Effect of Mixing Sequence of Polymer and Nanofillers on Thermo Mechanical as well as Morphological Property of the Nanocomposites

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Abstract

Blends of polybutylene terephthalate (PBT) and thermo tropic liquid crystalline polymer (LCP) and blend of PBT, LCP and nanosilica have been prepared by melt mixing technique. Polymer composites made by engineering thermoplastic PBT and reinforcing polymer LCP has been extruded in presence of nanosilica in different mixing sequence. Here the mixing sequence of PBT, LCP and nanosilica has been picked out so as to study the different changes that can be observed in the characteristics in each of the system. The resultant mixtures are then compression moulded in high temperature range. Microstructures of the blends have been studied by Field Emission Scanning Electron Microscope (FESEM). Thermal properties and dynamic behaviour of the composites have been analyzed by Thermo gravimetric Analysis (TGA) and Dynamic Mechanical Thermal Analyser (DMTA), respectively. From the TGA analysis it is evident that PNL has superior thermal stability than the other nanocomposites. FESEM analysis revealed that the nanosilica prefers the low viscous LCP phase than the high viscous PBT. PNL has the highest tensile modulus among all the nano composites due to migration of nanosilica from high viscous PBT to low viscous LCP phase. There is a remarkable enhancement in storage modulus value is observed in case of PNL system than the other nano composites.

Keywords: PBT, LCP, DMTA, storage modulus, Scanning Electron Microscope

1. Introduction

In the advent of rigid rod-like molecules and due to their spontaneous molecular orientation the thermo tropic liquid crystalline polymers (TLCPs) gains impressive rheological (low melt viscosity), thermal, and dynamic mechanical stability and thereby making them useful for a number of specialized application in conjunction with other thermoplastics. Recently studies onpolyblendssystem have been the subject of numerous investigations. Blending of LCP with other polymers are attractive for number of reasons, the most important of which is in the case of processibility and in situ fibrillation offered by the LCP component to the isotropic polymers (Siegmann, Dagan, & Kenig, 1985; Isayeb & Modic, 1987; Kiss, 1987). Polymer composites based on engineering thermoplastics have excellent wide ranging properties for which they are extensively applied in automobile industries, electronics, electrical appliances and many other fields. Nanoparticles have an extremely high surface to volume ratio which dramatically changes their properties when compared with their bulk sized equivalents. It also changes the way in which the nanoparticles bond with the bulk material. The result is that the composite can be many times improved with respect to the component parts. Some nanocomposite materials have been shown to be several times tougher and improved thermal and mechanical property than the bulk component materials (Ishida, Campbell, & Blackwell, 2000; Beecroft & Ober, 1997; Messersmith & Giannelis, 1995). Nano-sized filler such as nanosilica, nano clay, carbon black have been reported to have unique influence on the morphology of immiscible blends (Messersmith & Giannelis, 1995; Steinmann, Gronisk, Friedrich, 2002; Wang, Li, Chen, Yuan, Yang, & Yuan, 2007). It has been reported nanosilica and nano clay has a compatibilization effect in immiscible polymer blend (Steinmann, Gronisk, & Friedrich, 2002; Wang, Li, Chen, Yuan, Yang, & Yuan, 2007; Zhang, Yang, & Fu, 2004). Polymer blending presents the most attractive route for the production of high performance materials with desired property while suppressing the unwanted properties of individual component. Most of the engineering thermoplastics (polycarbonate, polyethersulfone, polybutylene

