Effect of $\text{Sr}_2\text{TiMnO}_6$ fillers on mechanical, dielectric and thermal behaviour of PMMA polymer

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Composites of poly(methyl methacrylate) (PMMA) and $\text{Sr}_2\text{TiMnO}_6$ (STMO) were fabricated via melt mixing followed by hot pressing technique. These were characterized using X-ray diffraction (XRD), thermo gravimetric analysis (TGA), differential scanning calorimetry (DSC), thermo mechanical analysis (TMA) and impedance analyser for their structural, thermal and dielectric properties. The coefficient of thermal expansion (CTE) was measured between 40°C and 100°C for pure PMMA is 115.2 ppm/°C, which was decreased to 78.58 ppm/°C when the STMO content was increased to 50 wt.% in PMMA. There was no difference in the glass transition (T_g) temperature of the PMMA polymer and their composites. However, the FTIR analysis indicated possible interaction between the PMMA and STMO. The density and the hardness were increased as the STMO content increased in the PMMA matrix. Permittivity was found to be as high as 30.9 at 100 Hz for the PMMA+STMO-50 wt.% composites, indicating the possibility of using these materials for capacitor applications. The thermal stability of polymer was enhanced by incorporation of STMO fillers.

Keywords: Polymer composite; dielectric properties; mechanical properties; thermal properties.

1. Introduction

Poly(methyl methacrylate) (PMMA) is an amorphous polymer which do not crystallize due to its semi-flexible and rigid backbone structure. The high stiffness of PMMA along with its biocompatibility, is commonly used in materials for bone-substitute applications.^{1,2} Despite its exceptional mechanical behavior, PMMA exhibits a rather low dielectric permittivity, which is typically lies between 3 and 8.^{3–5} PMMA is categorized into three species with respect to its tacticity, i.e., isotactic(i-), syndiotactic(s-) and atactic(a-), depending on the way that pendant methacrylate groups are arranged along the backbone chain of a polymer which led to different tertiary structures.⁶ PMMA has been the subject of numerous composite studies focusing on the improvement of strength and durability.^{7–10} Though polymers possess relatively low permittivity, they can withstand high fields due to its high dielectric strength. In order to enhance the permittivity of the polymers, particulate composites (comprising ceramic crystallites) possessing high permittivity have become increasingly important for capacitor applications.¹¹ Therefore, it became the subject of interest to combine the advantages of polymers (low processing temperatures and mechanical

flexibility) with those of ceramics with large permittivity for the development of composites with low leakage and high energy density for capacitors applications.¹² The most widely used dielectric ceramics for the development of high permittivity ceramic-polymer composites are those based on BaTiO_3 (BT), BaSrTiO_3 (BST), $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 (PMNPT), $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT) and $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO).^{13–27} The double perovskite have attracted considerable attention due to their unique electrical and magnetic properties. They exhibit interesting combination of conductivity, dielectric and magnetic properties depending on the degree of octahedral tilting that changes the extent of orbital overlap between the B-site octahedral networks. $\text{Sr}_2\text{TiMnO}_6$ (STMO) ceramic belongs to this double perovskites group and the permittivity was found to vary significantly with the thickness of the samples and nature of the contacts at low frequencies owing to its extrinsic nature. It has high permittivity which is important from the scientific and technological applications points of view.^{28,29} Ceramics were incorporated into the PMMA matrix to improve the overall permittivity of PMMA.^{30–33} The Al_2O_3 loading to the level of 45 vol%, in PMMA had increased the permittivity, which was attributed to the space charge

