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Preparation and Characterization of ZnO/polystyrene Nanocomposite Films Using Ultrasound Irradiation

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Abstract In the present work, thin films containing nano zinc oxide and polystyrene were prepared via sol-gel process followed by film casting with 5 wt% concentration of ZnO. The prepared nano composite films were characterized using atomic force microscopy (AFM), Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD) analysis, differential scanning calorimeter (DSC) and UV-Vis analysis. Atomic force microscopy showed that ZnO nano particles were homogeneously dispersed in the polystyrene matrix, and root mean square (RMS) was 5.24 nm for neat polystyrene and found to be 6.2 nm for ZnO/polystyrene composite film. The introduction of ZnO nano particles increased the glass transition temperature by 6.81°C. The transmittance and absorbance of UV-Vis light exhibited normal spectra for these films. The X-ray diffraction pattern verified the hexagonal structure of nano ZnO and FT-IR spectra evidenced the existence of ZnO nano particles and polystyrene in ZnO/Ps composite film.

Keywords Sol-gel, ZnO nanoperticles, Polystyrene, AFM, XRD, DSC, FT-IR and UV-Vis

1. Introduction

Nowdays, a lot of work has been done on organic/ inorganic nanocomposite films. A combination of organic and inorganic materials results in the formation of composites that show the properties of both components, creating wide scope of applications in science and technology. Besides, improvements of many properties are achieved at a very low loading of nanoinorganic materials, compared to micro-sized fillers [1-6].

Among many inorganic materials, ZnO is specifically interesting owing to its variety of application fields like solar cells, gas sensors, Varistors, luminescent devices and antibacterial activity. When the size of ZnO crystal decreases to nano scale, it can have mechanical, optical, electrical, thermal properties and antibacterial activity quite different from the bulk [7-16]. Nano particles are much more reactive than larger particles because of their small size and large surface area. They have many advantages like high surface to volume ratio, good chemical, biocompatibility and easy fabrication which makes them appropriate for preparation hygienic surfaces [17-24].

The polymer matrix composites are very important as they are most widely used because of their lightness, ease of fabrication and a variety of other properties [25-31]. ZnO nanoparticles can be prepared easily via sol-gel or wetchemical method, thermal decomposition and chemical vapor route [32-37].

A great deal of research has been focused on the development of ZnO/polymer nano composite materials using different polymer systems. Polystyrene polymer is transparent thermoplastic material, with lots of prospects for making composite material with nano structured ZnO. Introduction of ZnO filler into polymeric matrices can modify their optical, electrical and other properties [38-44].

The present work is a simple attempt to prepare and characterize of ZnO/polystyrene nano composite thin films via mixing and casting process.

2. Experimental Section

All chemicals were purchased from a Merck company and used without further purification. The solutions were prepared by using distilled water. Preparation of nano zinc oxide are illustrated else where [45]. In brief, gel of zinc oxide was prepared as follows: 12.6g of zinc acetate dihydrate was dissolved in 400ml of distilled water, then 600ml of ethanol was added slowly at 50°C, and 6ml of H_2O_2 (47%) was added dropwise then mixed for one hour. Then, this solution was placed in an ultrasonic vessel with rated output power of 750 W and frequency 24 kHz, to get clear solution and keptuntil use. Sonics vibra cell from USA sonics and materials, INC company was used in this

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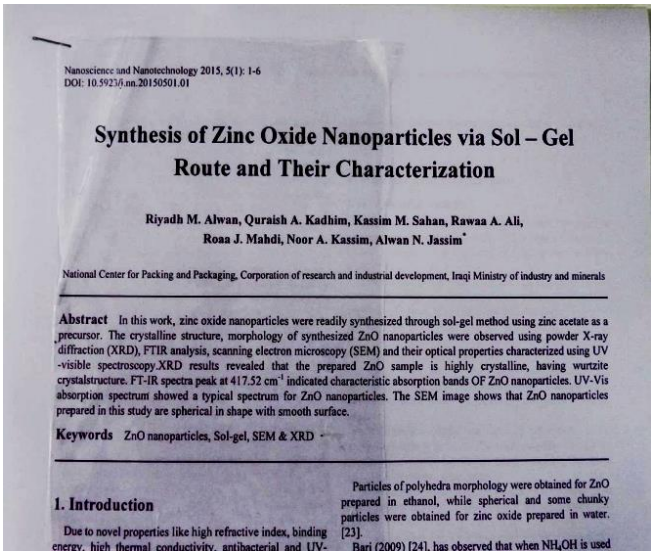
experment. For comparison purpose, we prepared nano zinc oxide powder by drying part of the above solution in oven for several hours at 80°C.

