

DEFORMATION OF PET NANOCOMPOSITES

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Abstract

The toughening mechanism in polyethylene terephthalate (PET) nanocomposites is investigated as a function of MLS concentration of 1 and 3% using effective area under the stress-strain curve coupled with infra red (IR) thermal wave imaging techniques. 1% MLS concentration, which had an exfoliated structure exhibited slight enhancement in toughness as compared to neat PET whereas 3% MLS composition showed drop in toughness by 87%. From IR thermography, it was concluded that the toughening mechanism in neat PET is due to the chain mobility induced by thermal heating. On the other hand in 1% MLS concentration, the increase in temperature (plastic deformation) is negligible. Differential scanning calorimetry results indicate the absence of cold crystallization peak. This implies that the interlamellar disorder is completely removed. In the case of 3% MLS nanocomposite, strain embrittlement is seen. This effect of embrittlement is pronounced at higher rate of testing where ductile-brittle transition is evident in 3% nanocomposite.

Introduction

Toughness of a material is defined as the area under stress-strain curve. This essentially means that a material with lower modulus can be tougher, if it can have high elongation. The toughening mechanism in polymers is mainly provided due to the mobility of chains and chain entanglement, which allows for chain extension. The addition of fillers can affect this toughening mechanism. The essential work of fracture in the case of thermoplastic fiber filled systems is a function of bond breaking, sliding of fibers, fiber pull out etc.¹ Weak interfacial bonding is often a means to increasing toughness by increasing the surface area of the crack. Musto et al² investigated a polyimide matrix with silica particles. The low interfacial adhesion between the matrix and filler resulted in increased toughness. This effect was attributed to cavitation caused by debonding between the matrix and fillers and further energy absorption through cavitation. Li et al³ have studied a compatibilized PET/PE reinforced system and have reported increased work of fracture in reinforced system attributing the effect to the compatibilization. This toughening mechanism in filled systems is studied by various methods like essential work of fracture⁴ and J-integral approach⁵.

Here we try to evaluate the effect of MLS addition on the toughness of PET matrix using infrared (IR) thermography.

Infrared thermography has been utilized in order to study fracture mechanics due to the sensitivity of technique^{6,7,8,9} in order to track the plastic zone, analyze stress induced crystallization, or to get a perspective on the temperature changes occurring over the stress-strain region.

Experimental

Materials

Extrusion grade semi-crystalline PET was supplied by KOSA. Cloisite 30B was obtained from Southern Clay.

Preparation of Nanocomposite

A 10% by weight master batch of clay with PET was prepared on a Thermoprism co-rotating twin-screw extruder of 16 mm screw diameter and L/D ratio of 24:1. Individual clay concentrations of PET nanocomposites (1,3 and 5% by weight) were made on a Thermoprism co-rotating twin-screw extruder. The films of these compositions were made on a twin screw extruder. Intrinsic viscosity measurements were done in an Ubbelohde viscometer and dichloroacetic acid as a solvent. The intrinsic viscosity of neat KOSA was found to be 1.2 and that of 5%MLS composition was found to be 0.89.

X-ray Diffraction

A Siemens D500 X-ray Diffractometer was used to study the diffraction behavior of clay composites. All the experiments were carried out between 2θ equal to 2° to 60° . PET nanocomposite pellets were crushed into powder by a cryo technique. Experiments were carried out at room temperature. The basal spacing or the d spacing was calculated by using Bragg's equation.

Transmission Electron Microscopy (TEM)

The TEM study was conducted on a JEOL JEM-100CX II electron microscope. A MT6000 Sorvall microtome was used to cut the thin sections of the sample.

Mechanical testing

Mechanical testing was done on MTS system with variable speed of testing i.e. 1mm/min and 10mm/min. sample dimensions were 70mm * 35mm * thickness of sample. The sample was notched at the center from both the sides to give 17* 5 of central region. The stretched sample was imaged with the help of FLIR- prism DS Infra red camera. This camera has the accuracy of 2% within the given temperature scale. Images were captured after every 4 seconds to understand the change in the temperature profile over the period of time.