polarization mechanism.³⁰ Similarly, permittivity as high as 19 has been reported for the PMMA composite comprising 40 vol% nanocrystallites of BaTiO₃.³¹ The PMMA-based ternary composites also exhibited improved dielectric properties.³² For PMMA/CSTO composite system, the permittivity as high as 15.7 at 100 Hz has been reported.³³ These investigation clearly demonstrated that the final properties of the composites are not only dependent on the type of polymer and its structure but it is also dependent on the type of ceramic, the interface bonding between the polymer and the ceramic, the thermal properties and the heat capacities of the individual components.^{34–36} Hence, it is essential to understand the thermal behavior of the composites, as the thermal behavior of polymer composites depends strongly on the matrix polymer and its chemical and morphological characteristics. Therefore, any study that deals with the polymer composite system must also understand the changes that are taking place in the host polymer due to the introduction of filler material. Even in the absence of specific interactions with the polymers, fillers behave as highly functional physical crosslinks and hence reducing the overall mobility of the polymer chains.³⁷ The introduction of fillers into the polymer matrix can also improve the thermal and mechanical properties.^{38–41} It is interesting to note that the addition of small amount of graphite particles (1–5 wt.%) in PMMA has increased the onset degradation temperature of the composite by 20°C.⁴² It is also observed that the stability of the composites has increased by 13.5°C as compared to that of pure PMMA, when the very low level (6.1% by weight) of nanosized SiO₂ (23 nm) was added into the PMMA. When the size of the crystallites was further reduced (17 nm), enhancement in the thermal stability has been achieved.⁴³ In the case of clay addition into the PMMA matrix, both the thermal stability and the glass transition temperature (T_g) of the composite has been increased as compared to that of virgin polymer.⁴⁴ Significant improvement in the thermal and mechanical properties of the composites has been achieved when the graphene loading as low as 0.07% by weight mass incorporated into the PMMA matrix.⁴⁵ Similarly, alumina/PMMA composites at extremely low filler weight fractions (<1.0 wt.%), the glass-transition temperature (T_g) of composite was reduced by 25°C as compared to that of pure PMMA.⁴⁶ All these research findings have clearly demonstrated that the improvement in the thermal, mechanical as well as electrical properties could be achieved by addition of ceramics fillers into PMMA matrix. There are no research papers wherein STMO has been used as fillers in the polymer matrix for the fabrication of composite material. Hence, one could explore the possibility of obtaining new hybrid composite materials with better thermal and dielectric properties by combining the merits of both PMMA and STMO. Herein, we report the details pertaining to the synthesis and thermal behavior of PMMA+STMO composites fabricated by melt mixing and hot pressing technique.

2. Experimental Methods

2.1. Synthesis of STMO ceramics

The solid-state reaction route was adopted for the synthesis of STMO ceramic powders.²⁹ The stoichiometric amounts of AR grade SrCO₃, MnO₂ and TiO₂ was weighed, mixed using acetone and ball milled (300 rpm) for 3 h. The homogeneous mixture thus obtained was dried in an electric oven for about 1 h. This stoichiometric mixture was taken in a re-crystallized alumina crucible and calcined in three stages at 1200°C, 1300°C and 1350°C, for the complete removal of the carbonates. Finally, the total mass was calcined at 1370°C/24 h to obtain phase pure STMO powder. In order to get submicron particles, the STMO powders were ball milled for about 4h using a planetary mill.

2.2. Fabrication of PMMA/STMO composite sheets

PMMA, having molecular weight of 1,10,000 (Make: LG Corporation) was used as matrix material. For the fabrication of PMMA/STMO composites, PMMA and STMO powder were melt mixed in a Brabender Plasticorder (Model: PLE331) for 15 min at 210°C, and then hot-pressed at this temperature to obtain a sheet of 150 mm² with 0.5 mm in thickness. A series of PMMA/STMO composites with varying concentrations (0% to 50%) of STMO by weight were fabricated. Figure 1 shows the flowchart depicting various steps involved in the fabrication of PMMA–STMO composites.

