

Investigation of thermally stimulated charge relaxation mechanism in SiO₂ filled polycarbonate nanocomposites

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Abstract The thermally stimulated charge relaxation properties of polycarbonate (PC) filled with SiO₂ nanofiller were studied by means of thermally stimulated discharge current (TSDC). The nanocomposite samples were further characterized by UV–vis spectroscopy, scanning electron microscopy, energy dispersive X-ray spectra, and differential scanning calorimetry (DSC) techniques to investigate the dispersion of nanofillers in polymer matrix and glass transition temperature. All pristine and nanocomposites samples of thickness about 25 μm were prepared using solution mixing method. The suitable weight percentage of SiO₂ nanofillers has been chosen to prevent the nonuniform dispersion. TSDC measurement of PC (Pristine) and PC+ (7% SiO₂) shows the single peak, while TSDC characteristic of other nanocomposites are showing two peaks. The higher temperature TSDC peak of pristine and nanocomposites samples is originated due to the charge relaxation from shallower and deeper trapping sites, however, low temperature peak is caused by dipolar relaxation of charge carriers. Since the position of higher temperature TSDC peak is generally an analysis of glass transition temperature of polymer/polymer nanocomposites. The authors have observed that the temperature of this peak is almost same as the T_g measured by DSC with 0 to ±5% variation. This article presents the deeper

understanding of charge relaxation mechanism caused by SiO₂ nanofillers in polycarbonate.

Keywords TSDC · Nanocomposites · Activation energy · Relaxation time · Nanofiller

Introduction

In last few years the filling of inorganic nanoparticles in polymer has paid much attention because of its excellent physical, mechanical, optical, electrical, and thermal properties [1–9]. Nanocomposites have the ability to reduce insulation thickness necessary for insulation of various electrical appliances. There are several reports on dielectric properties of these materials in recent years [10–12] but question arose that whether a new trapping level that can contribute to the improvement of insulation performance is formed by the addition of nanofiller or due to action of electric field on nanofillers separately or in composite material. The systematic and repeated study on composite material may able to answer the above questions.

Thermally stimulated discharge current (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, [13] etc. The effects of dipolar, direct current (dc), and space charge relaxations are closely linked to the temperature-dependent mobility of molecules, their fragments, protons, anions, electrons and depend on thermal treatment, temperature and field intensity of polarization and heating rate on depolarization or cooling rate on polarization. The nature of charge relaxation mechanisms

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is affected not only by the mentioned factors but also by morphological, structural, and chemical characteristics of materials. TSDC plays very important role for the study the interface formed due to filling of macro/nano inorganic fillers in polymer matrix in recent years [14].

The glass transition temperature (T_g) of polymer is influenced by several factors that include chain stiffness, ease of rotation of bonds, interactions between molecules, and chain length. In this regard, at least in bulk polymers, T_g reflects the structure of the polymer. Recently, it has been shown that T_g depends on the concentration of nanofillers in polymer matrix. The nano fillers may reduce to length scales comparable to the radius of gyration of the chain, the T_g of the polymer may increase or decrease, depending on the nature of its interactions with its environments [15, 16].

The authors report the preparation of PC and PC + SiO₂ nanocomposites samples by solution mixing method. These nanocomposites samples were characterized by UV-vis spectroscopy, scanning electron microscopy (SEM), energy dispersive X-ray spectra (EDX), differential scanning calorimetry (DSC), and thermally stimulated discharge current (TSDC) measurement.

Experimental

Polycarbonate (PC) pellets were supplied by Redox (India) and Silicon dioxide (SiO₂) nanoparticles of size 5 nm were supplied by Sigma-Aldrich have been used in this study. The pristine and nanocomposites samples in form of film were prepared by solution mixing method. The 5 g 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 solution thus prepared was poured onto an optically plane glass plate floating on mercury pool and the solvent was then allowed to evaporate inside an oven at room temperature for 24 h to yield circular film shape. The samples were further dried at room temperature with outgassing of 10⁻⁵ torr for a further period of 24 h to remove volatile residual solvent. For preparation of PC + SiO₂ nanocomposites samples of different weight ratio, the SiO₂ of certain amount was dissolve in 20 mL dichloromethane (DCM) and added drop by drop in solution of PC and again kept at magnetic stirrer for a period of 2 h at 333 K. This solution was used for preparation of PC + SiO₂ nanocomposites samples. All the samples of same thickness about (i.e., 25 μm) were used in present studies.

