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Thermal, Optical and Mechanical Characterization of ZnO Embedded PC/PMMA Blend Nanocomposites

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Abstract:
In present work, pre synthesized ZnO nanoparticles, have been dispersed in polycarbonate (PC) /Poly methyl methacrylate (PMMA) blend by solution casting method. Prepared blend nanocomposites have been subjected to X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Differential Scanning Calorimetry (DSC), Ultra Violet-Visible (UV-Vis) spectroscopy and Universal Testing Machine (UTM) for structural, thermal, optical and mechanical characterization. XRD and SEM confirm the formation of blend nanocomposites. DSC thermograms have been recorded at heating rate 5, 10, 15 and 20°C/min. Variation in glass transition temperature (T_g) and melting temperature (T_m) has been observed in DSC thermograms. Results reveal that glass transition temperature (T_g) increases with the increase in ZnO wt% and heating rate, due to polymer chain stiffening. Decrease in optical band gap has been observed by the addition of ZnO content. UTM results indicate that young's modulus increases with the increase of ZnO nanoparticles.

Keywords: *Blend nanocomposites, X-Ray Diffraction, DSC, glass transition temperature (T_g), tensile strength*

1. Introduction

Polymer materials have acquired a variety of outstanding applications including industrial applications [1-3]. Polymer nanocomposites are important materials for nanoelectronics, solar cells due to their unique properties like high homogeneity, cost-effective processability [4]. The potential applications of the nanocomposites include automotive, aerospace, opto-electronics [5] and many more. The glass transition temperature (T_g) has become the most thoroughly investigated property of polymers due to the abrupt change in mechanical and thermal properties at T_g. At these ambient temperatures many polymers exist in the amorphous glassy state. This is an inherently non-equilibrium state that, on heating, material relaxes toward the equilibrium liquid state. [6]. Nanostructured zinc oxide has unique properties like high isoelectric point, biocompatibility, nontoxicity, high chemical stability and high electron transfer capability [7]. ZnO nanoparticles have been proved promising candidates for various applications such as nanogenerator, gas sensors, bio sensors, solar cells [8-9]. Present study deals with the structural, thermal, optical and mechanical characterization of PC/PMMA-ZnO blend nanocomposites.

A plenty of work has been done on thermal, mechanical and optical properties of polymer nanocomposites. R. Zhou [10] studied the optical properties of PC, PS and PMMA composites containing inorganic particles in different sizes and concentrations, produced by direct melt mixing. Also, the optical properties have been characterized by total light transmittance, haze, and clarity. M. S. Islam [11] investigated the effect of nanoparticle loading on mechanical properties of silica-epoxy nanocomposites. The tensile, compressive and flexural behavior of nanocomposite has also been reviewed. J. Xiao [12] studied the effect of clay on thermal stability of polycarbonate (PC). It has been observed that montmorillonite can catalyze thermal degradation of PC chains and decrease thermal stability of the nanocomposites. The aim of the present work has been concerned with the study of structural, thermal, optical and mechanical characterization of PC50%/PMMA50% blend filled with ZnO nanoparticles.

2. Experimental

Polycarbonate (PC) and Polymethylmethacrylate (PMMA) have been used as precursor for blend nanocomposites. For Synthesis of PC/PMMA-ZnO blend nanocomposites, PC/PMMA in 50/50 wt%/wt% composition has been dissolved in Dichloromethane (DCM) and stirred until a homogeneous solution occurs. ZnO nanoparticles have been dispersed in this solution in 1, 2 and 3 wt % proportion and sonicated. The resulting solution has been casted on to the glass petridish and kept in dry atmosphere. Dried film has been peeled off from petridish and used for further characterization.

3. Results and Discussions

3.1. Structural Characterization

X-ray Diffraction (XRD) pattern of synthesized blend nanocomposites have been recorded using X-ray Diffractometer Bruker D8 Advance with Cu (Kα) radiation (λ=1.54 Å) in the range of 2θ = 20°-70°. The X-ray diffraction pattern has been recorded in a step-scanning mode. Figure 1 shows the X-ray Diffraction (XRD) pattern of PC/PMMA blend and its ZnO (1, 2 and 3 wt %) blend nanocomposites.

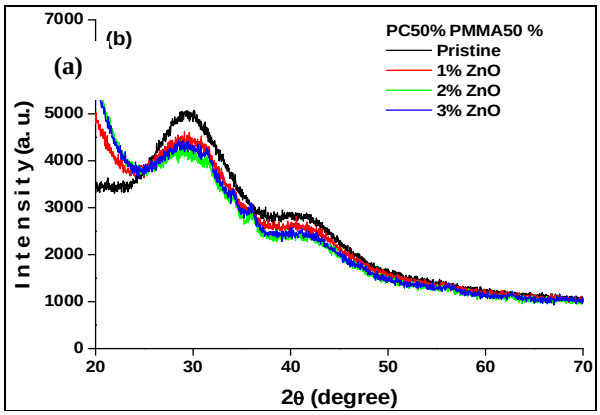

Figure1: XRD pattern of PC/PMMA- ZnO blend nanocomposites

In XRD pattern of blend nanocomposites, hump and three small but sharp peaks have been observed. Humps are due to amorphous nature of PC and PMMA. Peaks correspond to ZnO nanoparticles shows that the size of ZnO particles in the PC/PMMA matrix remains in nano regime.

