Elucidation of modification in structural and thermal properties of polystyrene nanocomposite films

TAMANNA SHARMA and MANEESHA GARG*

Department of Physics, J. C. Bose University of Science and Technology, YMCA, Faridabad 121006, India

*Author for correspondence (garg_maneesha@yahoo.com)

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Abstract. Organic–inorganic nanocomposites have endured our interest in research, as they possess unique physical and chemical properties in various fields of application. In the present investigation, ZnO nanoparticles and polystyrene/zinc oxide nanocomposite films were successfully synthesized by sol–gel and solution-mixing techniques, respectively. These thin films were prepared with varying concentrations of ZnO, i.e., from 0 to 20 wt%. The thickness of these synthesized films was measured experimentally. These films were characterized to investigate the structural, morphological and thermal properties using Fourier transform infrared spectroscopy, atomic force microscopy, scanning electron microscopy (SEM) and differential scanning calorimetry (DSC) techniques. The roughness of film surfaces has been calculated from Nanoscope analysis software and correlated to the SEM images. The glass transition temperature of pristine and nanocomposite films is observed from the analysis of DSC data.

Keywords. Nanocomposites; Fourier transform infrared spectroscopy; AFM; SEM; glass transition temperature.

1. Introduction

Nowadays, organic–inorganic nanocomposites experienced a lot of attention due to their excellent and remarkable properties. The introduction of filler into polymer leads to changes in mechanical, electrical and optical properties. This change was observed due to the nanosize of particles and showed great deviation in properties than pristine materials. Semiconductor oxide nanoparticles have been widely studied for the last few decades [1–4]. They were enduring attention due to their advanced applications in UV absorption and optoelectronics. They were being used with polymers for tuning the physical properties of polymer owing to unique applications of nanocomposites as solar cells, gas sensors as well as electrical and optical devices [5–7]. Among various inorganic and semiconductor materials, zinc oxide (ZnO) is a direct wide bandgap semiconductor, and it has large excitonic binding energy (= 60 meV) at room temperature. This energy allows an intense near-band-edge excitonic emission at both room and higher temperatures. ZnO is a superior material because of its potential applications in optoelectronic devices, viz. LEDs in both UV and visible regions. As energy corresponding to the bandgap of ZnO lies in UV region, it can work as an efficient UV absorber [8–13].

Filler-based polymer nanocomposites are an interesting research for several applications having advantage of both filler and polymer. These nanocomposites benefit from the improved physical properties due to the addition of nanofillers. The demand for polymer nanocomposites is increasing due to their lightweight, thermal, chemical and moisture resistance, biocompatible and transparent nature. Polymeric materials are preferred where other engineering materials fail. Making nanocomposites is one of the simplest methods to improve the properties of polymers. Out of the variety of polymers, polystyrene (PS) is chosen as a host matrix for present investigations due to its excellent physical and chemical properties. It is one of the most stable and commercial polymers having ease of processability, low cost, lightweight, thermally insulated and low water absorption capability [14–16]. It is a clear and transparent polymer and suitable for optical and UV-shielding applications [6, 12, 17–19]. The polystyrene/zinc oxide (PS/ZnO) nanocomposite films were prepared by different researchers using various techniques [14, 17]. The other synthesis techniques are responsible for the change in structural and morphological properties of the materials. The addition of nanofillers into PS matrix results in the improved properties of PS owing to its application in optoelectronics [15, 17].

In the present work, ZnO nanopowder and PS/ZnO nanocomposite films were synthesized at room temperature using sol–gel and solution-mixing techniques, respectively. These nanocomposite films were prepared with 0, 5, 10, 15 and 20 wt% content of ZnO and characterized to observe the change in physical and chemical properties of polymer...
and composites. These prepared nanocomposite films were abbreviated as PS-1, PS-2, PS-3, PS-4 and PS-5 for 0, 5, 10, 15 and 20 wt% of ZnO. Hence, the main focus of this study is to investigate the effect of ZnO on the structural, morphological and thermal properties of PS polymer.

2. Experimental

2.1 Sample preparation

For the synthesis of polystyrene/zinc oxide (PS/ZnO) nanocomposite films, firstly, ZnO nanopowder was synthesized via sol–gel method. Zinc acetate dihydrate (Merck Specialities Pvt. Ltd., Mumbai, India) and sodium hydroxide were taken as the precursor, ethanol as a solvent and distilled water as a medium. Here, 2.2 g of zinc acetate dihydrate is added to 15 ml of distilled water in a beaker to make its aqueous solution. Another beaker was used to prepare an aqueous solution of 8 g NaOH in 10 ml of distilled water. After a while, NaOH solution was added dropwise to the zinc acetate dihydrate solution with constant stirring until a clear solution was obtained. Further, 100 ml ethanol was added dropwise to the obtained solution which turns milky-white. After 24 h, white precipitates settled down on the bottom of the beaker. These precipitates were extracted from the beaker and centrifuged at 2000 rpm. Finally, these precipitates were dried at 80°C for an hour and annealed further at 300°C for 4 h to obtain purified ZnO nanopowder of average size 18.22 nm. This study was confirmed by X-ray diffraction, Fourier transform infrared (FTIR) and UV–visible spectroscopy [20].

