

Investigation of Optical and Thermally Stimulated Properties of SiO₂ Nanoparticles-Filled Polycarbonate

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ABSTRACT: Polycarbonate nanocomposite containing silicon oxide nanoparticles average size of 5 nm at different weight ratio has been prepared by solution mixing method. The dispersion of nanoparticles in polymer matrix was studied by transmission electron microscopy (TEM). The optical and thermally stimulated behavior of nanocomposites were analyzed by energy dispersive X-ray spectra (EDX), X-ray diffraction pattern (XRD), UV-vis spectroscopy, differential scanning calorimetry (DSC), and thermally stimulated discharge current (TSDC). TEM images show the dispersion and size of the nanoparticles, however, EDX indicate the presence of SiO₂ on the surface of the nanocomposite film. An XRD result reveals that the crystallinity increases with increase in concentration of

SiO₂ nanoparticles in polymer matrix. The direct and indirect optical energy band gaps decreased and number of carbon atom increased with concentration of SiO₂ nanoparticles. We have observed that the increase of SiO₂ nanoparticles in PC significantly reduces the refractive index. DSC and TSDC show that glass transition temperature increases according to SiO₂ weight ratio. The TSDC of nanocomposites samples could be understand in terms of non-Debye theory of charge relaxation and co-tunneling mechanism of charge transport. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: TSDC; nanocomposite; activation energy; relaxation time; co-tunneling

INTRODUCTION

The electret state in insulating materials arises from the induced polarization owing to the frozen in phenomenon of electric charges. The study of electret state in insulating polymers using thermally stimulated discharge current (TSDC) technique reveals the nature of various relaxation processes. TSDC is the study of charge decay by heating the electret at constant rate. These decay processes are investigated as a function of temperature. The application of polymer nanocomposites as an electret is the promising area of research.^{1–3} Electrets can store the charge for long time and will especially apply as a supercapacitor, piezosensor, pyro sensor, etc.^{4–10} The SiO₂ thin film electret is a promising electret for energy harvesting. It can be used to realize vibration-based capacitive energy harvester systems using CMOS-compatible processes.¹¹

Organic–inorganic nanocomposite materials are increasingly important because of their outstanding properties arises from synergism between the properties of the components. There are several routes to

these materials, but probably the most prominent one is the incorporation of inorganic fillers in organic polymers. These materials have gained much interest because of their excellent mechanical,¹² electrical,¹³ thermal,^{14–18} and magnetic¹⁹ properties when compared with pristine organic polymers.

There are many similarities in PC and SiO₂ nanoparticles. PC and SiO₂ both are amorphous, transparent, light weight, high stability and wide band gap materials.^{20–22} Therefore, the combinations of PC and SiO₂ have been chosen in this study.

The issues of dispersion of SiO₂ in composite system, as a result of poor interactions at nanofiller polymer interface, are very important. Because uniform dispersion of nanofiller could able to achieve the desired properties. Zheng et al.²³ recently applied the ultrasound waves for dispersion of nanoparticles in polymers and achieved uniform dispersion of silica nanoparticles in epoxy resin. A dramatic increase in interfacial area between fillers and polymer can significantly improve the properties of pristine polymers.²⁴ The well-dispersed nanoparticles can effectively enhance the comprehensive properties of nanocomposites, which are unique and different from any other composites.²⁵

In experimental point of view, the relaxation kinetics in the amorphous-glassy state can be characterized by means of thermally stimulated depolarization current (TSDC) whereas the relaxation kinetics

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in liquid state can be analyzed by means of dielectric relaxation spectroscopy (DRS).²⁶ TSDC technique is applied in variety of material for the study of dispersion phases such as disperse and porous metal oxides, polymers, liquid crystals, amorphous and crystalline solids, polymer nanocomposites, bio material, cells, tissues,²⁷ etc. This study is motivated by the interaction between organic polymer matrix and nanofiller via a huge interface.²⁸ This interaction produces strong effects on the polymer matrix, even with low filler concentration. Vollenberg and Heikens²⁹ have shown that a large proportion of the matrix is influenced by the formation of a polymer layer of higher density in the immediate vicinity of nanoparticle and thus enhance the mechanical properties.

There are several reports^{30–32} on polymer nanocomposites that show an increase of the glass transition temperature (T_g). It ascribed that the mobility of the entire volume of polymer is restricted by the presence of the nanofillers. However, reduction of T_g has also been reported in some cases³³ because of weak interactions between fillers and polymer. In other hand, the addition of nanoparticles causes no significant change in glass transition of the polymer presumably because effects causing the increase and decrease of polymer mobility are present simultaneously and effectively cancel out.³⁴

It was also shown that from different experiments, the restriction of chain mobility caused by the nanofillers does not extend throughout the material but affects only the chains within a few nanometers of the filler surface. The existence of an interfacial layer between polymer matrix of nanoparticles seems relatively well established in the case of silica filled some of the elastomers, however, their exact nature is not well understood. Despite complex phenomena to develop clear understanding, most of the experimental results have been described in terms of one or two distinct interfacial layers or a gradual change in dynamics with changing distance from the particle.

