

Structure and Properties of Polyblends of a Thermotropic Liquid Crystalline Polymer with an Alloy of Polyamide-6 and ABS

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SYNOPSIS

The relationship between the microstructure and corresponding mechanical properties developed during injection molding of blends containing a liquid crystalline polymer (LCP) as the minor component and an engineering polymer system has been studied. A wholly aromatic copolyester LCP (Vectra A950) was melt blended at different compositions with a thermoplastic matrix consisting of a commercial compatibilized blend of polyamide-6 and ABS (Triax 1180). These blends were prepared under two different sets of injection molding conditions. In the first case, a higher melt temperature, higher barrel temperature, lower injection pressure, lower mold temperature, and shorter residence time in the mold were used during injection molding, as compared with the second case. The mechanical properties of the blends were superior to those of the base polymer. In the second case, the resulting injection-molded specimens had a distinct skin-core morphology where elongated fibrils of LCP constituted the skin layer. The mechanical properties of the blends processed under the second set of processing conditions were superior to those of the first, though the trends in both cases were the same. To study the effects of process variables the 15% LCP blend and the second set of processing conditions were taken as the base. Samples were injection-molded by varying one parameter at a time. It was seen that the properties of the blend were increased by maintaining a lower barrel temperature, greater injection pressure, lower injection speed, higher mold temperature, and a greater residence time in the heated mold. Thus it was found that the processing conditions played a vital role in determining the mechanical properties and morphology of the polyblends. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The cost of developing new polymers is substantial compared with that of modifying existing polymers by various techniques, of which melt blending plays a key role. Thermotropic liquid crystalline polymers (LCPs) have been blended with engineering thermoplastics to form self-reinforced blends. This has been a subject of an enormous amount of research and is a topic that has been widely investigated.¹⁻¹⁹ The interesting use of these polymers is that they

can be blended with conventional thermoplastics to form blends which can be processed easily and which display improved mechanical properties. LCP, which is a minor component, forms fibrils *in situ* parallel to the flow direction, leading to the formation of self-reinforced composites.³ The inherent properties of LCPs such as high strength and stiffness contribute to the enhancement of the mechanical properties of the base polymer as well as minimize the drawbacks of both components.⁴ The systems studied include the use of both amorphous and crystalline matrices.¹⁻¹⁹

Prior to the development of LCPs as reinforcing fillers, glass fiber was the primary reinforcing agent. Though relatively inexpensive it has certain inherent disadvantages, such as leading to an increase in

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the viscosity of the system which causes excessive wear and tear of equipment. The product quality may also suffer due to change in critical dimensions of molds and dies.³ LCPs, on the other hand, have been known to decrease the extrusion energy by causing a decrease in the viscosity of the system.⁵ They also give relatively flash-free injection molding. The improvement in mechanical properties has been explained on the basis of the morphology of the LCP domains in the blends. The resulting injection-molded structure has a distinct skin-core morphology where elongated LCP fibrils present in the skin layer change to ellipsoidal and spherical globules in the core section.²

In this paper the effect of the reinforcement action of a thermotropic copolyester, namely Vectra A950, has been studied on a commercial compatibilized blend of polyamide-6 and ABS (Triax 1180). Polyamide 6 and ABS form a two-phase heterogeneous blend with little adhesion between the phases. Notched Izod impact, flexural, and tensile properties of the compatibilized blends of polyamide-6 and ABS are superior to that of the uncompatibilized blends.²⁰ La Mantia and coworkers found that in spite of the incompatibility of nylon and Vectra the latter polymer acts as a reinforcing agent of good effectiveness, and that the strength of the glass-reinforced nylon composites is only slightly larger than that of LCP-reinforced polymer whereas elongation at break is significantly lower.⁵

