INTRODUCTION

Bleeding of toughened matrices with short glass fibers provides an attractive route to achieve concomitant strengthening and toughening for engineering applications. Provided reasonable bonding at fiber-matrix interface, improvement in strength and stiffness was observed in short fiber reinforced toughened matrices (1, 2). Nevertheless, the presence of inorganic fillers inadvertently raises the melt viscosity of thermoplastics, whereby high energy consumption and constrained processability incur additional fabrication costs. Fiber reinforcement also catalyzes the tear and wear of the processing equipment and high loadings of inorganic fibers lead to heavier products. Reinforcement effect arising from fiber inclusions critically depends upon the retention of fiber length and its orientation. Unfortunately, the shear force during compounding and injection-molding processes often lead to fiber breakage. It is desirable to optimize fiber lengths and to promote good mixing during compounding process.

Addition of LCPs to a thermoplastic matrix demonstrates the promise to reduce the viscosity of the compounding process and hence processability could be improved. The LCP/thermoplastic blends also have other advantages over glass-fiber reinforced systems in addition to reduced melt viscosity and slashed energy consumption in processing. Most injection molded LCP-containing thermoplastics produce smooth surface finishes because of their propensity for skin-core morphology. LCP also imparts good recycle characteristics to glass fiber reinforced thermoplastics because glass fiber breakage is less severe in the presence of LCP during processing. Being an organic component by itself, LCP can form in situ fibers, offering light substitutes for inorganic glass. Of critical importance is that the mechanical properties of hybrid composites are potentially superior to those of glass filled composites (3) via synergistic interactions. Previous studies by He and collaborators (4, 5) reported attractive properties for LCP/glass/thermoplastic hybrid composites. They also demonstrated good processability using PEEK, PC and PES as matrices for LCP-containing systems. However, little is understood of the behavior of thermoplastics containing an engineered combination of short glass fibers, LCP and an elastomeric phase. The role of impact modifiers in reinforced hybrid materials is particularly abstruse. In a series of studies we attempt to uncover the desirable properties of such complex LCP hybrid systems. The ultimate goal is to elucidate the fracture behavior and synergistic properties in a hybrid structure.

In this paper, we focus on the effect of LCP on the processability of glass fiber reinforced thermoplastics. The use of LCP as a processing aid and reinforcing agent was investigated. The morphology of the hybrid composites was examined using SEM.

MATERIALS AND EXPERIMENTAL WORK

A hybrid composite consisting of rubber toughened nylon 6,6, short glass fibers and thermotropic LCP was investigated by varying the content of LCP. It was found that a hybrid composite offered better 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. The thermal stability of the glass fiber reinforced composite was improved by blending with LCP. However, a minimum of 15 wt% LCP was required to realize reinforcement effect from the hybrid composite. The fracture morphology was examined using SEM techniques. Some LCP fibrils could be observed on the tensile fracture surface.

Rubber-toughened nylon 6,6 (Zytel ST801 from DuPont) was dry blended with 20 wt% of short E-glass fibers (length = 12 mm; diameter = 17 μm) and...
independently with 5, 10, 15 and 20 wt% of liquid crystalline polymers (Vectra A950 from Hoechst-Celanese). The LCP comprised 27-mol% of 2-hydroxy-6-naphthoic acid (HNA) and 73-mol% of p-hydroxy benzoic acid (HBA). Melt blending was carried out using a high shear rate, inter-meshing, co-rotating twin-screw extruder (Leistritz Micro 18; with a screw diameter of 18 mm and L/D ratio = 30). Table 1 shows the processing conditions in the twin-screw extruder for the preparation of LCP hybrid composites. The extruded pellets were injection molded into 3.5-mm-thick dog-bone specimens (ASTM D638 type I) using a Battenfeld BA 300 CDplus injection-molding machine. The temperatures in zone 1 and zone 2 were kept at 285°C and 292°C respectively. The nozzle temperature was kept at 275°C and the mold temperature at 30°C. An injection pressure of 70 bar and holding time of 50 s were used. The screw speed was kept at 140 rpm. Rubber toughened nylon 6.6 containing 20 and 30 wt% glass fibers were processed and compared to the properties pertaining to the hybrid composites. All the materials were dried at 80°C for at least 72 h in a vacuum oven before processing.