The filling of nanoparticles in polymer matrix can form high refractive index nanocomposite. The filling of PbS nanoparticles into gelatin or poly (ethylene oxide) has been reported.^{35,36} Their studies prove that the PbS particle loading affects significantly the overall refractive index of the nanocomposite. Refractive index of 1.60–1.76 observed in solvent-based polyarylether (sulfone) containing $\text{SiO}_2\text{-TiO}_2\text{-ZrO}_2$ has also been reported.^{37,38} However, no report is available in effect of nanofillers on refractive index of PC.

The electret state in PC was recently reported in literature^{39–42} with poor electrical response. Because both PC and SiO_2 nanoparticles are amorphous material, however, there are no reports on effect of SiO_2 nanoparticles in electret state of PC. Therefore, it is decided to study the electret state by means of opti-

cal and thermally stimulated properties of SiO_2 nanoparticles-filled polycarbonate film.

In this work, the thermal relaxation dynamics related to the T_g in a series of PC and PC + SiO_2 nanocomposite samples are investigated by means of TSDC technique and differential scanning calorimetry (DSC). The combination of experimental techniques used in this study will allow to gain more complete understanding of the effect of the SiO_2 nanoparticles on relaxation properties of PC. Further, the optical properties could be investigated using X-ray diffraction pattern (XRD), ultraviolet-visible spectroscopy (UV-vis), transmission electron microscopy (TEM), and energy dispersive X-ray spectra (EDX) techniques by measuring the crystallinity, refractive index, and optical energy band gap.

EXPERIMENTAL

Polycarbonate (PC) pellets supplied by Redox (India) and SiO_2 nanoparticles of size 5 nm supplied by Sigma Aldrich have been used in this study. The preparation of the PC-based composites containing SiO_2 nanoparticles film is given as follow: first, the 5 gm PC was dissolved in 100 mL of dichloromethane (DCM) and then kept for 5 h in magnetic stirrer to become homogeneous—transparent solution at 333 K. The certain amount of SiO_2 according to weight ratio was dissolved in 20 mL DCM and added drop wise in solution of PC. This solution is kept in stirrer for 1 h. After 1 h, 100 μL of triethoxyvinylsilane 98% deposition grades" (Sigma Aldrich) as a coupling agent was added drop by drop in PC + SiO_2 solution and again stirrer for 1 h. Now the final solution was kept in sonicator at a frequency of 20 kHz for 10 min. The solution thus prepared was poured on optically plane glass plate floating on mercury pool and the solvent was then allowed to evaporate inside vacuum oven at room temperature for 24 h to yield circular thin film shape. The thin films were further dried at room temperature with outgassing of 10^{-5} Torr for a further period of 24 h to remove volatile residual solvent. All the samples of same thickness about 25 μm were chosen for this study. Morphological characterization of PC pristine and nanocomposite samples were observed by TEM (JEOL 2100F). The nanocomposite samples for TEM analysis were prepared by addition of single drop of composite solution onto carbon-coated copper grids and later the retained solvent to be evaporated at room temperature. EDX (ZEISS EVO 40) spectra were recorded to justify the formation PC + SiO_2 nanocomposites.

The percentage of crystallinity PC pristine and PC + SiO_2 nanocomposite samples have been investigated by X-ray diffraction (XRD). The XRD patterns were recorded using the $\text{Cu K}\alpha$ ($\lambda = 1.541\text{\AA}$) radiation in θ - θ locked couple mode from the Bruker AXS