2.3. Characterization

To examine the structure, an XPERT-PRO Diffractometer (Philips, Netherlands) instrument was used. Thermo gravimetric analyses (TGA) were done using the TA Instruments (UK, Model: TGA Q500) and thermo mechanical analyses (TMA) were done using the TA Instruments (UK, Model: TMA Q400). TGA experiments were conducted in nitrogen atmosphere at a flow rate of 60 mL min^{−1}, at a heating rate of 10°C min^{−1}. TMA experiments were conducted in nitrogen

Fig. 1. Flowchart depicting various steps involved in the fabrication of STMO ceramic and the PMMA+STMO composites.

atmosphere at a flow rate of 60 mL min^{-1} , at a heating rate of 5°C min^{-1} . Infrared spectra were recorded using a FTIR/ATR spectrophotometer, Model: Nicolet 6700 (Make: Thermo Scientific). Differential Scanning Calorimeter (Make: Mettler Toledo, Model: DSC 821e) was employed at a heating rate of $10^\circ\text{C min}^{-1}$ under nitrogen atmosphere at a flow rate of 60 mL min^{-1} , using Aluminium pan). The density of the composites was measured by Archimedes liquid displacement method. The hardness test was carried out as per the procedure outlined in the ASTM D 2240. LCR meter (Model: Agilent 4294A) was used for the capacitance measurements as a function of frequency (100 Hz–100 MHz) at room temperature.

3. Results and Discussion

Figure 2 shows the X-ray diffraction (XRD) pattern recorded for the STMO ceramics prepared by solid-state reaction route²⁹ and for the PMMA/STMO composites that were prepared by melt mixing technique. It is reported²⁹ that the phase pure STMO is formed only at 1370°C , and hence, the powders that were calcined in three stages at 1200°C , 1300°C and 1350°C (not shown here) exhibited secondary phases pertaining to SrMnO_3 , SrTiO_3 and TiO_2 . When the calcination temperature was increased to 1370°C , as shown in Fig. 2(a), phase pure STMO could be obtained at this temperature. All the reflections could be indexed to a tetragonal cell associated with $I4/m$ space group and consistent with the results reported.²⁹ The XRD pattern revealed the amorphous nature of PMMA (Fig. 2(b)). The XRD patterns recorded for the PMMA comprising 10 wt.% STMO and 30 wt.% STMO (Figs. 2(c) and 2(d)) revealed the composite

nature of the samples. In the case of PMMA with 50 wt.% STMO composite (Fig. 2(e)), XRD pattern revealed only STMO peaks as the intensities of these are dominant.

The FTIR spectra recorded for the pure PMMA and their composite samples are depicted in Figs. 3(a) and 3(b), respectively. For PMMA (Fig. 3(a)), the absorption peaks around 2992 and 2949 cm^{-1} correspond to C–H asymmetric stretching in CH_3 and CH_2 , respectively. The vibrational band at 2847 cm^{-1} is due to the C–H symmetric stretching in CH_3 .

Fig. 2. XRD patterns for (a) 1370°C /phase pure STMO ceramic, (b) pure PMMA, (c) PMMA+STMO-10 wt.%, (d) PMMA+STMO-20 wt.% and (e) PMMA+STMO-50 wt.%.

Fig. 3. (a) FTIR spectra recorded for the pure PMMA. (b) FTIR spectra recorded for (a) 10, (b) 20, (c) 30, (d) 40 and (e) for 50 wt.% PMMA+STMO composite.

The characteristic band for the pure PMMA is observed at 1721 cm^{-1} , which corresponds to C=O stretching band. The vibrations due to deformation modes of CH_3 groups appear at 1489 , 1434 cm^{-1} and 1385 cm^{-1} . Medium bands at 1268 and 1238 cm^{-1} correspond to C–O stretching modes. The vibration modes due to C–C stretching appear at 985 and 969 cm^{-1} . The peaks at 912 and 840 cm^{-1} are assigned to CH_2 rocking and the peaks at 809 and 749 are due to the C=O in plane and out of plane bending, respectively.⁴⁷ The FTIR spectra obtained for the composites (Fig. 3(b)) has been thoroughly analyzed and it has been observed that there are additional absorption peaks at 564 and 1541 cm^{-1} . These results indicate that there is a good interaction between the PMMA and STMO in the composite samples.