Torque measurements were carried out in a Haake Rheocord-90 intermeshing, counter-rotating, twin-screw extruder. One hundred grams (100 g) each of rubber-toughened nylon 6.6 with glass fiber content ranging from 10 to 30 wt% were extruded at a temperature of 280°C while maintaining a screw speed of 100 rpm. Accumulated torque and the instantaneous torque were measured. Similar measurements were carried out on the extruded 20 wt% reinforced rubber-toughened nylon 6.6 blended with extra 5, 10, 15, 20 wt% LCP. The temperature during the extrusion was 290°C and the screw speed 100 rpm.

Thermal stabilities of the blends were assessed by thermogravimetric analysis (TGA) using a Hires TGA 2950 equipped with thermal analysis software. TGA measurements were done at a scan rate of 10°C/ min purged with a stream of nitrogen.

Scanning Electron Microscopy (SEM) observations of the blends were performed on a JEOL 5410 LV model SEM. Morphological examination was conducted on the cross section of the extruded strand of LCP-containing composites after cryogenic fracture in liquid nitrogen. The fracture surface was coated with gold in an SPI sputter coater. The tensile fracture surface was also studied using SEM.

All specimens were kept dry prior to mechanical tests. The tensile tests to determine the tensile strength and modulus were performed according to ASTM D638 using an Instron 5565 at a crosshead speed of 5 mm/min. An extensometer was used to determine the modulus. The values reported were averages of at least five measurements.

### RESULTS AND DISCUSSION

#### Processability

Torque rheometry measures the work accomplished in the studied materials during melt mixing under controlled conditions, viz., temperature and shear rate. Torque is directly proportional to the melt viscosity at a certain time. Figure 1 illustrates the variation of torque with time for the extrusion of the glass fiber reinforced composites. As expected, the torque increases with the glass fiber content. This is due to the increase in the melt viscosity of the composite with increasing amount of glass fiber. It is interesting that the melt viscosities of the glass fiber containing compositions decrease with time and soon go below that of the rubber toughened nylon. This observation is attributed to the fact that, during increasingly elongational flow experienced by the melt in the converging section of the extrusion die, fibers in the composites get oriented in the flow field direction. This results in the reduction in viscosity and hence the decreasing torque with respect to time.

In extrusion and injection molding, the flow fields generated always promote some degree of fiber orientation. The extent of fiber orientation depends on the intensity of the flow field and the response characteristics of the fiber (6). Concentrated fiber suspensions are found to be more sensitive to elongational flows in promoting orientation. Crowson and co-workers (7) reported the studies on fiber glass reinforced polypropylene undergoing converging and shearing flows. Using a contact radiography technique, they found a high degree of fiber orientation parallel to the converging flow direction when the polymer melt enters the capillary die through a small cone angle from the reservoir. But much of this orientation was found to be lost during the shear flow. Green and Wilkes (8) studied the rheological properties of short fiber reinforced plastics using steady-state shear measurement. They found that at low shear rates the steady state shear viscosity increases with fiber concentration. With extended shearing time the viscosity becomes almost the same as the neat resin, regardless of the glass fiber content. All these previous studies are consistent with our observation of the decreasing torque with time and the fiber alignment in the direction of flow.

Figure 2 shows the variation in the total torque with glass fiber content for the glass fiber reinforced toughened nylon. The information generated from the total torque could be rather complex. It represents the resistance of the solids in the conveying region of and the melt resistance throughout the extruder and this torque is integrated with respect to time. The total torque is clearly indicative of the energy consumed for

<table>
<thead>
<tr>
<th>Zone 1 (°C)</th>
<th>Zone 2 (°C)</th>
<th>Zone 3 (°C)</th>
<th>Zone 4 (°C)</th>
<th>Die (°C)</th>
<th>Screw Speed</th>
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<tbody>
<tr>
<td>260</td>
<td>280</td>
<td>285</td>
<td>285</td>
<td>292</td>
<td>200 rpm</td>
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blending and it increases with the glass fiber content. A steep rise in the total torque is observed between 10 and 20 wt% of glass fibers. It appears that there exists a critical fiber volume fraction above which the viscosity increases more markedly with fiber content. Clearly, inclusion of glass fibers has greatly increased the energy consumption during processing.