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terephthalate, polypropylene oxide) are very difficult to process due to their high processing temperature as well as melt viscosity and are not compatible with each other. To improve the processibility these thermoplastics are often blended with the polymer of lower viscosity like liquid crystalline polymer (LCP) and to minimize the phase separation in binary or multi component system, some compatibiliser is to be added during blending (Sahoo, Das, Pandey, & Mathur, 2002; Datta & Weiss, 1991; Jose, Thomas, Biju, Koshy, & Karger-Kocsis, 2008). The properties of LCP/polymer composites fall far short of expectations, mainly due to poor interfacial adhesion between the dispersed LCP phase and the thermoplastic matrix phase (Datta & Weiss, 1996). Several approaches have been attempted to enhance the interfacial bonding between the two phases (Bassett & Yee. 1990; Datta, Chen, & Baird, 1993). The best way to avoid the above mentioned problem is to incorporate a compatibiliser, which can ensure better adhesion and hence reduces the interfacial tension. PBT is a semi crystalline engineering thermoplastic.PBToffers good electrical properties and good mechanical properties including high strength, rigidity, and toughness and chemical resistance to a wide range of chemicals, solvents, oils and greases. Polybutylene Terephthalate (PBT) has excellent dimensional stability, low moisture absorption, and powerful insulation resistance. Since the processing temperature of PBT is very high so the compatibiliser for this type of blend system should be thermally stable. Polyphosphazene compatibilised PEI/LCP (Bose, Pramanik, Das, Ranjan, & Saxena, 2010), PES/LCP (Bose, Mukharjee, Das, & Saxena, 2009) studied by Bose et al. and PEI /LCP (Nayek, Sahoo, Karthikeyan, Das, Saxena, & Ranjan, 2011) studied by Nayek et al. Nanosilica is one of the most common nano-fillers used in the preparation of nano composite. Han et al has shown that The formation of a high-performance SiO₂ network by well dispersed silica (formed by the surface modification) has improved the thermal stability of LLDPE (Han, Pan, Dong, & Zhang, 2011). Lai et al. has shown that PEEK nanocomposite filled with the modified silica would show higher storage modulus values as compared with those of the unmodified counterparts, also suggesting that the better dispersion of the nano-sized silica could reduce the polymer domain size and make greater improvement on the modulus of the PEEK matrix (Lai, Kuo, Huang, & Chen, 2007).

Here in this work we have shown that mixing sequence had a major role in the dispersion and migration of the nanofillers in the polymer blends. In this article a comprehensive study is carried out to investigate and highlight the thermal, rheological, and morphological properties of PBT/LCP and PBT/LCP/nanosilica blend systems. Here one blend system (PL) and the nanocomposite systems (PLN, LNP, PNL) have been prepared by melt blending process. This paper mainly highlights about the migration of nanofillers to the low viscous medium (LCP) and for this how the thermomechanical, morphological properties are altered for different composite system.

2. Experimental Details

In this section the materials used in this study has been mentioned. This section also contains brief discussion about the characterization techniques adopted for thermal, rheological, morphological and of PBT/LCP and PBT/LCP/nano-silica nanocomposite system.

2.1 Materials Used

- (1) The thermo tropic LCP used in this study was Vectra A950 supplied by Ticona (Shelby, NC). This LCP is a wholly aromatic co polyester consisting of 25 mol % of 2, 6 hydroxynaphthoic acid (HNA) and 75 mol% of p-hydroxybenzoic acid (HBA). The molecular weight could not be determined because it was difficult to find a suitable solvent in which it can be dissolved.
- (2) The thermoplastic used in this study was polybutylene terephthalate, grade [LUPOX, GP-1000, I.V. 1.00 dL/g (LG Polymers India Pvt)].
- (3) Nano silica was indigenously developed in the laboratory of Materials Science Centre, Indian Institute of Technology Kharagpur, India.

2.2 Preparation of PBT/LCP/nano-silica Nanocomposites

Prior to the mixing of PBT and LCP were kept at 80°C and nanosilica was kept at 150°C for 12h. PBT/LCP composite with nanosilica were prepared by melt blending method in an internal mixture, equipped with two sigma type counter rotating rotors, at 285°C and 100 rpm. The mixing was done for five minutes. A binary blend of PBT/LCP was also prepared under the same condition for comparison of properties with the ternary and quaternary blends. Samples for the mechanical testing were prepared by compression moulding, at 285°C and 10 MPa pressure. Then the samples were rapidly cooled to room temperature. The compounding formulations of the nanocomposites are presented in Table 1.

Table 1. Showing the Composition of the nanocomposites along with PL blend

Sample Code	Compositions of the Samples
PBT	PBT(100%)
PL	PBT (70%)+ LCP(30%)
PLN	PBT (69.5%)+LCP(29.5%) +Nanosilica (1%)
PNL	{PBT (69.5%)+Nanosilica (1%)}+LCP(29.5%)
LNP	{LCP(29.5%)+Nanosilica (1%)}+ PBT (69.5%)

2.3 Characterisation

2.3.1 Differential Scanning Calorimetry Study (DSC Study)

Differential Scanning Calorimetric study was carried out using a NETZCH DSC 200 PC instrument up to 250°C at a heating rate of 10°C/min.

