The focus of this work was to investigate the potential of enhancing the mechanical properties of thermoplastic resins, with an emphasis on those which are considered commodity resins, by blending with liquid crystalline polymers (LCPs). There is an inherent problem, however, in achieving this goal in that thermotropic LCPs often have higher melting (or processing) temperatures than most thermoplastic polymers such as poly(ethylene terephthalate) (PET) and polypropylene (PP). To overcome this limitation a novel blending technique was developed in our laboratory in which the LCP and matrix polymers were plasticated in two separate extruders, and the melts then were brought together in a mixing head. Blends of PET and PP with several LCPs were successfully generated by the above technique. Either rods or flat films were extruded by attaching an appropriate die to the exit of the mixing head. The morphology of the blends showed that the LCP phase formed continuous reinforcing fibrils in the respective matrix material. A high degree of molecular orientation was also observed by means of wide-angle x-ray diffraction studies. Significant enhancements in the mechanical properties of rods, flat films and injection molded plaques of the blends correlated well with the morphology and orientation measurements.
GENERATION OF CONTINUOUS LIQUID CRYSTALLINE
POLYMER REINFORCEMENTS IN THERMOPLASTICS BY A
NOVEL BLENDING PROCESS

A.M. Sukhadia, A. Datta and D.G. Baird
Department of Chemical Engineering
Virginia Polytechnic Institute and State University
Blacksburg, VA 24061
INTRODUCTION

The art of blending of polymers to obtain materials with superior mechanical and thermal properties is now well established and widely used [1]. In recent years, more attention has been devoted to blends of polymers with thermotropic liquid crystalline polymers (TLCPs or LCPs) as the reinforcing phase because of several advantages [9]. These include fast cycle times, very low mold shrinkage/warpage/sinking, excellent mechanical properties, good solvent resistance, high continuous use temperatures, low thermal expansion, excellent barrier properties and low water absorption [2]. Further, due to their rigid rod-like molecular structure, LCPs tend to be easily oriented in the melt by an external field [3]. The ordered LCPs are known to relax very slowly in the supercooled state [4,5] and therefore the orientation achieved during processing may be retained after solidification usually resulting in enhanced mechanical properties. Also, the melt viscosities of LCPs under processing conditions (elevated temperatures and high deformation rates) are often lower by one or two orders of magnitude than those of comparable flexible chain polymers [6,7]. In fact, the melt viscosity of the blend is usually lowered significantly compared to the matrix polymer viscosity upon addition of a LCP. In order to take advantage of some of the above properties of LCPs, a number of laboratories have reported studies using a discrete LCP phase as both a processing aid and a reinforcing phase for a variety of thermoplastic polymers [8-19].

Typically, under appropriate processing conditions [8,18] the LCP phase forms fine fibrils of high aspect ratio which can effectively reinforce the matrix. The morphology of the blend can resemble conventional short-fiber composites, except that the scale of the reinforcement is an order of magnitude smaller [20]. Mechanical properties of these blends may also be comparable with inorganic fiber-reinforced composites in applications where good processability and low density are important [25].

Most of the previous work, however, involves the blending of thermoplastics with LCPs provided that the two polymers have some overlap of their normal processing temperature regimes. LCPs tend to have high melting temperatures and are consequently processed at relatively higher temperatures compared to some commodity and even engineering thermoplastics e.g., polypropylene and poly(ethylene terephthalate). Mixing of a number of LCPs with polymers in which there is no overlap in their processing temperatures can not be carried out in the same extruder. In this paper we report on some results obtained on the generation of in situ LCP reinforcements in commodity resins using a new blending process which successfully overcomes the processing constraints discussed above. The morphology, orientation and resulting mechanical properties were studied. Several different matrix/LCP systems were blended to test the capabilities of the new process. Both strands (rods) and flat films were extruded and pertinent details are provided in the following sections.

