Structural, Optical and Morphological Properties of PVA/ Fe_2O_3 Nanocomposite Thin Films

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Abstract

The addition of inorganic nanoparticles to polymers allows the modification of the polymer physical properties as well as the implementation of new features in the polymer matrix. Thin films of pure Poly Vinyl Alcohol (PVA) and PVA mixed with 4 %, 8 % & 12 % by weight of Fe_2O_3 nanoparticles (NP) were prepared by spin coating technique. The average size of Fe_2O_3 nanoparticles were 30nm – 40 nm. Structural, Optical and Morphological properties of the prepared nanocomposite films were studied by using Fourier Transform Infra Red Spectrophotometer,(FTIR) Ultra Violet Visible Spectrophotometer (UV-Vis) and Atomic Force Microscopy (AFM). The peaks in FTIR spectra of the prepared films show interaction between PVA and NP. Film of PVA with 8% concentration of NP was found to be better than other prepared samples. There is a decrease in optical band gap of prepared films with increase in concentration of NP. Morphological studies using AFM shows uniform grain structures of pure PVA and change in surface morphology with addition of NP. RMS roughness of PVA decreases with addition of 4 % and 8 % concentration of NP which could be due to more nucleation sites produced by NP. However RMS roughness of PVA increases for 12 % concentration of NP as compared to pure PVA. This could be due to agglomeration of NP.

Key words: Fe_2O_3 Nanoparticles, FTIR, AFM, RMS roughness.

Introduction

The studies of metal oxide nanoparticles/Polymer thin films are generating increasing interest due to their potential applications in household electronics, recording heads, memory and microwave devices [1, 2]. The addition of inorganic nanoparticles to polymers allows the modification of the polymer physical properties as well as the implementation of new features in the polymer matrix [3]. With decreasing particle size, the ratio of surface/volume increases, so that surface properties become crucial. Smaller the particles are, more important will be the surface properties, thereby influencing interfacial properties,

agglomeration behavior, and also the physical properties of the particles. The intensity of these properties changes depending upon the nature, composition, concentration and size of the nanoparticles [4]. Theoretical considerations predicted size-dependent energy band gap for nanoparticles [5- 6]. The large specific surface area of the filler causes the formation of an interfacial polymer layer (shell) attached to the particle core and leads to better dispersion in the polymer matrix [7]. The presence of this shell also will reduce the maximum filling degree of nanoparticles in the polymer matrix [8]. The physical properties of the polymer localized in the shell are different from the bulk polymer due to immobilization [9]. In the present work, Poly Vinyl Alcohol (PVA) was selected due to its low cost and high transparency. Besides it can readily mix with inorganic fillers. The present study involves the polymer nanocomposite of ferrous oxide with PVA for its structural, optical and band gap properties.

Materials and Methods

PVA was purchased from S.D. Fine chemicals, India with molecular weight 85,000 - 1,24,000 and its solution was prepared by adding 20 ml of deionized water to 1 g of PVA granules. The solution was stirred for 3 hours at 1000 rpm at the temperature of 363 K using a hot plate with magnetic stirrer. It was kept overnight in an air tight container to increase its viscosity and a clear solution of PVA was obtained. Thin films were prepared on clean glass slides by spin coater spinNXG-P1 supplied by Apex equipments, Kolkata, India. Fe_2O_3 nanoparticles were procured from Central Institute for Research on Cotton Technology, Mumbai, India. The average size of Fe_2O_3 nanoparticles were 30 nm – 40 nm. Nanoparticles were kept in water suspension to prevent their agglomeration. Before adding nanoparticles to PVA solution, the suspension was sonicated for 30 minutes in bath Sonicator at 40 KHz at room temperature. The PVA/ Fe_2O_3 solution was further sonicated for 1 hour to improve dispersion of nanoparticles in PVA matrix. The obtained solution was used for spin coating. Thin films of pure PVA, PVA mixed with 4 %, 8 % and 12 % by weight of Fe_2O_3 nanoparticles were prepared by spin coating at 1000 rpm for 120 seconds .The prepared samples were dried in Oven at 60 °C and kept in desiccator.

The prepared samples were characterized by FTIR (Jasco make in the range of 4000 to 400 cm^{-1} with a scan rate of 4 cm^{-1}) and *UV-VIS* (UV-1700 Series in the wavelength range of 300 to 800 nm). AFM measurements were performed with diInnova from Veeco Instruments in tapping mode (for both trace and retrace information) using a silicon nitride tip at ambient temperature and WxSM Analysis software was used for quantitative analysis

Results and Discussions

FTIR Spectral Analysis

The FTIR spectrum of PVA in Fig. 1(inset) indicates the PVA peaks at 2950 and 3500 cm^{-1}. Additional frequencies and shift in the frequencies were found in PVA nanocomposite spectra compared to PVA indicating formation of composites. The peaks in pure PVA spectrum at 2950 cm^{-1} and 3500 cm^{-1}

get shifted towards lower frequencies at 2926 cm^{-1} and 3330 cm^{-1} respectively due to incorporation of Fe_2O_3 NP. This indicates the bonding nature between iron oxide and polymer.

