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This report is comprised of three separate aspects of the research dealing with in situ generated liquid crystalline polymer, LCP, reinforced thermoplastic composites. In the first part, the miscibility and its effect on morphology and thermoformability of Ultem/LCP composites have been discussed. In the next section, the results of reinforcing commodity thermoplastics using a novel blending technique are presented. In the final section of this report several processing methods that have been used to improve mechanical properties of PP/LCP composites are discussed. Also the outlines for future work are discussed for each of the three sections.

Blends of engineering thermoplastics with LCPs

This first part of our research was concerned with improving the performance of engineering thermoplastics by blending with liquid crystalline polymers (LCPs) to make "in-situ" composites. The research was concentrated on an amorphous matrix (polyetherimide or PEI; trade name ULTEM of General Electric), but a semi-crystalline matrix (polyether ether ketone or PEEK of ICI) was also studied. A series of liquid crystalline polymers (the "HX" series made by Du Pont) was used as the reinforcement. In addition other thermotropic liquid crystalline polymers such as Vectra A and Grantar were also used. Matrix/LCP systems studied include Ultem/Vectra, Ultem/HX1000, Ultem/HX4000, Ultem/HX6000, Ultem/Grantar and PEEK/Grantar. Vectra A is a copolyester of p-hydroxybenzoic acid and 2-hydroxy-6- naphthoic acid in the ratio of 73:27. Grantar is a copolyester of phenyl hydroquinone, ethylphenyl hydroquinone and terephthalic acid. HX4000 is an amorphous LCP while HX6000 is a LCP with improved toughness. These are propreitary LCPs of Du Pont and their composition is not known

"In-situ" composites were prepared by injection molding pellets of the matrix and the reinforcing LCP (which had been previously mixed by tumbling). Rheological data (cooling curves) helped to establish the processing windows available for injection molding. The

blends so prepared were characterized for their mechanical properties (tensile, flexural and torsional tests), morphology (scanning electron microscopy (SEM) and wide angle X-ray diffraction (WAXD)) and thermal transitions (differential scanning calorimetry (DSC) and dy-namic mechanical thermal analysis (DMTA)).

The miscibility of the LCP phase with the matrix was found to have a significant effect on the mechanical properties of the blend. It has been found that blends of Ultem with some liquid crystalline systems (like Vectra A and HX6000) show a negative deviation from the law of mixtures for properties such as the flexural modulus (Fig. 1), tensile modulus and tensile strength. In contrast, other liquid crystalline systems like HX1000, HX4000 (Fig. 2) and Granlar show a positive deviation from this law. The reason for the positive deviation may be attributed to the miscibility between the LCP and Ultem. The miscibility between different LCP systems and Ultem has been examined by means of DSC and DMTA. Representative DMTA data for Ultem/HX4000 blends are shown in Fig. 3. The tan δ peak corresponding to the PEI matrix phase can be seen to shift to lower temperatures as the amount of the LCP in the blend is increased. The reason for this is that part of the LCP dissolves into the PEI matrix phase and lowers the glass transition temperature of that phase. A similar shift in tan δ was not found for Ultem/Vectra A systems (which were concluded to be immiscible). DSC results lead to the same conclusions. Partial miscibility between the matrix and the reinforcing LCP is desirable because it improves the mechanical properties of these in-situ blends. Due to the partial miscibility of the Ultem/HX4000 system, the HX4000 microfibrils are hard to pull out of the Ultem matrix, whereas the Vectra microfibrils can be pulled out easily. Morphological evidence for this was obtained by scanning electron microscopy. Thus partial miscibility improves the adhesion between the matrix and the reinforcing LCP fibrils. The blending history was found to have a marked effect on the extent of miscibility for the partially miscible system. The miscibility was found to be improved by increasing the number of passes through a single screw extruder or using a twin screw extruder.

A disadvantage of these in-situ composites is that they tend to be highly anisotropic. The anisotropic mechanical properties of these composites are caused by the alignment of the

LCP microfibrils along the machine direction. As shown in Fig. 2, the transverse properties of HX4000 blends are much lower than those measured in the machine direction. In an attempt to improve the transverse properties, glass reinforced Ultem was used. As shown in Fig. 2, both, the transverse as well as the machine direction properties, were enhanced upon the addition of glass reinforcement.