To prepare ZnO/polystyrene nano composite film, in a typical experiment, 2g of polystyrene (Sabic company) was dissolved in 50ml of toluene and then directly added into the prepared gel of ZnO. The concentration of ZnO was taken as 5 wt% to polystyrene. The solution mixture was then poured into 10x15 cm clean and dry glass mold. The solvents were evaporated slowly in a dust free chamber at room temperature, then composite films were obtained after evaporation and then heated for several hours at 80°C to remove any solvents and to convert zinc gel into zinc oxide nano particles. Also, neat polystyrene film without nano material was prepared similarly to this procedure with similar thicknesses.

3. Results and Discussion

The prepared composite thin films were flexible crack free and the achievement of transparency can be readily seen by nacked eyes. Figure 1 shows the photograph image of the film cast from toluene with 130 µm thickness in average.



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Synthesis of Zinc Oxide Nanoparticles via Sol – Gel Route and Their Characterization

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Abstract In this work, zinc oxide nanoparticles were readily synthesized through sol-gel method using zinc acetate as a precursor. The crystalline structure, morphology of synthesized ZnO nanoparticles were observed using powder X-ray diffraction (XRD), FTIR analysis, scanning electron microscopy (SEM) and their optical properties characterized using UV -visible spectroscopy.XRD results revealed that the prepared ZnO sample is highly crystalline, having wurtzite crystalstructure. FT-IR spectra peak at 417.52 cm^{-1} indicated characteristic absorption bands OF ZnO nanoparticles. UV-Vis absorption spectrum showed a typical spectrum for ZnO nanoparticles. The SEM image shows that ZnO nanoparticles prepared in this study are spherical in shape with smooth surface.

Keywords ZnO nanoparticles, Sol-gel, SEM & XRD

1. Introduction

Due to novel properties like high refractive index, binding energy, high thermal conductivity, antibacterial and UV-

Particles of polyhedra morphology were obtained for ZnO prepared in ethanol, while spherical and some chunky particles were obtained for zinc oxide prepared in water. [23].

Bari (2009) [24], has observed that when NH_4OH is used

Figure 1. Photograph of the nanocomposite film prepared by casting. The thickness of the film is around 130 µm. The amout of ZnO was fixed to 5 wt%

AFM

AFM imaging technique has proved to be effective to study the morphology of ZnO/PS nanocomposite films. Due to soft polystyrene polymer surface we used tapping mode atomic force microscopy (AFM) at scan rate of 0.8 Hz using (INTEGRA) Scanning probe microscope from Russian NT-MDT company.

AFM images obtained for the nano composite films in all the samples verified spherical morphology for the ZnO nanoparticles. Figure 2 shows the AFM 2-D image and corresponding 3-D image of the ZnO /Ps nano composite film in a scan area of 2X2µm. Also, AFM analysis shows good distribution of ZnO nanoparticles in polymer film. Besides, a large amount of nano pits was found on polystyrene film surface. The nanoparticles had a size distribution centered around70 nm, with a few particles around 80nm, resulting in an average size of 70 nm. The Root mean square (RMS) roughness of the composite filmwere found to be 6.2nm, and was 5.24 nm for plain polystyrene film.