EXPERIMENTAL

Materials: Three LCPs were used in this study. The first LCP is known commercially as Vectra A900 and was purchased from Hoechst Celanese. Vectra A900 is a random copolyester of 73 mol % 4-hydroxybenzoic acid (HBA) and 27 mol % 6-hydroxy-2-naphthoic acid (HNA). Vectra B is another LCP obtained from Celanese and is described as a wholly aromatic liquid crystal poly(ester-co-amide). Its detailed composition is not available. The third LCP used (which will be referred to as LCP60) was a copolyester of 60 mol % HBA and 40 mol % poly(ethylene terephthalate) (PET) and was supplied by Eastman Tennessee Co.

Two matrix materials were used in this study. PET was supplied by Goodyear Tire and Rubber Company. The PET has the following characteristics: Tm = 255°C, Mw = 84000 and Mn = 42,000, according to the data supplied by the manufacturer.
The polypropylene (Pro-Fax 6823) (PP) was kindly supplied by Himont Company and has the following characteristics: Tm = 161°C, Mw = 600,000 (approx.) and a molecular weight distribution (MWD) equal to 5 according to the supplier's data sheet.

**Rheological Studies:** The rheological studies on all the materials were conducted on a Rheometrics Mechanical Spectrometer (RMS-800). Dynamic frequency sweeps were done at the temperatures of interest using a parallel plate arrangement with a plate radius of 12.5 mm and a gap between 1.4-1.6 mm. A strain of 5.0% was used for the LCPs in all the dynamic experiments whereas a strain of 10.0% was used for the matrix materials. These strains were necessary to give a reasonable torque reading at low frequencies. The frequency sweeps were conducted from 0.1 rad/s to 100 rad/s with 3 to 5 readings per decade. Cooling experiments were conducted, also using the parallel plate mode with a gap of 1.4-1.6 mm by monitoring the complex viscosity, $\eta^*$, the storage modulus, $G'$, and the loss modulus, $G''$, as a function of temperature as the polymers were cooled from different temperatures. An angular frequency of 10 rad/s and the same strain levels as before were used in all the cooling experiments. All tests were conducted in a nitrogen atmosphere to prevent any oxidation effects at the elevated temperatures.

**Morphological Studies:** The morphology was determined by scanning electron microscopy (SEM) using a Stereoscan-S200 instrument (Cambdrige) with an accelerating voltage of 25kV. All the samples were prepared by cryogenic fracture after immersion in liquid nitrogen for five minutes. The samples were then mounted on aluminum stubs and sputtered with gold using an SPI Sputter Coater for enhanced conductivity.

Some PET/LCP blends were also etched prior to fracture to remove the matrix PET phase. The solvent used was n-propylamine obtained from Fisher Scientific. The sample was placed in a small beaker and immersed in the solvent which was stirred using a magnetic stirrer apparatus for about 18-50 hours depending on the sample. The etched sample was then washed in water, dried in an oven at 120°C and then prepared as stated earlier for SEM.

**Mechanical Properties:** The tensile (Young's) modulus of the extruded rods was measured on an Instron Mechanical Tester (model 1122). All mechanical tests on the rods were performed with a gage length of 14 cm and a constant crosshead speed of 0.5 mm/min. Because of the brittleness of the samples, virtually all samples broke at the serrated grips and therefore the tensile strength was not evaluated. All the data points represent an average of at least six tests except for draw ratios above 60 where insufficient samples were available. In these cases the data is an average of two to four tests only. The properties of films and injection molded bars were evaluated using the same instrument as above. A crosshead speed of 1 mm/min was used for all the tests and the results represent an average of at least five tests.