To study the creep behavior of these blends, the dynamic torsional compliance was measured at various temperatures, both above and below the glass transition temperature of the LCP phase. The elastic compliance was found to always be dominant. The creep compliance was found to be lower at higher frequencies (corresponding to short times) but increased at lower frequencies (corresponding to long times) when the temperature was above the glass transition temperature of the LCP phase. Below the glass transition temperature of the LCP phase. Below the glass transition temperature of the LCP phase. Below the glass transition temperature dition of the LCP, the creep compliance was virtually independent of the frequency. The addition of the LCP reinforcement was found to substantially lower the creep compliance of the blend at temperatures below the glass transition temperature of the LCP.

Blending with Ultem increases the thermoformability of the LCPs. For example, neat HX4000 plaques could not be thermoformed even when preheated up to 370°C. However, for the Ultem/HX4000 blend containing 70 weight percent Ultem, thermoformed parts with smooth surfaces were obtained. The thermoformability of Ultem/Vectra A and Ultem/Granlar composites was studied as a function of the preheating temperature and the mold temperature. It is suggested by our research that the reinforcing microfibrils as well as their molecular orientation are retained even when the Ultem/Vectra blends are thermoformed above the melting point of the Vectra. This is due to the long relaxation time of the LCPs coupled with the much higher viscosity of the matrix polymer, Ultem (compared to that of Victra), and the drawing effect during thermoforming. This has been confirmed by morphological evidence obtained from WAXD and scanning electron microscopy. The Ultem/Granlar composites are too brittle to be thermoformed when the content of Granlar in the blends exceeds 30 weight percent. This is possibly due to the coexistence of free Granlar domains which can be easily crystallized during the preheating period.

In the earlier part of the research, a process was developed for generating in-situ reinforced films (a patent application, number 07/540,941, entitled "Polyblends comprising highly oriented liquid crystalline polymer fibrils" was filed on 20 June 1990). Films or sheets with moduli in the range of 30 GPa were generated using a two step drawing process. The films could be laminated in much the same way that thermoplastic composite prepregs are processed. However, because of the poor transverse properties of the films, the properties of the laminates were not outstanding.

The most exciting part part of the research centered around the discovery of partially miscible systems of certain LCPs with polyetherimide. The partial miscibility is probably re-sponsible for the synergistic enhancement of some of the physical properties. There may be considerable practical significance in these systems in certain areas where long fiber composites are presently being used.

There are, however, a number of areas which still need to be investigated. First, processing options which capitalize on the self-reinforcing nature of these blends need to be developed. The origin of the partial miscibility needs to be determined. Finally, the possibility of using polyetherimide to make LCPs miscible with PEEK and PEKK should be considered.

Blends of Commodity Thermoplastics with LCPs

The objective of the second part of the work was to develop a mixing process which would generate continuous LCP fibrils in the matrix polymer during processing (i.e. in situ) in order to yield blends with enhanced mechanical properties. A method was devised capable of blending polymers such as LCPs with other matrices such as polypropylene (PP) and poly(ethylene terepthalate) (PET) where there is no direct overlap of the nominal processing temperatures. In this section, we report on a blending method (hereon referred to as the dual-extruder mixing method) which has been developed in our laboratory to fulfil the above objectives simultaneously. Also, comparisons of the mechanical properties and morphology

of strands of blends generated using a single-screw extrusion process with those from the dual-extruder mixing method are given and reasons for the differences are discussed. The reinforcing LCPs that have been used are Vectra A and Vectra B (a polyestercoamide comprising of hydroxy napthoic acid, terepthalic acid and hydroxy acetanilide). Based on this part of the work, a patent application entitled "Mixing process for generating insitu reinforced thermolpastics" was filed on 5 May, 1991.

The rheology of the pure materials is discussed first so that the reasoning and need behind the development of the dual-extruder mixing method may be better appreciated. Several different types of rheological measurements were conducted on the matrix polymers and the LCPs. From isothermal time sweep measurements, it was seen that both PET and PP were stable at temperatures below 290°C but they started to degrade too rapidly above 300°C. As the desirable processing temperature of most LCPs is above 300°C, the blending of LCPs with these thermoplastics in the same extruder or molding unit becomes difficult due to the possible degradation of the matrix polymer. The results of the dynamic oscillatory tests showed that the viscosity of Vectra A at 290°C is higher than that of PET at 265°C for the entire frequency range from 0.1 to 100 rad/s. However, once Vectra A is heated up to 320°C (where the residual crystallites are melted out) the viscosity dropped by about two decades from that at 290°C. To generate fibrils of the minor (LCP) phase in the matrix polymer, it is now well recognized that the viscosity of the LCP phase should be lower or at most equal to that of the matrix polymer (i.e. viscosity of minor phase/viscosity of major phase \leq 1) at the processing conditions. Thus in order to obtain a viscosity ratio favorable for fibril formation, 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 as discussed earlier. 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 showed that the viscosity of Vectra at these low temperatures is still lower than that of PET (and PP) in the frequency range of 0.1 to 100 rad/s. (Similar lowering of viscosity was obtained for

frequency sweeps at 290 °C or lower for Vectra B initially heated to 325 °C) This is in essence the thermal history that the materials undergo in the actual blending process yielding a favorable viscosity ratio.