EXPERIMENTAL

Materials

LCP: Vectra A950, manufactured by Hoechst Celanese (Chatham, NJ, USA) is prepared by the melt condensation of 27 moles of HNA and 73 moles of HBA; it has an average molecular weight of 20,000 and a melting point of 280°C. Thermoplastic matrix: Triax 1180, manufactured by Monsanto Chemical Company (Springfield, MA, USA) is a commercial

Table I Conditions of Melt Blending

Case	Screw Speed (rpm)	Temperature (°C)				
		Barrel Zones			Die Zones	
		ZI	ZII	ZIII	DZI	DZII
I	40	260	290	280	280	280
II	40	260	280	260	220	220

Table II Conditions of Injection Molding

Parameter	Reading	
	Case I	Case II
Barrel Temperature (°C)	280	255
Nozzle Temperature (% Barrel Temperature)	95	95
Mold Temperature	35	70
Injection Speed (units)	11	9
Injection Pressure (kg/cm ²)	80	120
Screw Speed (units)	9	6
Holding (Pressure) time (s)	20	30
Total Cooling time (s)	30	60

compatibilized blend of polyamide 6 and ABS and has a melting point of 224°C.

Sample Preparation

Melt Extrusion

Melt blending of Triax 1180 and Vectra A950 was carried out on a Klockner Windsor single-screw extruder fitted with a general purpose screw and with an L/D ratio of 22. The polymer pellets were dried in a vacuum oven at 80°C for 48 h and then manually dry-mixed by tumbling in a closed container. These granules, dry-mixed at compositions of 5, 10, 15, and 20% LCP, were extruded under two different thermal profiles, one higher than the other. A screw speed of 40 rpm was maintained for both conditions. The extruded strands were cooled by quenching in a water bath and then were chopped into granules. The two thermal profiles are given in Table I.

Injection Molding

Injection molding of properly dried granules prepared by melt extrusion was carried out on a Windsor SP-1 screw-type injection molding machine with a maximum shot volume of 53 cm³. Seven test specimens were injection-molded for each composition in both cases I and II. The processing parameters for both cases are given in Table II. The samples extruded at a lower melt temperature were injection-molded at a lower barrel temperature, higher injection pressure, higher mold temperature, lower screw speed, and longer residence time in the mold. The 15% LCP blend and the second set of processing conditions were taken as the base and samples were injection-molded by varying one parameter at a time. These process parameters are given in Table III.

Table III Injection Molding Parameters of 15% LCP Blend with Case II as the Base

Parameter	Case II	A	B	C	D	E	F	G	H	I
Barrel Temperature (°C)	255	265*	255	255	255	255	255	255	255	255
Mold Temperature (°C)	70	70	55*	80*	70	70	70	70	70	70
Injection speed (units)	9	9	9	9	6*	11*	9	9	9	9
Injection Pressure (kg/cm ²)	120	120	120	120	120	120	80*	130*	120	120
Total cooling time (s)	60	60	60	60	60	60	60	60	30*	70*

Injection-molded specimens were cooled at room temperature. After flash removal, the dimensions of these specimens were noted. Five specimens of each composition prepared under both sets of processing conditions were tested to determine the mechanical properties.

Mechanical Testing

Tensile and flexural properties were determined at room temperature on an Instron 1121 Universal tensile tester equipped with tensile and flexural modes of testing. Dumbbell-shaped tensile specimens were used for determining tensile properties according to ASTM D638 procedures, using a cross-head speed of 50 mm/min. The full scale load was 200 kg and a chart speed of 200 mm/min was used, keeping a span length of 6 cm. The parameters determined were tensile strength, Young's modulus, and elongation at break. Flexural properties—namely, strength and modulus—were measured by testing rectangular bars 10 mm × 4 mm in accordance with ASTM D790 method, keeping a span length of 70 mm, crosshead speed of 50 mm/min, and full scale load of 50 kg. A chart speed of 200 mm/min was maintained. The mode of testing constituted three-point bending with loading at mid-span.