2.3.2 Dynamic Mechanical Analysis (DMTA Analysis)

Dynamic mechanical analysis (DMA) was performed in a TA instrument DMA 2980 dynamic mechanical analyzer model in a single cantilever bending mode with a frequency of 1 Hz and a heating rate of 10 °C/min. The temperature dependence of storage modulus E/ was measured from 20°C to 150°C.

2.3.3 Thermo-gravimetric Analysis (TG Analysis)

Thermo-gravimetric analysis is conducted using a DuPont TGA-2100 thermal analyzer at 100°C to 650°C with a heating rate of 10°C/min.

2.3.4 Mechanical Testing

Tensile tests were carried out on a dumb-bell shaped samples using a Hounsfield HS 10 KS (universal testing machine) operated at room temperature with a gauge length of 35 mm and a crosshead speed of 5 mm/min. Tensile values reported here are an average of the result for test run on at least four specimen.

2.3.5 Field Emission Scanning Electron Microscopy (FESEM)

Fracture surfaces are analyzed by Field Emission Scanning Electron Microscope (Tescan, Vega LSU) to reveal the fracture mechanism of the blend systems. Before the analysis samples are gold coated to make it conducting.

3. Results and Discussion

3.1 DSC Study

Figure 1 shows the DSC plots of PBT and its composites. Pure PBT showed an endothermic peak around 227°C corresponding to its melting temperature. Incorporation of Nanosilica in PBT matrix showed a slight deviation in the melting temperature. However, for PBT/LCP blend system there are two endothermic peaks were observed. The peak at around 110°C corresponds to the T_g of LCP which indicated towards the incompatible nature of the two blend partners. Incorporation of Nanosilica in the PBT/LCP blend shows two peaks in the melting range of PBT. This might be due to the non-uniform dispersion of Nanosilica in the PBT phase. Addition of Nanosilica first in PBT phase, followed by LCP addition shows no sign of bifurcation of melting peak of PBT. Similarly addition of Nanosilica first to the LCP phase followed by PBT addition showed no bifurcation. This indicates that the Nanosilica dispersion was better in case of two step mixing but it could not be clear from the DSC analysis that in which phase these nanofillers were dispersed. To further explore the dispersion state of Nanosilica in PBT/LCP matrix, FESEM analysis was carried out and discussed in the following section.

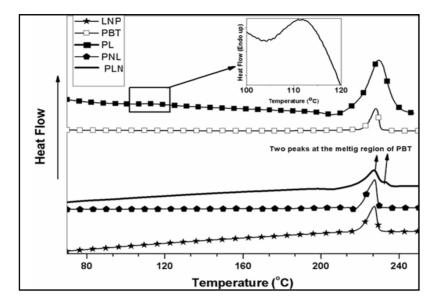


Figure 1. Showing the DSC plot of PBT and its naocomposites

3.2 Fracture Surface Analysis

Figure 2 shows the FESEM images of PL blend along with the PLN, PNL and LNP composite systems. In Figure 2a it can be seen that in case of PL blend system there matrix droplet morphology is observed. The LCP droplets are embedded in to the PBT matrix. The LCP droplets are pulled out from the PBT matrix. This occurs due to the incompatibility of PBT and LCP phase. There also open ring structure is observed at the interface of PBT and LCP phase. This kind of morphology is also observed in the work by Nayek et al. (2011) which again support the incompatibility of the two polymers. Figure 2b is showing the morphology of PLN system. Here the ellipsoidal LCP phase is observed. When PBT, LCP, Nanosilica simultaneously mixed together, the major percent of nanosilica remains in low viscous LCP phase and very few amount are migrated to the interface of two polymers. Hence the adhesion of two polymers at the interface becomes comparatively better. Due to this better adhesion the PBT phase exerts a strong dragging force on LCP phase hence that phase becomes ellipsoidal. Similar type morphology also observed in the paper by Hatui et al. (2012). In LNP system (Figure 2c), nanosilica remained in the LCP phase and the adhesion at the PBT LCP interface was very poor and no fibrillar morphology was observed but still there is some small fiber in the LCP phase due to presence of nanosilica in LCP phase. However, for the PNL system (Figure 2d), even though the nanosilica was found in the LCP phase, the phase adhesion was found to be better and a lot of fibrils were observed on the LCP phase. This indicates that during mixing when the nanosilica was added first to the LCP phase followed by PBT, the fillers were remain in the LCP phase and not migrated to the PBT phase. However, when the reverse mixing was done, i.e. nanosilica was first mixed with PBT followed by LCP, there was a migration of fillers from the PBT phase to LCP phase and hence the nanosilica was found in the LCP phase. This showed that mixing sequence had a major role in the dispersion and migration of the nanofillers in the polymer blends. To analyze the effect of dispersion and migration of nanosilica on the PBT/LCP blend system, tensile and dynamic mechanical analyses were carried out and the results were discussed in the following section.