**BLEND PROCESSING**

Details of the blending process are best explained with reference to the schematic of the apparatus shown in Fig. 1 [26]. The matrix material and the dispersed phase (reinforcing LCP) were plasticated separately in the two extruders (Killion-KL100, 2.54 cm diameter). The melt streams were then joined and blended in a mixing head further downstream. An adaptor was used at the exit of the mixer to which any appropriate capillary die or flat film die could be attached. Strand extrusion was done using a capillary die with a diameter of 3.176 mm (0.125") and a L/D ratio of 1. Films or sheets were prepared using a 10.16 cm (4") wide film die with an adjustable die gap and typical coathanger feed. The extrudate was then taken up between a pair of chill rolls whose speed could be varied to obtain different draw ratios. In the case of strand extrusion, a water bath for quenching the sample was used immediately downstream of the capillary die before drawing. For the purpose of this paper, any blends made using the above process will be referred to
as 'mixer blends' while blends made by simply tumbling the materials in a single extruder (without the mixing head) will be referred to as 'physical blends'.

Due to the nature of the blending process, it was not possible to determine a priori the composition of the blend. Therefore a series of experiments were conducted wherein the RPM of the matrix extruder was kept constant at 40 RPM and the RPM of the LCP varied from 2 to 25 RPM. The flow rates were then calculated by timing the disappearance of a known weight of polymer for each combination of RPMs. As a check, the output (total) flow rate was also measured and in cases where there was no leakage, the sum of the matrix and dispersed polymer flow rates compared well with the total measured flow rate.

RESULTS AND DISCUSSION

RHEOLOGY

In order to better appreciate both the reasoning and need behind the development of the new blending process, we discuss the rheology of the materials first. It is well known that most polymer melts are immiscible and thus form multiphase domains upon mixing. The morphology of this blend is governed by several factors including composition ratio, viscosity ratio, elastic and interfacial properties of the components, magnitude and type of flow field, residence time and post-processing (e.g. post-extrusion drawing). It is also now widely believed that the viscosity ratio (dispersed phase to matrix phase) must be lower than or equal to unity for the dispersed phase to be successfully elongated from droplets into highly elongated fibrils [7,8]. However, such a favorable viscosity ratio is difficult to achieve using a single extruder. This point is further discussed in the following section.

Results of dynamic oscillatory tests are shown in Fig. 2. It can be seen that the viscosity of Vectra at 290°C is higher than that of PET at 265°C for the entire frequency (or shear rate) range up to 100 rad/s. Once the Vectra is heated up to 320°C where the residual crystallites are melted out (as suggested in refs. [21,22]) the viscosity drops by about three decades from that at 290°C. Thus in order to obtain a viscosity ratio favorable to fibril formation, the Vectra needs to be heated up to 320°C. However, if this were to be achieved in a single screw extruder along with PET as the matrix material, then processing of PET at this high a temperature would very likely lead to degradation. Interestingly enough if the Vectra is heated to 330°C and held there for a few minutes and then cooled to lower temperatures, viz. 265°C and 285°C, and the dynamic frequency sweep conducted at these temperatures, it can be seen from Fig. 2 that the viscosity of Vectra at these low temperatures is still lower than that of PET in the entire frequency range. This is in essence the thermal history that the materials undergo in the actual blending process yielding a favorable viscosity ratio.

In order to get an idea regarding the temperature window within which a material may be processed, cooling experiments as described earlier were conducted. Results from these tests are shown in Fig. 3. The Vectra has a melting temperature of 283°C. However, when the material is cooled from 330°C it does not solidify (crystallize) until as low as 250°C which is judged by the rapid rise in either η* or G'. The actual solidification temperature is somewhat lower but the test is stopped here so as not to overload the transducer. This difference in the solidification and actual melting temperatures is often referred to as the processing or 'supercooling' window wherein the material is still viscous enough to flow but also has the requisite melt strength. For processes such as sheet extrusion, film blowing and blow-molding, where the melt emerging from the die is subject to further deformation usually by way of drawing, it is imperative that the melt have sufficient strength to sustain this deformation. Of interest in Fig. 3. is the behavior of pure PET when cooled from 290°C (open triangles) and 330°C (closed squares). In the former case the PET solidifies at about 200°C giving a processing window of ca. 65°C. When cooled from 330°C, the solidification is not complete until about 170°C. Thus the processing window has been increased to almost 100°C. But of greater
consequence is the magnitude of the viscosity from the two cases. When the PET is cooled from 290°C, its viscosity is higher than that of Vectra in the entire temperature range of interest. If, however, it is cooled from 330°C, its viscosity is lower than that of the LCP in the entire temperature range. The viscosity ratio in the former case is favorable to fibril formation whereas in the latter case it works against fibril formation. Thus being able to give independent thermal histories to the two polymers allows one to obtain optimal processing conditions.