Differential scanning calorimetry (DSC)

The effect of stress on crystallization was studied with help of a Perkin-Elmer Pyris 6 differential scanning calorimeter (DSC), with indium calibration. The films of PET/montmorillonite nanocomposite ranging in weight from 5-10mg were used for each run. The sample is heated from 30°C to 280°C at rate of 10°C/min and held at 280°C for 30 minutes and cooled at a rate of 10 °C.

Results and Discussions

Dispersion Analysis

From the XRD (figure 1), the basal MLS peak is either absent (in case of 1%MLS nanocomposite) or significantly suppressed (in 3% MLS concentration). An analogous result is obtained from TEM analysis (figure 2). Analysis of the dark line thickness reveals a thickness of 25Å , which divided by the MLS d-spacing. This indicates that the number of layers corresponding to a black line is around two. The distance between the individual dark lines however is 42Å , 41Å for the 1 and 3% composites. Hence it is inferred from this analysis that 1%MLS concentration shows exfoliated dispersion whereas 3% MLS concentration leads to slightly intercalated-exfoliated structure.

Mechanical Testing

The PET nanocomposites were tested at two different crosshead speeds to investigate the effect of chain entanglement on the fracture mechanism i.e. at 1mm/min and at 10mm/min. For the stretching rate of 1mm/min; all the PET compositions showed ductile fracture with prominent plastic zone seen in IR thermography. The area under curve, the total work of fracture (W_f) was taken as the measure of toughness

(Figure 3). A prominent yield point was noted in these curves and the area under yield region was taken as the elastic work (W_e) done. For 1%MLS composition, the total fracture work as well as the elastic work of fracture was the maximum. As the amount of clay is increased, the area under the curve shows a significant decrease. It is to be noted that the maximum stress does increase. For a loading of 3% MLS, the toughness decreased by 87%. Thus it was observed that addition of 1%MLS increases the toughness of matrix only by a fraction of amount whereas further addition of MLS reduces the toughness of matrix significantly. From an earlier study¹⁰ it was seen that the addition of MLS has reduced the entanglement and also the crystallinity of PET matrix. The decrease in entanglements affects the toughness.

Figure (4) shows the DSC heating scan of neat PET film before and after fracture. The cold crystallization temperature which was present before the fracture is completely absent in the DSC scan of fractured PET in both neat as well as 1%PET nanocomposite. For the 1%PET nanocomposite, there is increase in enthalpy of 13J/g in fractured sample as compared to the pre-fractured sample's DSC curve. This shows that there is stress induced crystallization occurring in PET, which is enhanced by presence of MLS. DSC samples of 3%nanocomposite in fractured zone were not prepared as there was no stress whitened region present in fractured zone.

This effect was further studied at higher rate of testing, where the effect of entanglements is evident. At the rate of 10mm/min, neat PET shows ductile fracture whereas for the 3% MLS composition, the ductile-brittle transition takes place with instantaneous fracture occurring at this rate. This result is also correlated to the dispersion phenomena. 1%MLS with its exfoliated structure shows ductile fracture whereas 3%MLS with slightly intercalated dispersion shows brittle fracture. This may imply that an exfoliated dispersion in a matrix provides a crack inhibitive mechanism, due to well dispersed MLS. Conversely owing to an aggregated state in the intercalated matrix, the crack is not inhibited. Chen et al¹¹ have studied amorphous PET system at rates as high as 1000mm/min and attribute the high temperature behavior to ductile- brittle transition and to adiabatic heating.

Also the temperature changes occurring on stretching the sample were measured with the help of IR wave imaging. Figure (6) shows the fracture occurring in neat PET at the crosshead speed of 1mm/min. the plastic region can be located in the center. It can be seen that neat PET shows a maximum of temperature increase of 1.6°C , whereas this value was only 0.5°C in case of 1%MLS composition (figure 5). In the case of neat PET, this increase is accompanied by the decrease in temperature. Hence we propose the strain induced crystallization occurring in this composition. In the case of a 3%MLS, there is no significant temperature change

occurring as sample is getting stretched since yielding was absent. This increase in temperature provides mobility of chains, which increases the toughness of the system. In the case of 1%MLS, the toughening mechanism is due to crack inhibition. Hence these two compositions vary distinctly in mechanism of toughening.