The preparation of PS/ZnO nanocomposite films was carried out via Solution-mixing method. To synthesize pristine polystyrene (PS) film, 2 g of polystyrene powder (Polysciences) was dissolved in 50 ml of toluene. The solution was stirred for 30 min using a magnetic stirrer. The above solution is further sonicated using Probe Sonicator (Labsonic Ultrasonic Homogenizer) for 1 h to obtain homogeneous solution of PS. This homogeneous solution is poured onto a plain glass plate and placed to a perfectly levelled surface at room temperature for 24 h for the complete evaporation of solution in a dust-free chamber. Hence, transparent PS film was obtained. Further, to obtain PS/ZnO nanocomposite films, ZnO nanopowder was added to the homogeneous solution of PS. Then, the above solution is sonicated using Probe Sonicator for 1 more hour owing to the complete dispersion of ZnO powder into PS solution. This solution is now poured onto the plain glass plate and placed it in dust-free place at room temperature for 24 h for the complete evaporation of the solution. Repeat this process to obtain PS/ZnO nanocomposite films for different ZnO nanoparticle concentrations (5, 10, 15, 20 wt%; figure 1).

3. Results and discussion

3.1 Thickness measurement of films

The thickness of synthesized PS/ZnO nanocomposite films with different concentrations of ZnO (0, 5, 10, 15, 20 wt%) was measured using a Digital microscope (OLYMPUS DSX1000 High Resolution Model). The thickness of all prepared samples was observed in the range of 45–50 microns and some of the images are depicted in figure 2.

3.2 Characterizations

The synthesized PS/ZnO nanocomposite films were characterized using different techniques like FTIR, atomic force microscopy (AFM), scanning electron microscopy (SEM) and differential scanning calorimetry (DSC) for their structural, morphological and thermal investigations. The presence of inorganic and organic materials and their chemical composition was confirmed from infrared spectroscopy. The FTIR spectrum was recorded on Bench-top Spectrum Two Perkin Elmer Spectrometer in the wavenumber range 4000–400 cm–1 in ATR-transmission mode. The AFM images of synthesized films was recorded on Bruker (Dimension Edge with Scan Asyst) system. The SEM images of ZnO and nanocomposite films were taken on Zeiss (EVO18) Scanning Electron Microscope. The thermal investigation of these films was carried out for finding their glass transition temperature using LABSYS EVO 1150°C DSC131 EVO analyzer in the temperature range RT (room temperature) to 200°C.

3.2a FTIR spectroscopy: FTIR spectroscopy is the technique which tells about chemical and molecular structure of the samples. Figures 3 and 4 show the FTIR spectra of synthesized pristine PS and PS/ZnO nanocomposites at different concentrations, respectively.

These spectra have characteristic absorption bands at 3108 cm–1, 3083 cm–1, 3062 cm–1, 3024 cm–1 (C–H stretching vibrations in benzene ring), 2999 cm–1, 2921 cm–1, 2849 cm–1 (C–H asymmetric and symmetric vibrations in aliphatic chain attached to phenyl group), 1601 cm–1, 1581 cm–1, 1542 cm–1, 1492 cm–1 (C=C and simple stretching vibrations in aromatic ring), 1452 cm–1 (C=O stretching vibrations), 1372 cm–1 (C–H out-of-phase bending vibrations in aliphatic chain), 1238 cm–1, 1132 cm–1 (simple vibrations in aliphatic chain), 1067 cm–1 (C–O stretching vibrations), 1003 cm–1, 963 cm–1, 943 cm–1, 907 cm–1 (–CH=CH– cis/trans out-of-phase bending vibrations), 842 cm–1 (–CH2 wagging bending), 753 cm–1 (–C–H, –CH=CH– out-of-phase vibrations). The bending vibrations at 1601 cm–1, 1492 cm–1, 1451 cm–1, 1027 cm–1, 753 cm–1 and 696 cm–1 may also be due to deformation and skeletal vibrations of C–H in PS [4, 21, 22]. PS/ZnO nanocomposites have some extra absorption bands at
3421 cm⁻¹, 465 cm⁻¹ and 419 cm⁻¹, which confirm the presence of ZnO nanoparticles in the host matrix. The broad band at 3392 cm⁻¹ is attributed to hydroxyl group [12]. This peak is absent in the spectrum of pure PS. This suggests that a small quantity of water is absorbed by ZnO powder during the fabrication of nanocomposite films. Band observed at 465 and 419 cm⁻¹ is due to the stretching of Zn–O bond [21]. The intensity of peaks is increased with the increase in concentration of ZnO among host matrix and it confirms the interaction between functional groups of PS polymer matrix and ZnO powder. Similar result has also been reported by Abutalib [9], Alghunaim and Alhusaiki-Alghamdi [23], Al-Naim et al [24] and Srinivasulu et al [25].

