J Therm Anal Calorim (2010) 101:315–321
DOI 10.1007/s10973-010-0675-2

Thermally stimulated current and differential scanning calorimetry spectroscopy for the study of polymer nanocomposites

Mulayam Singh Gaur · Bhupendra Singh Rathore · Pramod Kumar Singh · Ajaypal Indolia · Anand Mohan Awasthi · Suresh Bhardwaj

Received: 20 July 2009 / Accepted: 6 January 2010 / Published online: 30 January 2010

Abstract The thermally stimulated discharge current (TSC) and differential scanning calorimetry (DSC) spectroscopy have been recorded in 25 μm thick samples of pristine polycarbonate (PC) and zinc oxide nano particle-filled polycarbonate. Polycarbonate (PC)/zinc oxide (ZnO) nanocomposites of different mass ratio (e.g., 1, 3, and 5%) were prepared by sol–gel method, followed by film casting. The glass transition temperature of nanocomposite samples increases with increase in concentration of ZnO nano fillers. It is due to the strong interaction between inorganic and organic components. The TSC peaks of nanocomposite and pristine PC indicate the multiple relaxation process. It has been observed that the magnitude of TSC decreases with increase in concentration of nanofillers. The TSC characteristics of 5% filled nanocomposites shows exponential increase of current at higher temperature region. This increase in current is caused by formation of charge-transfer complex between inorganic phase (e.g., ZnO) and organic phase (e.g., PC). Thus, the nano material like zinc oxide transfers the charge carriers from inorganic phase to organic phase rapidly and resultant current increases exponentially. This current is known as leakage current or breakdown current. TSC peak height is observed as a function of the polarizing field. The height of TSC peak increases as the field increases in pristine PC, while TSC peak height is suppressed in nanocomposite samples. This indicates the amount of space charge is smaller in the nanocomposites with a proper addition of ZnO nano fillers than in the pristine PC.

Keywords TSDC · Nanofillers · ZnO · Activation energy · Secondary relaxation

Introduction

The development of polymer nanocomposite of polymers using nanoparticles is common in the production of modern technology. Polymer nanocomposites (PNCs) or materials represent a radical alternative to these conventional-filled polymers or polyblends. In contrast to conventional systems where the reinforcement is on the order of microns, PNCs are exemplified by discrete constituents on the order of a few nanometers—million-times finer than a human hair. Uniform dispersion of these nanoscopically sized filler particles produces an ultra-large interfacial area per unit volume between the nanoelement and host polymer. For example, interfacial area approaching 700 m^2 cm^{-3} occurs in dispersions of layered silicates in polymers. This is comparable to a football field within a raindrop. These dimensions also imply that the distance between nanoelements is comparable to their size. For a 1-nm-thick plate, the distance between plates approaches 10 nm at only 7 vol% of plates. This is a morphology truly dominated by nanoscale properties. Due to the nanoscale structure of PNCs, a new combination of properties offers new advantages for the development of advanced materials, including polymer materials, with high transparency, thermal resistance, electrical resistance, dielectric properties, and dimensional stability. These materials seem to be promising candidates for such practical areas as optics and electronics [1–5].

M. S. Gaur (✉) · B. S. Rathore · P. K. Singh · A. Indolia
Department of Physics, Hindustan College of Science
and Technology, Farah (Mathura), India
e-mail: mulayamgaur@rediffmail.com

A. M. Awasthi · S. Bhardwaj
UGC-DAE Consortium, Indore, MP, India

Recently, a lot of attention has been paid in polymer nanocomposites because of their applications as an emerging insulating material for electric power apparatus. They have the ability to reduce insulation thickness necessary for insulation of various electric appliances. There are several reports on dielectric properties of these materials in recent years [6–10] but question arises that whether a new trapping level that can contribute to the improvement of insulation performance is formed by the addition of nano-filler or due to action of electric field on nano fillers separately or in composite material. This phenomenon is still unclear inspite of many efforts made by researchers. Therefore, TSC is expected to be a powerful tool to explain underline phenomenon.

The T_g of polymer is influenced by several factors that include chain stiffness, ease of rotation of bonds, and 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 [11–13].

