to break of composites.

nanoparticles (see SEM analysis). These aggregates are the weakest point in the composite which lead to earlier tensile break.

DSC Analysis

Study of the thermal transitions of PVA and the composite samples was performed by DSC measurements. The DSC curves obtained for various samples are represented in Figure 7. It shows that T_g of the nanocomposites shift to a higher temperature with the increasing of nano-ATO content. Such an effect on T_g has been reported to obey motion restrictions of the polymer chains in the nanoparticle-matrix interface [15]. When the polymer chains present strong interfacial affinity with the filler, a region of strongly bound polymer chains is formed. This region has been speculated to be within a few nanometers and called the “bound polymer layer” [16] and at higher lengths, it has been called the “interaction zone”. In this zone or region, the polymer chains exhibit a different behavior than that in bulk; the strong packing hinders chain segmental mobility, which occurs under standard conditions at T_g . Thus, more energy is required to allow the first thermal transition, shifting T_g to a higher temperature.

TGA Analysis

The TGA curves for the pure PVA and PVA/ATO nanocomposites with 5 wt% and 10 wt% ATO content in atmosphere are shown in Figure 8. As observed in Figure 8, pure PVA exhibited two weight-loss steps. The weight

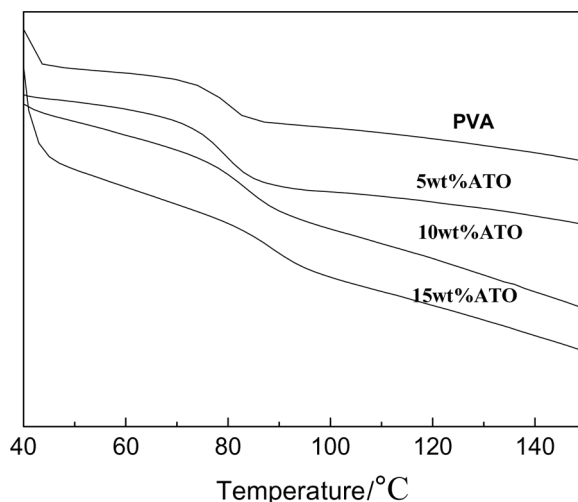


Figure 7: DSC curves of PVA and PVA/ATO.

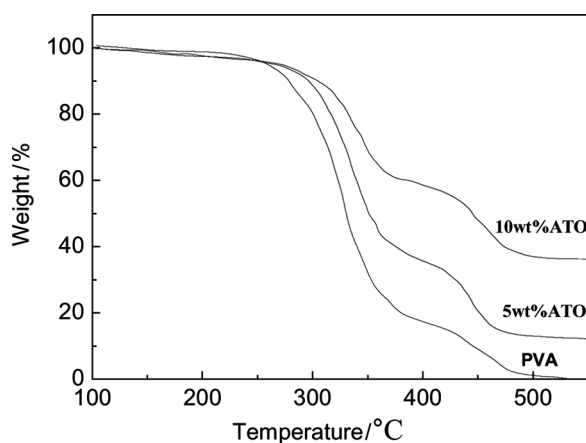


Figure 8: TGA curves of PVA and PVA/ATO composites.

loss around 350 and 450°C was considered to reflect the decomposition of the side chain and main chain of PVA [17,18], respectively. However, for PVA/ATO nanocomposites, three degradation steps could be observed. The first step was between 100 and 300°C, the second step was between 300 and 400°C, and the third step was after 400°C. The first weight loss process, which was associated with the loss of absorbed moisture and/or with the evaporation of trapped solvent, was independent of the composition for all samples. The second weight loss process corresponded to the degradation of PVA by dehydration on the polymer side chain, whose decomposition temperature was around 350°C. In the third weight loss process, the polymer residues were further degraded at approximately 450°C, corresponding to the decomposition of the main chain of PVA. As seen in Figure 8, the degradation temperature was ambiguous with the increase of the ATO. These suggested that some bonding between the polymer and ATO formed.

CONCLUSIONS

Conductive PVA/ATO nanocomposites exhibiting a reduced low threshold have been successfully prepared by solution blending. Electrical properties of the composites were characterized and the morphology were investigated via SEM, XRD, TGA and DSC. It was found that the 5 wt% ATO sample gave the highest tensile strength and elongation at break value among all the ATO compositions from 0 to 15 wt%. Thermal stability of the nanocomposites was found to be remarkably enhanced by the incorporation of ATO.

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