UV-vis transmittance spectra for PC (Pristine) and nanocomposites samples were recorded by double beam spectrophotometer (Hitachi Model U-2800) in the range of 200–800 nm.

The DSC thermograms of the pristine and nanocomposites samples were recorded in temperature range from 303 to 460 K with constant heating rate of 10 K min⁻¹. These thermograms were recorded from DSC (Model 2910 MDSC) available in UGC-DAE Consortium Indore (India).

The TSDC was recorded with digital picoammeter (Scientific Equipments Roorkee, India, model DPM-111) at a linear heating rate of 3 K min⁻¹. In order to avoid the effect of ground loop and extraneous electrical noise, the digital picoammeter was properly shielded and grounded. The detail of TSDC assembly and methods of polarization is reported in literature [17].

Result and discussion

Figure 1 shows the transmittance of PC (Pristine) and PC nanocomposites samples. The transmittance of the nanocomposites samples decreases with increase in SiO₂ concentration is due to Rayleigh scattering from the embedded SiO₂ nanoparticles. However, the transparency of samples at lower and higher wavelength is the same for all samples. These results of nanocomposites samples as compare to pristine indicate the proper dispersion of nanoparticles in polymer matrix. These results are similar to the nanocomposites based on epoxy resin and SiO₂ nanoparticles [18].

The surface morphologies of PC pristine and SiO₂ nanofillers dispersed in polymer matrix were carried out by SEM images. Figure 2a shows the micrograph of PC pristine and Fig. 2b–d shows the micrographs of 3, 5, and 7 wt% SiO₂ nanofillers dispersed in PC, respectively. SEM images show the uniform dispersion of the nanofillers in polymer matrix.

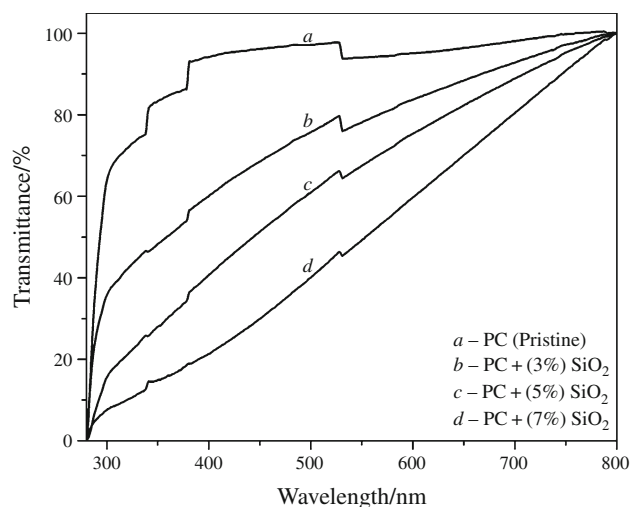
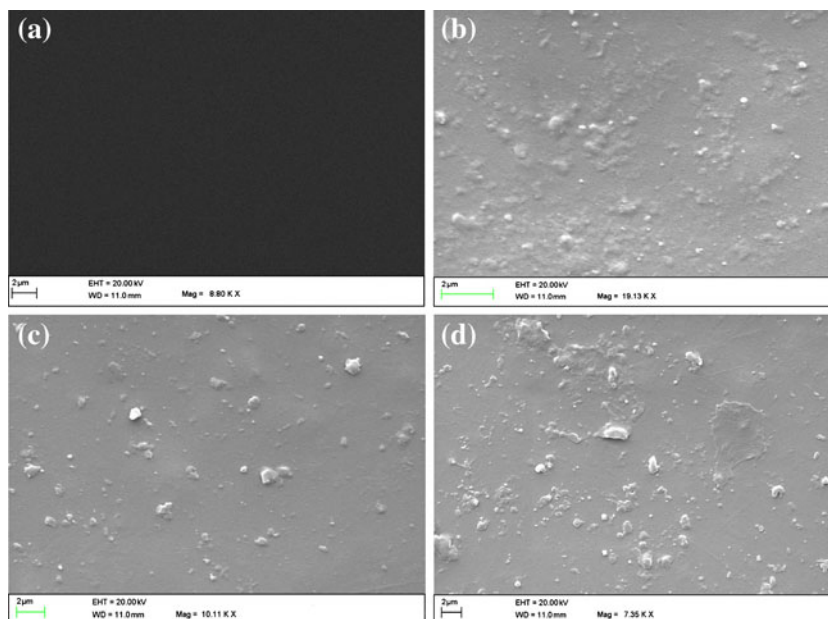