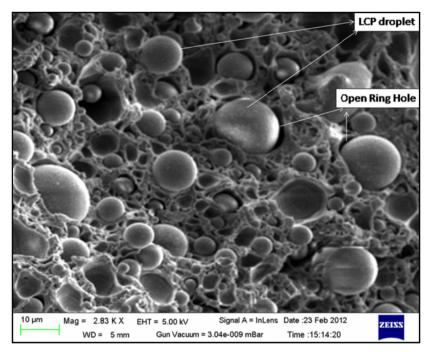


Figure 2a. FESEM image of PL blend system

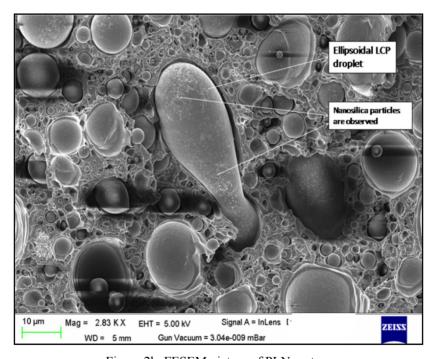


Figure 2b. FESEM picture of PLN system

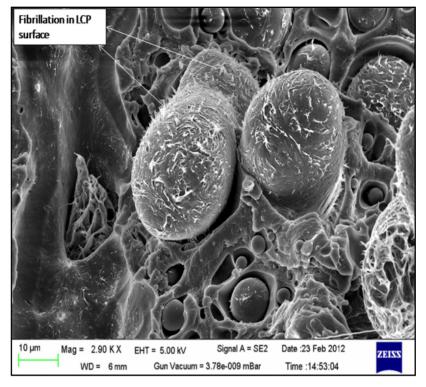


Figure 2c. FESEM picture of LNP system

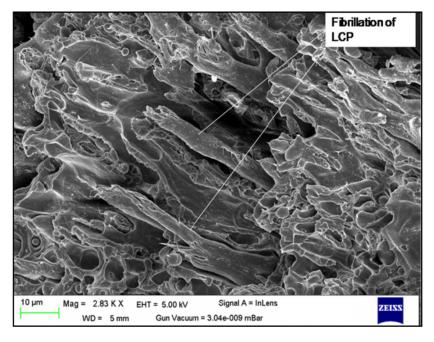


Figure 2d. FESEM picture of PLN system

3.3 Tensile Property Measurement

Figure 3 shows the tensile modulus properties of all the blend systems. As can be seen, pure PBT possessed the lowest tensile modulus among all the systems. Blending with LCP, increased the modulus of PBT/LCP blend in comparison to pure PBT due to the incorporation of rigid LCP phase in the PBT matrix. Further incorporation of nanosilica (PLN) increased the modulus of PBT/LCP blend system due to the reinforcing effect of nanosilica. However, better modulus was achieved for the two step blending process (PNL and LNP) as compared to one

step blending (PLN). Among the PNL and LNP systems PNL possessed the better modulus. This can be correlated with the dispersion and migration of nanosilica. As discussed in the previous section, in case of LNP system nanosilica was remained in the LCP phase (which was the minor phase) and the adhesion between the PBT and LCP was very poor due to which the modulus decreased (Bose, Pramanik, Das, Ranjan, & Saxena, 2010). Due to the poor adhesion at the PBT-LCP interface the load transfer from PBT to the rigid LCP domain was hampered and hence the modulus decreased. But in case of PNL system better adhesion at the PBT-LCP interface enhanced the load transfer from matrix to the dispersed phase and hence the modulus increased.

