Structural and Thermal Study of ZnO filled Polymer Blend

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Abstract- In the present work Polycarbonate and Polystyrene (PC/PS) have been blended with different weight percentages (100/0, 50/50, 0/100) and filled with different concentration of Synthesized ZnO Nanoparticles (1, 2, 3 wt.%) using solution casting method. The size of nanoparticles has been confirmed by X-ray diffraction (XRD). The effect of filler content on PC blends have been investigated by means of Fourier transform infrared (FT-IR) and Differential Scanning Calorimeter (DSC). Significant changes in FT-IR analysis have been observed which reveals interactions between the two polymers. Blends formation have been confirmed from FTIR. It is observed by DSC thermograms that glass transition temperature of samples have influenced by the heating rate and filler content.

Keywords - DSC, FT-IR, XRD and PC/PS

INTRODUCTION

Polymers are ideal materials for many industrial applications but developing nanocomposites based on polymers and nanoscale fillers has an attractive approach to achieving good properties. Various nanoscale fillers, including montmorillonite, silica, calcium carbonate, aluminium oxide and titanium dioxide have been reported to enhance mechanical and thermal properties of polymers, such as toughness, stiffness and heat resistance [1, 2]. Among the nanostructured metal oxides, ZnO have been considered to be one of the best metal oxides that can be used at a nanoscale level. ZnO itself has normally a hexagonal or wurtzite structure and it is a well-known n-type II–VI semiconductor with a wide direct band-gap of about 3.37 eV and a large exciton binding energy of 60 meV, which have made this material important both for scientific as well as industrial applications such as gas sensors, solar cells, varistors and photo catalyst with high chemical activity [3, 4]. From the literature survey, it has been found that various approaches for the preparation of ZnO nanopowders have been developed, namely; sol-gel, microemulsion, thermal decomposition of organic precursor, spray pyrolysis, electrodeposition, ultrasonic, microwave-assisted techniques, chemical vapour deposition, hydrothermal and precipitation methods. Most of these techniques have not extensively used on a large scale, but chemical synthesis has been widely used due to its simplicity and less expensive [5].

EXPERIMENTAL

(1) Synthesis and characterization of ZnO nanoparticles

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Zinc Oxide Nanoparticles have been synthesized by chemical route method using zinc acetate and potassium hydroxide precursors. In this method 0.2M zincacetatedihydrate $((CH_3COO)_2Zn.2H_2O)$ have mixed in 20 ml Di-methylsulphoxide (DMSO) under constant stirring using magnetic stirrer to completely dissolve the zinc acetate and 1.2M potassium hydroxide (KOH) solution in 10 ml ethanol has also been prepared in the same way with stirring. After complete dissolution of zinc acetate, KOH solution has been added drop by drop, under high speed constant stirring. In this, 0.12 ml thioglycerol has added and solution is stirred for one hour. After the completion of reaction, the solution turns milky, the solution has centrifuged for 10 min, and the precipitate has been removed. Thus, precipitated ZnO nanoparticles have been washed three times with ethanol to remove the by-products which were bound with the nanoparticles and then dried in air atmosphere. The prepared ZnO nanoparticles have been characterized by X-ray diffraction [6].

(2) Preparation of PC/PS and ZnO nanocomposites

Polycarbonate (PC), Polystyrene (PS) and PC/PS blend (50/50 wt %) based Zinc Oxide nanocomposites with different weight percent e.g. (1%, 2% and 3%) of ZnO nanoparticle have been prepared by solution casting method followed by film casting. For this purpose Dichloromethane (DCM) has been used as solvent. The effect of nano filler and heating rate on the PC/PS blend has been investigated by using NETZSCH DSC 204 F1 phoenix Differential Scanning Calorimetry (DSC). T_g and T_m have been calculated and analysed using DSC thermograms.