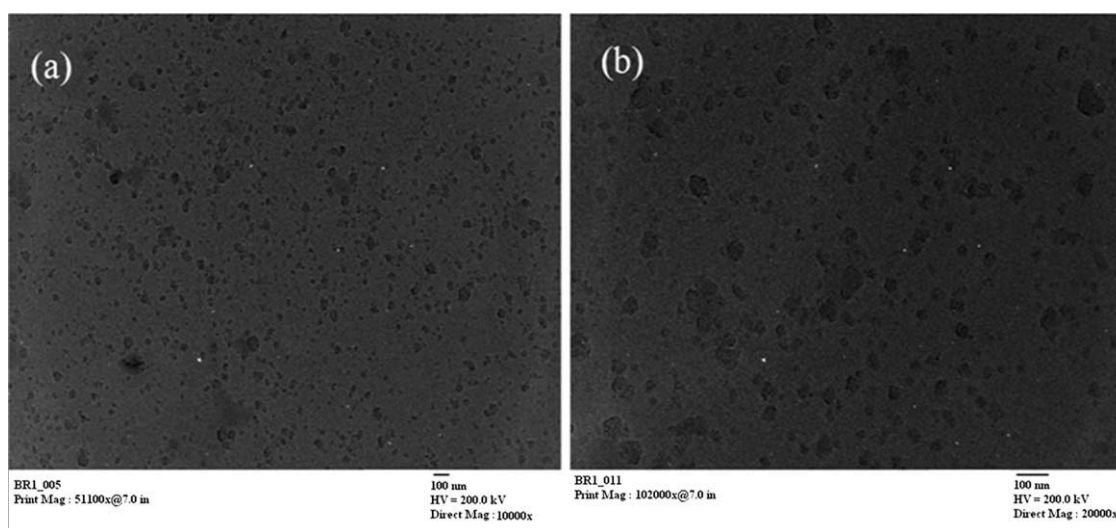


Figure 1 TEM images of PC + (2%) SiO₂ and PC + (12%) SiO₂ nanocomposites films.

D8 diffractometer with scan speed of 1°/min. The diffraction angle (2θ) has been varied from 5 to 40 degree with step size of 0.02. The optical energy band gaps, carbon atoms per cluster, and refractive index were observed by using UV-vis spectrophotometer. The envelop method is used to calculate the refractive index from UV-vis spectra.³ UV-vis spectra were recorded by double beam spectrophotometer (Hitachi U- 2800) in the range of 250–800 nm. The DSC measurement was used to investigate the T_g of the pristine and nanocomposite samples. The DSC thermograms of polymeric samples were recorded in temperature range from 330 to 460 K with constant heating rate of 10 K/min. These thermograms were recorded from DSC (2910 MDSC) available in UGC-DAE Consortium Indore (India).

The TSDC technique was used to investigate the activation energy, relaxation time, charge released, and T_g of the pristine and nanocomposite samples. For TSDC measurement, both sides of the PC pristine and PC + SiO₂ nanocomposite samples were vacuum aluminized by using vacuum equipment (VEQCO) Delhi, India, for good ohmic contact. The polymeric samples were mounted into the sample holder. The sample holder forming aluminum-polymeric sample-aluminum system was placed in an “Ambassador” oven, which is programmed to linear rise of temperature. The thermo electrets of PC pristine and PC + SiO₂ nanocomposite samples were prepared by using dc field of 200 kV/cm at 423 K temperature for 2 h, then the sample cool down up to room temperature under dc field. When the sample temperature becomes equal to room temperature, then we removed dc field and it is short-circuited during 15 min through an electrometer (Model DPM-111, Scientific Equipments Roorkee, India). The TSD current was recorded as a function of temperature

with a digital picoammeter (Scientific Equipments Roorkee, India, DPM-111) at a linear heating rate of 3 K/min. To avoid the effect of ground loop and extraneous electrical noise, the digital picoammeter was properly shielded and grounded. The more detail of TSDC measurement is reported in literature.^{43,44}

RESULT AND DISCUSSION

The dispersion of SiO₂ nanoparticles in PC matrix is characterized by TEM. Figure 1(a,b) shows the TEM images of PC + (2%) SiO₂ and PC + (12%) SiO₂, respectively. It is found that SiO₂ nanoparticles are uniformly dispersed in PC matrix. SiO₂ shows in form of dark parts and PC shows in gray part. The particle size is increasing with content of SiO₂ and the average size of SiO₂ nanoparticles was calculated about 7–10 nm.

In order to show the direct evidence of PC + (12%) SiO₂ nanocomposite, the EDX spectra was recorded as shown in Figure 2. The EDX is showing the presence of Si, oxygen, gold, carbon, and chlorine. The presence of chlorine is due to the solvent (i.e., DCM) used for preparation of film. The presence of gold is because of coating material of sample. The presence of Si and oxygen in nanocomposite film is a direct evidence for formation of nanocomposite.

XRD (Fig. 3) shows the amorphous nature of PC pristine and PC + SiO₂ nanocomposite films with different concentrations of 2, 4, 8, and 12 wt % of SiO₂ in PC. The percentage crystallinity of the films are calculated by the following relation,⁴⁵

$$B = \frac{A}{A'} \times 100\% \quad (1)$$

where A is the total area of the peaks, and A' is the total area under the diffraction pattern. It is observed