It is also of great importance to know the kinetics of the solidification (or crystallization) of the material upon cooling. From this data one can get a feeling of how long the material can be processed at a particular temperature before it solidifies. Thus isothermal time sweeps for Vectra were conducted at 265°C and 285°C upon cooling from 330°C as shown in Fig. 4. As can be seen, the material is quite stable at 285°C (crystallizing very slowly as observed by the gradual rise in the complex viscosity) for over 15 minutes where the experiment was terminated. At 265°C, however, the material shows a fairly rapid rise in complex viscosity but still indicates that about six minutes of processing time is available before the material solidifies. This is much longer than the estimated residence time of 1.5-2.5 minutes that the material actually spends in the mixer, adaptor and die combined.

**STRAND EXTRUSION**

Morphology: Strands of PET/Vectra 70/30 were extruded using the mixing process as described earlier. The morphology of these strands was examined using SEM. A 5 cm long section of the strand was also etched in n-propylamine for about 24 hours to remove much of the PET phase and then prepared for SEM as discussed earlier. In Fig. 5 is shown the fracture surface of PET/Vectra 70/30 mixer blend rod as extruded. Two things are very clearly evident from Figs. 5a and 5b. First, the distribution of the Vectra phase in the PET matrix is extremely good judging from the presence of fibrils in the entire cross-section of the strand (Fig. 5a) and there is no evidence of a skin-core structure. Second, the fibrils appear to be extremely long and thin (high aspect ratio) with average fibril diameters of about 0.5-2.0 μm. Both these factors i.e. high aspect ratio fibrils and a good distribution in the cross-section are important and conducive to obtaining significant reinforcements in the matrix polymer. In Fig. 6a is shown an SEM of the strand which was etched and a photograph of the Vectra phase left behind shows a rather dramatic morphology consisting of a bundle of infinitely long fibrils (Fig. 6b). In sharp contrast, a low magnification SEM (Fig. 7a) of the physical blend rod shows a skin-core structure with most of the LCP fibrils present in the skin region. The core region, however, shows distinct droplet structure of the LCP (Fig. 7b). The diameter of the fibrils were observed to be about 1-5 μm. On the basis of these observed morphological differences, it is expected that the mixer blends would show higher mechanical properties.

Mechanical Properties: The tensile (Young’s) moduli of strands of several different PET/Vectra compositions was measured using standard test methods described earlier. The moduli of several different PP/LCP blends was also measured. The results of these tests for the PET/Vectra system are shown in Table 1. Before discussing the results, it should be noted that pure PET rods were also extruded for comparison and the modulus of PET strands was measured to be 2.5 GPa. Further, the modulus of pure PET strands remained unchanged, within experimental limits, with draw ratio which is likely due to the short relaxation time of molecular orientation. In fact, this was confirmed using WAXS where a strand with draw ratio of 40 did not show any evidence of a preferred direction of molecular orientation. With reference to Table 1, it may be observed that there is a substantial increase in the value of Young’s modulus with an increase in both the LCP composition as well as the draw ratio at a fixed composition. For example, with only 4 wt% of the LCP at a draw ratio of 67.0, the modulus of PET is enhanced by a factor of two. Similarly, at the 70/30 blend and draw ratio of 49.7, the blend modulus of 18.99 GPa represents an seven-fold increase over pure PET. In contrast, the blend from the single screw extrusion process exhibits a modulus of only 13.39 GPa at this draw ratio. Thus as
was anticipated from the morphological observations made earlier, the moduli of the PET/Vectra 70/30 blend from the mixing method are higher than the corresponding physical blend for all the draw ratio tested.