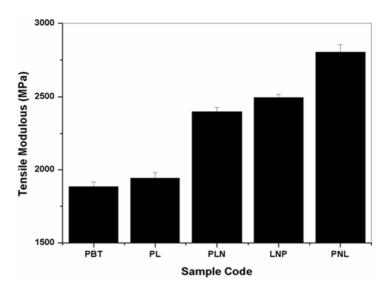


Figure 3. Tensile Modulud of nano composites and blend

3.4 DMTA Study

To further confirm this we had carried out DMA analysis and the plots are represented in Figure 4. The storage modulus plots (Figure 4a) follow the same trend as that of tensile modulus. Pure PBT possessed the lowest modulus among all the systems. Addition of LCP enhanced the storage modulus of PBT/LCP blend system as compared to pure PBT (Bose, Mukharjee, & Das, 2009). Incorporation of nanosilica further enhanced the storage modulus. However, remarkable enhancement was observed for the two step mixed samples. The storage modulus of PNL was found to be superior to LNP. This also supports the tensile modulus results. The tan δ plots are represented in figure 4b. As expected pure PBT possessed the lowest Tg among all the blend systems and PNL possessed the highest T_g. As can be seen addition and incorporation of LCP and nanosilica (PL and PLN) did not affect the Tg much. However, for the LNP and PNL samples there was a change in Tg which suggests the better dispersion of nanosilica in the blend system. As discussed in the FESEM section the nanosilica for the LNP system were remained in the LCP phase which restricted their migration to the PBT phase due to the viscosity mismatch. Since LCP have the lower viscosity as compared to PBT so during mixing the nanofillers were remain in the low viscous LCP phase and possessed very limited dispersion in the PBT phase due to which the Tg of PBT was not affected much. However, for the PNL system, since the nanosilica was first mixed with PBT phase they dispersed in the PBT matrix and during the addition of LCP they tried to migrate towards the LCP phase. But due to the shorted time period of mixing (5 min) all the nanosilica were not migrated to the LCP phase and hence there was even dispersion in both PBT and LCP phase which reflected in the enhanced T_g value.

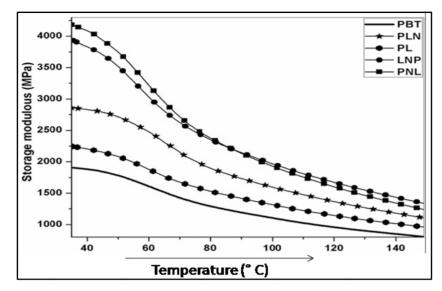


Figure 4a The storage modulus of the nanocomposites along with PL blend

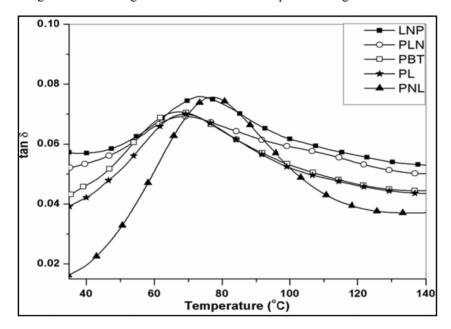


Figure 4b. The tan σ plot of the nanocomposites along with blends

3.5 TG Analysis

The thermal stabilities of the blends were analyzed by TGA and represented in Figure 5. Pure PL possessed the lowest thermal stability among all the blend systems even lower than pure PBT. This might be due to the incompatible nature of the PL blend system. Incorporation of nanosilica enhanced the thermal stability of PLN system due the restricted vibration of the polymer chains in the immediate vicinity of the nanosilica which required higher energy for the degradation process. However, for the LNP and PNL systems better thermal stabilities were achieved due to the better dispersion of nanosilica. Thermal stability of PNL was found to be superior to LNP which may be due to the presence of nanosilica in the matrix phase as compared to in the dispersed phase for the LNP system.

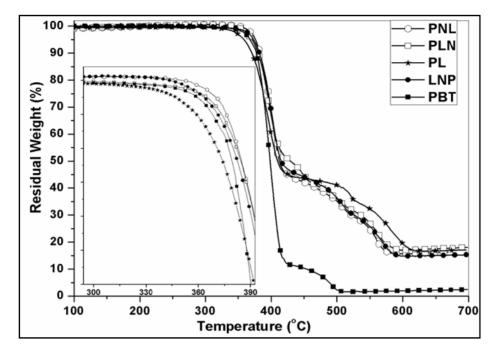


Figure 5. The TGA curve of nano composites

4. Conclusion

The blend nanocomposite of PBT and LCP, in presence of nanosilica was successfully prepared by melt blending process. FESEM analysis revealed the fibrillation of LCP for the PNL system. The storage modulus was also found to be superior for the PNL system. DSC analysis revealed the glass transition temperature of the nanocomposites. Thermal stability of the nanocomposites was determined by TG analysis instrument and it is evident that PNL is thermally most stable nano composites. Mechanical analysis revealed that PNL has the highest storage modulus among all the nanocomposites.

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