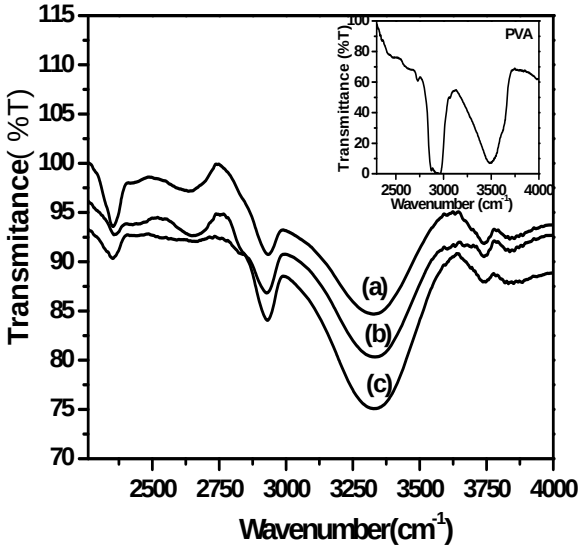

Fig.1. FTIR transmittance spectra of PVA (inset) and PVA with (a) 4 % ,(b) 8% and (c) 12 % concentration of Fe_2O_3 Nanoparticles.

Ultra Violet Visible Spectroscopy

As seen in the Fig.2, pure PVA is highly transparent with transmittance of around 98 %. After addition of 4% by weight of iron oxide nanoparticles, the transmittance of nanocomposite drops to 90%. Further addition of nanoparticles reduced the percentage transmittance to 88% and 86% for 8% and 12% samples respectively.

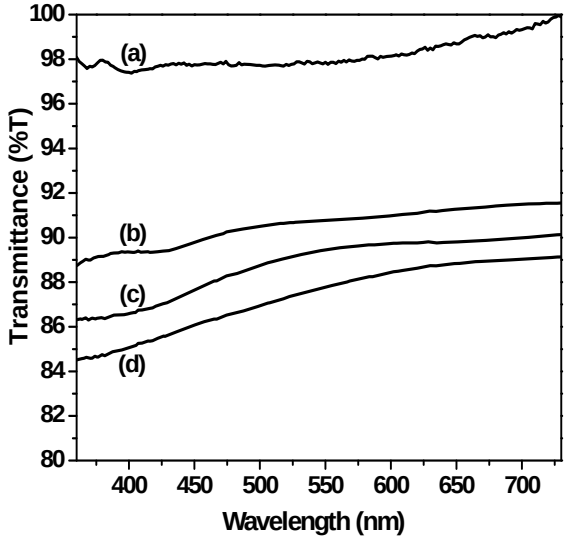

Fig.2. Transmittance Spectra of PVA (a) Pure, (b) with 4 %, (c) 8 % and (d) 12 % concentration of Fe_2O_3 Nanoparticles.

The absorption coefficient calculated from transmittance spectra was found to remain almost constant in the entire wavelength range of UV Visible spectra for pure PVA. The addition of nanoparticles brings in the wavelength dependence of absorption coefficient which increases with increase in filler concentration. This leads to optical band gap properties of nanocomposite films .The optical band gap of nanocomposite film with 4% concentration of Fe_2O_3 is 2.79 eV (Fig.3 (a)). Further addition of Fe_2O_3 reduces the band gap to 2.09 and 1.86 eV in case of 8% and 12 % samples (Fig.3(c, b)).

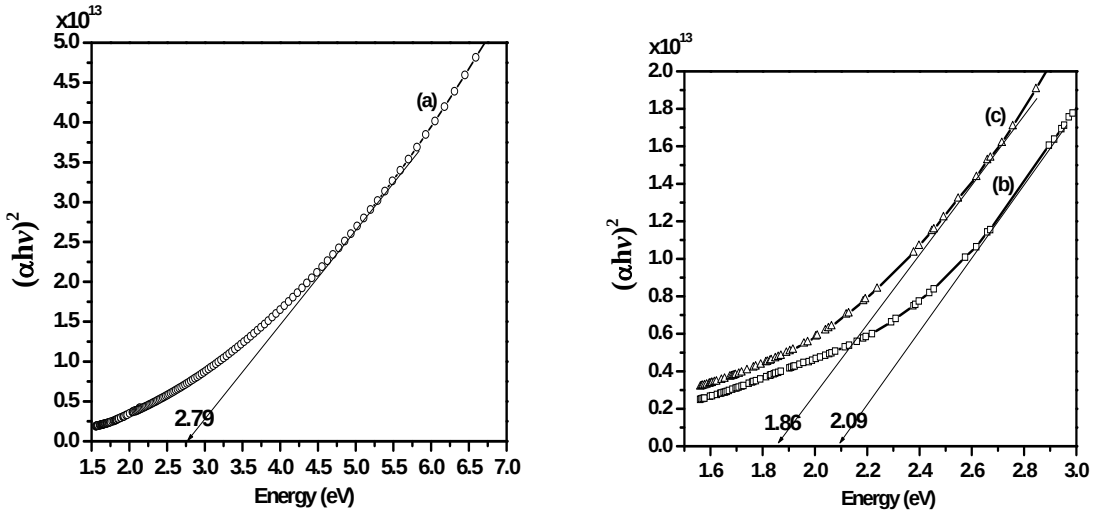

Fig.3. Optical Band Gap of PVA with
(a) 4 %, (b) 8 % and (c) 12 % concentration of Fe_2O_3 Nanoparticles.