Morphology Studies

Scanning Electron Microscopy (SEM)

Injection-molded flexural specimens prepared under the first set of processing conditions were fractured in liquid nitrogen. The surfaces of pure Triax and blends with 5, 10, 15, and 20% LCP were coated with silver to a thickness of 50–100 Å and were scanned under a Cambridge Stereoscan 360 electron microscope. Similar studies were carried out for the injection-molded specimens with 5, 10, 15, and 20% LCP composition prepared under the second set of processing conditions. The skin and core sections were scanned separately.

RESULTS AND DISCUSSIONS

Mechanical Properties

The tensile and flexural properties of injection-molded blends of Triax and LCP with varying LCP contents and injection-molded at the selected two sets of conditions are given in Tables IV and V respectively. Figures 1, 2, and 3 show the corresponding plots of tensile strength, tensile modulus, and percent elongation at break versus percent of LCP

Table IV Tensile Properties of Cases I and II

Composition Triax 1180/LCP	Tensile Strength (MPa)		Tensile Modulus (MPa)		Elongation at Break	
	Case I	Case II	Case I	Case II	Case I	Case II
100/0	30.9	30.9	732.0	732.0	183.2	183.2
95/5	32.1	33.0	768.6	785.0	64.2	65.5
90/10	34.8	37.5	841.8	883.0	38.5	40.8
85/15	36.6	42.7	863.8	915	13.8	16.4
80/20	35.4	38.8	920.0	1009	12.9	14.5

Table V Flexural Properties of Cases I and II

Composition Triax/LCP	Flexural Strength (MPa)		Flexural Modulus (MPa)	
	Case I	Case II	Case I	Case II
100/0	49.1	49.1	1187.0	1187.0
95/5	49.3	49.8	1282.0	1332.0
90/10	53.2	55.8	1401.0	1472.0
85/15	57.9	61.1	1650.0	1714.0
80/20	58.7	62.3	1674.0	1739.0

in the blend. It was seen that the tensile strength and modulus of the blends of Triax and Vectra were superior to those of pure Triax. The latter case was more conducive to giving enhanced properties of the self-reinforced blends. For both sets of samples, the tensile strength increased with a rise in LCP concentration up to 15% and decreased thereafter. In both cases the composition with 15% LCP showed the highest tensile strength values and the general trend in both cases was the same. In the second case, the composition consisting of 15% LCP showed the highest value, a 40% increase in tensile strength

compared with pure Triax 1180. This may be attributed to the fibrillar formation in the blend leading to enhanced tensile properties in the direction of flow. Siegmann and coworkers¹³ studied the structural development during the injection molding of polyblends containing amorphous nylon and LCP. They showed that fibrillar structure develops in the skin area where elongational flow prevails. This system gave outstanding tensile strength compared with that of the base polymer. The composition with 25% LCP gave an increase in tensile strength of 41% compared with that of amorphous nylon.

The tensile modulus (Fig. 2) showed a steady increase as a function of LCP concentration and the blend with 20% LCP showed the highest tensile modulus even though its tensile strength was lower than that corresponding to 15% LCP. The increase in modulus can be explained by the reduction in strain. Thus the slight reduction in tensile strength is compensated by the decrease in strain. As for the reinforcing effect of the LCP, the blend with 20% LCP in case II showed a 38% increase in tensile modulus. Kiss obtained a 30% increase in modulus when nylon was blended with 30 wt % of a liquid crystalline copolyester.³

The elongation at break (Fig. 3) decreased drastically with the incorporation of small amounts of

Table VI Effect of Barrel Temperature on Mechanical Properties

Barrel Temperature (°C)	Sample Code	Tensile Strength (MPa)	Tensile Modulus (MPa)	Flexural Strength (MPa)	Flexural Modulus (MPa)
255°C	Case II	42.7	915	61.1	1714
265	A	38.7	882	59.5	1681

