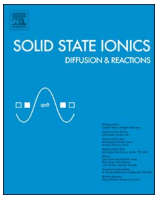
Solid State Ionics 320 (2018) 132–147

Contents lists available at ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi



Studies on free volume controlled electrical properties of PVA/NiO and PVA/TiO_2 polymer nanocomposites

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ARTICLE INFO

Keywords:
Free volume
Dielectric constant
Conductivity
Critical free volume
Interface

ABSTRACT

Microstructural characterization of poly(vinyl alcohol)/nickel oxide (PVA/NiO) and titanium dioxide (PVA/TiO_2) polymer nanocomposites has been performed by Positron Lifetime Technique (PLT). The increased positron lifetime parameter viz., o-Ps lifetime (τ_3) up to 1.0 wt% of NiO and up to 0.4 wt% of TiO_2 loading suggests the reduction in overall packing density of the polymer network and the formation of interface between PVA polymer matrix and NiO, TiO_2 nanoclusters. The decreased o-Ps lifetime (τ_3) at the higher concentration of TiO_2 loading indicates the improved interfacial interaction between the surface of TiO_2 nanoparticles and side chain of PVA polymer matrix. This is evident from Fourier Transform Infrared Spectroscopy (FTIR) studies. Scanning Electron Microscopy (SEM) studies demonstrate the formation of nanoclusters by the agglomeration of nanoparticles at higher wt% of nanofiller loading. The increased AC/DC conductivity of PVA/NiO and at lower concentration of TiO_2 in PVA/TiO_2 polymer nanocomposites suggests the increased mobility of ions and electric charge carriers. The decreased conductivity at higher concentration of TiO_2 indicates the reduced conducting pathways for the mobility of ions and electric charge carriers due to the increased ion aggregation. The increased dielectric constant and dielectric loss up to 1.0 wt% of NiO and 0.4 wt% of TiO_2 suggests the increased dipole polarization. The decreased dielectric constant after 0.4 wt% of TiO_2 is attributed to the reduced dipole polarization by the formation of thin immobile nano-layers and hence the polymeric chain mobility.

1. Introduction

Nowadays, studies on polymer nanocomposites have attracted much attention in view of their wide range of applications in the field of polymer nanotechnology. The polymer nanocomposites heavily rely on geometry, size distribution, aggregation and surface chemistry of organic/inorganic nanoparticles as well as matrix–nanoparticle interactions. Nevertheless, the properties of nanocomposites were found to depend on the type of nanoparticles, the content of nanofillers and nature to bridge chemically and physically with the polymer matrix [1,2].

The improvement in electrical properties of polymer nanocomposites for variety of electrical applications have been considerably investigated in the past [3–8]. The electrical properties of polymer nanocomposites can be suitably modified by the addition of nanofillers depending on their reactivity with the host matrix. The conductivity of polymer nanocomposites depends upon inter-particle distance of conducting fillers in the polymer matrix [9]. The polymeric nanocomposites are emerging as the excellent materials for energy storage devices with desirable high dielectric constants. However, the effect of nanofillers on the dielectric properties of polymer nanocomposites is not clear.

Generally, the interfacial interaction between polymer matrix and inorganic nanofillers are very important for determining the final performance of polymer nanocomposites. Depending on the chemical nature of the incorporating nanoparticles and the way in which they interact with the polymeric host matrix, the nanoparticle alters the physical properties to different degrees. The metal oxide nanofillers incorporated polymer matrix represents a new class of nanocomposite materials that has attracted significant scientific attention due to their wide range of dielectric and electrical insulation applications. Most of the metal oxide nanoparticles exhibit net negative surface charge and form strong ionic interactions with positively charged polymeric surfaces.

Due their good dispersibility in the polymeric system, nickel oxide (NiO) and titanium dioxide (TiO_2) are considered as the potential candidates in the fabrication of engineering nanomaterials for multifunctional applications. NiO and TiO_2 nanofillers are being incorporated into the polymeric matrix for developing polymer nanocomposites with improved electrical and dielectric properties. Nickel

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https://doi.org/10.1016/j.ssi.2018.03.006
Received 17 November 2017; Received in revised form 7 February 2018; Accepted 3 March 2018

and titanium based transition metal oxides with remarkable electrochemical properties have become a new kind of energy-storing materials [10,11]. Previously, the authors have studied PSAN/TiO_2, PVA/GO, PSF/TiO_2 and PSF/NiO polymer nanocomposites and reported the improved electrical properties [5,12,13].

Poly vinyl alcohol (PVA) is a potential material having high dielectric strength, good charge storage capacity and dopant dependent electrical and dielectric properties. PVA exhibits flexible polar side groups with a polar bond having intense dielectric transition. The electrical conductivity of PVA can be tailored to a specific requirement by the incorporation of suitable inorganic nanoparticles. The conducting nature of doped PVA is thought to be due to the high physical and chemical interactions between polymer chains and dopants.

The addition of NiO and TiO_2 nanoparticles into polyvinyl alcohol (PVA) matrix is expected to achieve conductive polymer nanocomposites with unique properties, which can be used as multifunctional material for different applications. The extensive studies on various properties of PVA based polymer nanocomposites by incorporating different types of nanoparticles such as gold, molybdenum disulfide, cuprous iodide, graphene, graphite oxide and graphene oxide etc., have been reported in the literature [3–8]. However, the effect of NiO and TiO_2 nanoparticles on free volume parameters, electric and dielectric performances of PVA/TiO_2 and PVA/NiO are nowhere reported. Therefore, in the present study authors report the effects of TiO_2 and NiO nanoparticles loading on the microstructural, electrical and dielectric properties of PVA/TiO_2 and PVA/NiO polymer nanocomposites. In addition, the variation in critical free volume with respect to nanofiller loading as a function of frequency of the applied AC field also discussed. The microstructural characterization of the polymer nanocomposites has been carried out by making use of one of the well-established technique viz., Positron Annihilation Lifetime Spectroscopy (PALS). Furthermore, attempt has been made to analyze the effect of concentration, size and type of the nanofillers on the conductivity, dielectric and free volume properties of polymer nanocomposites.