Conclusion

Neat PET showed adiabatic heating in the plastic zone. Due to this heating effect, the molecular mobility was enhanced leading to increased toughness. In the 1%nanocomposite, there was no significant rise in temperature, yet the toughness is improved. This effect is mainly attributed to the exfoliated nature of matrix providing inhibitive mechanism to fracture. On the other hand the 3% MLS nanocomposite, which had a slightly intercalated structure showed reduced toughness. At higher speed of testing, neat PET remained in the ductile fracture zone but 3% MLS nanocomposite showed ductile-brittle transition at the rate of 10mm/min. Hence embrittlement is caused due to aggregated state of MLS in PET matrix. Hence even though the two compositions (neat PET and 1% nanocomposite) showed similar toughness values, from IR thermography the difference between the fracture mechanisms can be resolved easily. From the DSC analysis it was further proved that there is stress induced crystallization in 1% nanocomposite. Also both neat and 1% nanocomposite show absence of cold

crystallization after fracture which indicate that stress induced ordering in amorphous region as well, especially the interlamellar region is getting ordered on stressing.

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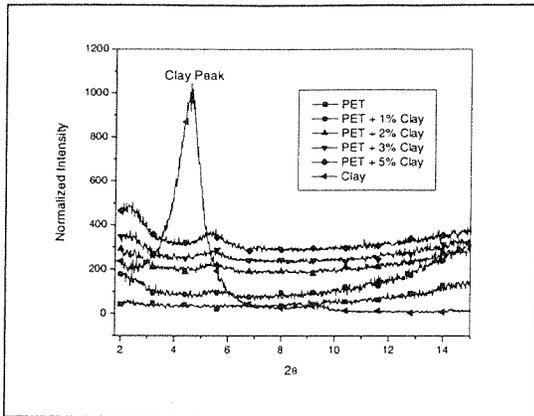


Figure 1. X-ray Diffraction of PET Nanocomposites.



Figure 2. TEM of 1% PET Nanocomposite.