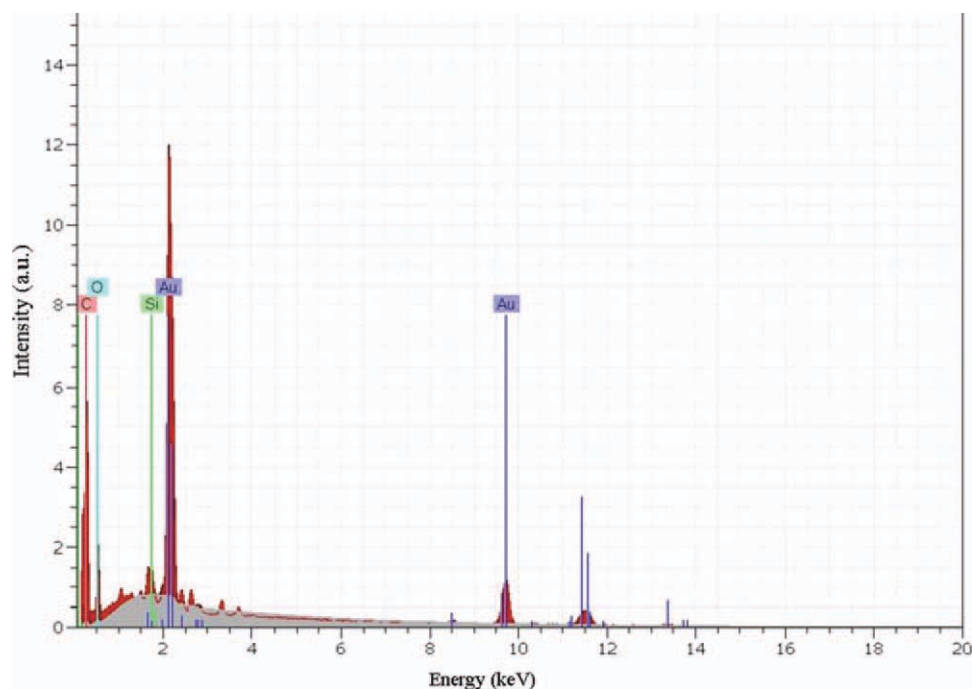


Figure 2 EDX spectra of PC + (12%) SiO₂ nanocomposite film. Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.

from Figure 4 that the crystallinity increases with increasing concentration of SiO₂, which may be attributed to increase in the density of nanoparticles and

crosslinking/chain scission of polymeric structure. It means that the amorphicity of the composites films decreases with concentration of SiO₂ nanoparticles.

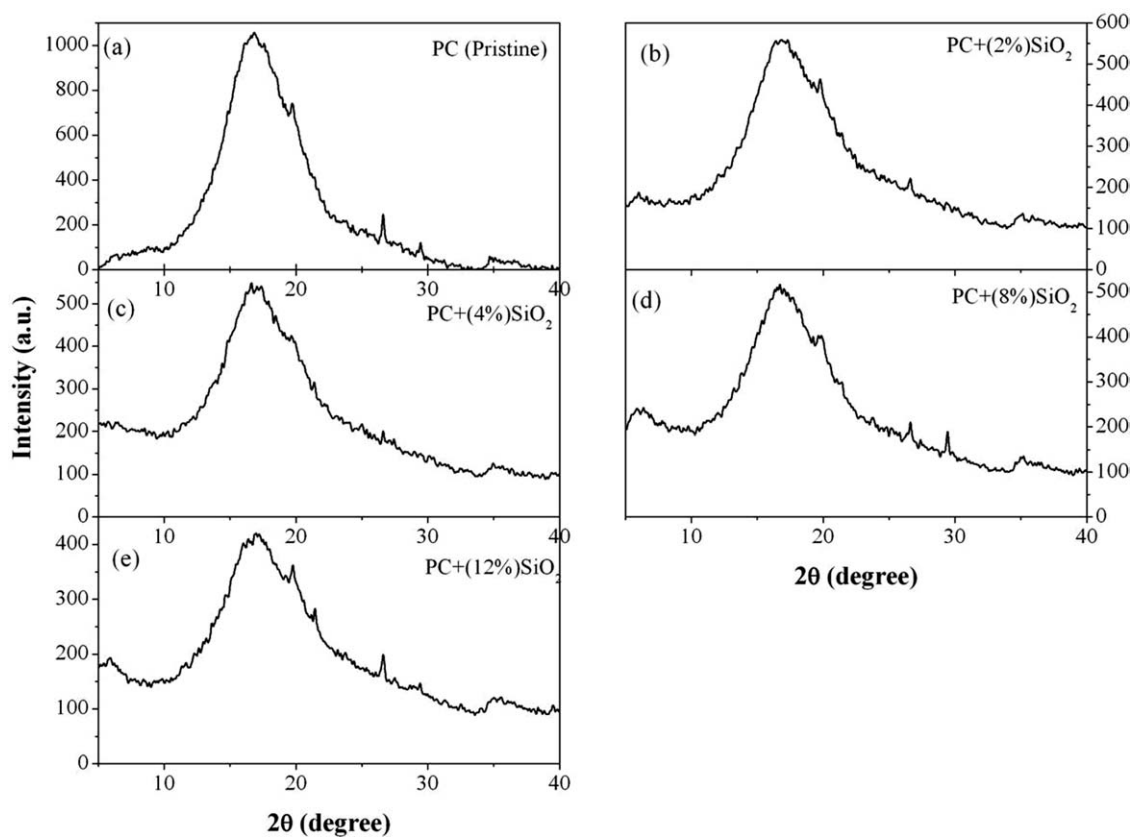


Figure 3 XRD patterns of PC and PC + SiO₂ nanocomposites films.