Results from several PP/LCP systems also indicated that significant enhancements in the modulus over that of pure PP were obtained by blending with LCPs. These results are shown in Table 2. The PP/Vectra 72/28 blend shows almost a seven fold increase over that of pure PP at the highest draw ratio. Results for the PP/Vectra B 74/26 blend are even more dramatic and show an increase of over nineteen times that of pure PP. The results of the PP/LCP6O 76/24 blend, although not dramatic, still show an enhancement of more than three times over PP. It should be added here that the morphology of the PP/LCP blend strands also showed infinitely long LCP fibrils in the PP matrix. For the PP/Vectra and PP/Vectra B blends, the fibrils were continuous, similar to the PET/Vectra blend discussed earlier.

SHEET EXTRUSION

Morphology: The morphology of the sheets was also examined to see if the LCP fibrillar development was similar to that obtained in the case of the strands. Figs. 8a and 8b show the SEMs taken normal to the machine direction for PP/LCP6O 73/27 film and PP/Vectra 81/19 film, respectively. The SEMs show that the LCP phase is present as both highly extended fibrils as well as ellipsoidal structures. This is an indication that the fibrillar development is not optimized. It is believed that the inability to obtain high draw ratios in the films is responsible for these morphologies.

Mechanical Properties: In Table 3 are shown the mechanical properties of flat sheets or films of polypropylene with LCP60 and Vectra. The properties show a two to three fold enhancement in the properties of the blends over pure PP. The tensile strength is also increased about 1.5-2 fold at comparable draw ratios. Although the reinforcing effect is no doubt present, the property enhancements are not as much as in the case of PET/LCP or PP/LCP rods. It should be mentioned here that the properties of PET/LCP films were also relatively poor. As mentioned earlier, this is believed to be mainly due to the fact that because of processing limitations, the draw ratios obtained were low (3-7) and both the degree of LCP fibrillar development and the level of molecular orientation achieved was low.

CONCLUSIONS

A method to blend high melting liquid crystalline polymers with lower melting thermoplastics and commodity resins has been successfully established. Blends of PET or PP with several LCPs have been made. The mechanical properties of strands (or rods) of blends containing 30 wt % Vectra in PET exhibited a seven-fold increase in the Young’s modulus over that of pure PET. In comparison, the properties of the blend of the same composition using a single extruder were enhanced only by a factor of 4 to 5. Similar enhancements in the properties of PP/Vectra rods were also obtained. The properties of the films of PP/LCP blends also showed a 3 fold enhancement in properties. These properties, though not as high as inorganic fiber composites, are certainly in the same region. We believe that there is a potential for further enhancement in the properties by optimizing the process.

The mixing process enhances the distribution of the LCP phase in the matrix and also leads to the development of the infinitely long fibrils which provide the significant reinforcement as observed from the mechanical properties. Another point that should be made is the fact that due to the nature of the mixing process, it was possible to give the two materials a thermal history independent of one another. Consequently, it was possible to preheat the Vectra to 330°C where complete melting of the residual crystallites takes place. The presence of residual crystallinity has been observed to inhibit the chain alignment and development of
uniform fibrillar structure of the LCP phase by some other researchers [23,24]. Thus it is important to appreciate this potential advantage gained by the mixing process.

One final comment that should be made here is that although one might argue that the morphological development in the new method is due to the mixing head used and thus similar properties might be obtained by attaching the mixing head to the exit of a single extruder, the real point is that one cannot melt blend certain materials in the same extruder due to the temperature differences. Therefore the value of this technique lies in the fact that it has overcome this limitation successfully and further that in principle it may be applied to the blending of any two (or more) phase systems where there is a significant mismatch of processing temperature regimes. The potential use of this new process to conduct film-blowing and blow-molding experiments in a unified single step operation is currently under investigation. Studies to determine if the mechanical property advantages of the strands (pellets) of the blends made by the mixing method can be retained in further processing such as injection molding are also currently underway. It is believed that having a system in which the LCP reinforcements have a melting temperature that is much higher than the matrix polymer, it may be possible to process these pellets such that the fibrillar morphology and molecular orientation of the LCP are retained upon further processing. In other words, it may be possible to get the blend to behave as an inorganic fiber-filled system with the LCP fibrils behaving as the filler in this situation.