The density measurements were carried out as per the procedure outlined in the ASTM standard (ASTM D 792).⁴⁸ The density data obtained for the PMMA/STMO composites with the behavior of unfilled PMMA are presented as box and whisker plots (Fig. 4(a)). The weight of the sample in air and weight of the sample in water is noted and density is calculated using the following equation

$$\rho_{\text{sample}} = \frac{W_a}{W_a - W_1} \times \rho_{\text{water}}, \quad (1)$$

where ρ_{sample} is the density of the sample, W_a is the weight of the sample in air, W_1 is the apparent immersed weight of the sample in water. The density of the pure PMMA increased when the STMO content increased in PMMA. The pure PMMA has the density/ g cm^{-3} of about 1.18, which has

increased to 1.94 when the STMO content is increased to 50 wt.% in PMMA. It is clearly seen that (Fig. 4(a)), the density of the composite increases gradually with the increase in STMO filler loading.

The hardness test was also carried out as per the procedure outlined in the ASTM standard (ASTM D 2240).⁴⁹ The hardness data obtained for the PMMA/STMO composites with the behavior of unfilled PMMA are presented as box and whisker plots (Fig. 4(b)). The hardness of the composites increases as the STMO content increased in the PMMA matrix. There is a linear increase in hardness from 61 to 79 (Shore D) value as the STMO content increases from 0 to 50 wt.% in the PMMA matrix. These results indicate that the hardness in a composite has a linear relationship with the density/ g cm^{-3} of the composite. In an essence, material with higher density would exhibit improved hardness.

Figure 5(a) shows the permittivity recorded for the pure PMMA and PMMA–STMO composites. It is seen that for pure PMMA, the permittivity is around 4.0 at 100 Hz and constant over the frequency range under investigation (100 Hz to 100 MHz). The enhanced dielectric constant in our study was achieved by introduction of STMO particles. As expected, as the STMO content increased in PMMA, the permittivity also increased. When the STMO content increased to 50 wt.% in PMMA, the permittivity value of composites was increased to 30.9 at 100 Hz from 4.0 at 100 Hz which is due to the much higher dielectric constant of the STMO particles in comparison with the PMMA matrix. The charges will move and get accumulated at the interface in

Fig. 4. (a) Variation of density with respect to STMO filler loading in PMMA+STMO composites. (b) Variation of hardness with respect to STMO filler loading in PMMA+STMO composites.

Fig. 5. (a) Frequency dependent of dielectric permittivity measured at room temperature (300 K) for different wt.% PMMA+STMO composites. (b) Frequency-dependent dielectric loss measured at room temperature (300 K) for different wt.% PMMA+STMO composites.

PMMA matrix under applied field. As a result, a field will be generated which could polarize the surrounding matrix, creating an interfacial polarization.¹¹ As the STMO content increases, the interparticle distance in PMMA matrix gets reduced. Composites shows improved dielectric constant due to overlapped diffused electrical double layer around each particle and an enhanced electromagnetic coupling between nearest neighboring particles. In the case of PMMA–CCTO composite system, the permittivity value was reported to be 15.7 at 100 Hz for 38 vol% of CCTO in PMMA.³³ Introduction of Al_2O_3 in PMMA to the level of 45 vol% has increased the permittivity, which has been attributed to the space charge polarization mechanism.³⁰

Dielectric loss demonstrates the capacitor performance of material where high dielectric loss indicates dissipation of stored energy in the form of heat. The room temperature dielectric loss data obtained for the pure PMMA demonstrated frequency-independent behavior (Fig. 5(b)). However, when STMO ceramic added into the PMMA, there exists two relaxations, one at low frequency and another at high frequency. As reported,²⁷ the relaxation peak at low frequency can be attributed to the α -relaxation, whereas at higher frequencies to the β -relaxation, which arises due to the dissimilar distribution of cooperative motions composed of dipolar groups belonging to the main chain of PMMA.^{50,51} The increased dielectric loss at low frequencies is attributed to the interfacial polarization and free charge motion in material.^{27,30,32}

TMA is a highly sensitive method for the measurement of expansion and contraction of cross-linked or filled materials.