Fig. 1 UV-vis spectra of a PC (Pristine), b PC + (3%) SiO₂, c PC + (5%) SiO₂, and d PC + (7%) SiO₂

Fig. 2 SEM micrographs of PC Pristine and PC + SiO₂ nanocomposites



To determine the chemical composition of the nanocomposites, the EDX spectra was recorded. In Fig. 3a–c shows the EDX spectra of 3, 5, and 7 wt% SiO₂ nanofillers dispersed in PC, respectively. The presence of Si and O in EDX spectra is a direct evidence for formation of PC + SiO₂ nanocomposites.

The DSC characteristics of PC (pristine) and nanocomposites samples are presented in Fig. 4. The DSC measurement shows that T_g of the nanocomposites increases with SiO₂ concentration. This effect is more pronounced with high concentration of nanofillers in short and rigid polymer chains, like PC in this study, and obviously overcompensates the reduction of molecular mobility imposed by the presence of the SiO₂ particles. In other hand, at low concentration of SiO₂ in PC creates the region of low mobility polymer and nanoparticles due to strong interaction gives the single T_g , it is also responsible for increase in T_g . This behavior is corresponds to high-temperature peak (say space charge relaxation peak) appeared in TSDC characteristics of the samples.

Figure 5 shows the TSDC spectra of PC (pristine) and PC + SiO₂ nanocomposites poled at poling field of 100 kV cm⁻¹ at 423 K. The PC (Pristine) and PC + (7%) SiO₂ shows single peaks, while PC + (3%) SiO₂ and PC + (5%) SiO₂ shows two peaks. The TSDC peak in pristine PC is due to the motion of main chain segment and trapping of charge carriers in surface traps. The charge carriers of energy 0.6 eV show that surface traps are more dominant. This TSDC behavior of pristine PC is well-known and reported in literature [19].

The TSDC characteristic in pristine PC shows a single peak at about 420 K, which corresponds to the α -relaxation associated with the glass transition of the amorphous phase of PC. The α -peak temperature of the pristine and