To determine the temperature range within which a material may be processed, cooling experiments were conducted. Results from these rheological tests showed that when Vectra A and Vectra B (which have melting temperature of 283 and 280 °C, respectively) are cooled from 325°C, they do not solidify (crystallize) until a temperature as low as 250°C is reached. This difference in the solidification temperature and the nominal melting temperature is often referred to as the processing or 'supercooling' window wherein the material is still viscous enough to flow and yet 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 melt strength to sustain this deformation to prevent breaking or tearing of the extrudate. However when PET is cooled from 290°C and 330°C, it solidifies at about 200°C and 170 °C. respectively (and not at its usual melting temperature of 265°C). Thus the processing window has been increased by almost a 100°C. But of greater consequence is the magnitude of the viscosity for 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 is not. Similarly, when cooled from 270 or 280°C, PP has a favorable viscosity ratio when compared to Vectra A or Vectra B cooling from 330 °C.

Details of the blending process which allows us to impart separate thermal histories to the matrix and the LCP to yield a favorable viscosity ratio are best explained with reference to the schematic of the apparatus shown in Fig. 4. The matrix material and the dispersed phase (reinforcing LCP) were plasticated separately in the two extruders. The melt streams were then joined and blended in a mixing head (in this case a static mixer) 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. Films or sheets were prepared using a 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'.

Strands of blends of PET/Vectra A in several different composition ratios were extruded using the dual-extruder mixing method. In Table 1, tensile properties of PET/Vectra A 70/30 mixer blend are compared to those of the physical blends with same composition generated using a single-screw extruder. Pure PET strands were also extruded using a single-screw extruder. These strands had a tensile modulus of about 2.5 GPa and the modulus did not vary significantly with draw ratio. The tensile moduli of the mixer blends and the physical blends improve with draw ratio (as seen in Table 1). However, the 70/30 PET/Vectra A physical blend moduli are lower than that of the 70/30 PET/Vectra A mixer blends at all draw ratios tested. Specifically, at the highest draw ratio of ca. 49, the mixer blend has a modulus value of 18.99 GPa as compared to 13.39 GPa for the physical blend. There is a significant difference of over 5 GPa in the tensile modulus between these two differently processed blends. Although both the physical and mixer blends showed high degree of molecular orientation, their morphologies differed greatly. In the case of the single-screw extruder blends, the morphology was observed to have a skin-core structure with most of the LCP fibrils present in the skin region and the core region showing distinct droplet structures. Also the LCP fibrils were not continuous. In contrast, the blends from the dual-extruder mixing method exhibited very high aspect ratio LCP fibrils in the entire cross-section (as seen in Fig. 5). Fig. 6 show the photograph of an etched PET/Vectra A 70/30 mixer blend strand 5 cm long and approximately 0.5-2 μ in diameter. The aspect ratios of the fibrils are essentially infinite and the reinforcement is continuous and can run the entire length of the extrudate. These differences

in morphologies resulted in blends from the dual-extruder mixing method having higher tensile moduli than those from the single-screw extrusion process. Also, PP/LCP mixer blend strands show significant improvement in tensile properties as seen in Table 2 and the morphology of the strands are similar to the PET/Vectra A mixer blend strands.

The above mentioned differences in the morphology were attributed to the differences in the mode of fibril formation in the dual-extruder mixing method and single-screw extrusion process. In the case of single-screw extrusion, the LCP phase was seen to be dispersed into the matrix polymer in the form of droplets in the extruder. These droplets, in the presence of appropriate extensional flow fields, may then be elongated into fibrils. In the dual-extruder mixing method, the LCP phase does not get dispersed in the thermoplastic matrix in the form of droplets but is continuously divided into layers and recombined in the static mixer, while maintaining the axial continuity of the LCP phase. This results in continuous LCP fibrillar reinforcement of the extruded strand or sheet.

Sheets of PET/LCP and PP/LCP blends were also extruded from the dual-extruder mixing method and the morphology showed high aspect ratio LCP fibrils in the matrix. However, due to some processing limitations, the draw ratios that could be obtained were low which resulted in low molecular orientation and consequently lower enhancement in mechanical properties for the blended sheets.