The objective of the present study is to elucidate the effect of ZnO nanofillers on TSC and DSC spectroscopy.

Experimental

Polycarbonate used in the present study was procured by BDH. The ZnO nano particle of size less than 100 nm was supplied by Sigma–Aldrich. All samples were prepared by using the sol–gel technique. The solution of particular concentration was prepared in a glass beaker by dissolving PC (5 g) in 100 ml of dichloromethane (DCM) at 333 K. The solution was then kept for 4 h to become homogeneous and transparent. 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 desired samples. The dried thin films of pristine PC were subjected to room temperature outgassing at 10^{-5} torr for a further period of 24 h to remove any residual solvent. In order to obtain the thin film of nanocomposite, we followed a process containing important steps for preparation of mother solution:

1. In this technique, the ZnO particles of certain mass ratio are taken in 20 ml dichloromethane (DCM) and then solution was kept at 333 K in magnetic stirrer for the period of 30 min. The milky solution (e.g., solution 1) was prepared.
2. The polycarbonate dissolved in 100 ml DCM. The solution was kept at 333 K in magnetic stirrer for a period of 30 min. A transparent homogeneous solution (e.g., solution 2) was obtained.
3. In order to prepare the mother solution, the solution 1 is added drop by drop in solution 2 and this new solution was stirred again for minimum 30 min. The mother solution was thus prepared.

The remaining method is same as for as preparation of pristine PC thin film. The 3.5-cm diameter of both surfaces of the samples was coated by aluminum using Hind High vacuum coating unit.

The TSC measurement assembly consists of two aluminum electrode of 3.5 cm diameter. The vacuum aluminized sample was sandwiched between two electrodes. The samples were thermally polarized with different value of polarizing field at 373 K. The sample holder forming metal–sample–metal system was placed in a digitally controlled oven heated up to 373 K. The sample was then allowed to remain at that temperature for about 30 min, and then desired strength of electric field was applied for 1 h. The sample was allowed to cool down at room temperature in the presence of applied field. On attaining room temperature, the sample was kept shorted for an arbitrary time of 10 min so as to remove frictional and stray charges. Then, the sample is reheated at a constant heating rate of 276 K min^{-1}; a discharge current is then generated as a function of rising temperature, which is measured by means of a sensitive digital electrometer (Scientific Equipments, Roorkee, India, DPM-111) was carefully shielded and grounded to avoid ground loops or extraneous electrical noise. The TSC thermograms were thus obtained consists of various peaks whose shape and location are characteristic of the relaxation mechanisms of the polymer nanocomposites.

The filling of ZnO nanoparticles allows the preparation of polyfunctional polymer hardener. This modification is performed through the interaction of ZnO with carbonate groups of polymer. The number of carbonate group on the surface of nanoparticle or vice versa modified the polymer matrix. As a result, the whole polymer system is transformed into an organo inorganic nanocomposite material that contains linear chains and polyfunctional units.

The glass transition temperature of the pristine PC and nanocomposites samples were measured using temperature-modulated differential scanning calorimeter (TA instrument model 2910) at UGC-DAE Consortium, Indore (M.P.) India. Sample of mass 4–12 mg was heated at a rate of 283 K min^{-1}. The experimental chamber is flushed for a few minutes with purge gas at high flow rate to get rid of any minute impurities. The sample and the reference are placed on raised platform cast on the thermoelectric constantan disk, which serves as the primary means of heat transfer to the sample and the reference from the temperature programmed furnace. The resulted heat flow to the sample is measured by area thermocouples fixed to the under side of disk platforms. T_g was determined by fitting straight lines through the data obtained from the glassy and rubber regions. The temperature at which these lines intersect is identified as the T_g of the sample. All the observations were carried out with the accuracy of ±5% experimental error and results are reproducible.

Results and discussion

TSC spectroscopy

The TSC thermograms of pristine PC and polymer nanocomposites (PC + ZnO) are shown in Figs. 1, 2, and 3. The thermograms are polarized with 30, 60, and 90 kV cm^{-1} at polarizing temperature of 373 K.