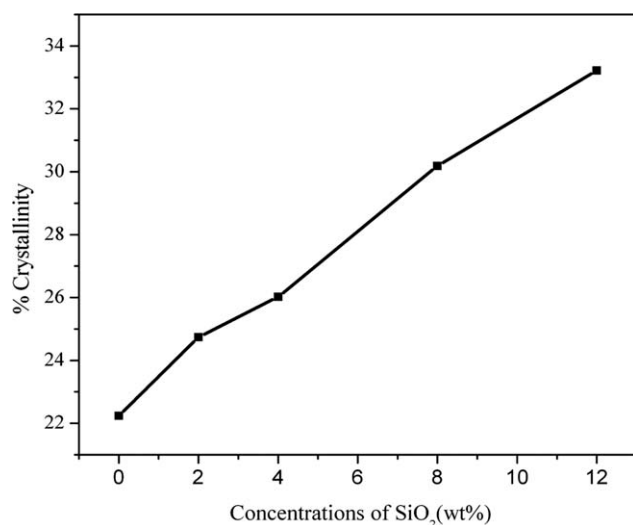


Figure 4 Concentration vs. percentage crystallinity of PC and PC + SiO₂ nanocomposites films.

Figure 5 shows the UV-vis spectra of PC pristine and PC + SiO₂ nanocomposite films with different wt % of SiO₂. It is clear that the fundamental absorption edge is shifted toward higher wavelength side with increase of concentrations. The optical band gap have been calculated by Davis and Mott relation,

$$\alpha(\nu) = \frac{B_{\alpha}(h\nu - E_g)^n}{h\nu} \quad (2)$$

where B_{α} is a constant, E_g is the energy band gap, $\alpha(\nu)$ is the absorption coefficient at a frequency of ν , and n is an index which can assume values of 1 for direct energy band gap and 1/2 for indirect energy band gap. The formation of a hydrogenated amorphous carbon with optical energy gaps depending on the H/C atom ratio.⁴⁶

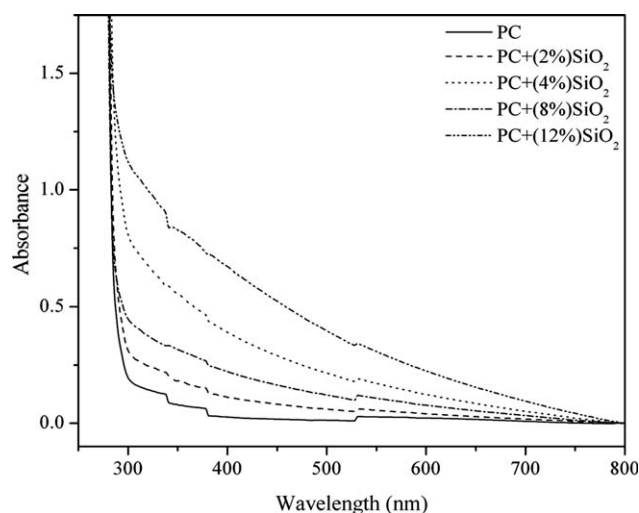


Figure 5 UV-vis spectra of PC and PC + SiO₂ nanocomposites films.

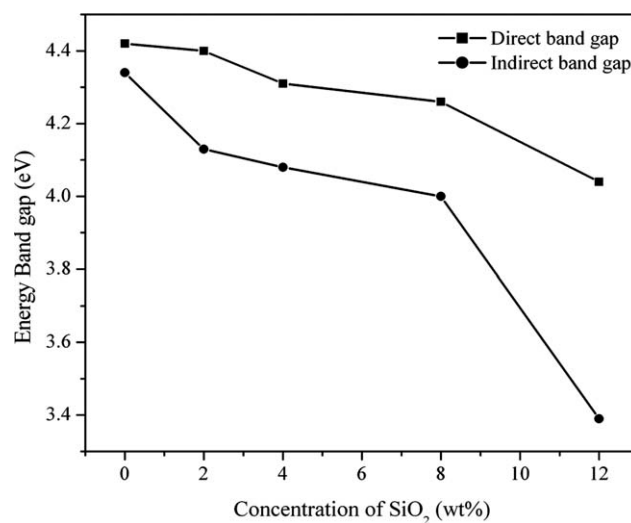


Figure 6 Concentration vs. energy band gap of PC and PC + SiO₂ nanocomposites films.