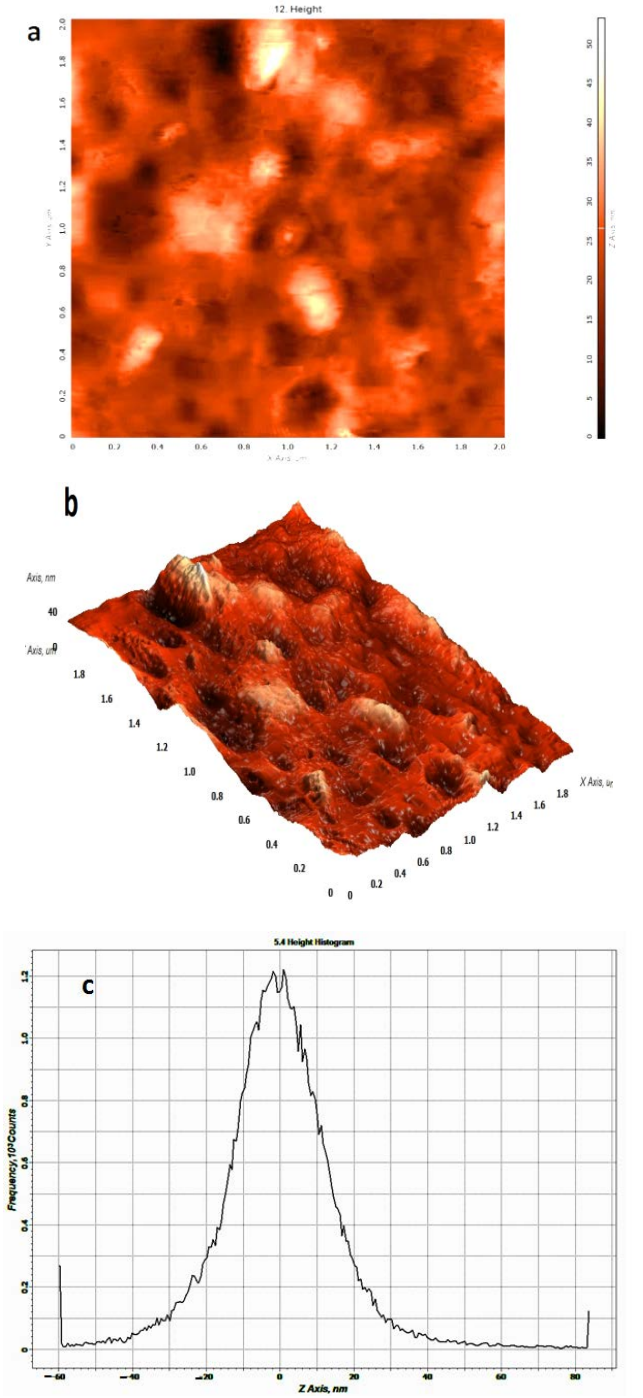

Figure 2. AFM 2-D image (a) and its corresponding 3-D image (b) of the ZnO/PS nano composite film in a scan area of 2X2 µm, and (c) shows good dispersion of nanoparticles in PS matrix

FT-IR spectroscopic studies

The FT-IR spectra of ZnO/PS nano composite film are shown in figure 3. The FT-IR spectra show absorption at 1760.66, 1532.97 and 1369.12 cm^{-1} which are characteristic vibration bands of aromatic C=C contributing from styrene units. The absorption peaks at 3028 cm^{-1} and 2849.81 $cm^{-1}$are assigned to the asymmetric and symmetric stretching vibrations of $–CH_2$ group respectively. The absorption bands ranging from 3600-3028.02cm^{-1} are assigned to aromatic C-H stretching vibration. In addition, the main peak of ZnO nanoparticles in ZnO-PS nano composite film was observed at 419.07 cm^{-1}. These results were consistent with previous works reported by others [39, 30, 31].

XRD

X-ray diffraction can be used for characterization and identification of nano particles. In this study, XRD patterns were taken on XRD SHMADZU 6000 diffractometer equiped with Cu-Ka (1.5418 A°) radiation operation at 40kv and 30mA. Scanning was carried out in the 2θ range from 5° to 80° The powder samples were scanned at a scan speed of 5° per minute, and the film samples, at a scan speed of 2° per minute.

The XRD pattern of ZnO/PS nano composite film is shown in Figure 4. The pattern shows a broad, noncrystalline peak of PS, and more intense and crystalline diffraction peaks of ZnO. The diffraction peaks with 2θ values of 31.74°, 36.83° and 47.62° corresponding to (100), (101) and (102) planes which indicate the hexagonal structure of ZnO. The average particle size is determined from the X-ray lines broadening using the scherrer equation:

$$\beta = k\,\lambda / d\cos\theta$$

Where β: is the full width at half maximum (f w h m) in radians of the diffraction peak,

λ: is the X-ray wavelength,

k: is a constant (0.89);

θ: is the Bragg angle of the peak and

d: is the average particle size.