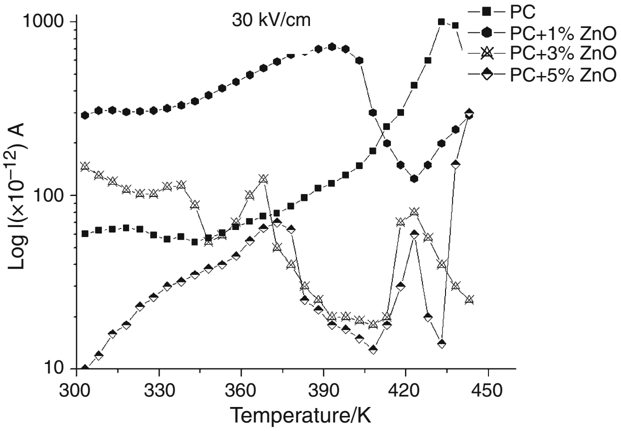

Fig. 1 TSC thermograms recorded at 373 K with polarizing field of 30 kV/cm

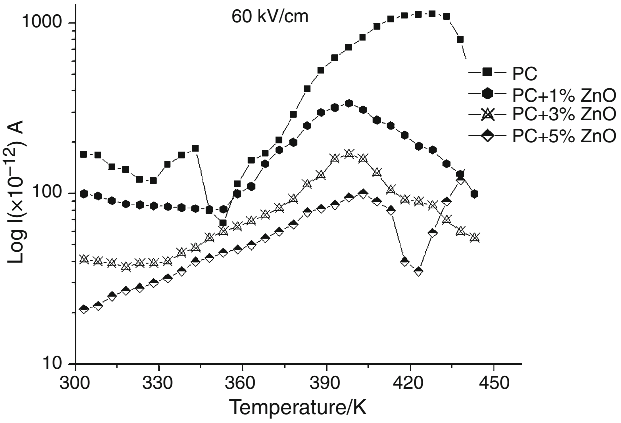

Fig. 2 TSC thermograms recorded at 373 K with polarizing field of 60 kV/cm

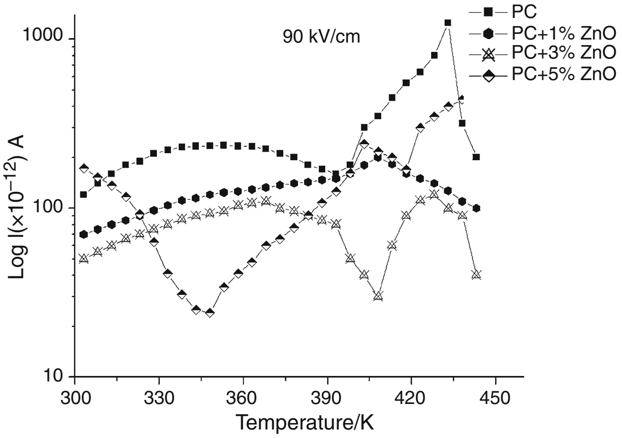

Fig. 3 TSC thermograms recorded at 373 K with polarizing field of 90 kV/cm

The TSC characteristics are showing three relaxation regions; (i) 303 to 348 K, (ii) 349 to 373 K and (iii) above 373 K. These relaxation regions are generally known as ρ, β, and α relaxation processes. ρ relaxation occurs due to influence of surface traps, β relaxation occurs due to dipolar polarization and α relaxation is due to space charge polarization followed by trapping of charge carriers in deeper traps. The low temperature peak (i. e., ρ relaxation peak) has been observed in pristine samples polarized with 60 kV cm^{-1} (Fig. 2) and in nanocomposite samples (3% ZnO-filled PC) polarized with 30 kV cm^{-1} (Fig. 1). However, β relaxation peak is only observed in 3 and 5% ZnO-filled nanocomposites polarized with 30 kV cm^{-1} as shown in Fig. 1.

