

Thermo-Mechanical Analysis of Lead Monoxide Filled Unsaturated Polyester Based Polymer Composite Radiation Shields

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ABSTRACT: Particulate polymer composites of Isophthalate based unsaturated polyester resin filled with different concentrations of lead monoxide were prepared and investigated for physical, thermal, mechanical, and gamma radiation shielding characteristics. The results of thermo-mechanical studies have been discussed in this article. The composites were investigated to understand the effect of filler on glass transition temperature (T_g) and thermal expansion coefficients (α) at various temperatures under cyclic heating and cooling conditions. The results show that T_g values of composites appear to decrease slightly with increasing filler content. The composites were observed to exhibit three phases of thermal expansion during first heating and cooling cycles where as they exhibit only two

phases during second heating cycle. An anomalous expansion of the composites was observed in the temperature range from 60°C to 110°C only during first heating and it disappears in subsequent heating cycles. Further, all the composites were observed to exhibit a dimensional contraction only during first heating and cooling cycles. The cyclic heating and cooling technique using thermo-mechanical analyzer was observed to be very efficient in determining actual values of T_g and also in determining the post curing temperatures of the polymer and its composites. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 3623–3629, 2010

Key words: thermo-mechanical analysis; polymer composites; radiation shields; unsaturated polyester

INTRODUCTION

To protect life and other matter from hazardous radiations emanating from unshielded radiation sources, appropriate shielding materials are always necessary. Generally, materials made of high density compositions, such as lead bricks, high density concrete, and metal or metal alloys are often used for radiation shielding purpose.^{1,2} However, these materials are heavy and bulky as well as lack in service flexibility³ and hence cannot be used under all conditions. When flexible shields are required, a protective cloth or an apron made of lead or lead oxide filled polymer composites are preferred.⁴ Such shields are being used by occupational workers in nuclear reactors, radiotherapy, or X-ray radiography, space applications, etc.

In performance of radiation shielding, even though the polymer materials are inferior to metals, they have merits in usage flexibility, workability, chemical stability, low cost, volume reduction after

use, etc. In view of this, several investigators have used variety of polymers as matrix material with different metal or metal oxides as fillers while fabricating the polymer based composite radiation shields. However, only a few investigators are successful in preparing the composites with lead oxides as filler in polyethylene,⁵ co-polymers of ethylene with vinyl alkylate, alkyl methacrylate,⁶ polyethylene glycol,⁷ styrene butadiene rubber,⁸ natural rubber,⁹ and polystyrene.¹⁰ Further, many of these authors have focused mainly on radiation shielding characteristics, but not on many other aspects of composites, such as thermal stability, mechanical characteristics, swelling characteristics, chemical stability, electrical conductivity, and radiation stability. These characterizations are also very much essential to evaluate any material and to call it as efficient and flexible radiation shield.

Incorporation of appropriate fillers either in the form of fibers or particles is a very traditional way of improving the properties of the polymer materials. The diameter of these reinforcements is usually in the range of few nanometers to several micrometers, and they provide an increase in thermal stability, stiffness, and strength of the polymer matrix used. Many of the fillers are also instrumental in inducing special properties in the polymer materials,

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which enable them to act as smart materials, such as shape memory polymer materials.^{11,12} There are, however, some drawbacks by such fillers, as for example a reduction in strain to failure, impact strength, and sometimes also in fracture toughness.^{13,14} Even though many of these composite properties are because of several factors such as filler type, filler size, filler shape, and interface area, they mainly depend on the polymer-filler adsorption interactions. The matrix-filler interactions are generally quite complex in nature and involve chemical reactions, physical interactions, changes in morphology of interacting components and mechanical interlocking. These processes modify the surface layers of both the interacting materials (filler and matrix) and form an interphase which differs in properties from the bulk matrix.¹⁵ The formation of the interphase is responsible for changes in the physical and mechanical properties of filled materials. Thermo-physical measurements can reveal these changes, which occur because of restrictions in molecular motions of the resin surrounding the filler particles. Molecular transformation in the vicinity of filler particles is a local phenomenon dependent on the concentration of filler particles.¹⁶ At low loadings, the particles are surrounded by a tightly bound polymer covered by a layer of loosely bound chains. As the loading increases, the areas of loosely bound polymer begin to overlap, containing the entire matrix to be influenced by the filler. If filler loading is high, there is little space left for loosely bound polymer and the participation of the layers of tightly bound polymer increases. At different filler loadings, a change in the interaction mechanism is likely to occur. In addition, the fillers also influence the structure of the polymer matrix because of contribution from filler surfaces to interphase organization. Thermo-mechanical analysis at compression mode is a very efficient tool in characterizing the thermo-physical interactions of a multicomponent or multiphase systems in a simpler way.