The coefficient of linear thermal expansion (CTE, α , or α_1) is a material property that is indicative of the extent to which a material expands upon heating. Over small temperature ranges, the thermal expansion of uniform linear objects is proportional to temperature change.^{52–54} The pure PMMA and their composites were subjected to TMA to understand their thermal expansion behavior as this is crucial for several device applications.^{55–57} Figure 6(a) shows the dimensional change (μm) as a function of temperature for pure PMMA and the composites. The coefficient of thermal expansion (CTE) was calculated using Equation (2), prior to glass transition temperature⁵⁷ with the help of software available within the equipment.

$$\alpha = \frac{\Delta l}{l_i \Delta T}, \quad (2)$$

where α is linear thermal expansion coefficient, Δl is change in length (μm), l_i is Initial length (m) and ΔT is change in temperature ($^\circ\text{C}$).

All the specimens were well polished using abrasive to have plane-parallel and smooth surfaces and specimens with identical thicknesses were prepared and these samples were subjected to TMA analysis to observe the trend in the results. It has been observed that as the STMO content increased in PMMA, CTE, measured between 40°C and 100°C (just before the T_g), has decreased (as compared to that of pure PMMA). The CTE for the PMMA is $115.2 \text{ ppm}/^\circ\text{C}$, which has decreased to $78.58 \text{ ppm}/^\circ\text{C}$ when the STMO content increased to 50 wt.% in PMMA. Similar trend has been observed for other PMMA-based composites.^{33,55–57}

Fig. 6. TMA for the (a) pure PMMA, (b) 10, (c) 20, (d) 30, (e) 40 and (f) for 50 wt.% PMMA+STMO composite and (b) DSC traces for the for the (a) pure PMMA, (b) 10, (c) 20, (d) 30, (e) 40 and (f) for 50 wt.% PMMA+STMO composite.

For the PMMA/CCTO composites, there is a drastic reduction in the CTE value (48.25 ppm/°C) when the CCTO content increased to 38 vol% in PMMA.²⁷ In the case of PMMA/Al composite,⁵⁵ as the temperature is raised, the expansion of polymer is restricted by the metal phase, which has lower thermal expansion coefficient. The addition of BN Nanotube (BNNT) to PMMA, the CTE has decreased dramatically from 215 to 115 ppm/°C which indicate that BNNTs significantly restrict the mobility of polymer chains. As reported,^{56,57} the introduction of ceramics restricts the mobility of polymer chain and hence decreases the CTE. The CTE values obtained for PMMA/STMO composites in

this work is in variance with that of the PMMA/CCTO composites,²⁷ clearly indicate the role played by the ceramic, its surface morphology and the mechanical reinforcement with the polymer apart from the density and the crystallite size of the fillers.

Differential Scanning Calorimetry (DSC) measurements were carried out to determine the thermal properties such as melting temperature (T_m), heat of crystallization (H_c) and glass transition (T_g) of PMMA and PMMA composites. The DSC traces obtained for PMMA and PMMA/STMO composites are shown in Fig. 6(b). It is well established that the glass transition (T_g) temperature either increases or decreases depending on the type of filler, its morphology and the intercrystallite distance.^{42,44,58} It is also reported that the T_g of PMMA depends upon the degree of tacticity (isotactic, heterotactic, syndiotactic or atactic), thermal history and the type of free radical initiator used during processing.^{38,39} Since the ceramics and polymers have different heat capacities, DSC analysis is important to understand the change in the heat flow behavior due to the addition of particles into the polymer matrix. For calculating glass transition (T_g) temperature, the DSC data obtained from the second run were taken into account. PMMA has exhibited a heat flow at approximately 117°C, corresponding to the glass transition (T_g) of “syndiotactic PMMA” (Fig. 6(b)(a)). There is no change in the glass transition (T_g) temperature for the polymer and the composites and similar results were reported in the case of PMMA/CCTO composite system also.²⁷