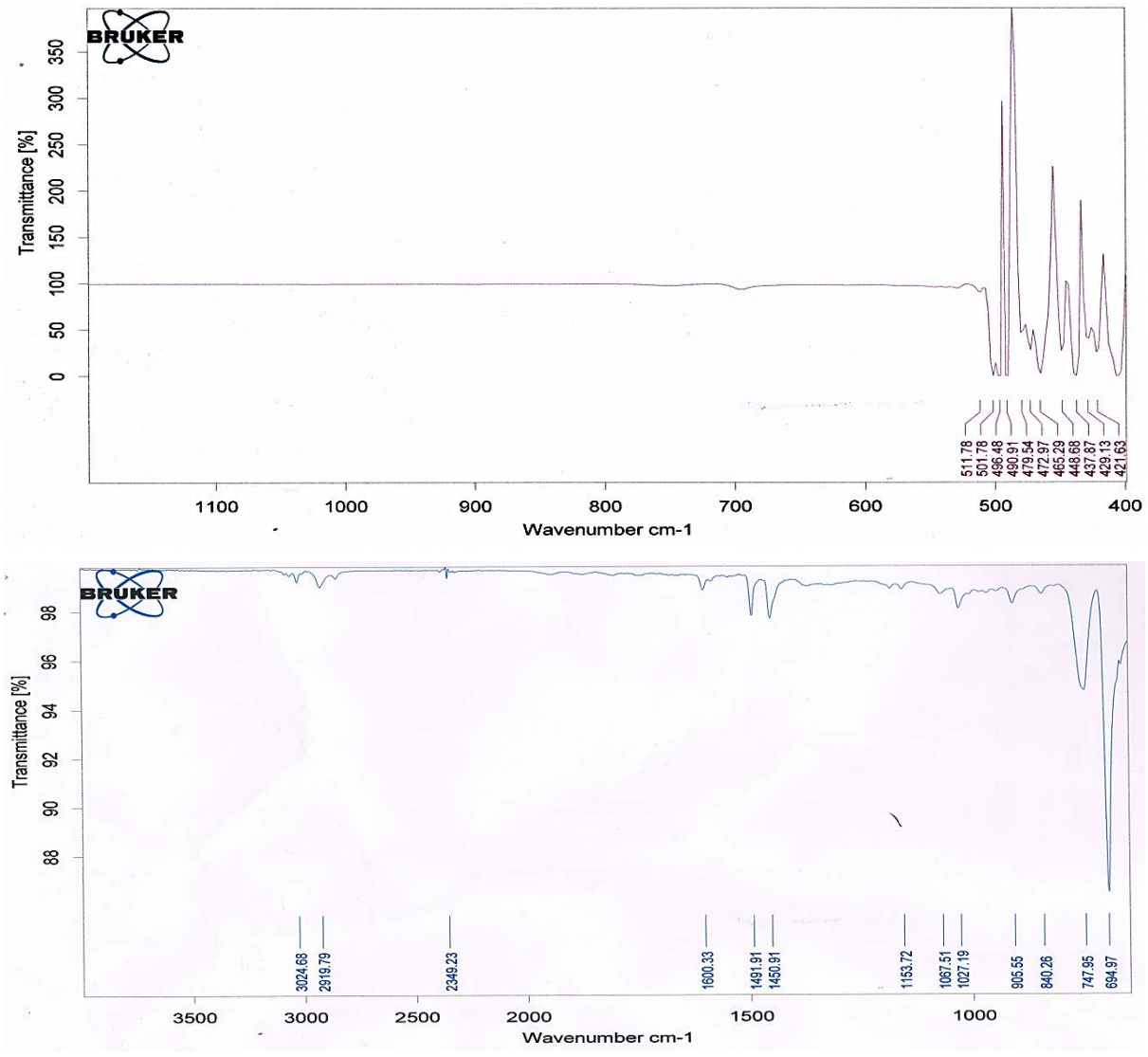

Figure 3. FT-IR transmission spectra of ZnO/PS nanocomposite film

The average particle size found to be 38nm.