In view of the above, the polymer composites of isophthalate based unsaturated polyester resin¹⁷ filled with lead monoxide particles^{18,19} have been

prepared and investigated for the above said aspects. In this article, only the results of thermo-mechanical analysis have been presented.

EXPERIMENTAL

The particulate polymer composites of unsaturated polyester filled with different concentrations of lead monoxide (PbO) were prepared using open mould casting technique. The details of which are already reported elsewhere along with the results of radiation shielding studies.²⁰

The composite samples of $3 \times 3 \times 3$ mm dimension were obtained by cutting the sample carefully from the laminates using a high speed cutting machine with a cutting blade studded with diamond edge. Initially the samples of slightly bigger dimension were obtained and later the edges were grinded carefully to the required dimensions using a fine emery paper. From each composition three set of samples were taken from different regions of the laminates and were characterized for thermo-mechanical behaviour using Thermo-mechanical Analyzer (TMA) supplied by TA Instruments. The samples were heated at a heating rate of $5^\circ\text{C}/\text{min}$ in air atmosphere from room temperature (26°C) to 250°C under compression mode with a constant load of $0.02N$ applied on the sample through a probe similar to one described by Olkhov and Jurkowski.²¹ The upper limit of temperature was decided based on the thermo-gravimetric analysis of the samples in which the onset of thermal degradation of the samples was observed to be well above 300°C . The Initial degradation temperatures (IDT) of the samples have been shown in column 3 of Table I. On observing an anomalous expansion in all the composite samples in the temperature range from about 60°C to 110°C , the samples were also subjected to cooling from 250°C to 60°C and re-heating from 60°C to 250°C to verify the repetitive behavior. Further, all the data obtained from TMA were analyzed for glass transition temperature (T_g), dimensional contraction and thermal expansion coefficients (α) using

TABLE I
Results of Thermo-Mechanical Analysis Due To First Heating of Samples from 26 to 240°C

Composite sample	Wt % of PbO	IDT $^\circ\text{C}$	T_g ($^\circ\text{C}$)	Coefficient of thermal expansion ($\mu\text{m}/\text{m}^\circ\text{C}$)		
				α_1 (26 to 60°C)	α_2 (120 to 160°C)	α_3 (160 to 240°C)
ILM1	0	337	109.93	56.76	159.1	137.9
ILM2	5	336	113	79.26	161.2	134.2
ILM3	10	330	117.94	77.5	161.8	146.6
ILM4	20	310	114.32	75.84	165.4	167.4
ILM5	30	308	105.42	78.01	115.3	90.89
ILM6	40	305	104.1	90.05	127.7	83.23
ILM7	50	304	102.86	77.56	103.5	73.32

TABLE II
Results of thermo-mechanical Analysis Due to cooling of Samples from 240°C to 60°C

Composite sample	T_g (°C)	Coefficient of thermal expansion ($\mu\text{m}/\text{m}^\circ\text{C}$)		
		α_4 (240 to 220°C)	α_5 (200 to 110°C)	α_6 (100 to 60°C)
ILM1	110	249.7	194.9	124.1
ILM2	108.87	245.6	195.4	134.7
ILM3	109.88	231.7	193.6	130.56
ILM4	108.12	227.1	195.3	145.6
ILM5	109.2	567.3	170.9	91.11
ILM6	108.92	780.8	147.3	83.45
ILM7	110.1	528.4	149.8	89.18

Universal Analysis 2000, Version-3.9A software supplied by TA Instruments-Waters LLC.

X-ray powder diffraction measurements were carried out to investigate the phase changes due to heating and cooling of the composite samples for Cu-K α line with 2θ ranging from 10° to 60° using MiniFlex-II, Rigaku Benchtop X-ray diffractometer supplied by Rigaku Corporation, Japan.

RESULTS AND DISCUSSION

To understand the effect of filler on T_g and α at various temperature regions, TMA of the composites was carried out and the results are shown in Tables I, II, and III and also in the form of Figures 1, 2, and 3. Further, Figures 2 and 3 also show the thermal expansion/contraction behavior of the composites under cyclic heating and cooling conditions. All the samples were found to exhibit a dimensional contraction only during first heating and cooling cycle as shown in Figure 2 and 3 and not in subsequent cycles of heating and cooling.