Table VII Effect of Mold Temperature on Mechanical Properties

Mold Temperature (°C)	Sample Code	Tensile Strength (MPa)	Tensile Modulus (MPa)	Flexural Strength (MPa)	Flexural Modulus (MPa)
55	B	41.0	896	60.2	1698
70	Case II	42.7	915	61.1	1714
80	C	42.8	920	61.8	1719

Table VIII Effect of Residence Time on Mechanical Properties

Residence Time (s)	Sample Code	Tensile Strength (MPa)	Tensile Modulus (MPa)	Flexural Strength (MPa)	Flexural Modulus (MPa)
30	H	41.2	897	60.3	1701
60	Case II	42.7	915	61.1	1714
70	I	42.9	918	62.3	1725

Table IX Effect of Injection Pressure on Mechanical Properties

Injection Pressure (kg/cm ²)	Sample Code	Tensile Strength (MPa)	Tensile Modulus (MPa)	Flexural Strength (MPa)	Flexural Modulus (MPa)
80	F	42.0	902	60.0	1709
120	Case II	42.7	915	61.1	1714
130	G	42.9	910	61.7	1718

Table X Effect of Injection Speed on Mechanical Properties

Injection Speed Temperature (°C)	Sample Code	Tensile Strength (MPa)	Tensile Modulus (MPa)	Flexural Strength (MPa)	Flexural Modulus (MPa)
6	D	42.8	920	61.8	1719
9	Case II	42.7	915	61.1	1714
11	E	41.4	907	60.1	1710

LCP. Limtasiri and Isayev showed that the increase in modulus and strength is accomplished by the dramatic drop of elongation at break even after incorporation of a small amount (2.5–5%) of LCP.⁸ The low elongation at break corresponding to high tensile strength and modulus are typical for fiber-reinforced composites.

Figures 4 and 5 show the plots of flexural strength and modulus, respectively, as functions of LCP con-

tent in the blend. The flexural strength of the blends showed a steady increase with rise in LCP concentration. In the second case the composition with 20% LCP showed the highest value, a 30% increase in flexural strength compared with Triax. The flexural modulus also increased in a similar manner with increasing amounts of LCP in the blend. This could be attributed to the high alignment of LCP microfibrils along the direction of flow.

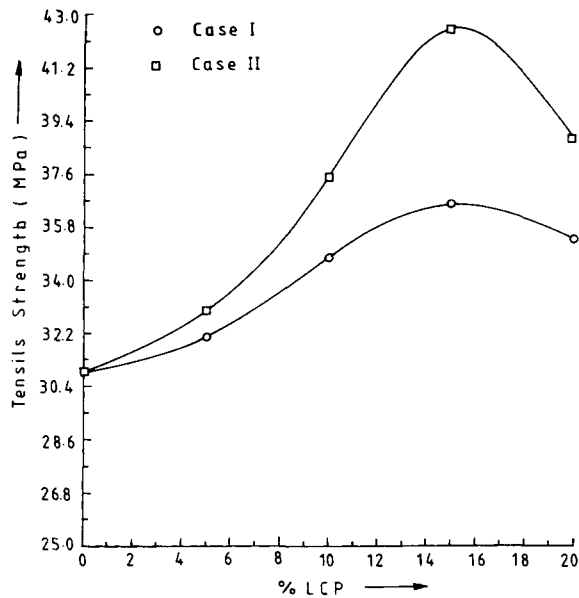


Figure 1 Plot of tensile strength versus % LCP content in blends of Triax 1180 and Vectra A 950.