No characteristic peaks of impurities are found. This revealed the high purity of the sample. We believe that the presence of ZnO produces neither new peaks nor peak shifts with respect to PS. This indicates that nano ZnO filled PS composites consist of two phase structures. The result is in accordance with the result of Jeep (2012) [25].

UV-Vis

The UV-Vis absorbance and transmittance spectra of polystyrene thin film and of the ZnO/PS nano composite films were recorded on Spectro UV-Vis Double Beam type UV-3500 spectrophotometer in the wavelength range from 190 nm to 900 nm. The transmittance spectra of plain polystyrene and ZnO/PS nano composite films, with similar thicknesses, are shown in Figure 5. The composite film shows transparency around 80.3% in the visible region, comparing with 85.3% for plain polystyrene film in the same region. The absorbance spectra of the composite thin film and the plain polystyrene are shown in Figure 6. It is clear that dramatic change in the absorption of the ZnO/PS nanocompsite film can be observed and the spectra exhibited strong absorption around 355nm, which indicates almost uniform size of the nano particles. For comparison purpose, the absorption spectrum of ZnO gel is shown in Figure 7. Our results are in agreement with those of other authors [46-49].

DSC

DSC analysis was performed with (DSC type shimadzu-DSC 60) with plain polystyrene film and ZnO/PS nanocomposite film. The samples were heated from room temperature to 400°C at the heating rate of 5°C per minute under a constant flow of argon gas.