Analysis of the TMA plots was carried out based on the ' α ' values. During first heating of the samples from the temperature 26°C to 60°C, the samples exhibit more or less same value of α (α_1) as shown in

Figure 1. From 60°C to about 110°C the samples exhibit an anomalous expansion which is evident from Figure 1. Further from about 120°C to 160°C and 160°C to 240°C the samples exhibit two different α (α_2 and α_3 respectively) values, which are also evident from Figure 1. Hence, the plot was broadly divided into four regions of thermal expansion. Excluding the anomalous expansion region, the average α values for the other three regions have been shown in Table I.

Generally, in the composites below T_g the expansion behavior of both glassy amorphous chains and crystalline chains are quite similar. However, above T_g the amorphous chains may experience large scale segmental motions and contribute largely to the expansion.²² All the composites show the temperature dependence in α values and also similar trend in thermal expansion/contraction. However, the magnitudes of expansion and contraction are different for different samples because of the difference in the filler concentration of the composites. Thermal expansion can also be used as simple method of verifying the adhesion between the filler and the matrix. If the adhesion is poor the composite will have high thermal expansion with the increasing filler content.²³ The α values shown in Table I to III

TABLE III
Results of Thermo-Mechanical Analysis Due to Re-heating of Samples from 60°C to 240°C and Contraction of the Samples after First Heating and Cooling Between 60 and 240°C

Composite sample	T_g (°C)	Coefficient of thermal expansion ($\mu\text{m}/\text{m}^\circ\text{C}$)		Contraction in the samples (%) Heating and Cooling 60°C-250°C-60°C
		α_7 (60 to 100°C)	α_8 (110 to 230°C)	
ILM1	108.66	103.8	192.8	1.2105
ILM2	106.87	111.2	195.3	0.8401
ILM3	107.36	103.4	190.5	0.7829
ILM4	106.41	116.2	190.6	0.6742
ILM5	102.69	98.09	146.8	2.4834
ILM6	103.84	71.04	124.9	3.1328
ILM7	104.03	73.58	142.5	2.3095

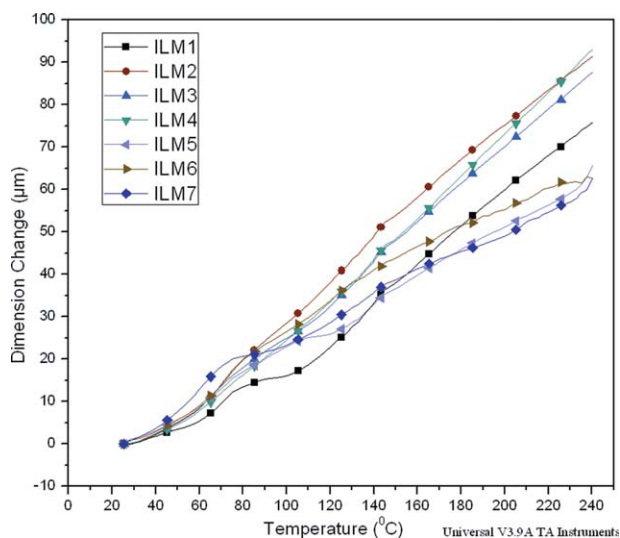


Figure 1 Thermo-mechanical plots of ILM1 to ILM7 for first heating from 26 to 240°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

indicate that except α_1 and α_4 all other α values (α_2 to α_8) decrease with the increasing filler content because of a good adhesion between the filler and the matrix.

In all the samples amorphous polymer chains are expected to experience large scale segmental motions and contribute largely to the expansion in the temperature range 26°C to 60°C because of the presence of more resin content by volume than filler in the composites. It is quite difficult to draw any conclusion from the α_1 values shown in Table I regarding the effect of filler fraction in the composite on thermal expansion characteristics. In addition to segmen-

