Effect of LCP Inclusion on Processability and Thermal Stability of Glass Fiber Reinforced Hybrid Composites

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Abstract

A series of studies were conducted to investigate the effect of LCP inclusion on the processability of short glass fiber reinforced toughened nylon 6,6. The objective was to identify the role of each component phase and obtain composite synergism arising from a multi-component system. It was found that a hybrid composite offered superior processability over the glass fiber reinforced polymers alone. The total torque in melt mixing increased with short glass fiber addition but decreased with an increase in LCP content. Cryofractured extrudates were examined using scanning electron microscopy (SEM). Improved processability of hybrid composites was ascribed to the orientation of LCP domains in the direction of flow. Hybridization also introduced new thermal-morphological interactions among component phases. The thermal and crystallization behaviors were studied by differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), SEM, and wide angle X-ray scattering (WAXS). DMA results indicated that the maximum miscibility between the blended components was in the 5 wt% LCP composition and the miscibility decreased with increasing LCP content. The possible role of elastomer acting as a compatibilizer was critically assessed. LCP hybridization increased the interplanar spacing of the hydrogen-bonded sheets of the nylon crystals rather than the spacing between the hydrogen bonded chains making the sheets more mobile than the chains.

1-INTRODUCTION

Elastomer toughening is one of the promising strategies of enhancing the toughness of otherwise brittle thermoplastics. However, rubber toughening sacrifices vital material properties like modulus and strength. To annul this decrement, reinforcing toughened matrices by utilizing inorganic fillers has been suggested as a strategy (1). Unfortunately addition of fillers inadvertently raises matrix melt viscosity whereby high-energy consumption and constrained processability incur additional fabrication costs. Addition of liquid crystalline polymers (LCPs) to a thermoplastic matrix demonstrates the promise to reduce the viscosity of compounding process and processability could be improved (2). As an amorphous phase, LCP additions also influences thermal behavior and crystalline state of the semi crystalline thermoplastic matrix to which it is blended. The objective of this paper is to investigate the effect of LCP hybridization on the processability, thermal behavior and crystalline state of short glass fiber reinforced toughened nylon 6,6 (GFRT nylon 6,6). Processability was assessed by torque rheometry. Thermal and crystallization behavior were studied by differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA) and wide-angle X-ray scattering (WAXS).

2-EXPERIMENTAL

Rubber toughened nylon 6,6 (Zytel ST801 from Dupont) was dry blended with 20 wt% short E-glass fibers (length=12mm; diameter=17µm) and independently with 5, 10, 15 and 20 wt% of liquid crystalline polymers (Vectra A950 from Hoechst Celanese). Melt blending was carried out using a high shear rate, inter-meshing, co-rotating twin-screw extruder (Leistritz Micro 18). The temperature profile in extruder was 260-280-285-285-292°C. Screw speed was maintained at 200 rpm. The extruded pellets were injection molded into 3.5-mm thick dog-bone specimens using a Battenfeld BA 300 CD+ injection-molding machine. The temperatures in Zone 1 and Zone 2 of the barrel were 285°C and 292°C respectively. The nozzle temperature was 275°C and the mold was kept at ambient
temperature. Torque measurements were carried out in a Haake Rheocord-90 intermeshing, counter-rotating, twin-screw extruder. Measurements were done during the extrusion of 100 g each of 20 wt% glass fiber reinforced rubber toughened nylon 6,6 with extra 5, 10, 15, 20 wt% LCP. Temperature during the extrusion was 290°C and screw speed 100 rpm. Instantaneous torque and total torque were measured. Scanning Electron Microscopy (SEM) observations were done on cryo-fractured extrudates using a JEOL 5410 LV model SEM. A TA Instrument differential scanning calorimeter (DSC 2920) equipped with TA thermal analysis software for data analysis was used for calorimetric studies. Samples weighing around 7 mg were cut from the injection molded samples and all experiments operated with a stream of nitrogen. The sample was first heated from room temperature to 310°C at a rate of 20°C/min and kept at that temperature for 10 min and then cooled to room temperature at a rate of 10°C/min. The cooled sample was reheated to 300°C at a rate of 10°C/min. The peak maximum provided the melting/crystallization temperature and the area under the thermogram provides the heat of crystallization/fusion. Dynamic mechanical analysis was performed using TA DMA 2980 equipped with TA thermal analysis software. The measurements were made on injection-molded plaques at a scan rate of 3°C/min with a frequency of 1 Hz in a temperature range of 25 to 200°C. A double cantilever clamp in a bending mode was used for the tests. X-ray diffraction measurements were conducted on injection-molded plaques using a Shimadzu Lab XRD-6000 X-ray diffractometer employing Ni-filtered CuKα radiation (λ=1.54 Å) operating at 50 kV and 20 mA. The scans were obtained in a continuous scan mode by counting for 6 s at 0.1° step (θ/2θ scan). The scanning range was restricted between 10.00-35.00 degrees to observe the relevant peaks pertaining to nylon 6,6.