The number of carbon atom per cluster could be calculated by the following relation,

$$E_{bg} = \frac{34.3}{\sqrt{M}} eV \quad (3)$$

where M is the number of carbon atoms per cluster and E_{bg} energy band gap (average of direct and indirect band gap). The energy band gap (direct and indirect) and number of carbon atom per cluster for PC pristine and PC + SiO₂ nanocomposite films are shown in Figures 6 and 7, respectively. Energy band gap decreases with concentrations (wt %) of SiO₂ nanoparticles because density of nanoparticles increases as a result of cross-linking/chain scission of polymeric structure. Because the number of carbon atoms per cluster is reciprocal of energy band

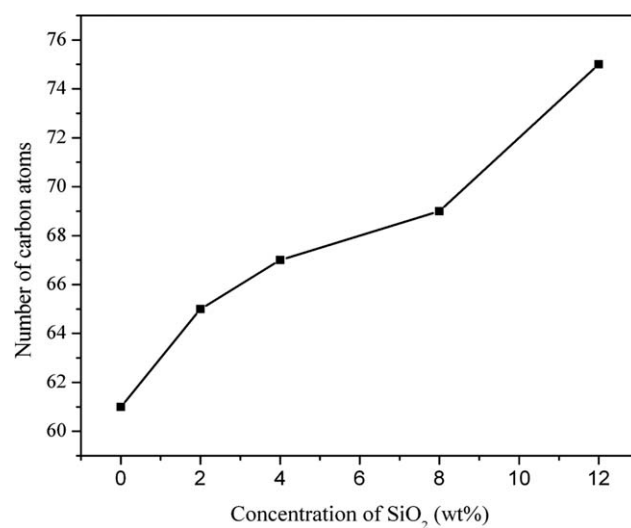


Figure 7 Concentration vs. carbon atoms of PC and PC + SiO₂ nanocomposites films.

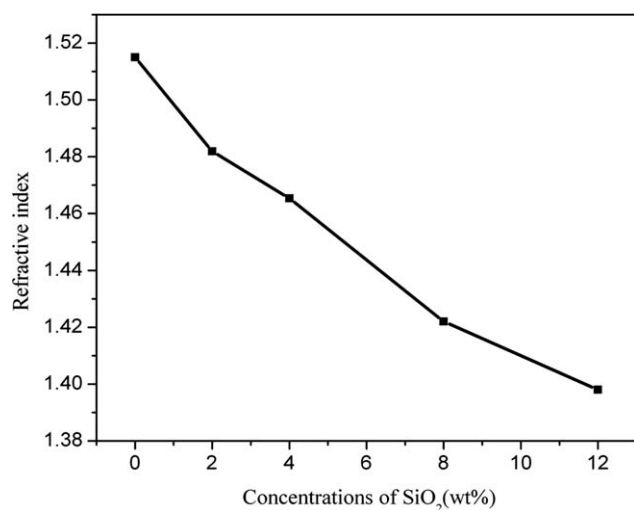


Figure 8 Concentration vs. refractive index of PC and PC + SiO₂ nanocomposites films.

gap, therefore, calculated value of carbon atoms increases with the concentration of SiO₂ nanofillers.

The refractive index at different concentration of SiO₂ nanoparticles in PC matrix were calculated by using the envelope method.^{3,47} Figure 8 shows the variations of refractive index with PC and PC + SiO₂ nanocomposites. The refractive index decreases with increase in SiO₂ concentration (i.e., 2, 4, 8, and 12 wt %). It is reported that refractive index of polymer nanocomposites is subjected to packing of nanoparticles with polymers. The refractive index in polymer nanocomposite is generally found to be the function of nanoparticles packing.⁴⁸ The decrease in refractive index indicates the loose packing of SiO₂ with PC as observed in present investigation.

The refractive index of nanocomposites depends on the nature of nanoparticles and its interaction with polymer matrix. Generally, the refractive index of polymer nanocomposites increases with increase in concentration of nanoparticles because nanoparticles are uniformly dispersed in the bulk of the material. Therefore, the uniform dispersion of nanoparticles decreases the velocity of light with increase in concentration of nanoparticles, causing the increase of refractive index. The interaction of nanoparticles with polymer molecules also affected the refractive index. However, if the nanoparticles are interacted strongly and dispersed uniformly, then the velocity of light will increase through polymer medium. Probably, this is happened in this experiment, which causes the decrease in refractive index. TEM images represent the uniform dispersion of nanoparticles and their elongation in a certain region forming the nanoclusters. The formation of nanoclusters in PC matrix is well expected. We have calculated the number of carbon atoms for verification of their existence. The size of nanoclusters is the function of carbon atoms. In pres-