Atomic Force Microscopy (AFM)

Morphological studies were performed by Atomic Force Microscopy. It shows uniform grain structures of pure PVA (Fig.4 (a)) and change in surface morphology with addition of NP as shown in Fig. 4 (b, c, d). The various parameters like variation of Average roughness, RMS roughness and Average height of PVA and its nanocomposites with various concentrations of Fe_2O_3 nanoparticles in PVA are calculated from AFM data (Table). RMS roughness of PVA decreases with addition of 4 % and 8 % concentration of NP and it increases for 12 % concentration of NP as compared to pure PVA. This could be due to more nucleation sites produced by NP. The increase in RMS roughness of 12 % concentration of NP is due to agglomeration of NP.

Table: Variation of Average roughness, RMS roughness, and Average height of Pure PVA and its nanocomposites with various concentrations of Fe_2O_3

Sample	Average surface roughness R_a (nm)	RMS surface roughness R_q (nm)	Average height (nm)
Pure PVA	1.45	2.18	10.45
PVA+4% NP	0.73	1.18	7.86
PVA+8% NP	1.23	1.43	5.79
PVA+12% NP	1.81	2.50	27.00

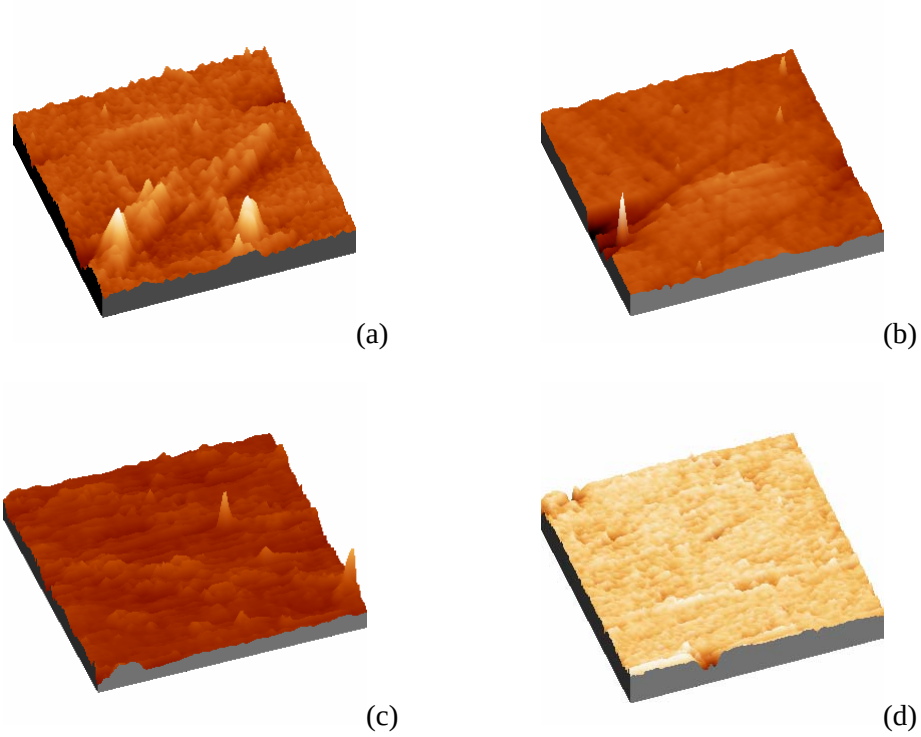

Fig.4. AFM 3D images (4µm x 4µm) of PVA, (a) Pure, (b) with 4 % , (c) 8 % and (d) 12 % concentration of Fe_2O_3 Nanoparticles.

Conclusions

In the present work, the polymer nanocomposite of PVA and Fe_2O_3 nanoparticles were prepared by spin coating method in different proportions. FTIR spectra analyses confirmed the incorporation of NP in polymer matrix. With the addition of 4 % iron oxide nanoparticles in PVA, the transmittance of nanocomposite decreased by 10 % whereas after further addition in steps of 4 % NP the transmittance decreased by just 2 %. One of the remarkable properties of PVA/ Fe_2O_3 nanocomposites was the change in the optical band gap with addition of NP. The optical band gap of nanocomposite film decreased with the increase of nanoparticles concentration. AFM images confirmed better incorporation of NP with 4 % and 8 % concentration.

References

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