3.2b Atomic force microscopy: The two-dimensional and three-dimensional images of pristine PS and PS/ZnO nanocomposite films are shown in figures 5 and 6, respectively. These were scanned in the area range from 1 × 1 μm to 4 × 4 μm. This study was carried out to investigate the surface morphology of pristine and nanocomposite films. AFM analysis is generally correlated to the optical properties of the samples. It describes the quantitative surfacial information of transparent films, which might not be possible to study with other techniques. AFM provides the surface architecture of insulating, semi-conducting and highly conducting films. It gives information about surface morphology in terms of amplitude of peaks and valleys. For the investigation about the surface corrugations in a range from few nanometres to micrometres, quantitative analysis of AFM technique is employed in the present investigation. It gives results in terms of metrological measurements like grain size, grain boundaries and roughness (i.e., irregular morphology) of the samples [26, 27]. The grain size of the material is calculated with respect to its diameter or height. The irregularity on the surface using height deviations can be explained in terms of roughness. The roughness parameters include $R_{rms}$ (root mean square roughness) and $R_a$ (average roughness). Average roughness has been calculated using the difference between top of the peaks and the bottom of the valleys. The irregularity on the surface (roughness) of the material may also be due to the synthesis method and diffusion or nucleation sites that were created during doping. Roughness of the surface ($= R_{rms}$) can be calculated using height of the tip ($x_i$) and number of data points ($n$) using equation (1) as [28],

$$\sum \frac{x_i^2}{n} = R_{rms}$$

The average grain size of these films was measured from AFM images using Nanoscope analysis software. The grain size of 100.12 nm is observed for pristine PS. The sudden decrease in grain size from 100.12 to 54.21 nm was recorded for 5 wt% ZnO nanocomposite films. This is due to the ZnO which may be resting on an uneven surface. For 10 and 15 wt% of ZnO among PS matrix, agglomeration starts due to which grains are not distinguishable, hence cannot be measured. However, with increase in ZnO concentration to 20 wt%, the grain size again increases to 85.52 nm and becomes separately visible. The calculated grain size of pristine and nanocomposite films has been reported in table 1.

The root mean square (rms) and average roughness of pristine film are 25.1 and 19.4 nm, respectively, obtained through AFM analysis. The roughness of nanocomposite films reduces at 5 wt% ZnO and increases for 10 and 15 wt% ZnO, but again decrease at 20 wt% ZnO. The decrease
in roughness is may be due to the strong coordination between particles of PS and ZnO. However, the increase in roughness of the samples may be due to the improper diffusion in thin films. The change in roughness of the films with different fluences of irradiation was reported by Chauhan and Kumar [28].
Skewness and Kurtosis are two functional parameters that are necessary for finding the symmetry, asymmetry and sharpness like features of the surface topography. Skewness explains the symmetry in terms of the surface height distribution of the samples. The moment of skewness will be positive when the surface has disturbed symmetry, i.e., asymmetrical surface and contains a large number of irregular peaks than valleys. The moment of skewness is zero when the distribution of height profile is symmetrical, i.e., symmetrical surface. It is negative when the surface is highly planar and valleys are present predominantly [29]. The coefficient of skewness can be calculated using the equation (2) as follows:

\[ S_{sk} = \frac{1}{NR_q^3} \left[ \sum_{i=1}^{N} x_i - \bar{x} \right]^3 \]  

The fourth parameter of the surface amplitude function is kurtosis and is the measure of sharpness. It measures the distribution of positive and negative spikes. In terms of Gaussian amplitude distribution, if the coefficient of kurtosis is 3, then the surface is known as Mesokurtic and if it is less than 3, then the surface is called Platykurtic (i.e., flat surface and proper distribution) [29]. However, if the surface has large number of peaks than valleys, then the coefficient of kurtosis is more than 3. The coefficient of kurtosis can be calculated using the relation given by equation (3) as

\[ S_{ku} = \frac{1}{NR_q^4} \left[ \sum_{i=1}^{N} x_i - \bar{x} \right]^4 \]  

In the present investigation, the value of skewness is observed positive for all pristine and nanocomposite films except the film having 10 wt% concentration of ZnO. The positive value of skewness shows the surface has many irregular peaks than valleys but the negative value shows

Figure 3. FTIR spectrum of synthesized pristine polystyrene (PS-1) film.