3- RESULTS & DISCUSSION

3.1-Processability

Instantaneous torque is directly proportional to the melt viscosity at a certain time and total torque is indicative of the total energy expended on extruding a given amount of material integrated to fixed time. Fig.1 shows the torque profiles.

![Figure 1- Torque versus time profiles for hybrid composites](image1)

The torque experienced during the extrusion of LCP hybrids is lower than that for GFRT nylon 6,6. Figure 2 shows the accumulated torque for hybrid composites integrated to 2-min.

![Figure 2- Total torque versus LCP content.](image2)
Clearly, energy expended on extruding the hybrid materials decreases with increasing LCP content indicating improved processability of GFRT nylon 6,6 with addition of LCP. Figure 3 shows the SEM micrograph of cryo-fractured extrudate of 20-wt% LCP hybrid composite sectioned along the flow direction.

**Figure 3**- Extrudate morphology of 20-wt% LCP hybrid of GFRT nylon 6,6.

We ascribe the improved processability to the orientation of LCP domains in the flow direction (Fig.3), thereby lubricating the melt flow.

### 3.2 Thermal behavior

Figure 4 shows the variation of melting point of hybrid composites with the square of volume fraction of LCP content.

![Graph showing melting point versus square of LCP volume fraction](image)

According to Nishi-Wang theory, interaction parameter between the blend components can be quantitatively correlated to the slope of melting point versus square of LCP volume fraction curve. The more negative the slope is the higher the miscibility. As evident from Fig.4, slope of melting point variation is most negative in 0.05-to 0.1-volume fraction of LCP (corresponding to 5-10 wt% LCP), indicating higher miscibility between nylon 6,6 and LCP. At higher volume fractions, the slope levels off indicating reduced interaction between the blend components. Figure 5 shows the $\alpha$-peak relaxation spectra of GFRT nylon 6,6 and its LCP hybrid composites from DMA studies.

![Graph showing tan delta versus temperature](image)

Glass transition temperature ($T_g$) of nylon 6,6 in GFRT nylon 6,6 increases from 63°C to 66°C with the addition of 5-wt% LCP, which is more than that predicted by Fox’s equation for completely miscible blends. Such a high temperature shift is not evident in other hybrid compositions. Moreover, 5-wt% LCP composition exhibits the broadest transition peak of all the compositions suggesting high interaction between the blend components. DMA results are consistent with the melting point data obtained from DSC. Maleic anhydride grafted elastomers are widely used for toughening nyons. Coincidently, these elastomers can also act as effective compatibilizers in polyamide/LCP systems. We believe that, elastomer in toughened nylon 6,6 acts as a compatibilizer, resulting in higher miscibility between nylon 6,6 and LCP.
3.3 Crystalline state

At room temperature, two peaks distinguish nylon 6,6 crystal structure, namely, $\alpha_1 (2\theta = 20.6^0)$ and a doublet $\alpha_2 (2\theta = 23.3^0)$ (3). Peak $\alpha_1$ arises from the distance between hydrogen-bonded chains and $\alpha_2$ occur from separation between hydrogen-bonded sheets in the triclinic crystal structure. Figure 6 shows variation of intensities of $\alpha_1$ and $\alpha_2$ peaks with LCP content.

![Figure 6](image)

**Figure 6** - X-ray intensity variation with LCP content for $\alpha_1$ and $\alpha_2$ peaks.

Intensity of $\alpha_1$ peak remains steady and, that of $\alpha_2$ peak decreases with increasing LCP content. This indicates that, LCP blending apparently increases the interplanar spacing between the hydrogen bonded sheets rather than the spacing between the hydrogen bonded chains.

As anticipated, the d-spacing value increases up to 10 wt% and drops gently thereafter (Fig.7). We believe that the increase in d spacing of 5 and 10 wt% hybrids is due to enhanced polymer-polymer interaction leading to high miscibility in these compositions as observed in DSC and DMA results.

4. Conclusions

Based on the results reported, the following conclusions can be drawn:

- LCP additions improve the processability of GFRT nylon 6,6. DSC and DMA results show that, miscibility between nylon 6,6 and LCP is highest in the 5 to 10 wt% LCP concentration range. Role of the elastomer as a compatibilizer was likely. WAXS studies indicated that LCP blending apparently increases the interplanar spacing between the H-bonded sheets rather than the distance between the H-bonded chains.

5. References