Figure 2 shows the Scanning Electron Microscopy (SEM) images of PC/PMMA (pristine) and PC/PMMA-ZnO (2wt %) blend nanocomposites as representative cases. SEM images of polymer blend have been found to be homogenous for PC/PMMA (pristine) sample. It is apparent that the addition of nano ZnO particles in PC50%/PMMA50% polymer blend exhibits changes in the surface morphology of such system. As the content of ZnO increases the film surface becomes rough with some segregation of ZnO in the polymeric system.

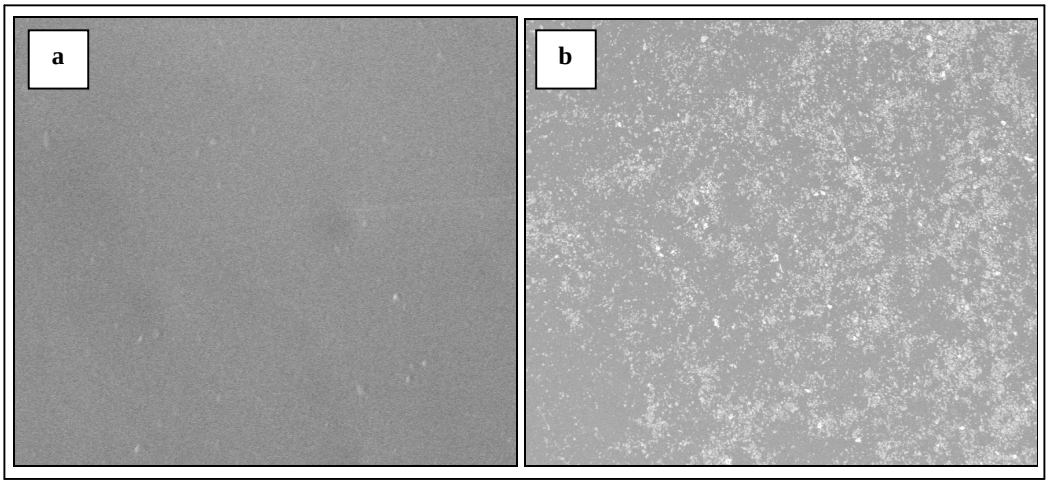

Figure 2: SEM images of (a) PC/PMMA pristine (b) PC/PMMA-ZnO (2wt%) blend nanocomposites

3.2. Thermal Characterization

Thermal characterization has been investigated using NETZSCH 204 F1 Differential Scanning Calorimetry (DSC). Typically, 6±0.3 mg of sample has been sealed in standard aluminum pans and heated at different heating rates (e.g. 5, 10, 15 & 20°C /min) under dry nitrogen atmosphere. DSC thermograms at heating rate 10°C/min and 20°C/min have been shown in figure 3 as representative cases. Similar DSC thermograms have been recorded for each composite at different heating rate 5°C/min and 15°C/min. From these thermograms, glass transition temperature (T_g) and melting temperature (T_m) have been obtained and listed in table 1. It is evident by table 1 that T_g and T_m increases as heating rate increases. Also, the enhancement in T_g values has been observed with the increase in ZnO wt%. ZnO filler serves to decrease the mobility of chains close to the surface of nanoparticles and increase stiffness of the polymer chains which results as the increase in the T_g values.