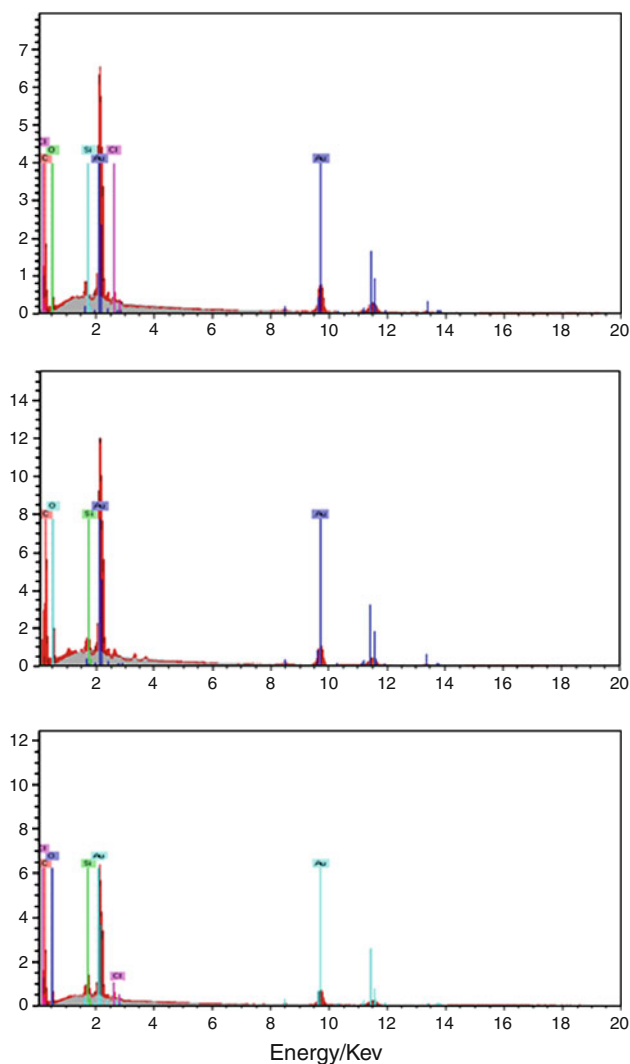


Fig. 3 EDX spectra of 3, 5, and 7% SiO₂ in PC

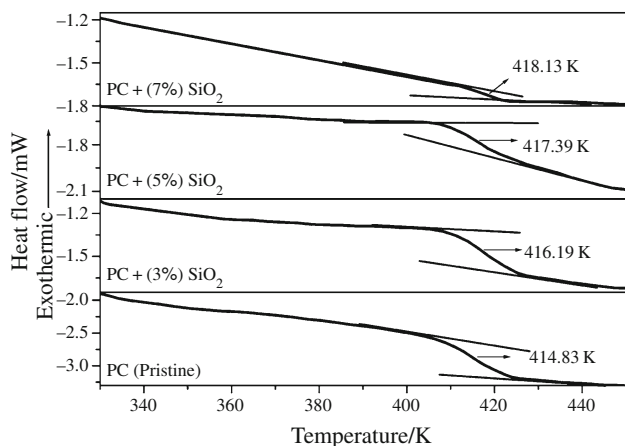


Fig. 4 DSC characteristics of PC Pristine and PC + SiO₂ nanocomposites

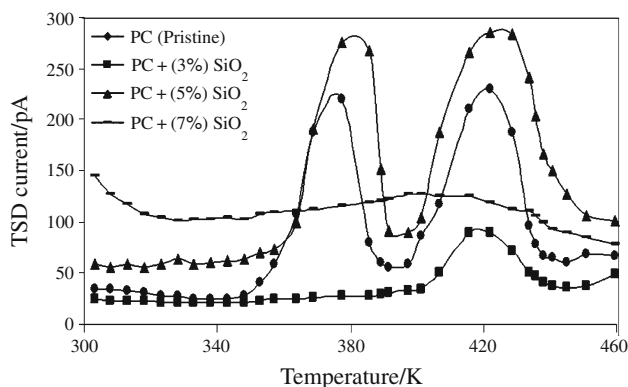


Fig. 5 TSDC characteristics of PC (Pristine) and PC + SiO₂ nanocomposites polarized at 423 K temperature

nanocomposites, which is in general a good measure of T_g , is in good agreement with the DSC data.

The modification of space charge behavior is a general feature of the various polymeric nanocomposites due to formation of interface between polymer and nanofillers. It has been observed in several polymeric nanodielectric [20–23] polymers that there may be a Guoy–Chapman layer associated with these interfaces. The dispersion of nano particles induces interaction zones to creating a pathway

for local conduction without affecting the bulk conductivity. This mechanism would provide an explanation for the change in internal charge behavior and also would be expected to reduce the space charge [24, 25]. The TSDC parameters such as activation energy, charge released and relaxation time are shown in Table 1.

It has been observed that (i.e., Table 1) the charge released for 3, 5, and 7% filled nanocomposite samples is more as compare to pristine PC. These results suggest the SiO₂ nanofiller enhance the charge storage capacity of PC. The nanocomposite sample shows the nonlinear behavior of activation energy with SiO₂ concentration. Therefore, on the basis activation energy it is difficult to discuss the charge relaxation mechanism. It is also difficult to treat the observed TSDC peaks quantitatively, since there is no theory of the TSD currents for nanocomposites samples. Nevertheless, it is clear from the shape of the peaks that relaxation processes in PC + SiO₂ nanocomposites deviate considerably from the ideal Debye case of non-interacting relaxing units. This can be taken into account by assuming that polarization decays with time according to the stretched exponential law

$$P(t) = P_0 \exp\left(-\frac{t}{\tau}\right)^\alpha \quad 1 \geq \alpha > 0 \tag{1}$$

where t is the time constant, P_0 is the initial polarization. If a sample is linearly heated at the rate $b = dT/dt$, then

$$P(t) = P_0 \exp\left(-\frac{1}{\beta} \int_{T_0}^T \frac{dT'}{\tau(T')}\right) \tag{2}$$

where T_0 is the initial temperature. It is reasonable to assume that temperature dependence of τ obeys the Arrhenius law

$$\tau(T) = \tau_0 \exp\left(\frac{A}{kT}\right) \tag{3}$$

where A is the activation energy, k is Boltzmann’s constant, τ_0 is the characteristic time. The expression for the TSD current density is obtained from Eqs. 1, 2, and 3