RESULTS AND DISCUSSION

(1) X-Ray Diffraction (XRD)

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Figure 1 shows the X-ray diffraction pattern of ZnO nanopowder. A definite line broadening of the XRD peaks indicates that the prepared material consist of particles in nanoscale range. From this XRD pattern analysis, we have determined peak intensity and full-width at half-maximum (FWHM) data. The diffraction peaks located at 31.49°, 34.18°, 35.97°, 47.25°, 56.30°, 62.57° and 67.81° have been keenly indexed as hexagonal wurtzite phase of ZnO (JPCDS card number: 36-1451).
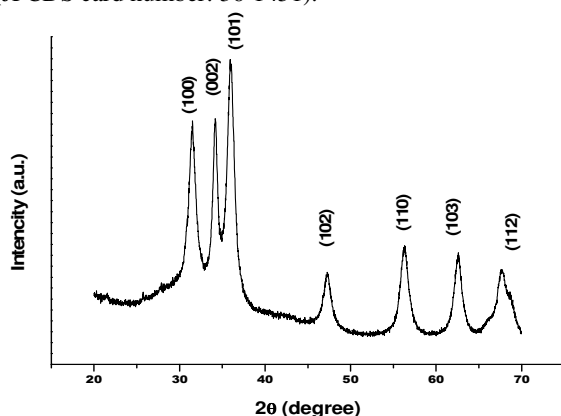

Figure 1: XRD pattern of prepared ZnO nanoparticles.

The average particle size of synthesized ZnO nanoparticle have been calculated using Debye-Scherrer equation, which is given as;
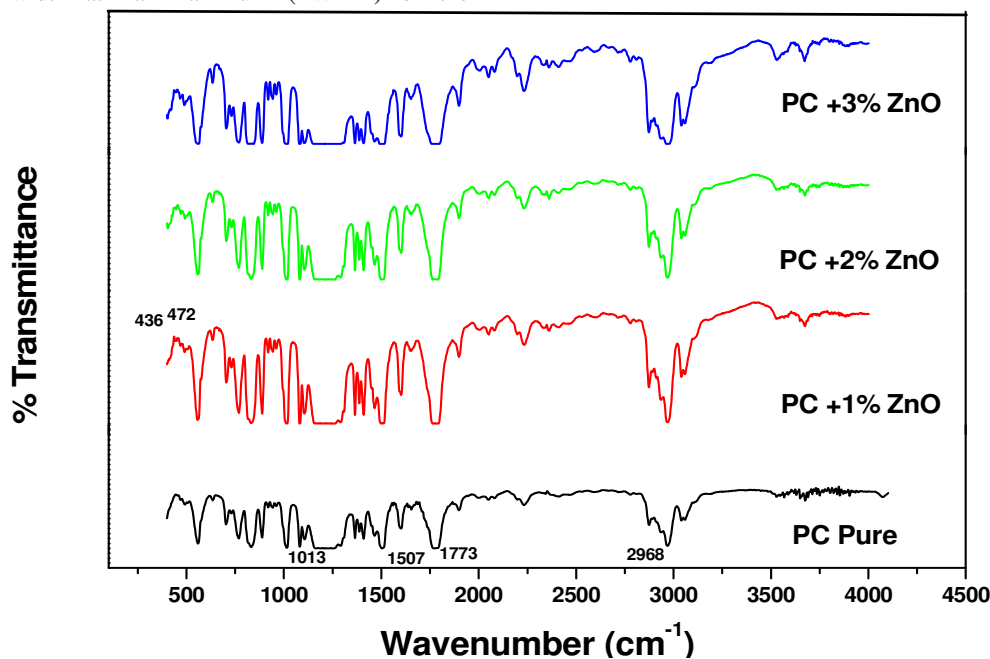
$$d = \frac{0.9\lambda}{\beta \cos\theta}$$

Where, 0.9 is Scherrer's constant, λ is the wavelength of X-rays (1.5406 Å), θ is the Bragg diffraction angle, and β is the full width at half-maximum (FWHM) of the diffraction peak [7]. The average particle size of the sample was found to be 11 nm.