A change in the trend of instantaneous torque and the total torque profile arises upon addition of LCP to the glass fiber reinforced materials. The torque during extrusion for all hybrid compositions with varied content of LCP is lower than that experienced during the processing of rubber toughened nylon 6,6 reinforced with 20 wt% glass fiber as shown in Fig. 3. The
difference in the instantaneous torque for 0% LCP in Fig. 3 and that in Fig. 1 is caused by the significant change in time scale and the 10°C change (from 280°C to 290°C) in temperature under two different sets of experiments. At 290°C viscosity drops and it takes less time to extrude the fiber-reinforced toughened nylon but the major cause of the difference is still with the time scale in the two different figures. When the total torque is plotted against the LCP content in Fig. 4, the decrease in accumulated torque appears to follow a volume-averaged rule. In contrast to the case shown in Fig. 2, it is clear from Fig. 4 that the total torque for LCP-containing hybrid composites decreases with increasing LCP content. It is evident that addition of LCP to glass fiber reinforced toughened nylon reduces the energy consumption in processing. The low energy consumption can be envisaged in light of the reduction in viscosity owing to the addition of LCP. The glass fiber content is kept at 20 wt% throughout and it is unlikely to contribute to the reduction in torque.

The role of LCP as a processing aid for thermoplastics is well established (9). Siegmann and co-workers...
(10), studying the polyblends of amorphous polyamide and liquid crystalline polyester, observed a marked decrease in viscosity for all the blends with the addition of as little as 5% LCP. This viscosity drop was attributed to the characteristic melt orientation of the LCP domains. Malik et al. (11) found that blends of LCP with polycarbonate (PC) had lower viscosities and exhibited more shear thinning than that of PC alone. Blizard and Baird (12) also observed a significant reduction in viscosity when they investigated blends of an LCP with nylon 6.6. Investigating the torque during extrusion of nylon 6/LCP blends, La Mantia et al. (13) observed a pronounced decrease in the torque with the addition of the LCP. Nevertheless, little work has been done on the effect of LCP on the processability of fiber-reinforced thermoplastics. Based on these previous studies (10–13) on LCP-containing thermoplastics, we conjecture that LCP domains orient themselves in the direction of the flow so that these interlayered alignments could facilitate the flow of polymer, and thereby the viscosity of the short glass fiber reinforced matrix is also reduced.

To facilitate LCP fibrillation in hybrid composites, the viscosity of the dispersed phase (LCP) should be lower than that of the continuous phase (14). It was interesting that Beery and co-workers (14) could barely observe the deformation of Vectra A950 in a nylon 6 matrix even at a high shear rate of 2500 s\(^{-1}\). At this shear rate the ratio of viscosity of LCP to that of nylon 6 was found to be 4. On the other hand, Chung and co-workers (15) investigated the dynamic rheological behavior of Vectra A950 reinforced nylon and observed that the viscosity ratio of Vectra A950 to nylon 66 was less than 1 at processing temperatures higher than 290°C. Their optical micrographs of blends of Vectra A950 and nylon 66 showed good fibrillation of the LCP above 290°C, but it could not fibrillate well at 280°C.

Figure 5 compares the torque profile of toughened nylon containing 20 wt% glass fibers and that of Vectra A950 at 290°C. The torque in the extrusion process of Vectra A950 is much lower than that for the fiber containing nylon. This condition appears to satisfy Chung’s observation (15) that the melt viscosity of Vectra A950 is lower than that of the matrix. Under this condition LCP fibrillation should be enhanced during melt processing.

**Extrudate Morphology**

The morphology of the extrudates was observed under the SEM after the extrudate was cryo-fractured following immersion in liquid nitrogen. Figure 6 compares the fracture surface morphologies of the extrudate from 5 wt% (Figs. 6a and b) and 20 wt% (Fig. 6c) LCP containing hybrid composites. The micrographs show two main features. The continuous phase is toughened nylon reinforced with 20 wt% short glass fibers and the LCP fibrils appear sparsely drawn out from the surface in Fig. 6b. The LCP phase is not completely distinctive from the predominant nylon matrix even though some individual LCP fibrils are visible. Such surface morphology suggests that some degree of complex interchange reactions (16) between the LCP and the nylon may take place at a molecular level. Further evidence of the interchange reactions is discussed elsewhere (16, 17). At 5 wt% LCP (Fig. 6b) the
fibrils seem to be uniformly and sparsely distributed all over the surface, but as the LCP content increases to 20 wt% (Fig. 6c) the LCP phase seems to coalesce and forms some sheet-like structures. This fibril formation and orientation of LCP phase are the primary driving force behind enhanced processability and mechanical properties for LCP composites.