Table 1 TSDC parameter of PC and nanocomposite samples

Polarization on field/kV/cm	Name of sample	Peak	Peak current/pA	Peak temperature/K	Activation energy/eV	Charge released/ $\times 10^{-12}$ coul.	Relaxation time/s
100	PC	II	90.49	418.96	0.12	273.29	2180×10^{-14}
	PC + (3%) SiO ₂	I	203.82	366.89	0.68	606.56	46.28×10^{-14}
	PC + (3%) SiO ₂	II	241.36	421.56	0.12	764.62	16.98×10^{-14}
	PC + (5%) SiO ₂	I	275.25	367.35	0.08	850.85	1.01×10^{-16}
	PC + (5%) SiO ₂	II	295.05	424.60	0.09	1275.74	26.70×10^{-14}
	PC + (7%) SiO ₂	II	128.43	402.63	0.01	2877.6	5.64×10^{-16}

$$i(T) = \frac{\alpha P_0}{\tau_0} \exp\left[-\frac{A}{kT}\right] [s(T)]^{\alpha-1} \exp[-(s(T))^\alpha] \quad (4)$$

where

$$s(T) = \frac{1}{\beta\tau_0} \int_{T_0}^T \exp\left(\frac{-A}{kT'}\right) dT' \quad (5)$$

Equation 4 confirmed the conclusions for the origin of TSDC and the thermal stability of relaxation processes. It shows that the depolarization current peak in 3 and 5% SiO₂ nanocomposites is originated due to two-relaxation process (i.e., may be dipolar and space charge relaxation), however, the appearance of single broad peak in 7% SiO₂ filled nanocomposites samples indicates the two components (i.e., dipolar and space charge) of relaxation are merge together. It is one of the reasons that activation energy could not able to explain the behavior of this peak. In the presence of SiO₂ in PC matrix, the resultant polarization may be caused by not only polycarbonate but also by SiO₂. The high concentration (i.e., 7, 9, and 11%) of SiO₂ filled nanocomposite is strongly affected the TSDC behavior. The appearance of single broad peak may also be due to the saturation of resultant polarization as well as diffusion of large number of oxygen atoms in polymer matrix. The similar results have been observed in 9 and 11% SiO₂ filled nanocomposites samples, but only representative TSDC and DSC characteristics of 7% SiO₂ filled samples are shown.

The sharp TSDC peak at higher temperature for the samples filled with 3 and 5% SiO₂ indicates the existence of deep traps related to the high charge stability. The traps are formed at the interface between SiO₂ nanoparticles and PC. Generally, space charge relaxation peak is shifted toward higher or lower temperature side with increase of polarizing field [26, 27]. Increasing the concentration of SiO₂ from 3 to 5%, no shifting of TSDC peak was observed with increase of polarizing field (i.e., figure not shown), it is considered as a modification of space charge phenomenon in polymer nanocomposites. The two sharp TSDC peak in nanocomposite sample filled with lower concentration of SiO₂ shows the strong modification of TSDC spectra for pristine PC. It may be due to the increase in permittivity and decrease in dielectric losses; therefore, the peaks are farley sharp. The first peak is followed by dipolar relaxation process, which is corresponding to low value of activation energy as presented in Table 1. Indeed, dipolar peak does not appear in pristine PC because of its nonpolar behavior. However, the peak appeared in 3 and 5% filled nanocomposites samples at same position for all polarizing field is a strong evidence for its dipolar nature. This behavior is caused by increase in dipole moment due to addition of nanoparticles.

The activation energy is maximum for 3% SiO₂ filled samples for the second peak and then reduces gradually with increase in concentration of SiO₂. This reverse behavior of activation energy could be understood in terms of modified space charge relaxation process. The second peak is expected to be due to creation of new traps ranges from shallow to deeper with variation of surface roughness by introduction of nanofillers. The trapping of charge carriers in shallow/deeper traps is the possible reason of this peak.

Conclusions

The thermally stimulated charge relaxation of a series of PC samples filled with different concentration of SiO₂ nanoparticles was investigated using differential scanning calorimetry and thermally stimulated discharge currents. These experimental techniques are complementary and allow the observation of charge relaxation, and gave results in very good agreement with each other. It is concluded that the variation of T_g in nanocomposite samples is due to the strong interaction of SiO₂ nanoparticle with PC matrix. The nonlinear behavior of TSDC parameters with SiO₂ nanofiller concentration indicates the deviation of ideal Debye theory for charge relaxation process.

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