(2) Fourier Transform Infrared Spectra (FTIR) of Nanocomposites

A Fourier transform infrared spectra have been employed for structural characterization of nanocomposites. FTIR spectroscopy is one of the powerful tools for identifying and investigating the presence of various functional groups in polymers [8, 9]. Fig.2 (a-c) depicts the FTIR spectra of PC, PS and their 50/50 (wt%) blend sample with undoped and doped ZnO nanoparticles. The IR spectrum of PC has showed absorption band at 2968 cm^{-1}, which attributes to CH_3 stretching vibration. Characteristics C=O stretching band has been reflected at 1773 cm^{-1}. The ring (C-C) vibrational mode appears at 1507 cm^{-1}. Peak at 1013 cm^{-1} is due to O-C-O stretching vibrational mode. The IR spectrum of PS showed absorption bands at 3026 cm^{-1} and 2849 cm^{-1} corresponding to aromatic and aliphatic C-H stretching, respectively. The peaks at 1601 cm^{-1} and 1493 cm^{-1} have been assigned to aromatic C=C stretching. The C-H deformation vibration band of benzene ring hydrogen's has appeared at 758 cm^{-1}. Ring deformation vibration has been observed at 700 cm^{-1}. The C-H stretching vibrations of ring hydrogen's have seen from 3000 cm^{-1} and 3100 cm^{-1}. The absorption band appeared at 436 cm^{-1} and 472 cm^{-1} has been reflected the presence of ZnO vibrational group. These data clearly indicates the formation of polymer blends and nanocomposites.
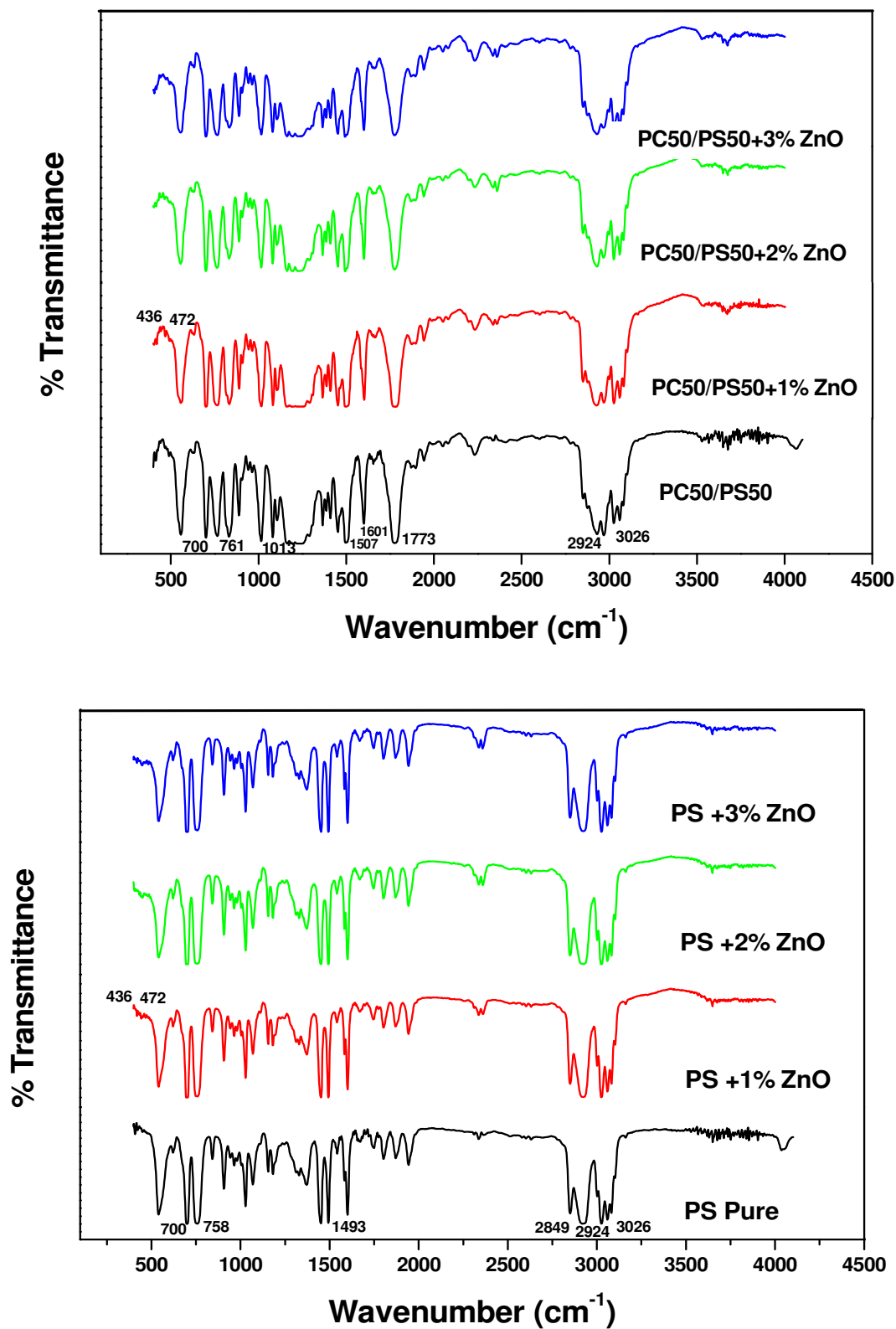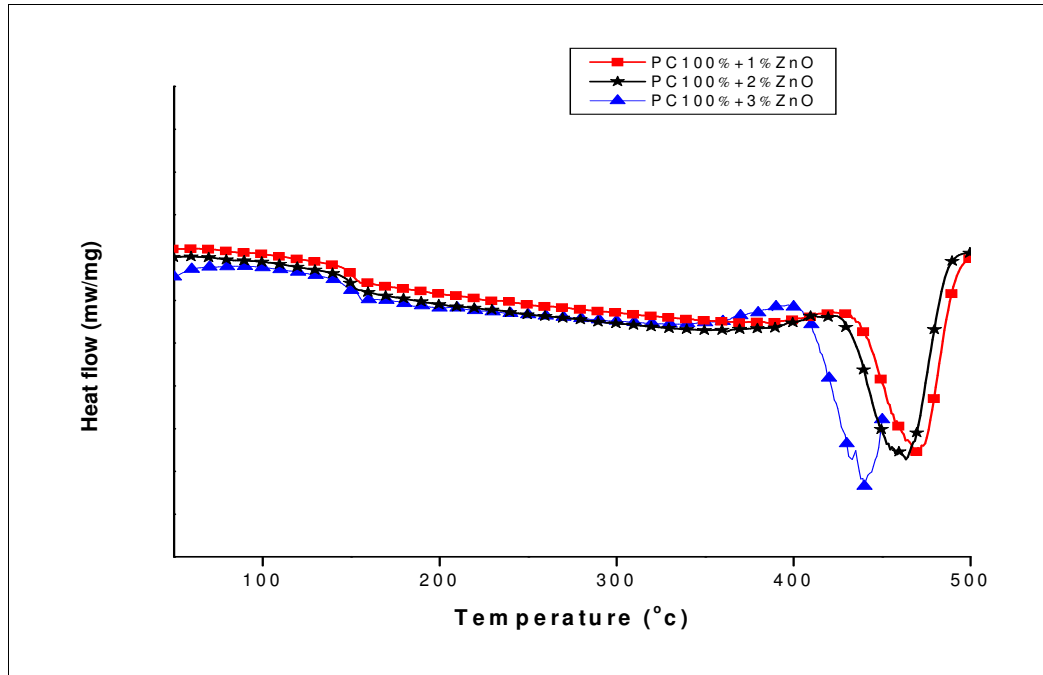
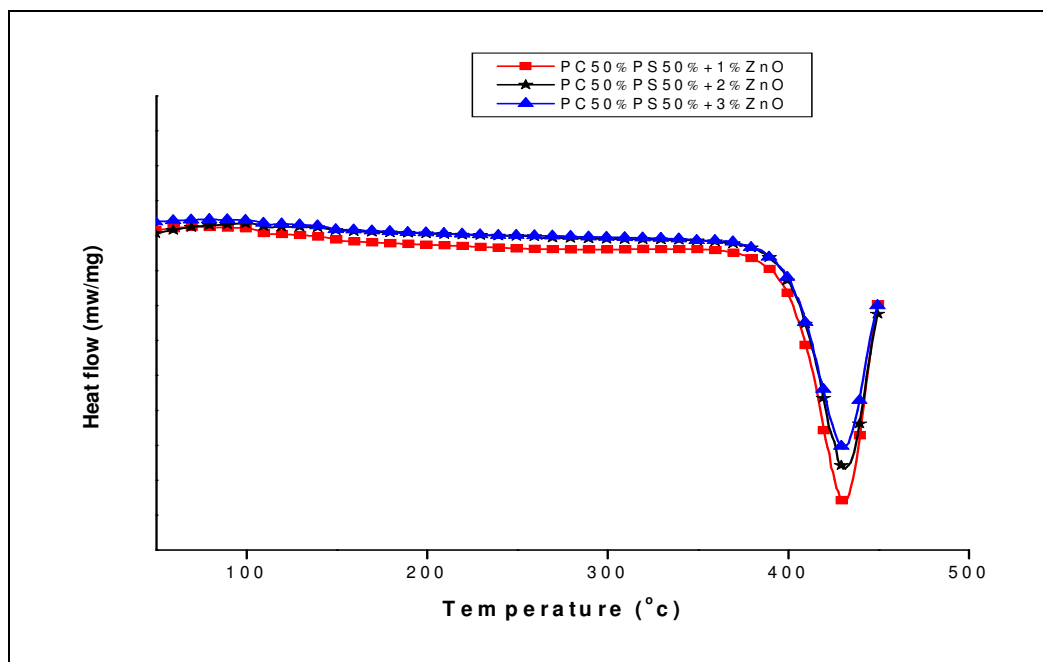Figure 2: FTIR Spectra (a) PC + ZnO (b) PC50%PS50% + ZnO (c) PS + ZnO