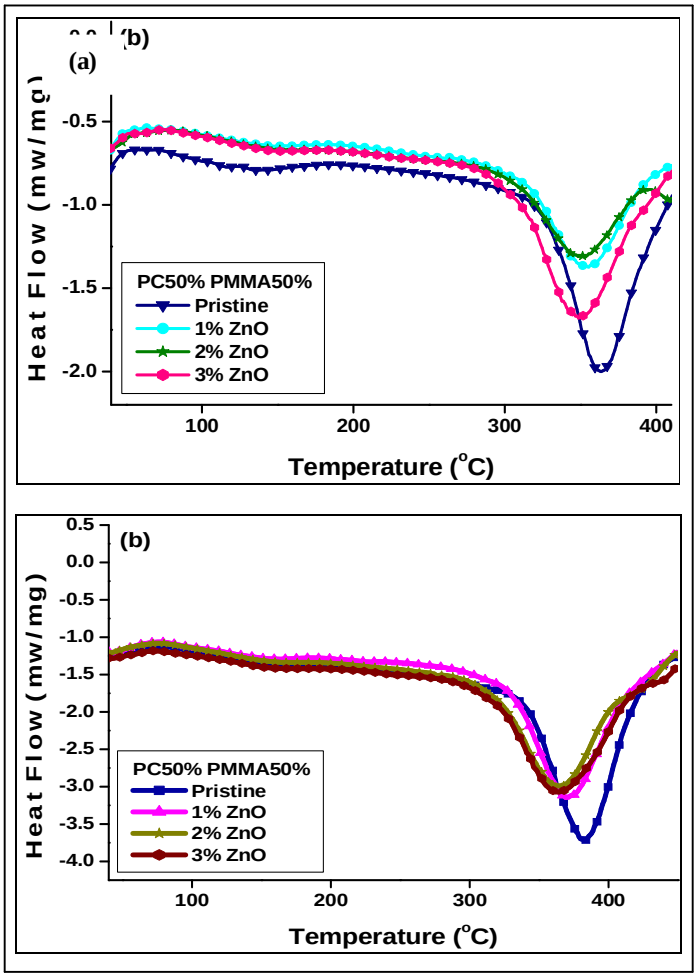

Figure 3: DSC thermograms at heating rate (a) 10°C/min (b) 20°C/min of PC/PMMA-ZnO blend nanocomposites

Heating rate (°C/min)	Pristine		1% ZnO		2% ZnO		3%ZnO	
	T_g (°C)	T_m (°C)	T_g (°C)	T_m (°C)	T_g (°C)	T_m (°C)	T_g (°C)	T_m (°C)
5	110.4	353.4	111.6	342.8	111.1	338.3	111.2	337.6
10	111.9	363.7	112.1	352.7	112.2	352.0	112.3	348.7
15	112.1	374.3	112.5	362.4	112.8	359.7	113.3	359.9
20	113.7	383.4	114.2	369.4	114.3	364.6	114.4	363.6

Table 1: T_g and T_m of PC/PMMA-ZnO blend nanocomposites

3.3. Optical Characterization

UV-Visible absorption spectroscopy is widely being used technique to examine the optical properties of polymer blend nanocomposites. Measurement of the UV-Vis absorption spectra of material is the most direct method to investigate the band structure of the materials. In the absorption process an electron is excited from a lower to higher energy state by absorbing a photon of known energy. The changes in the transmitted radiation can decide the types of possible electron transitions. Fundamental absorption refers to band-to-band or exciton transition. Figure 4 shows the absorption spectra of ZnO filled PC/PMMA blend nanocomposites. Absorption spectra demonstrates the onset of absorbance for these films in the range 250 nm-300 nm, which can be attributed to the excitation of electrons from the valence band to the conduction band of ZnO. Furthermore, one can observe that the intensity of this band increases with an increase in ZnO content. ZnO is a wide band gap semiconductor, and it has a high-absorption coefficient in the UV. Thus, in contrast to the visible, the composite films are strongly absorbing in the UV region, so, the result could be attributed to high absorbance of ZnO [13, 14]. The fundamental absorption, which corresponds to electron excitation from the valence band to conduction band, can be used to determine the nature and value of the optical band gap, E_g^{opt}. The relation between the absorption coefficient, α, and the incident photon energy, hν, has been given by Tauc [15]. The usual method to calculate the band gap energy is to plot a graph between $(\alpha h\nu)^2$ and photon energy, hν, for direct band gap. The value of E_g^{opt} can be given by intercept on the hν-axis. Figure 5 depicts the variation of $(\alpha h\nu)^2$ against hν of ZnO filled PC/PMMA blend nanocomposites. The optical energy gap has been determined from the intercepts of extrapolations to zero

with the photon energy axis $(\alpha h\nu)^2 \rightarrow 0$ as shown in figures. From figure 5, it has been seen that an increase of concentration of ZnO in the system leads to a decrease in the optical band gap.