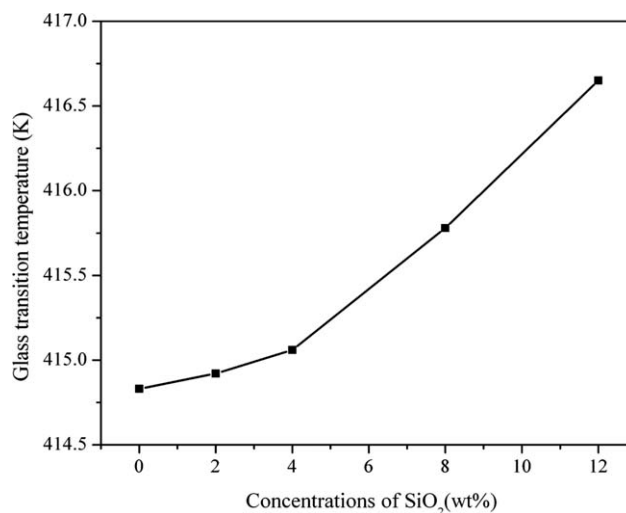


Figure 9 Concentration vs. T_g of PC and PC + SiO₂ nanocomposites films.

ent investigation, it is observed that the number of carbon atoms increase with increase in concentration of SiO₂ nanoparticles as shown in Figure 7. It is an evidence for formation of nanoclusters. Thus, the velocity of light is affected by nanoclusters and reduces the refractive index of nanocomposites samples.

Figure 9 shows the concentration vs. T_g of PC pristine and PC + SiO₂ nanocomposite films. The PC pristine material showed a T_g about 415 K, which is agreement with values reported in literature.^{30,44} After nanofilling, the T_g increases with SiO₂ wt %. It was well known that the polymers nanocomposites would result in strong or weak interfacial interaction. Therefore, the higher endothermic conversion can be interpreted by the restricting effect of SiO₂ nanoparticles on the polymers matrix. Thus, the SiO₂ nanoparticles are responsible for increase of T_g in nanocomposite sample.⁴⁹

Figure 10 shows the TSDC spectra of PC pristine and PC + SiO₂ nanocomposite samples poled at

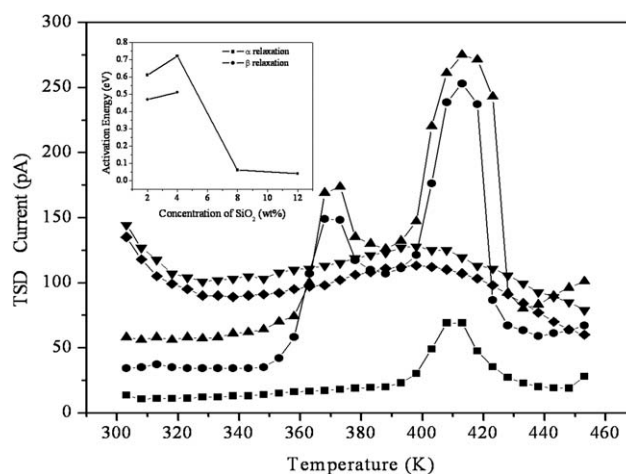


Figure 10 TSDC thermograms recorded with poling field of 200 kV/cm at 423 K.

TABLE I
TSDC Parameters of PC and PC + SiO₂ Samples

Polarization field (kV/cm)	Sample	Peak	Peak current (pA)	Peak temperature (K)	Activation energy (eV)	Charge released ($\times 10^{-12}$ coul.)	Relaxation time (s)
200	PC	II	71.83	410.59	0.44	143.29	1.01269×10^{-16}
200	PC + (2%) SiO ₂	I	253.82	412.88	0.47	818.72	1.01347×10^{-16}
200	PC + (2%) SiO ₂	II	150.49	370.40	0.67	318.99	1.02917×10^{-16}
200	PC + (4%) SiO ₂	I	274.92	414.56	0.51	1216.16	1.01411×10^{-16}
200	PC + (4%) SiO ₂	II	174.92	370.80	0.72	323.18	1.02289×10^{-16}
200	PC + (8%) SiO ₂	II	127.89	398.40	0.06	1048.98	5.94584×10^{-14}
200	PC + (12%) SiO ₂	II	113.30	398.08	0.04	950.19	9.56182×10^{-14}

poling field of 200 kV/cm at 423 K. The PC pristine and nanocomposites (8 and 12 wt %) shows single broad peak (α -relaxation peak) located at about 410 and 395 K, respectively, whereas PC + (2 wt %) SiO₂ and PC + (4 wt %) SiO₂ shows two peaks (α -relaxation and β -relaxation), which are located at about 412 and 365 K, respectively. The α -relaxation peak shows the T_g of PC pristine and nanocomposites sample. The α -peak temperature of the PC pristine and nanocomposites, which is in general, a good measure of T_g is in good agreement with the DSC results.

A material like a nanocomposite is a highly inhomogeneous material; on the scale of the filler-particle size, the conductivity is high at the positions of the particles and low in the matrix. TSDC is one of the techniques to give the information of conductivity, normally; it is measured over a length and area that are much larger than the size of the particles. In such a macroscopic measurement, the "average" conductivity is found in the sense that the measured current (which will mainly flow through the particles and not through the matrix) is treated as if it were flowing through the total material with a constant current density.