TGA is a technique in which changes in physical and chemical properties of materials are measured as a function of increasing temperature (with constant heating rate), or as a function of time (with constant temperature and/or constant mass loss).^{59–61} In order to examine the thermal stability, thermal analyses were carried out on the PMMA/STMO composites as well as on pure PMMA for comparison. Figure 7 shows the TG curve recorded for the pure PMMA (a) and for PMMA/STMO composites (10 to 50 wt.%) (b–f) in nitrogen atmosphere (flow rate: 60 ml min⁻¹), at a heating rate of 10°C min⁻¹. The onset of decomposition temperature (temperature at 10% weight loss)⁶² was examined. It has been observed that the decomposition temperature onset accompanied by 10% weight loss for the composite PMMA/STMO-10% is 354.75°C and for the PMMA/STMO-50%, is 363.69°C, while for pure PMMA, it is 353.5°C. The onset of decomposition temperature is higher by 10°C than that of virgin PMMA. The mid-point temperature (temperature at 50% weight loss) found to increase gradually as the STMO content increased in PMMA, indicating the interaction between the ceramic and the polymer, which is in line with the reported literature.^{62,63} Few composites samples were subjected to burnt (950°C/24 h) out test by the gravimetric determination and the weight loss obtained are in good agreement with the experimental values based on TG. The derivative curves (DTG) from the TG were plotted for the PMMA and for the composites and the same is shown in

Fig. 7. (a) TG for the (a) pure PMMA, (b) 10, (c) 20, (d) 30, (e) 40 and (f) for 50 wt.% PMMA+STMO composite and (b) Derivative thermo gravimetric (DTG) analysis for the (a) pure PMMA, (b) 10, (c) 20, (d) 30, (e) 40 and (f) for 50 wt.% PMMA+STMO composite.

Fig. 8. (a) TG: (a) 5°C min⁻¹, (b) 10°C min⁻¹, (c) 15°C min⁻¹ and (d) 20°C min⁻¹ heating rate for the pure PMMA. (b) TG: (a) 5°C, (b) 10°C, (c) 15°C and (d) 20°C min⁻¹ heating rate for the PMMA+STMO composite.

Fig. 7(b). It has been observed that both the virgin PMMA and the composites undergo only single step degradation. There is a clear shift in the decomposition temperature for PMMA+STMO-50% composite as the filler content is increased in the PMMA indicating that there is good interaction between the polymer and ceramic. It is reported⁶⁴ that PMMA undergo more than one steps of degradation and this can be clearly visualized using different heating rates.⁶² Hence, the experiments were conducted at different heating rates for PMMA and for the composite (PMMA+STMO-50%) to identify the number of steps of degradation temperatures and the results obtained are given in Figs. 8(a) and 8(b), respectively. However, both the PMMA (Fig. 8(a)) and the composite (PMMA+STMO-50% by weight) (Fig. 8(b)) exhibited only a single step degradation behavior, which is agreed with the results obtained for the PMMA/CCTO and PMMA-clay systems.^{27,62} These results indicate that the addition of STMO filler does not alter the degradation behavior, except that the degradation temperature was shifted to higher temperature in the composites. Overall the composites have better thermal stability than that of PMMA.