Our TSC results suggesting that secondary (e. g., α relaxation) relaxation is the main mechanism of TSC. For α relaxation processes, the activation energy is more than 0.5 eV. However, calculated activation energy for nanocomposite samples is comparatively less than pristine PC samples. This shows the reduction of space charges due to addition of nanoparticles. The motion of carbonate group is strongly observed in our TSC results but it seems that motion of hydroxyl group is merged together with motion of carbonate group in pristine PC. The peak seems to be due to trapping of space charges in deep trapping levels and motion of carbonate groups. The shifting of α peak is mainly observed when nanocomposites polarized with polarizing field of 60 and 90 kV cm^{-1}. This shift could not be observed in polarizing field of 30 kV cm^{-1}. The shift of α peak in naocomposites indicated the motion of carbonate group is impeded by addition of nanoparticles.

It is widely accepted that the TSC peaks are the results of different types of relaxation processes, the relaxation processes are clearly distinguished on the basis of peak position. The relaxations in the glassy state basically imply intermolecular processes, and perhaps only the α-relaxation (e.g., secondary relaxation) is related to intermolecular effects. Infact, some authors considered the α relaxation as the precursor of the glass transitions, therefore, many authors [14–17] considered TSC as a tool to deduce glass transition temperature of polymeric materials, and in this sense it would be a "universal feature" of the glass-forming materials, including low molecular mass compounds. The α relaxation is due to polymer segmental motion associated with the onset of the glass transition and the other due to the dipolar motion associated with low temperature peak.

In general, it is considered that molecular units associated with a dipole tend to rotate within a cage, cluster, by the effect of the electric field. The motion is restricted by limits of the cluster (i.e., mobility of charge carrier) made up of other polymer atoms acting as the boundaries of the cage. The motion of the unit is described in terms of the coordinates fixed with respect to the coordinates of the cavity, and an intermolecular potential barrier expressed as a function of these coordinates. Consequently, subglass relaxation processes can be considered as a thermally activated motion between two potential wells separated by a potential barrier [18]. The probability of location of molecules at each side of the barrier is determined by the Boltzmann distribution. The application of an external electric field alters the equilibrium distribution by changing the relative depths of the minima, thus causing a redistribution, the rate of which is controlled by the activation energy barrier [10].

The dielectric relaxation in polymeric insulators is mainly caused by the molecular motions [19, 20], which could be considered: (i) local main chain motions can give rise to secondary dielectric relaxations as in the case of PC (ii) motions of side groups about the bonds linking them to the main chain, as in the case of poly-n-alkyl methacrylates, are probably the best studied examples of the polymers containing dipolar groups in their lateral chains (iii) internal motions of the side chain groups without cooperation of the main chain are typical of polymers containing flexible units or polar group (iv) another possibility concerns the motions of small molecules, as water, for example, embedded in a polymer matrix .

Polymers such as polyvinyl chloride (PVC), polycarbonates (PCs), and aromatic polyesters derived from terephthalic acid (PET) and similar polymers or isophthalic (PEIT) acid show secondary relaxation. The interpretations of these peaks are made by several authors as reported in literature [21–26]. Therefore, we do not think the interpretation of these peaks is essential, we mainly concern with how ZnO nanofillers affect the behavior of TSC in PC?

Our results indicate that charge carriers tend to be captured more strongly by the addition of ZnO nano fillers. Figure 4 shows the TSC peak current versus polarizing field characteristics. The opposite trends of 3 and 5% ZnO-filled nanocomposites may be due to nonuniform dispersion of nanoparticles. The peak height increases as the field increases in pristine PC. On the other hand, generally the nonlinear dependence of peak height on polarizing field and comparative suppression of the peak height in 1% ZnO-filled nanocomposites indicate the charge carriers tend to be captured more strongly. If these captured charge carriers induce homocharge layers in the vicinity of the electrodes, thus further formation of space charge would be suppressed. This seems to explain the fact that the amount of space charge is smaller in the nanocomposite than in the pristine PC. The activation energy was calculated using Arrhenius equation [11]:

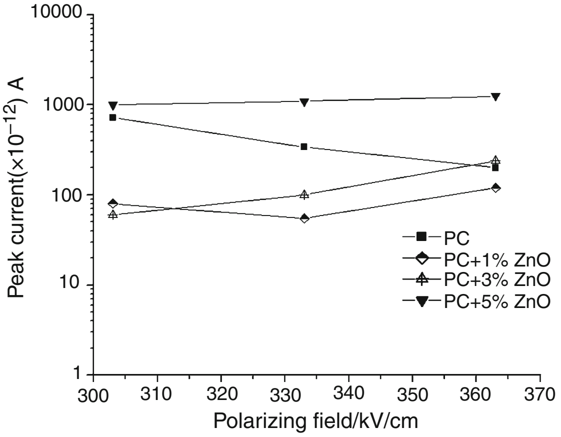

Fig. 4 Peak current versus polarizing field characteristics for α peak

$$I = I_0 \exp[-E_a/kT] \tag{1}$$

The activation energy have the higher value ranges from 0.5 to 1.2 eV for α relaxation peak of pristine PC, but activation energy of nanofilled PC is not exceeding the value of 0.6 eV.

We observe, a significant decrease of the current magnitude of the nanocomposite samples and a shift to lower temperatures. It could be further understood in terms of loosened packing of PC chain fragments in the nanocomposites due to tethering on the ZnO nano particles, resulting in increase of free volume. This effect is more pronounced in the case of amorphous polymer chains like PC in the present study, and obviously over compensates the reduction of molecular mobility imposed by the presence of the ZnO nano particles.

It has been observed that the TSC of 5% ZnO-filled nanocomposite samples increases exponentially at higher temperature region in all polarizing conditions (Figs. 1, 2, 3). The increase in current caused by presence of nanoparticle in polymer matrix at the high charging field and temperature due to formation of charge-transfer complex between inorganic and organic molecules. The charge-transfer complex (CTC) is an intraction between two or more molecules, or of different parts of one very large molecule, in which the attraction between the molecules (or parts) is created by an electronic/ionic transition into an excited state, such that the friction of charge is transferred between molecules. Since ZnO nano particles in the PC matrix introduces ionic species that contribute ionic charge carriers. These friction charges (e.g., ions) rapidly tunnel from inorgnic phase to organic phase and responsible for leakage or breakdown current. This state is experimentally observed in TSC of nanocomposite (e.g., 5% ZnO-filled PC) recorded at 100 kV cm^{-1} field.

The position of α peak (i.e., high temperature peak) in TSC characteristics of pristine and PC–ZnO nanocomposite samples have been found to be near the glass transition temperature region. This peak is caused by dielectric manifestation of the glass transition temperature [27–29]. The position of α peak varies from 422 to 443 K, however, T_g observed from DSC is varying from 414.83 to 415.98 K. This difference in position of α peak with T_g observed by DSC is occurred due to different heating rate used in both the experiment.

Differential scanning calorimetry (DSC)

The DSC characteristics of pristine and nanofilled PC is shown in Figs. 5, 6, 7, and 8. In general, the glass transition temperature (T_g) increases with increase in concentration of nanofillers. The filling of nanoparticles is not only act as plasticizers but also interact with the molecular motions that causes subglass activity and finally affecting the glass transition temperature of polymers.

The oxygen groups in PC have unshared electrons, which can share the electron with ZnO nanofillers and form a bond. These interactions hinder the mobility of chain