Figure 4. FTIR spectra of (a) PS-2, (b) PS-3, (c) PS-4 and (d) PS-5 nanocomposite films.

Figure 5. Two-dimensional AFM images of nanocomposite films (a) PS-1, (b) PS-2, (c) PS-3, (d) PS-4 and (e) PS-5.
maximum planar surface in which valleys are primarily present. This was clearly observed from 3D images of the films. The value of kurtosis for pristine and nanocomposite films is observed more than 3 in the present study. It indicates the film surface has a large number of peaks as compared to valley and are confirmed from 3D images. The calculated value of corrugation parameters, viz., average roughness, rms roughness, skewness and kurtosis for the synthesized pristine and nanocomposite films are listed in Table 1.

3.2c Scanning electron microscopy: Scanning electron microscopy is an analytical technique that gives highly magnified images to study the topography of the samples. These images were obtained with the help of focused high-energy beams. Figure 7 shows the SEM images of ZnO nanopowder, pristine PS and PS/ZnO nanocomposite films. The micrograph of ZnO was taken with X15000 magnification in scale of 1 μm. It shows the nanorods and nanoflowers-like structure of synthesized ZnO. These nanoflowers consist of a bunch of nanorods centrally outward. The images of pristine and nanocomposite films were taken with X3000 magnification in a scale of 5 μm. The pristine PS film consists of circular patterns as depicted in the micrograph. These circular patterns do not have long-range order confirming the amorphous nature of pristine PS. The surface of the film having 5 wt% ZnO is very clear and shows long-range order compared to pristine PS. In this film, the ZnO shows its presence along with PS circular patterns. The nanocomposite films having a higher concentration of ZnO (i.e., 10 and 15 wt%) depicts disturbed surface due to the uneven agglomeration of ZnO. The surface of nanocomposite films with 20 wt% ZnO shows a regular pattern having disturbed symmetry of circular PS pattern. It shows the embedding of ZnO on the surface of PS polymer due to its nucleating effect. These images are in good agreement with AFM results of this study.

3.2d Differential scanning calorimetry: Differential scanning calorimetry is a thermal characterization technique that is used to investigate the response of polymers to heating. It gives us insight into finding the glass transition temperature and melting temperature of polymeric materials. The physical and thermal transitions of these materials can be observed with this technique. During the heating cycle, glass transition temperature and melting temperature are measured and by subsequent cooling crystallization temperature can be determined. The glass transition temperature is an important parameter for any thermoplastic polymer, as its property changes drastically above this temperature [11, 30]. In the present investigations, the pristine and nanocomposite films were studied using DSC and change in glass transition temperature has been measured. The glass transition temperature of pristine PS is 351.42 K (= 78.42°C) measured experimentally. The glass transition temperature for pristine PS has been reported by different research groups in the range of 355–370 K [1, 31, 32]. This temperature increases to 396.56 K for the film having 5 wt% ZnO and then decreased to 376.54 K for 10 wt% ZnO nanocomposite film. For 15 wt% ZnO films, the temperature is slightly increased to 370.49 K but further decreased to 357.64 K for higher concentrations of ZnO, i.e., 20 wt% (listed in Table 2).

Table 1. Various parameters from AFM analysis of PS/ZnO nanocomposite films.

<table>
<thead>
<tr>
<th>Samples</th>
<th>PS-1</th>
<th>PS-2</th>
<th>PS-3</th>
<th>PS-4</th>
<th>PS-5</th>
</tr>
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<tbody>
<tr>
<td>Grain size (nm)</td>
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<td>—</td>
<td>—</td>
<td>85.52</td>
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<td>54.9</td>
<td>10.4</td>
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<td>0.563</td>
<td>—</td>
<td>5.87</td>
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<td>5.56</td>
<td>6.34</td>
<td>16.4</td>
<td>56.1</td>
</tr>
</tbody>
</table>

Figure 6. Three-dimensional AFM images of nanocomposite films: (a) PS-1, (b) PS-2, (c) PS-3, (d) PS-4 and (e) PS-5.
4. Conclusions

The ZnO nanopowder, pristine PS and PS/ZnO nanocomposite films at different wt% of ZnO were successfully synthesized via sol–gel and solution-mixing techniques, respectively. These were characterized using FTIR, AFM,
SEM and DSC techniques to study structural, morphological and thermal changes in PS matrix due to the addition of ZnO. The thickness of prepared pristine and nanocomposite films was measured in the range 45–50 μm. The peak observed at 417 cm–1 in Raman spectra of nanocomposite films shows the incorporation of ZnO into PS. The glass transition temperatures of pristine and nanocomposite films are observed in the range 351–397 K. The result of all characterization shows coordination of PS polymer with ZnO and are in good agreement with each other. The nanocomposite films having 10 and 15 wt% of ZnO show some deviation in characteristics as compared to the films having 5 and 20 wt% of ZnO.

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