ACKNOWLEDGEMENT

We gratefully acknowledge support of this work from the Army Research Office, Grant No. DAAL03-88-K0104.

REFERENCES

10. U.S. Patent No. 4,438,236 (March 20, 1984) F.N. Cogswell et al. (to the Imperial Chemical Industries PLC)
FIGURE 1. Schematic of the mixing apparatus
FIGURE 2. Dynamic frequency sweeps of PET and Vectra A900 with different thermal histories
FIGURE 3. Cooling curves for PET and Vectra A900
FIGURE 4. Isothermal time sweeps of Vectra A900 cooled from 330°C

- 265 C
- 280 C

STRAIN = 4%
RATE = 10/S
FIGURE 5. Scanning electron micrographs of the fracture surface of PET/Vectra 70/30 mixer blend rod (D.R. = 49) at (a) low (183X) and (b) high (1390X) magnifications
FIGURE 6. PET/Vectra 70/30 rod etched in n-propylamine: (a) scanning electron micrograph and (b) photograph
FIGURE 7. Scanning electron micrographs of the fracture surface of PET/Vectra 70/30 physical blend rod (D.R. = 49) at (a) low (224X) and (b) high (3790X) magnifications
FIGURE 8. Scanning electron micrographs of fracture surfaces of films taken normal to the machine direction, (a) PP/LCP60 73/27 and (b) PET/Vectra 81/19
TABLE I. Results from tensile testing of strands (rods) of several PET/VECTRA A900 blends by two mixing methods

<table>
<thead>
<tr>
<th>Sample-#</th>
<th>Draw Ratio (D.R.) vs Young’s Modulus (E)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>96/4 (M)</td>
</tr>
<tr>
<td></td>
<td>D.R.</td>
</tr>
<tr>
<td>1</td>
<td>5.0</td>
</tr>
<tr>
<td>2</td>
<td>10.4</td>
</tr>
<tr>
<td>3</td>
<td>17.3</td>
</tr>
<tr>
<td>4</td>
<td>26.04</td>
</tr>
<tr>
<td>5</td>
<td>45.28</td>
</tr>
<tr>
<td>6</td>
<td>67.0</td>
</tr>
</tbody>
</table>

Reported values are an average of at least four tests and standard deviations are given in parenthesis.
(M) = Blends prepared by the mixing technique
(P) = Blends prepared in a single-screw extruder under similar conditions as ‘(M)’ for the corresponding composition
TABLE II. Results from tensile testing of PP/LCP films made using the mixing apparatus

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>DRAW RATIO</th>
<th>TENSILE STRENGTH* [MPa]</th>
<th>YOUNG’S MODULUS* [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polypropylene (PP)</td>
<td>4.0</td>
<td>15.73 (3.11)</td>
<td>0.56 (0.098)</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>21.95 (3.42)</td>
<td>0.615 (0.047)</td>
</tr>
<tr>
<td>PP/LCP60 73/27</td>
<td>4.8</td>
<td>26.45 (1.81)</td>
<td>1.57 (0.156)</td>
</tr>
<tr>
<td></td>
<td>5.6</td>
<td>28.85 (1.25)</td>
<td>2.11 (0.121)</td>
</tr>
<tr>
<td>PP/Vectra A 81/19</td>
<td>4.4</td>
<td>39.42 (4.19)</td>
<td>2.10 (0.170)</td>
</tr>
</tbody>
</table>

*Standard deviations are given in parenthesis