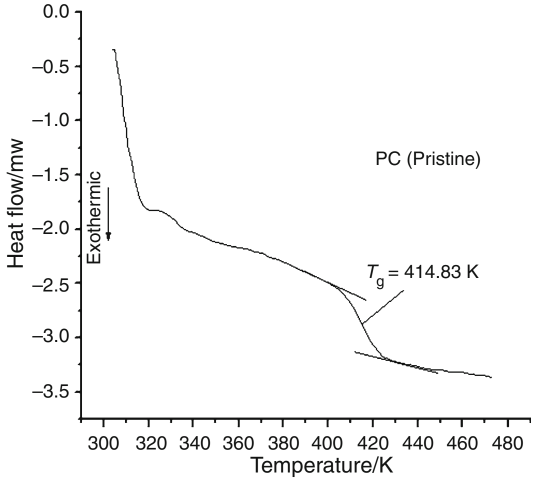

Fig. 5 DSC of pristine PC

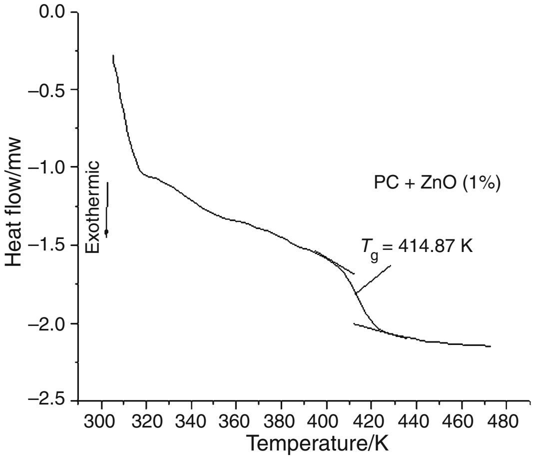

Fig. 6 DSC of polymer nanocomposites (PC + 1% ZnO)

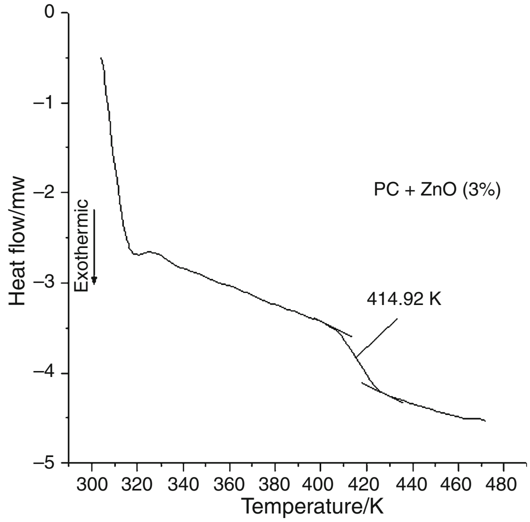

Fig. 7 DSC of polymer nanocomposites (PC + 3% ZnO)

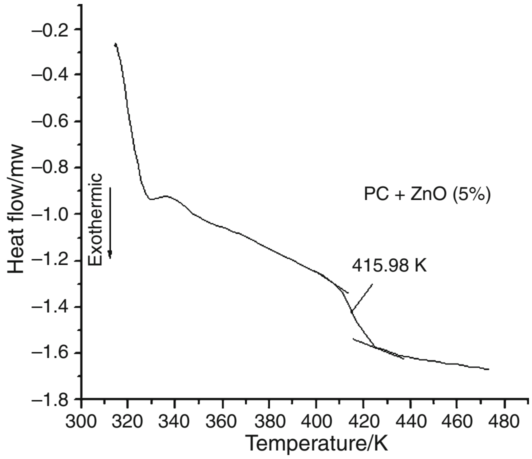

Fig. 8 DSC of polymer nanocomposites (PC + 5% ZnO)

segments and create a region of low mobility in the vicinity of the polymer–nanofiller interface. This region in the vicinity of the polymer matrix evidently exhibits a dominant effect on the average glass transition temperature of composite, leading to the increase in the effective T_g due to interaction with nanofillers and formation of nanophases. This behavior is similar to that observed in polystyrene (PS), poly (methyl methacrylate) (PMMA), and poly (2-vinyl pyridine) (P2VP) nanocomposites containing 10–15 nm-diameter silica nanospheres or 47 nm-diameter alumina nanospheres [30].

Wei et al. [31] through molecular dynamics simulations, showed that the density of composites is larger than that of a pristine polymer and that there is an associated increase in the glass transition. The increase in T_g, they argued, the dynamics of the polymer chains are reduced in composites. One could argue further that a broader distribution of dynamical processes should characterize the behavior of the composites. The structure of the composites should be heterogeneous on a small scale comparable to the chain dimensions; chains locally in contact with the nano fillers would exhibit slower dynamics than chains in an environment rich with polymer chains. It has been observed that T_g is appeared in α relaxation region of TSC. T_g increases slightly on addition of nanoparticles from the value of 414.83 K for PC to the value of 415.98 K for the nanocomposites. This improvement in T_g suggests that the nanofillers stiffen the polymer matrix at high temperatures. Due to the large surface area of the nanoparticles, large amount of polymer chains have strong interaction with the particle surfaces and prevents segmental motion of the polymeric chains [32].