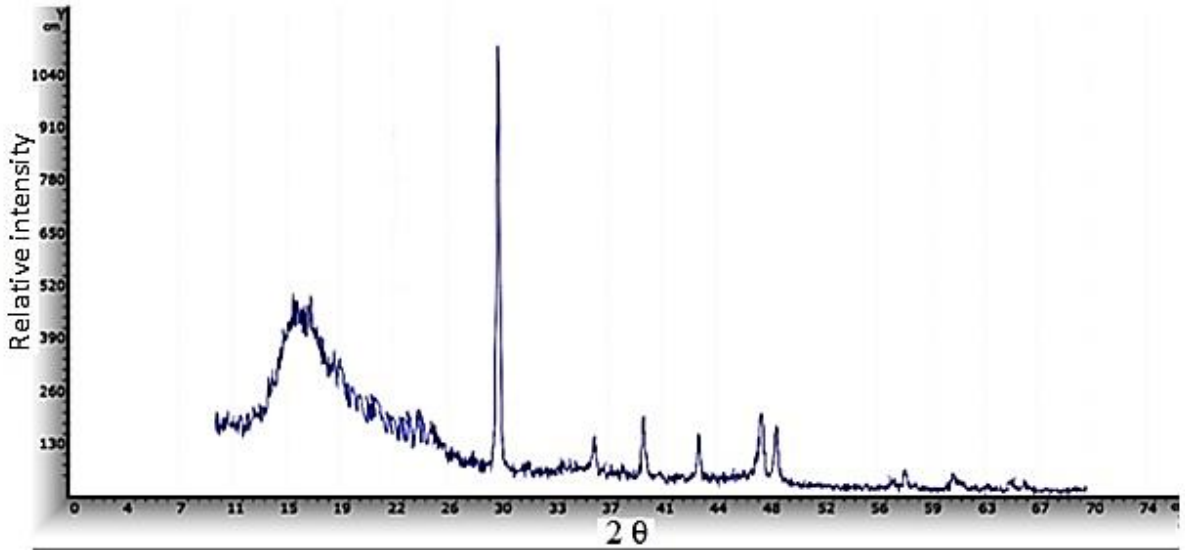

Figure 4. XRD pattern of ZnO/PS nanocompsite film prepared at room temperature

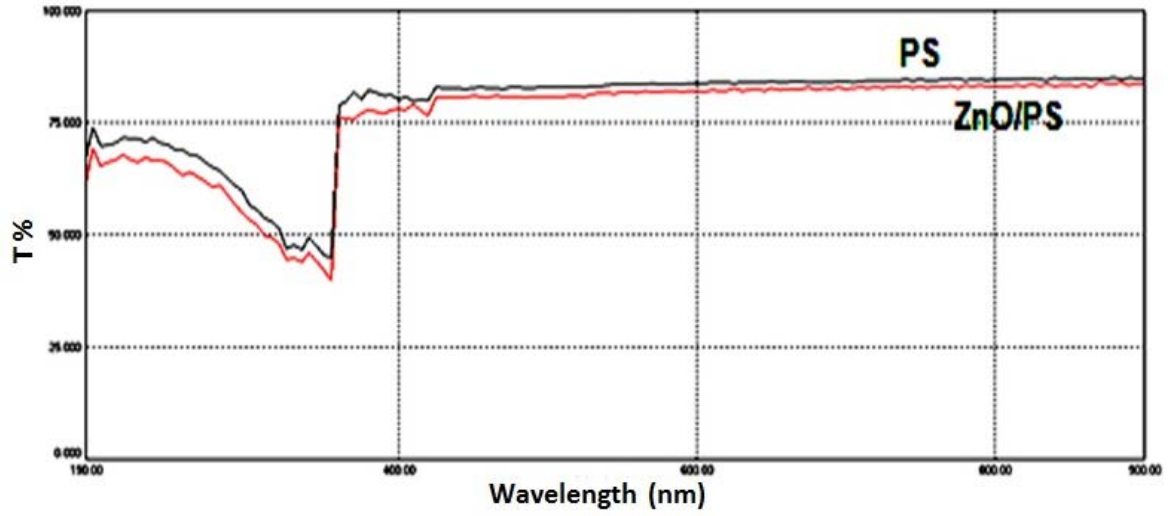

Figure 5. UV-Vis transmission spectra of the ZnO/PS nanocomposite film, and of plain polystyrene film

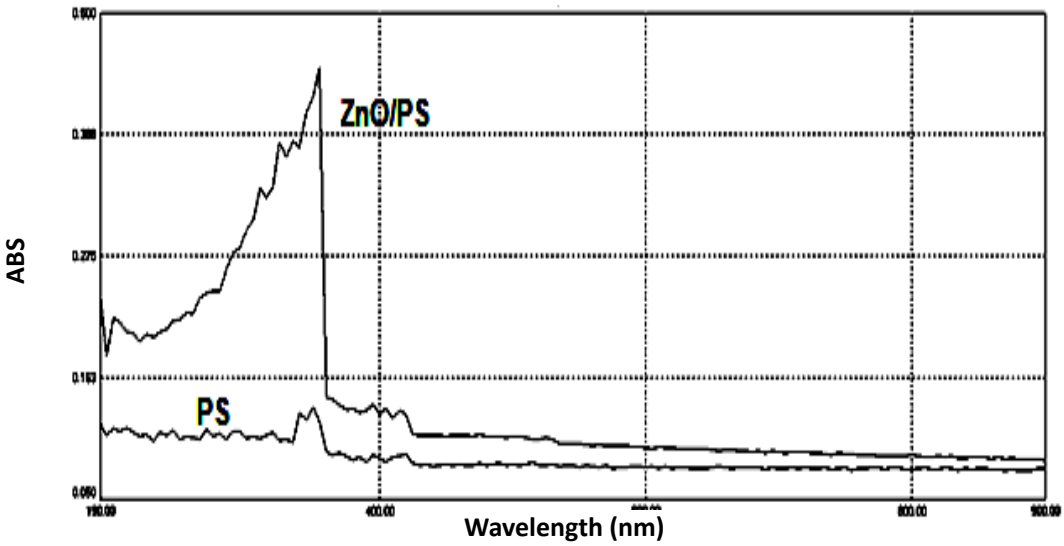

Figure 6. UV-Vis absorption spectra of ZnO/PS film and PS film at room temperature