2. Experimental

2.1. Materials

The nanopowders of nickel oxide (NiO) and titanium dioxide (TiO_2) with particle diameter 50 nm and 7 nm, density 6.67 g/cm^3 and 5 g/cm^3 was purchased from Sigma Aldrich, USA and Sisco research laboratories, Mumbai respectively. Polyvinyl alcohol (PVA) having molecular weight of 124,000 and density 1.08 g/cm^3 was procured from SDFCL, Mumbai.

2.2. Preparation of polymer nanocomposites

Polymer films of PVA, PVA/NiO and PVA/TiO_2 nanocomposites filled with different concentrations of 50 nm size nickel oxide (NiO) and 7 nm size titanium dioxide (TiO_2) were prepared by solution casting method. Polymer solution of PVA was prepared by adding 5 g of PVA into 100 ml deionized water and stirred at 60 °C until a viscous transparent solution was obtained. Nickel oxide and titanium dioxide nanopowders dissolved in deionized water was added into the polymeric solution of PVA and stirred well to get homogeneous mixture. The solution was allowed to reach a suitable viscosity. The viscous solution was then poured into the glass dish and kept to dry in atmospheric air at room temperature. The prepared PVA, PVA/NiO and PVA/TiO_2 nanocomposites films were kept at 80 °C in Thermotek tubular oven for 6 h to eliminate the residual solvent. The polymeric films of thickness about 0.5 mm and dimension of 1 cm × 1 cm were cut and kept at the desiccators for 48 h at room temperature. These samples were used for XRD, FTIR, SEM, PALS, electrical conductivity and dielectric constant measurements.

2.3. Measurements

2.3.1. Positron annihilation lifetime measurements

Positron annihilation lifetime spectra of PVA, PVA/NiO and PVA/TiO_2 polymer nanocomposites were acquired using fast-fast coincidence Positron Lifetime spectrometer. Consistently reproducible spectra were analyzed into three lifetime components with the help of computer program PATFIT-88 [14] with proper source and background corrections. The detailed experimental description can be found elsewhere [5,12].

2.3.2. X-ray diffraction studies

X-ray diffraction spectra of PVA, PVA/NiO and PVA/TiO_2 nanocomposites were recorded using Rigaku Mini Flex 11 diffractometer with Ni filtered CuK∝ radiation of wavelength 1.5406 Å with graphite monochromator. X-ray diffraction spectra of as received PVA and PVA/NiO and PVA/TiO_2 nanocomposites for different filler concentration were taken in a glass sample holder. The X-ray scans were recorded in the 2θ range from 6°–60° with the scan speed of 5°/min in steps of 0.02°. The working voltage and current were 30 kV and 15 mA respectively. The crystallinity of PVA/NiO and PVA/TiO_2 polymer nanocomposites is evaluated by the deconvolution of XRD spectra using PEAKFIT4.1 software.

2.3.3. Scanning electron microscopy studies

The surface morphology of pure PVA, PVA/NiO and PVA/TiO_2 nanocomposites were characterized by means of scanning electron microscope (SEM) (ZEISS EVO 15, Germany) with the accelerating voltage of 15KV. The polymer nanocomposites were mounted on aluminum stubs and gold coated to avoid electrical charging during examination. All SEM images were taken at the magnification of 2KX.

2.3.4. FTIR studies

FTIR spectroscopic experiments were carried out using a Perkin Elmer Spectrum Version (model spectrum 2 series, NIOS2 Main software, USA) interfaced with Personal Computer (PC) for data processing. FTIR spectra of as received PVA, PVA/NiO and PVA/TiO_2 polymer nanocomposites for different filler concentration were run at ambient temperature using KBr disk method at a wave number range of 4200–600 cm^{-1}. The FTIR spectra were recorded by performing 4 scans for each sample at a resolution of 4 cm^{-1}.

2.3.5. Electrical conductivity measurements

The DC electrical conductivity of PVA, PVA/NiO and PVA/TiO_2 polymer nanocomposites as a function of nickel oxide and titanium dioxide nanoparticles wt% was measured by Keithley 2636A dual channel Source Meter. The samples of PVA, PVA/NiO and PVA/TiO_2 nanocomposites of dimension (1.2 cm × 1 cm × 0.47 mm) coated with silver paste were sandwiched between two electrodes. The computer program Lab Tracer 2.0 was used to record the voltage and current data. From the recorded voltage and current data, the value of bulk resistance (R_b) is calculated. The electrical conductivity (σ) was obtained by the relation $\sigma = t/R_bA$, where, “t” and ‘A’ are the thickness and the area of the contact respectively.

2.3.6. AC conductivity and dielectric measurements

The AC conductivity and dielectric measurements of PVA, PVA/NiO and PVA/TiO_2 nanocomposites as a function of nickel oxide and titanium dioxide nanoparticles loading have been carried out using HIOKI 3532-50 Hi-tester (Japan) model. The prepared samples of PVA, PVA/NiO and PVA/TiO_2 nanocomposites of dimension (1.2 cm × 1 cm × 0.47 mm) coated with silver paste on both sides for good electrical contact were sandwiched between two electrodes. The computer interfaced digital LCR meter in the frequency range from 100 Hz to 5 MHz at room temperature was used to record the conductance, tanδ and capacitance data. From these recorded data, the