It is demonstrated by many group of researcher that in the case of a hard surface in polymer matrix the configurational freedom of the chains is lower due to the interactions [33–35]. Thus, for a polymer nanocomposites confined at both interfaces, one would expect the T_g of this system to be higher than the bulk analog. In general, the configurational freedom of the entire system determines the sign of ΔT_g. Hence, if the interactions between the polymer matrix and the fillers like nanoparticles are strong then the observation that $\Delta T_g > 0$, which is an agreement of the results of present study. If the effect of the interactions of the PC with the ZnO nanofillers is to increase the chain segmental density, which is resulting in an increase of configurational entropy, then an increase in T_g will be anticipated and observed.

Conclusions

The TSDC peaks in pristine PC is due to the secondary relaxation processes caused by motions of the main chain, motion of side chain, and formation of space charge at the metal oxide polymer interface. The secondary relaxation process is justified on the basis of calculated activation energy of TSC peaks. Secondary relaxation process is further observed in nanocomposite provided reduction of current and space charges due to filling of nanoparticles in polymer matrix. It is concluded that the charge carriers captured more strongly in new traps produced by nanofillers.

DSC emphasizes the influence on polymer–ZnO interactions versus polymer–interface interactions on the T_g of the nanocomposites. The results presented here not only have important to study the glass transition temperature in polymer nanocomposites, but they provide an important basis for the further development of theories of the glass transition in polymer nanocomposites.

Acknowledgements Author M. S. Gaur and Ajaypal Indolia are gratefully acknowledge the financial support of Defence Research Development Organization (DRDO), New Delhi, India (Vide letter no. ERIP/ER/0804419/M/01/1113). We are also thankful to Dr. A. Gupta, Director, UGC-DAE Consortium, Indore for providing DSC facility.

References

1. Barabanova AI, Shevnin PL, Pryakhina TA, Bychko KA, Kazantseva V, Zavin BG, et al. Nanocomposites based on epoxy resin and silicon dioxide particles. Polym Sci Ser A. 2008;50:808–19.
2. Nam JD, Hwang SD, Choi HR, Lee J, Kim KJ, Heo S. Electrostrictive polymer nanocomposites exhibiting tunable electrical properties. Smart Mater Struct. 2005;14:87–90.
3. Godovsky DY. Device applications of polymer-nanocomposites. Adv Polym Sci. 2000;153:163–205.
4. Lewis TJ. Nanometric dielectrics. IEEE Trans Dielectr Electr Insul. 1994;5:812–25.
5. Tanaka T, Montanari GC, Mülhaupt R. Polymer nanocomposites as dielectrics and electrical insulation–perspectives for processing technologies, material characterization and future applications. IEEE Trans Dielectr Electr Insul. 2004;11:763–84.
6. Zhang C, Mason R, Stevens GC. Dielectric properties of alumina-polymer nanocomposites. Electr Insul Dielectr Phenom. 2005; 16:721–4.
7. Shen Y, Lin YH, Nan CW. Interfacial effect on dielectric properties of polymer nanocomposites filled with core/shell-structured particles. Adv Funct Mater. 2007;17(14):2405–10.
8. Ning H, Masuda Z, Yan C, Yamamoto G, Fukunaga H, Hashida T. The electrical properties of polymer nanocomposites with carbon nanotube fillers. Nanotechnology. 2008;19:215701–10.
9. Koo JH. Polymer nanocomposites: processing, characterization and application. New York: McGraw-Hill Professional; 2006. p. 33.
10. Riande E, Daz-Calleja R. Electrical properties of polymers. Boca Raton: CRC Press; 2004. p. 374.
11. Torres JA, Nealy PF, Pablo DJJ. Molecular simulation of ultrathin polymeric films near the glass transition. Phys Rev Lett. 2000;85:3221–4.
12. Forrest JA, Dalnoki-Veress K, Dutcher JR. Interface and chain confinement effects on the glass transition temperature of thin polymer films. Phys Rev. 1997;E56:5705–16.