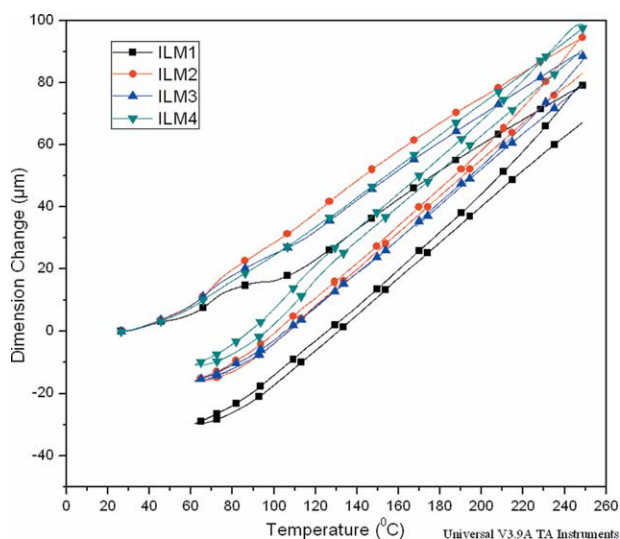


Figure 2 Thermo-mechanical plots of ILM1 to ILM4 for heating-cooling-heating cycle between 26°C and 250°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

tal motions of polymer chains, other processes which lead anomalous expansion also initiate in this temperature range. Hence, both these processes appear to compete against each other and hence a random expansion of the samples. Further, an anomalous expansion of the composites observed in the temperature range 60°C to about 110°C can be attributed to the possible expulsion of the residual solvents and unreacted components mainly styrene monomers/oligomers present in the composites and it disappears in subsequent heating cycles.^{23,24} With a rise in temperature in that range, the probability of intermolecular interaction increases and the size of the composites changes significantly exhibiting an anomalous expansion.²⁵ From 100°C to 120°C, the samples undergo glass transition from glassy phase to elastic flow phase. After glass transition, all the samples exhibit larger α_2 because of more elastic flow nature of the composites. Here, the composites of lower filler concentration (ILM1 to ILM4) exhibit larger α_2 in comparison with those of ILM5 to ILM7 and are as shown in Table I. The presence of the higher filler concentration in the composites inhibits the movements of polymer layers.²⁶ Further, above 160°C all the samples were observed to undergo transition into next phase showing low α_3 than α_2 indicating the maximum possible reorientation/crystallization of amorphous chains. ILM5, ILM6, and ILM7 samples show next transition at about 240°C and this may be because of change of state from hyper-elastic state into viscous flow state.

During cooling of the samples from 250°C, the composites show large dimensional changes (α_4) due to shrinkage between 240°C and 220°C as shown in Figures 2 and 3. As can be seen from Table III that

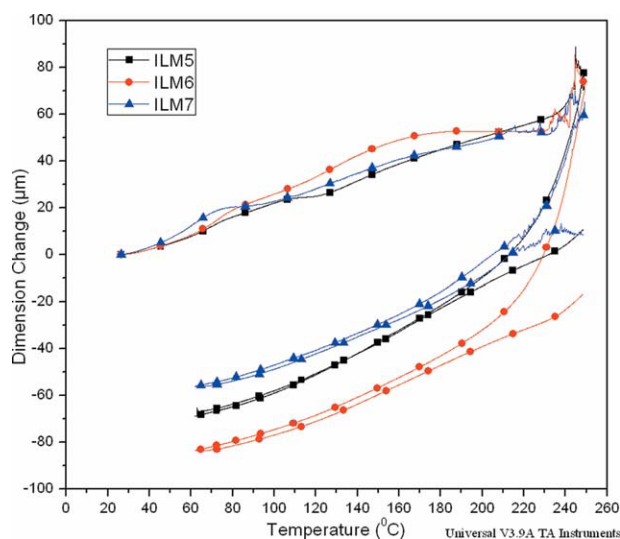


Figure 3 Thermo-mechanical plots of ILM5 to ILM7 for heating-cooling-heating cycle between 26°C and 250°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

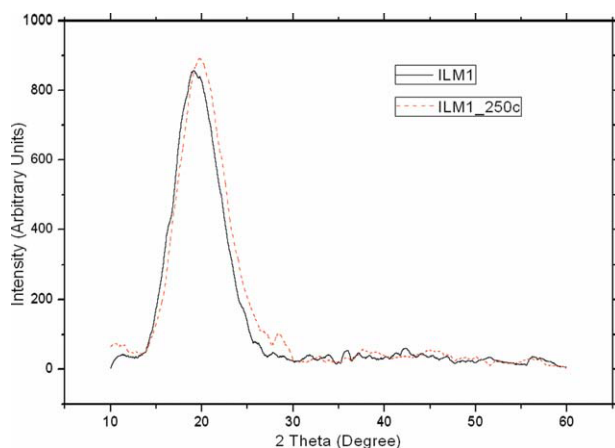


Figure 4 X-ray powder diffractograms of ILM1 before and after heating-cooling cycle. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