Furthermore, extensive research efforts have been directed at examining the postprocessibility of the blends made by the above mixing method. Specifically, injection-molding, lamination and thermoforming studies have been conducted so far. The preliminary results show that the LCP reinforcing characteristics i.e. orientation and morphology can be retained upon post-processing provided that the melting point of the LCP is not reached or exceeded in the post-processing step. The retention of the morphology was confirmed using scanning electron microscopy and the orientation levels were examined using wide-angle x-ray scattering. Thus the potential to treat the blend sheets as prepreds certainly exists.

Future work will focus on establishing the mechanical properties of the laminated composites. Also, one of the long term goals is to further extend the capabilities of the new mixing method to blow-molding and film-blowing operations.

Compatibilization of PP/LCP blends

In the last segment of the current study, the role of the compatibilization on mechanical properties and surface finish of PP/LCP blends has been investigated. Preliminary studies in our laboratory on blends of PP with several LCPs had shown that the blends exhibited some improvements in modulus. However, they tended to have decreased tensile strength compared to that of pure PP and poor surface finish, both of which might be attributed to their incompatibility. Compatibilization has been shown to improve the dispersity, adhesion and the mechanical properties of other non-compatible blends. It was thus decided to investigate whether compatibilization can lead to further improvements in various mechanical properties of PP/Vectra B blends.

Injection molded plaques of PP/Vectra A and PP/Vectra B plaques were made with and with out compatibilization. Compatibilization of PP/Vectra was carried out by a reactive extrusion process in which the PP was grafted to the LCPs. The effects of the compatibilization on the tensile properties of PP/Vectra B blends are presented in Table 3. There are significant improvements in the tensile moduli of the compatibilized PP/Vectra B blends over those blends which were not compatibilization as compared to those of the non-compatibilized PP/Vectra B blends. Overall about 2.5 to 3.2 fold increase in the tensile properties for the 20 and 30 wt % LCP blends, respectively, over that of pure PP has been obtained. The tensile strengths of the PP/Vectra B blends dropped below that of pure PP, but on compatibilization the tensile strength recovered and was further enhanced beyond that of the PP matrix. Fig. 7 shows the torsional modulus versus temperature curve of PP/Vectra B

blends. The torsional properties improve on addition of LCP and they further improve on compatibilization. At elevated temperatures, the higher moduli of the blends over that of pure PP would possibly result in better heat distortion properties for the blends than PP. Similar improvements in tensile modulus, tensile strength (as seen in Table 4.) and torsional properties were observed on compatibilization for PP/Vectra A blends. Additionally unlike the blends without compatibilization, the compatibilized blends have a smooth, polished and homogeneous appearance. Although the presence of reinforcing fibrils is observed in both compatibilized and non-compatibilized blends, the fibrils are more evenly distributed and appeared less bunched together in the former than in the latter. The enhanced modulus, strength, better surface finish and more uniform fibril distribution were attributed to better adhesion and improved dispersion in compatibilized blends of PP with Vectra A and Vectra B. Based on this part of the work, a patent application, number 07/686,603, entitled "Compatible Blends of Polypropylene and a Liquid Crystalline Polymer" was filed on April 17 1991.

Solid phase forming is another possible method to improve the mechanical properties of polymers and we wanted to determine the feasibility of further enhancing the mechanical properties of the LCP reinforced PP composites by solid phase forming techniques. The solid phase forming technique used by us is basically non-isothermal compression molding and involves deforming the composites in a cold press after heating the blends at temperatures below the melting point of the LCP.

The effect of non-isothermal compression molding at different preheating temperatures for the two compatibilized PP/Vectra B blends are summarized in Table 5. It is observed that for the compatibilized PP/Vectra B composites containing 20 and 30 wt % LCP, the moduli increased by 20 to 30 % when pressed at room temperature after preheating at 155 or 165°C. Overall there is almost a three to four fold increase in modulus over that of pure PP. Similar trends are observed for the compatibilized PP/Vectra A blends that were pressed nonisothermally. The tensile strengths of the blends were not altered by pressing. The scanning electron microscopy of the unpressed and the pressed plaques showed no noticeable differences. However, the WAXD patterns showed that the Vectra phase in the pressed samples

had higher molecular orientation which possibly led to the higher moduli of the pressed plaques.

Currently, we are trying to optimize the compatibilization process to further increase the mechanical properties. We are trying to determine the functionality of the compatibilizer, the permanency of the compatibilizer and the dimension of the dispersed LCP phase as effected by the compatibilizer. The effect of compatibilization on blends having higher LCP content are also being studied. The effect of compatibilization on impact and creep properties of PP/Vectra blends are being investigated. Further we are examining the possibility of processing the PP/Vectra blends using techniques like calendering, thermoforming and blow molding.