13. Fukao K, Miyamoto Y. Glass transition temperature and dynamics of α relaxation process in thin polymer films. Europhys Lett. 1999;46:649–54.
14. Gaur MS, Shukla P, Tiwari RK, Tanwar A, Singh SP. New approach for the measurement of glass transition temperature of polymer. Ind J Pure Appl Phys. 2008;46:535–9.
15. Turnhout JV. Thermally stimulated discharge of electrets. In: Sessler GM, editor. Topics in applied physics (Electrets). Berlin, Heidelberg: Springer-Verlag; 1980.
16. Richeret R, Blumen A, editors. Disordered effects on relaxation processes. Berlin, Heidelberg: Springer-Verlag; 1994.
17. Strobl G. The physics of polymers. Berlin, Heidelberg: Springer-Verlag; 1996.
18. Ibar JP. Do we need a new theory in polymer physics? Polym Rev. 1997;37:389–458.
19. Bernes A, Martinez JJ, Chatain D, Lacabanne C. Thermally stimulated current spectroscopy for the study of thermoplastics. J Therm Anal Calorim. 1991;37:1795–804.
20. Litt MH, Torp S. Strain and temperature dependence of relaxation phenomena in polycarbonate. J Appl Phys. 1973;44:4282–7.
21. Kluin JE, Yu Z, Vleeshouwers S, McGervey JD, Jamieson AM, Simha R. Temperature and time dependence of free volume in bisphenol—A polycarbonate studied by positron lifetime spectroscopy temperature and time dependence of free volume in bisphenol A polycarbonate studied by positron lifetime spectroscopy. Macromolecules. 1992;25:5089–93.
22. Aoki Y, Brittain JO. Isothermal and nonisothermal dielectric relaxation studies on polycarbonate. J Polym Sci B Polym Phys. 1976;14:1297–302.
23. Narula GK, Pillai PKC. Dielectric measurements in an amorphous polymer—Poly(methyl methacrylate). J Polym Sci B Polym Phys. 1990;42:469–72.
24. Bernes A, Chatain D, Lacabanne C. Thermally stimulated current study of relaxation in glassy polycarbonate. Polymer. 1992;33:4682–6.
25. Sauer BB, Avakian P, Howard W, Starkweather Jr. Cooperative relaxations in semicrystalline fluoropolymers studied by thermally stimulated currents and ac dielectric. J Polym Sci B Polym Phys. 1995;34:517–26.
26. Graeme JP, Michael J, Smith A. Multiple dielectric relaxation processes in an unequilibrated bisphenol-A polycarbonate. Polym Int. 1996;40:239–49.
27. Delbreilh L, Negahban M, Benzohra M, Lacabanne C, Saiter JM. Glass transition investigated by a combined protocol using thermostimulated depolarization currents and differential scanning calorimetry. J Therm Anal Calorim. 2009;96:865–71.
28. Alves NM, Ribelles JLG, Mano JF. Enthalpy relaxation studies in polymethyl methacrylate networks with different crosslinking degrees. Polymer. 2005;46:491–504.
29. Bacharan C, Dessaux C, Bernes A, Lacabanne C. Thermally stimulated current spectroscopy of amorphous and semi-crystalline polymers. J Therm Anal Calorim. 1999;56:969–82.
30. Rittigstein P, Torkelson JM. Polymer-nanoparticle interfacial interactions in polymer nanocomposites: confinement effects on glass transition temperature and suppression of physical aging. J Polym Sci B Polym Phys. 2006;44:2935–43.
31. Wei C, Shrivastava D, Cho K. Thermal expansion and diffusion coefficients of carbon nanotube-polymer composites. Nano Lett. 2002;2:647–50.
32. Chang JH, Seo B, Hwang DH. An exfoliation of organoclay in thermotropic liquid crystalline polyester nanocomposites. Polymer. 2002;43:2969–74.
33. Dixit M, Gupta S, Mathur V, Rathore KS, Sharma S, Saxena NS. Study of glass transition temperature of PPMA and CdS-PPMA composite. Chalcogenide Lett. 2009;6:131–6.
34. Xu W, Ge M, Pan WP. Glass transition temperature in polyvinyl chloride/monotmorillonite nanocomposite and mechanical properties. J Therm Anal Calorim. 2004;78:1–9.
35. Binder K, Baschnagel J, Bennemann C, Paul W. Monte Carlo and molecular dynamics simulation of the glass transition of polymers. J Phys Condens Matter. 1999;11:A47–55.