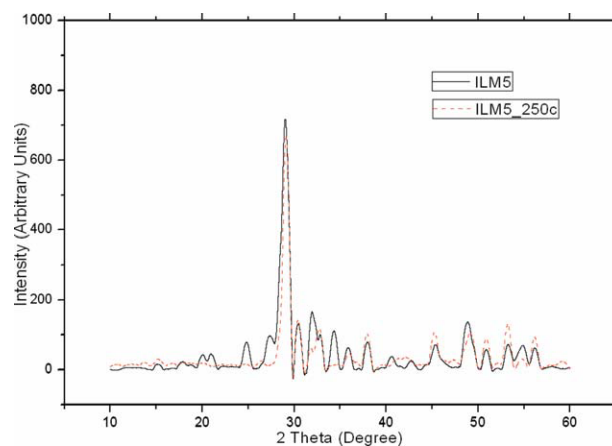


Figure 6 X-ray powder diffractograms of ILM5 before and after heating-cooling cycle. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the % of contraction is low and in decreasing order for the samples ILM1 to ILM4, whereas it is quite high for the samples ILM5, ILM6, and ILM7. Contraction in ILM1 to ILM4 can be attributed to both the reasons that during anomalous expansion unreacted components are expelled out and also the polymer chains undergo rearrangement due to thermal annealing. Interestingly, it can be seen that during anomalous expansion the samples ILM5 to ILM7 show large expansion than the other samples. These observed facts confirm the possibility that, at lower concentration of filler in the composite the filler loading is below the optimum filler content and polymer-filler adsorption interactions are not much. But above 20% by weight of filler content, it seems to exceed the optimum value and further by analogy with the reported results, larger contraction at higher filler content may be attributed to a consider-

able polymer-filler adsorption interactions, which inhibit the formation of the cross-linked structure^{27,28} and may also due to the possible maximum thermal crystallization above 240°C at higher filler concentration (ILM5 to ILM7). Further, from 200°C to 110°C the α_5 values were observed to decrease with increasing filler concentration in the composites. Between 110°C and 100°C the samples undergo glass transition. When the samples were cooled further till 60°C no anomalous expansion was observed. The α_6 values were also observed to decrease further and exhibit a similar decreasing trend with respect to filler concentration.

During re-heating of the composites from 60°C to 250°C only two regions of thermal expansion were observed in all the samples (α_7 and α_8 respectively as shown in Table III and are shown in Figures 2 and 3). After a cyclic heating and cooling, the

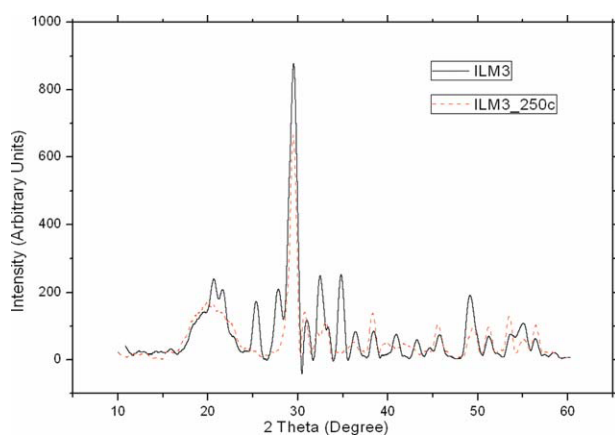


Figure 5 X-ray powder diffractograms of ILM3 before and after heating-cooling cycle. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

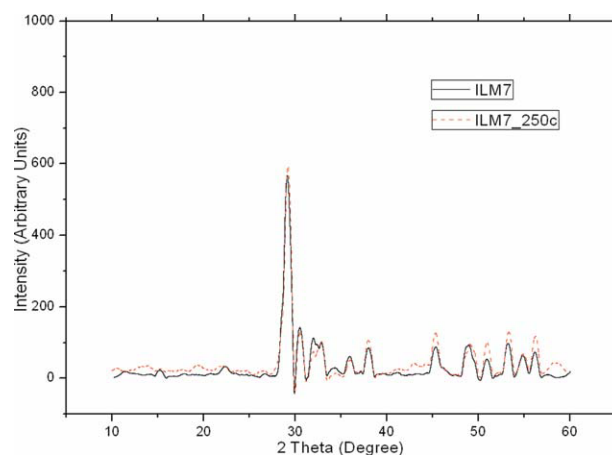


Figure 7 X-ray powder diffractograms of ILM7 before and after heating-cooling cycle. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