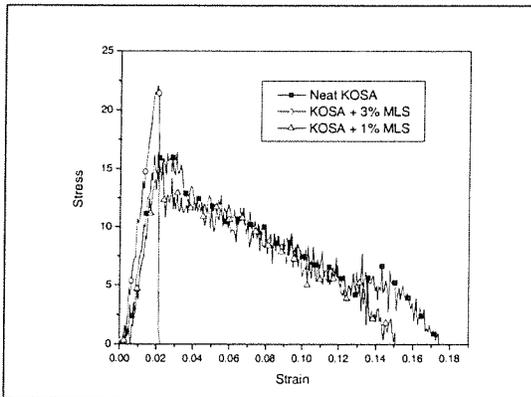


Figure 3. Effect of MLS concentration on fracture

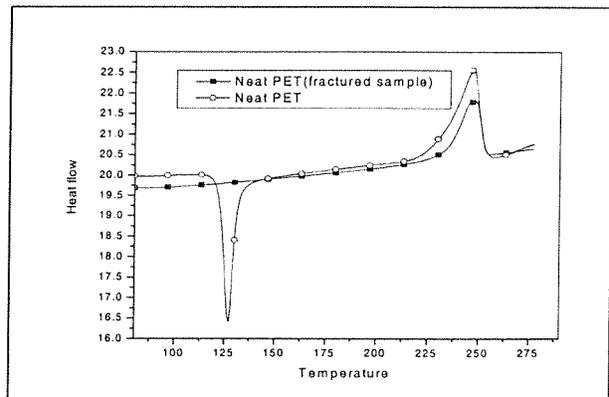


Figure 4. DSC thermogram of PET-pre and post fractured results

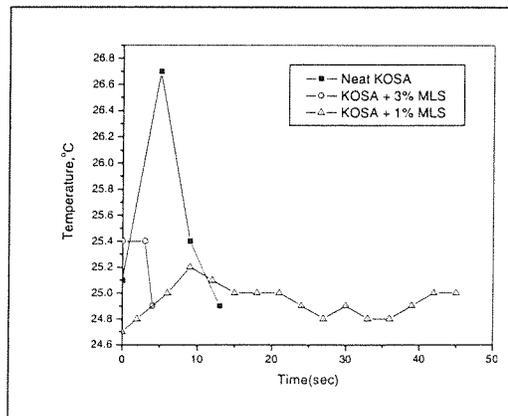


Figure 5. Changes in temperature on stretching the samples of different

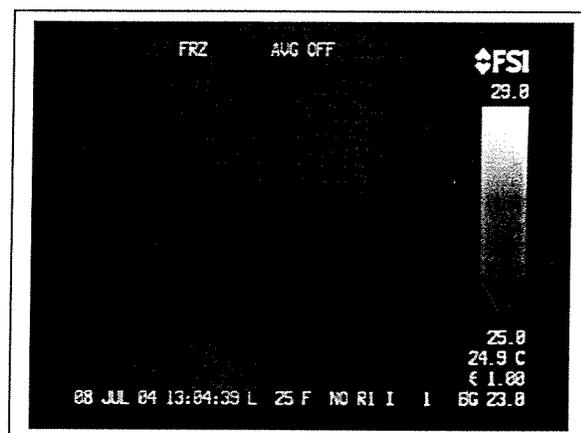
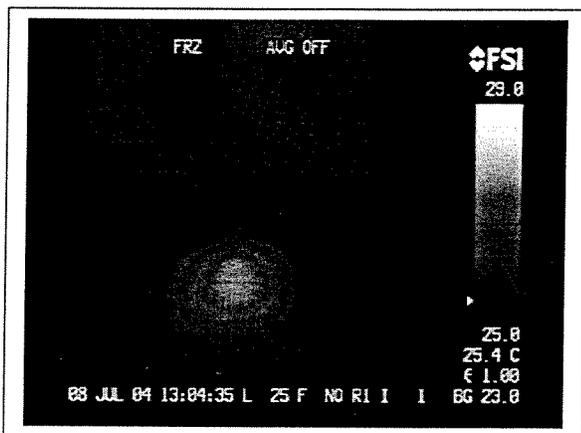
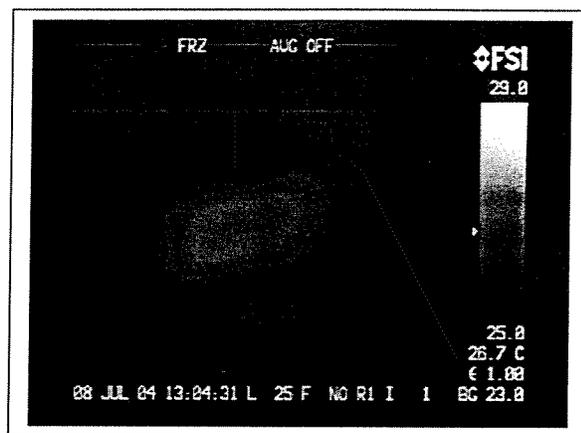
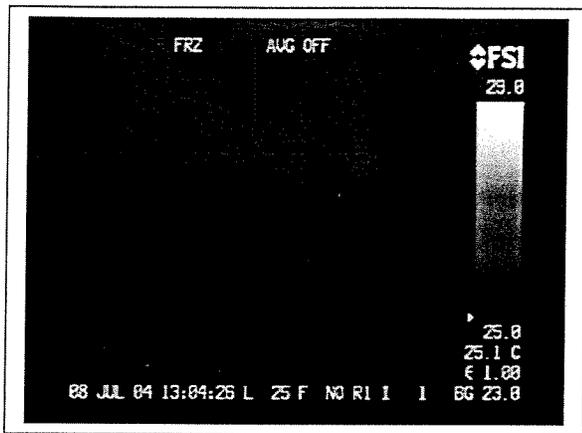


Figure 6(a,b,c,d). Plastic region growth in neat PET on stretching at 1mm/min captured by IR thermography

Composition	W_f (MPa)	W_e (MPa)
Neat KOSA	1.3	0.1
KOSA + 1%MLS	1.6	0.2
KOSA + 3%MLS	0.2	0.1

Table 1. Effect of MLS concentration and rate of testing on

	Neat KOSA	Neat KOSA fractured	KOSA + 1%MLS	KOSA + 1%MLS fractured
T_m (°C)	247	248	247	248
ΔH (J/g)	44	48	52	65

Table 2. DSC results of PET nanocomposites -pre and post fractured results