In nanocomposite system, the tunneling over two distant junctions can take place by using a virtual state of material that is in between the two junctions. This process is called the co-tunneling. There exist two forms of co-tunneling: elastic co-tunneling and inelastic co-tunneling. In elastic co-tunneling, the energy in all the steps⁵⁰ is conserved, whereas in inelastic co-tunneling, an excited state arises in the material between the junctions. Tunneling process for which the electron penetrate in forbidden gap region and create a short of tunnel between valance and conduction band. However, when electron escape to valance band via an intermediate virtual state, where two simultaneous tunnel events have an overall negative change in free energy. If a different electron from top tunnels for short time to conduction band, then overall an electron escaped from valance band to conduction band. This process is called inelastic co-tunneling, because it produces an electron-hole interaction.⁵¹⁻⁵⁴ However, the elastic co-

tunneling corresponds to the same electron tunneling into and out of a virtual state.

The latter is only possible when more than one electron is involved in the process. It seems that the electrons involved simultaneously change in state; one electron hops over the first junction (i.e., polymeric junction) to the other material (i.e., the junction formed by SiO₂) between the two junctions and another electron hops at the same time from this nanomaterial over the second junction. For inelastic co-tunneling, the former electron hops to a state that has energy differs from the energy of the state from which the latter electron comes, whereas for elastic co-tunneling, these energies are equal. Co-tunneling needs not to be restricted to two junctions; it can also cover three or more junctions. In co-tunneling, large distances can be hopped to states with favorable energies. Therefore, in materials like semiconductive nanocrystals, granular metals, or quantum dots, the temperature dependence typical for variable-range hopping can be observed.⁵⁵⁻⁵⁷ The charge transport process in TSDC is due to the co-tunneling mechanism is expected. It is further verified due to the nonlinear behavior of activation energy with concentration of SiO₂ (Fig. 10).

The position of TSDC peak in PC + SiO₂ nanocomposite is shifted toward higher temperature side with increase of SiO₂ wt %. Initially, the TSDC increases in all observation, however, TSDC decreases in nanocomposite samples, if concentration is more than 4%. In PC + SiO₂ (8 wt %) and PC + SiO₂ (12 wt %), the second peak (β -relaxation) is disappeared and first peak (α -relaxation) shifted toward lower temperature side. The TSDC peak in PC pristine is due to the motion of main chain segment and trapping of charge carriers in surface traps. This TSDC behavior of PC pristine is well known and reported in literature.⁴⁴ The TSDC parameters such as activation energy, charge released, and relaxation time are shown in Table I.

The charge released shows the linear behavior of 2, 4, 8, and 12 wt % SiO₂ nanocomposites samples when compare with PC pristine sample. These results show that SiO₂ nanofiller enhance the charge storage capacity of PC because of formation of deep

traps. The nanocomposite sample shows the linear behavior of activation energy with polarizing field and concentration but after 4 wt % SiO₂, the activation energy decreases. These results could be understood in terms of co-tunneling transport of charge carriers followed by the change in conductivity of material. The TSDC of nanocomposite samples increases up to 4% wt ratio of SiO₂ and then decreases. The behavior of TSDC is an evidence for increase and decrease of conductivity. SiO₂ increases the mobility of charge carrier in lower concentration range but reduces the mobility of charge carriers in higher concentration. It is due to the polymer nanoparticles interface impeded the motion of charge carrier in higher concentration. In other hand, the large particle density induced its own resistance and reduces the conductivity of nanocomposite.

Generally, the charge relaxation in polymer obeyed the Debye theory for charge relaxation process. In this study, the nonlinear behavior of TSDC parameters (Table I) with SiO₂ nanofiller concentration and polarizing field indicates the deviation of ideal Debye theory for charge relaxation process in polymer nanocomposite.

CONCLUSION

This article report the detailed investigation of the crystallinity, energy band gap, number of carbon atoms, refractive index, and dielectric relaxation in PC pristine and PC + SiO₂ nanocomposite. It has been concluded that these parameters are significantly affected by filling of SiO₂ nanoparticles in PC matrix. The increases of crystallinity is significantly affected the T_g and TSDC behavior of nanocomposite. DSC and TSDC techniques are observed to be complementary and allow the observation of charge relaxation and gave the results in good agreement with each other. Finally, it is understand clearly that the improvement in all these properties is due to the modification of surface and bulk structure of PC by filling of SiO₂ nanoparticles. The comparative analysis of the various structural parameters and dielectric parameters of complex structures for nanocomposite materials are strongly coupled properties, which establish the suitability of TSDC as a novel tool for the online testing and monitoring of nanocomposite materials.

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