Thermal Properties

TGA results are summarized in Table 2. Blending of glass fiber reinforced nylon 6,6 with Vectra A950 has improved the thermal stability of the blends. LCPs having better thermal properties than the flexible chain polymers impart improved thermal stabilities to the reinforced matrix. Campoy and co-workers (18) studied the thermal stabilities of blends between nylon 6 and Vectra A950. They found that the thermal stability of the Vectra A950 is much better than that of nylon 6 and thermal stabilities of the blends are progressively improved by the addition of the LCP. Tjong and co-workers (19) also observed an improvement in thermal stability of the polypropylene on blending it with Vectra A190. Our results presented here indicate that the thermal stabilities of glass fiber reinforced composites could be considerably improved by some inclusion of LCP.

Mechanical Properties

The plots of tensile strength and modulus versus LCP content are shown in Fig. 7. The trends of variation in both strength and stiffness with respect to LCP content appear to be similar. With the addition of 5 wt% of LCP there is a slight drop in strength and stiffness. Further increase in the LCP content enhances both properties. At 20 wt% LCP there is a rapid rise in the tensile strength and stiffness. Figure 8 compares the tensile modulus and strength of the unreinforced, glass-fiber reinforced and LCP-containing hybrid material. The tensile strength of the hybrid composite at 20 wt% LCP (70 MPa) is higher than that of a rubber toughened nylon 6,6 reinforced with 30 wt% glass fiber (67 MPa). Clearly, the presence of LCP not only provided good processability but also a strengthening role for glass fiber reinforced polymer matrix.

Figure 9 shows the skin and core regions of tensile fracture surface of injection molded 20 wt% glass fiber reinforced composites with (a) 5 wt% LCP (low mag.), (b) 5 wt% LCP (high mag.) and (c) 20 wt% LCP.
reinforced LCP hybrid composites. Injection molding inevitably wiped out some of the thermal history of extruded LCP hybrid composites. As a result, some changes in morphological features were expected. The size and nature of LCP fibrils change with LCP content. From the micrographs in Fig. 9, it is evident that sparse fibril formation exists in 5 wt% LCP near the skin (Fig. 9a) but the LCP phase appears in the form of spherical aggregates for 10 and 15 wt% LCP (Figs. 9b and c). Blizard and Baird (12) could not observe any deformed LCP domains at low content of LCP in nylon 66/LCP blends. Figure 9d displays the micrograph at the skin of 20 wt% LCP hybrid composite revealing some fibrils and predominantly oriented sheet-like structures, which are characteristic skin morphology in LCP-containing thermoplastics (20).

### Table 2. TGA Results of Hybrid Composites.

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<tr>
<th>Sample description</th>
<th>Degradation temperature $T_d$ (°C)</th>
<th>Residue at 450°C (%)</th>
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<tr>
<td>Toughened nylon reinforced with 20 wt% short glass fibers</td>
<td>382.59</td>
<td>42.8</td>
</tr>
<tr>
<td>Toughened nylon reinforced with 20 wt% short glass fibers and 15 wt% LCP</td>
<td>397.06</td>
<td>63.8</td>
</tr>
<tr>
<td>Toughened nylon reinforced with 20 wt% short glass fibers and 20 wt% LCP</td>
<td>400</td>
<td>64.5</td>
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Note: Degradation temperature was determined by TGA at 5% weight loss.
The oriented structures also contributed to the rapid enhancement in strength and stiffness as discussed in Fig. 7. All micrographs (Figs. 9e–9h) in the core region show prevalent LCP droplets within the nylon matrix. These LCP droplets increase in size and number with rising LCP content. Fibrillation of Vectra A950 in injection molded hybrid composites is extremely limited. It is believed that the lack of LCP fibrillation curtails the improvement in strength and stiffness of the injection molded hybrid composites only until 20 wt% of LCP is reached. Strengthening in the latter arises primarily from the oriented sheet-like structures near the skin.

This paper aims to address the benefits of enhanced processability and tensile properties of the hybrid composites consisting of toughened nylon 6,6, short glass fiber-LCP. Future work will focus on the role of
the elastomer and micromorphology in fracture toughness and the synergistic performance in toughened hybrid composites.

CONCLUSIONS

Based on the results reported in this paper the following conclusions can be drawn:

1. The processability of LCP-nylon-glass hybrid composites was assessed by measuring the accumulated torque as a function of glass fiber reinforcement and LCP content. The inclusion of small amount of LCP into glass fiber reinforced nylon 6.6 markedly improved the processability of fiber-reinforced toughened thermoplastics.

2. The hybrid composites so obtained exhibited better thermal stability than the glass fiber reinforced polymers alone.

3. It was concluded that LCP not only served as a processing aid but also a reinforcing agent in hybrid composites when its domains were oriented along the load bearing direction. At 20 wt% LCP, the hybrid composite exhibited the best combination of processability and mechanical properties.

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