The activation energy and thermal degradation kinetics under nitrogen atmosphere were analyzed by Ozawa–Flynn–Wall (OFW) method. The degree of conversion, α , is the ratio of the actual weight loss to the total weight loss,

$$\alpha = (m_0 - m)/(m_0 - m_\infty), \quad (3)$$

where m is the actual weight, m_0 is the initial weight, and m_∞ is the weight at the end of isothermal or non-isothermal experiments. The rate of degradation $d\alpha/dt$ depends on the temperature and the weight of the sample, as given by Eq. (4).

$$\frac{d\alpha}{dt} = Ae^{\left(\frac{-E_a}{RT}\right)(1-\alpha^n)}, \quad (4)$$

where A is the pre-exponential factor, E_a is the activation energy, R is the gas constant, T is the absolute temperature and n is the reaction order.

$$\frac{d\alpha}{(1-\alpha)^n} = \left(\frac{Ae^{\left(\frac{-E_a}{RT}\right)}}{\beta} \right) dT, \quad (5)$$

where β is the heating rate. Isoconversional graphs of $\ln\beta$ versus $1000/T$ were plotted (Figs. 9(a) and 9(b)) according to Eq. (5) using the TGA curves of PMMA, PMMA-STMO composite at heating rate (β) of 5°C, 10°C, 15°C and 20°C min⁻¹. The activation energies in the thermal decomposition process were calculated from the slopes of the lines.

Figure 10 shows the relationship between activation energy and degree of conversion ($\alpha = 0.1$ – 0.9) for thermal degradation of PMMA and PMMA-STMO composites. The activation energy of PMMA was observed greater than PMMA-STMO composites at first stage of degradation ($\alpha = 0$ – 0.25) due to random chain scission in PMMA composites which requires less activation energy. In first stage,

Fig. 9. OFW plots for (a) PMMA and (b) PMMA+STMO for the following degrees of conversion: (1) $\alpha = 0.1$, (2) $\alpha = 0.2$, (3) $\alpha = 0.3$, (4) $\alpha = 0.4$, (5) $\alpha = 0.5$, (6) $\alpha = 0.6$, (7) $\alpha = 0.7$, (8) $\alpha = 0.8$ and (9) $\alpha = 0.9$.

the average activation energy for PMMA and PMMA-STMO composites were calculated as 70 and 59 kJ/mol, respectively. In the second stage of degradation ($\alpha = 0.25$ – 0.5), the activation energy for PMMA-STMO exceeded those of pure PMMA which shows the thermal stability of composites in further decomposition. The average activation energy for the PMMA-STMO and PMMA were observed as 92 and 68 kJ/mol in second stage of degradation, respectively. In PMMA, the lower activation energy is due to increase in the number of free radicals with increasing degree of conversion, which accelerates the degradation process. In case of PMMA-STMO composites, the ceramic fillers act as catalysts so that less energy is needed to initiate the degradation process, but in later stages, the interaction between the ceramic and monomer traps the volatile degradation product which results

Fig. 10. Variation in activation energy at different conversion obtained by OFW method for PMMA and 50 wt.% PMMA-STMO composite.

into increase in activation energy. From the calculated results, the thermal stability of PMMA are improved by STMO ceramic fillers.

4. Conclusions

Double perovskite giant dielectric STMO ceramics were synthesized successfully by solid-state reaction route and the same has been confirmed by X-ray powder diffraction technique. A series of composites (0–50% by weight) were fabricated by incorporating STMO ceramics into the PMMA matrix by melt mixing followed by hot pressing technique. The thermal analysis carried out on both the polymer and on the composites exhibited single step degradation behavior. This was further confirmed by the thermal analysis carried out at different heating rates. Overall, the composite exhibited better thermal stability as compared to that of polymer as observed by Ozawa's method. DSC studies revealed that there is no change in the glass transition (T_g) temperature for both polymer and for the composites, and these results are in agreement with the results reported²⁷ for the PMMA-based composite system. The decrease in CTE values due to the addition of ceramics has clearly indicated the role played by the ceramic, its surface morphology and the mechanical reinforcement with the polymer apart from the density and the crystallite size of the fillers. Improvement in polymer density and hardness has been observed when the STMO ceramic content has increased in the polymer. The permittivity as high as 30.9 @ 100 Hz has been achieved for the PMMA+STM-50 wt.% composite.

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