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(3) Differential Scanning Calorimetry (DSC) of Nanocomposites

The Differential Scanning Calorimetry (DSC) thermograms of Polycarbonate (PC), Polystyrene (PS) and PC/PS blend based Zinc Oxide (ZnO) nanocomposites with different weight percent of ZnO nanoparticle have been recorded at two heating rates; 10°C/min & 20°C/min. Figure 3 shows thermograms recorded at 20°C/min.

A

B

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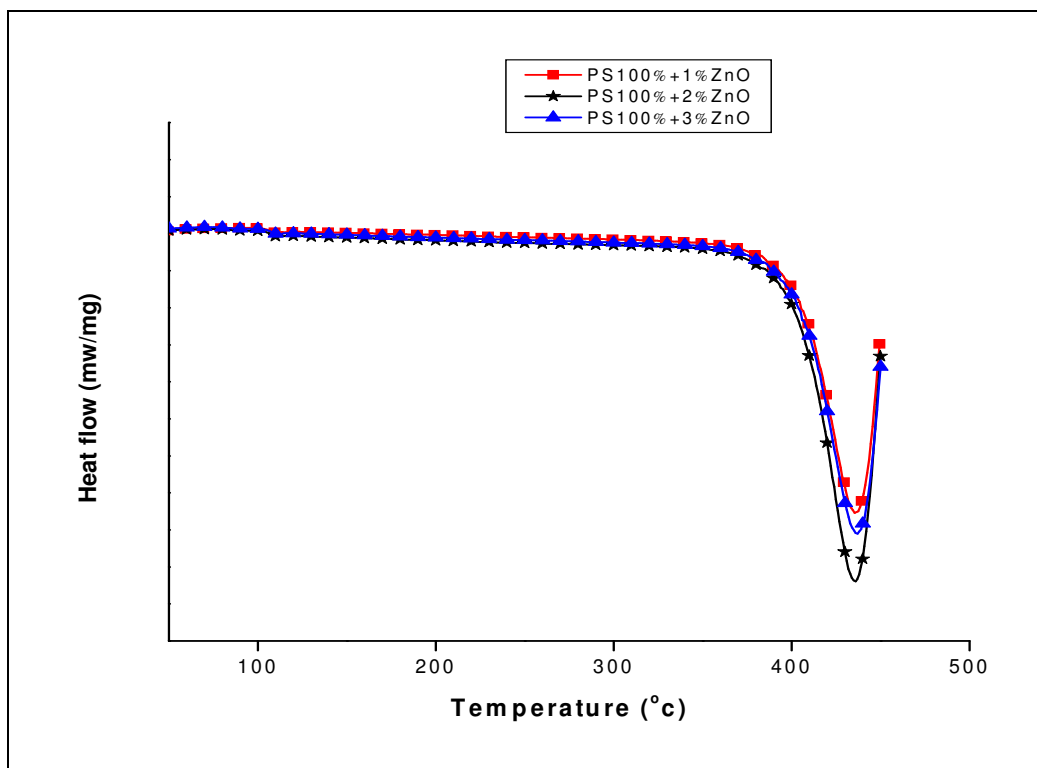
C

Figure 3(a-c): DSC thermograms (a)PC + ZnO (b) PC50%PS50% + ZnO (c) PS + ZnO

Table 1 shows the values of T_g and T_m at *different* heating rates ($10^oC/min$ and $20^oC/min$) for different samples. DSC results show that the glass transition and melting temperature have been affected by the presence of ZnO nanoparticles. Table 1 indicate the increase in the glass transition temperature (T_g) with heating rate and ZnO content. The Tg value has associated with the mobility of polymer chains. ZnO filler serves to increase the Tg value by decreasing the mobility of the chains close to the surfaces of nanoparticles. So, it has been found that thermal stability of nanocomposites increases with increasing ZnO wt% heating rate. In contrast, the melting temperature was not so much affected by the addition of the nanosized ZnO. It is quite evident from table 1 that nearly constant values of T_m appear for Nanocomposites.

Table 1: variation of glass transition temperature (T_g) and melting temperature (T_m) with heating rate.

Heating Rate ↓ Nanocomposites	$10^oC/min$		$20^oC/min$	
	$T_g(^oC)$	$T_m(^oC)$	$T_g(^oC)$	$T_m(^oC)$
PC100%+1% ZnO	149.68	437.81	151.77	470.89
PC100%+2% ZnO	150.26	441.80	152.70	463.29
PC100%+3% ZnO	150.77	424.22	153.12	439.84
PC50%PS50%+1%ZnO	103.12	416.68	110.09	430.25
PC50%PS50%+2%	104.79	416.98	111.05	430.68
ZnO	106.83	417.75	111.68	430.22

PC50%PS50%+3% ZnO				
PS100%+1% ZnO	106.35	422.10	108.15	435.50
PS100%+2% ZnO	106.46	419.70	109.07	435.90
PS100%+3% ZnO	106.75	421.57	109.42	437.25

CONCLUSION

ZnO nanoparticles have been synthesized by easy and rapid chemical route method and characterized by XRD. The formation of ZnO nanoparticles have been confirmed by X-ray Diffraction (XRD) technique. The average particle size of the nanoparticles has been found to be 11nm. FT-IR analysis has been observed which reveals interactions between the two polymers. Blends formation have been confirmed from FTIR. The thermal analysis of prepared ZnO nanocomposites have been carried out using DSC and it has been found that thermal stability of nanocomposites increases as ZnO wt% increases. This stability factor increases for higher heating rate. Also, a increase in T_g has been observed with the increase in heating rate and ZnO content in the nanocomposite. This could be attributed to the mobility of polymeric chains.

Acknowledgement

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