composites exhibit more stability to thermal expansion below T_g which is evident from α_6 and α_7 values. Further above T_g , all the composites show a similar trend in thermal expansion but over a wide temperature range from 110°C to 230°C as shown by α_8 against α_5 . Disappearance of anomalous expansion region as well as an intermediate transition at about 160°C after cyclic heating and cooling might be due to the rearrangement of the composite structure minimizing defects because of thermal annealing.

The results also show that the glass transition temperature values appear to range between 102°C and 108°C as shown in Table III. An anomalous T_g values above 110°C were also observed for some samples as shown in Table I and 2, but only during first heating which are quite common in either uncured or improperly postcured composite samples. The subsequent heating cycles reduce the broadening of the phase transition stage at glass transition temperatures i.e., a smooth transition from glassy state to hyperelastic state.

The X-ray powder diffractograms of all the samples were taken and analysed for the difference in appearance of peak positions, peak intensities, and peak shifts. From the observation it was found that these parameters were not much appreciable when all the samples were considered together. Hence, the samples that were alternatively numbered (ILM1, ILM3, ILM5, and ILM7) were considered for discussion. The X-ray powder diffractograms of ILM1, ILM3, ILM5, and ILM7 composite samples before and after thermo-mechanical heating-cooling cycles have been shown in Figures 4, 5, 6, and 7, respectively. A broad peak centered around 19.2° and diffused scattering from 30° to 60° with some minor peaks observed in Figure 4 show mainly the amorphous nature of the neat sample ILM1. The observed broad peak and diffused scattering pattern is mainly because of their long chain structure with a relatively large number of defects. Further, the presence of polymer crystallites if any are relatively very small with a large surface to volume ratio enhance the contribution of interfacial disorganization on the diffraction pattern.^{29–31} The plot for the same sample after heating-cooling cycle shown as ILM1_250c shows a slight shift in the broad peak toward higher 2θ , modification of many of the minor peaks that appeared at 30° to 60° and also appearance of new peak at 28.4°. These observations clearly indicate the possible phase changes occurring in the sample because of thermal annealing effects.

In Figures 5, 6, and 7 the patterns observed is the result of overlapping of peaks due to both polymer and the filler. The filler does not undergo any phase modifications during heating-cooling cycles within the maximum temperature (250°C) and hence prominent

and relatively sharp peaks were observed at 2θ values equal to 29.12, 30.35, 32.62, 37.80, 45.21, 49.33, 50.76, 53.14, and 56.10 degrees. In all the samples these peaks were found to be unique and remain in the same positions. The peaks observed are found to be in good agreement with ICDD-JCPDS database.³² Further, the additional peaks observed at 2θ values equal to 24.66, 27.14, 34.22, 40.43, 42.74, etc., degrees in the samples ILM3, ILM5, and ILM7 (Figs. 5, 6 and 7) are attributed to scattering from polymer layers. These peaks were also observed to undergo modifications during heating-cooling cycles and the changes in peaks may be attributed to the possible rearrangement of polymer molecules during heating-cooling cycles.

CONCLUSIONS

The composites were observed to exhibit four phases of thermal expansion during first heating and found to exhibit only three phases during cooling and only two during reheating cycle. An anomalous expansion of the composites was observed in the temperature range from about 60°C to 110°C during first heating which disappears in subsequent heating cycles. Further, all the composites were observed to exhibit a temperature dependent α values at all temperature regions of heating and cooling cycles. Also at each temperature region, α values were observed to depend on filler content in the composite. With the increase in filler content, α values found to decrease. Which indicates that the presence of more filler content adds more stability against the thermal expansion of the composites. X-ray powder diffractograms of the samples confirm the occurrence of phase changes in the composite samples during heating-cooling cycles. The glass transition region and hence T_g values become more clear after a heating-cooling cycle. The T_g values of the composites appear to decrease slightly at higher filler loading. The cyclic heating and cooling technique using thermo-mechanical analyzer was observed to be very efficient in determining the actual values of T_g and also in determining the postcuring temperatures of the polymers and their composites.

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