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Table 4 Tensile properties of PP/Vectra A plaques w/w/o compatibilization

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TABLE 1

COMPARISON OF YOUNG'S MODULUS OF PET/VECTRA A900 70/30 RODS FROM TWO BLENDING METHODS

Mixing [Device Rods	Single Sc	rew Rods
Draw Ratio	Young's Modulus (GPa)	Draw Ratio	Young's Modulus (GPa)
2.36	5.45 (0.58)	4.55	3.98 (0.23)
3.25	6.97 (0.34)	7.10	7.08 (0.82)
3.80	8.93 (0.39)	13.0	8.05 (0.09)
39.0	13.31 (0.37)	20.0	8.49 (0.54)
43.2	17.21 (0.13)	49.0	13.39 (0.45)
49.7	18.99 (0.17)		

TABLE 2

Tensile modulus as a function of draw ratio of blends of PP/LCP MB strands extruded via the mixing method.

MATERIAL	DRAW RẠTIO	YOUNG'S MODULUS* (GPa)
Polypropylene (PP)	6.25 21.16	. 0.688 (0.047) 0.432 (0.066)
PP/Vectra B 88/12	3.11 6.25 13.97 40.85	1.59 (0.25) 2.07 (0.13) 2.09 (0.19) 2.73 (0.21)
PP/Vectra B 74/25	4.33 20.16 35.40	6.5 (1.25) 10.96 (1.14) 13.47 (1.78)
PP/Vectra A 72/28	3.80 8.07 39.06	3.837 (0.351) 4.211 (0.5) 4.711 (0.474)
PP/LCP60 76/24	5.70 -18.16	1.66 (0.149 2.67 (0.49)

*Standard deviations are given in parenthesis

TABLE 3

Materials	Tensile Modulus GPa	Tensile Strength MPa
PP	1.354 (0.075)	26.89 (1.10)
PP/Vectra B 80/20	2.553 (0.169)	24.04 (1.14)
PP/Vectra B 80/20 (Compat.)	3.209 (0.262)	34.01 (1.06)
PP/Vectra B 70/30	3.003 (0.289)	19.71 (0.59)
PP/Vectra B 70/30 (Compat.)	4.101 (0.401)	37.55 (3.97)

Tensile Properties of PP/Vectra B Plaques w/w.o Compatibilization

Standard Deviations are given in parenthesis. (Compat.) - Compatibilized

Table 4

Materials	Tensile Modulus GPa	Tensile Strength MPa
PP	1.354 (0.075)	26.89 (1.10)
PP/Vectra A 80/20	2.555 (0.216)	27.70 (1.06)
PP/Vectra A 80/20 (Compat.)	3.059 (0.185)	33.23 (0.70)
PP/Vectra A 70/30	2.868 (0.280)	28.26 (1.15)
PP/Vectra A 70/30 (Compat.)	3.791 (0.299)	34.45 (1.23)

Tensile Properties of PP/Vectra A Plaques w/w.o Compatibilization

Standard Deviations are given in parenthesis. (Compat.) - Compatibilized

Table 5

	Tensile	Properties	of	Non-isothermally	pressed	PP/Vectra	В
Composities	(Compa	tibilized)					

Materials	Process. Cond. (°C) Heat. Temp./ Press Temp.	Percent Thickns. Reductn.	Tensile Modulus GPa	Tensile Strength MPa
PP	N.P.	-	1.354 (0.075)	26.89 (1.10)
PP/Vectra B 80/20 (C)	NP	-	3.209 (0.262)	34.01 (1.06)
PP/Vectra B 80/20 (C)	155/20	4.7	3.945 (0.282)	35.53 (1.95)
PP/Vectra B 80/20 (C)	165/20	21.0	3.885 (0.406)	34.23 (0.95)
PP/Vectra B 70/30 (C)	NP	-	4.101 (0.401)	37.55 (3.47)
PP/Vectra B 70/30 (C)	155/20	6.1	4.780 (0.252)	38.37 (1.02)
PP/Vectra B 70/30 (C)	165/20	17	5.297 (0.300)	39.23 (2.23)

Standard Deviations are given in parenthesis. NP: non-pressed (C) : Compatibilized

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ULTEM / VECTRA

------ CALCULATED BASED ON: $E_{1b} = E_m V_m + E_f V_f$ \odot EXPERIMENTAL



Figure 3. Torsional Experiments on Ultem/HX1000 Blends.





Figure 4. Schematic of dual extruder mixing method.



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