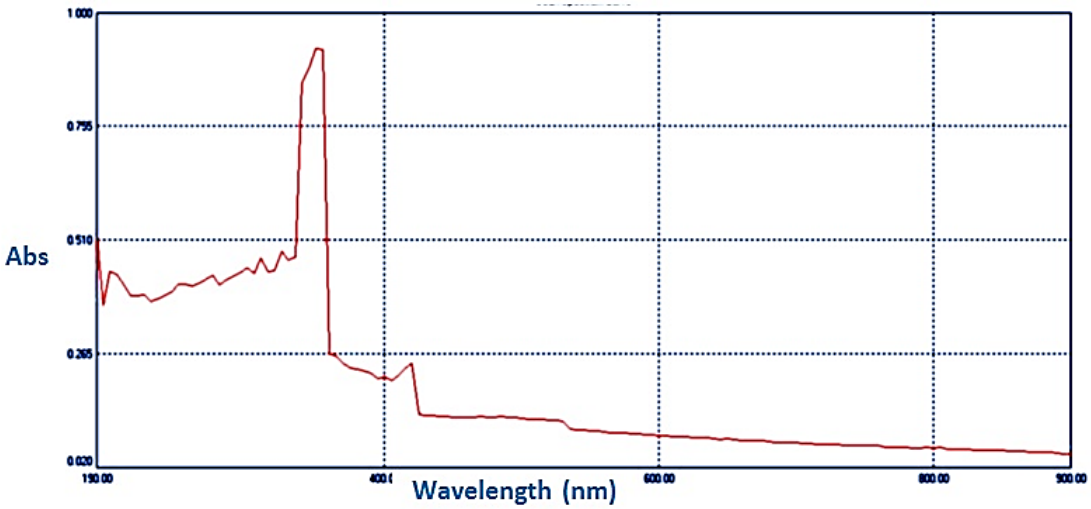

Figure 7. Absorption spectrum of ZnO gel

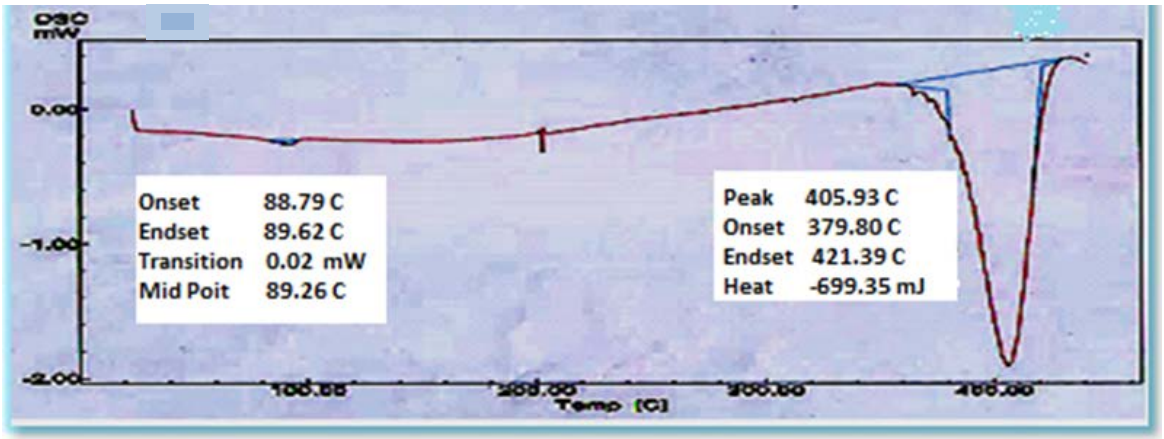

Figure 8. DSC thermogram of ZnO/PS nanocomposite film

The glass transition temperature (Mid Point), Tg, of plain polystyrene film is found to be nearly 82.45°C and increased to 89.26°C for ZnO/PS nanocomposite film. This indicates that presence of ZnO nanoparticals does not reduce the intermolecular H-bonding interactions to such a great extent that much thermal energy is required for transformation from glassy to rubbery state. In other words, at embient temperature the ZnO/PS film exists in glassy state. Almost similar type of discussion has been reported by Sunil B. et al [46]. The thermograms of ZnO/PS films is shown in Figure 8.

4. Conclusions

We have demonstrated the synthesis of ZnO/polystyrene nanocomposite film with 5% of ZnO through the mixing process. The nano zinc oxide improved the thermal properties of the prepared composite film and increased the root mean square of their surfaces, beside a dramatic change in the absorption intensity in the UV region. Also, the XRD, FT-IR and UV-Vis analyses exhibited the high purity of the prepared nanocomposite film. Further work remains to be done on various other thin film combination uesing different materials.

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