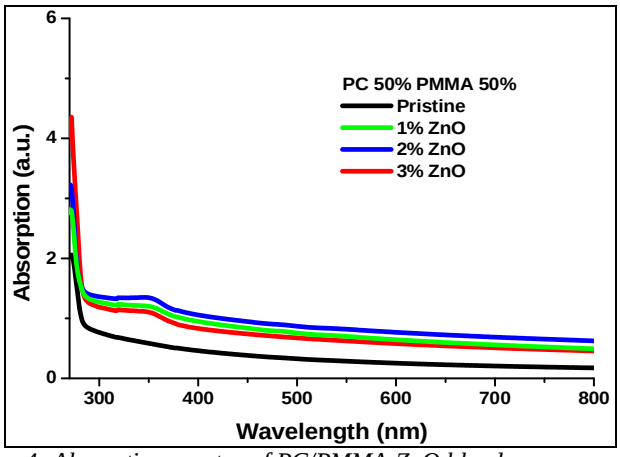

Figure 4: Absorption spectra of PC/PMMA-ZnO blend nanocomposites

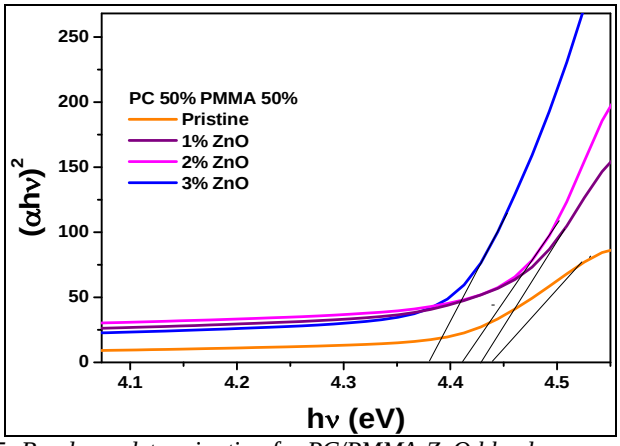

Figure 5: Band gap determination for PC/PMMA-ZnO blend nanocomposites

3.4. Mechanical Characterization

Mechanical study, to determine the tensile parameters for all the samples, has been carried out using Universal Testing Machine (UTM). Young's modulus is a measure of the stiffness of a material and is a quantity used to characterize materials. It is defined as the ratio of the stress to the strain along that axis in the range of stress in which Hooke's law holds. Tensile strength is also known as ultimate tensile strength. It is the maximum stress that a material can withstand while being stretched or pulled before breaking. Stress-strain curves obtained from the tensile test has been shown in figure 6. The values of tensile parameters have been determined by these curves and listed in table 2. It has been observed that young's modulus increases as ZnO wt% increases. Maximum value of tensile strength, fracture energy and fracture strain have been found for PC/PMMA-ZnO 3 wt % blend nanocomposite. The result could be attributed to the agglomeration of ZnO nanoparticles.

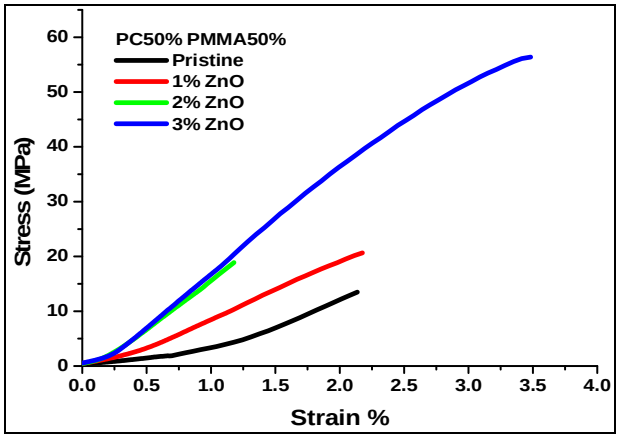

Figure 6: Stress-strain curves for PC/PMMA-ZnO blend nanocomposites

Sample	ZnO wt %	Young's Modulus (MPa)	Tensile strength (MPa)	Fracture energy (J)	Fracture strain (%)
PC50% PMMA 50%	0	5.56	16.02	25.77	3.10
	1	7.71	20.51	21.14	2.19
	2	18.71	19.32	10.07	1.17
	3	26.49	56.52	104.88	3.48

Table 2: Tensile parameters for PC/PMMA-ZnO blend nanocomposites

4. Conclusion

Pre-synthesized ZnO nanoparticles, in different wt%, have been dispersed in polycarbonate (PC) /Poly methyl methacrylate (PMMA) blend by solution casting method. Structural, thermal, optical and mechanical characterization of prepared blend nanocomposites has been carried out using XRD, SEM, DSC,UV-Vis and UTM. XRD patterns and SEM images confirms the formation of blend nanocomposites. Glass transition temperature (T_g) and melting temperature (T_m) have been recorded using DSC thermograms at different heating rates e.g. 5, 10, 15 and 20°C/min. Results reveal that T_g increases with the increase in ZnO wt% because ZnO filler serves to decreasing the mobility of chains close to the surface of nanoparticles and increase in stiffness of the polymer chain ,which results the increase in the T_g values. UV-Vis results show that an increase of concentration of ZnO in the system leads to a decrease in the optical band gap. Optical absorption of these samples in UV region is high so these can be used as transparent coating with UV protection ability. UTM results reveals that maximum value of young's modulus, tensile strength, fracture energy and fracture strain is for PC/PMMA-ZnO 3 wt % blend nanocomposite, due to the agglomeration of ZnO nanoparticles.

5. Acknowledgement

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6. References

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