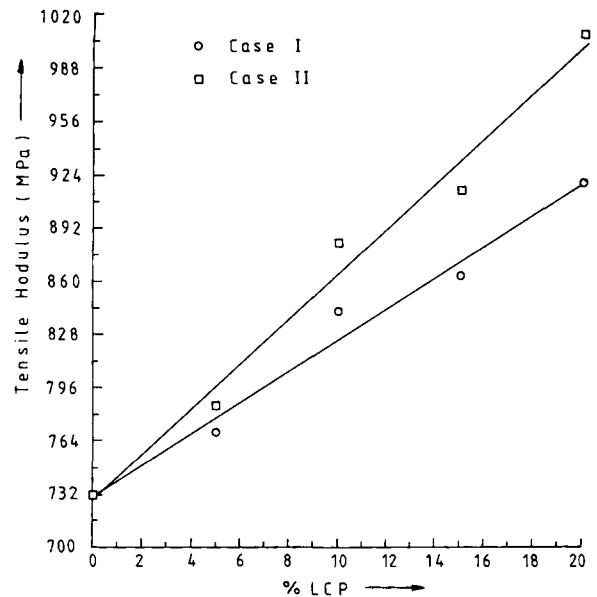


Figure 2 Plot of tensile modulus versus % LCP content in blends of Triax 1180 and Vectra A 950.

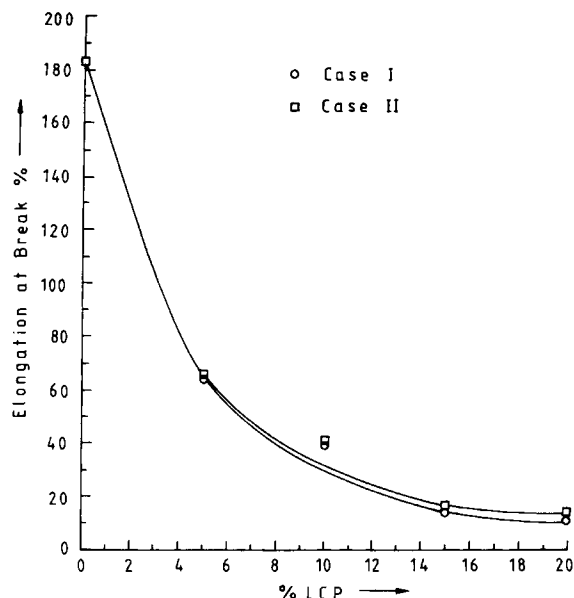


Figure 3 Plot of elongation at break versus % LCP content in blends of Triax 1180 and Vectra A 950.

Effect of Process Variables

On comparison of the mechanical properties of samples prepared under cases I and II it was observed that Case II showed markedly superior properties compared with case I. Case II employed the use of a lower melt temperature, higher mold temperature, greater injection pressure, lower injection speed, and greater residence time in the heated mold. To study the effects of these processing parameters

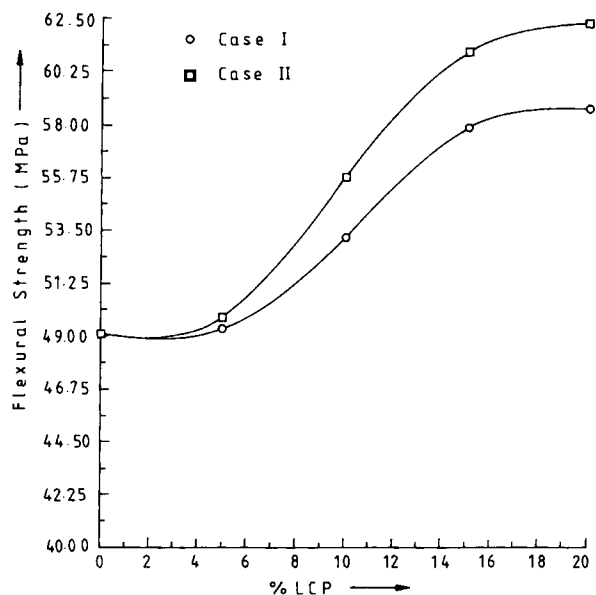


Figure 4 Plot of flexural strength versus % LCP content in blends of Triax 1180 and Vectra A 950.

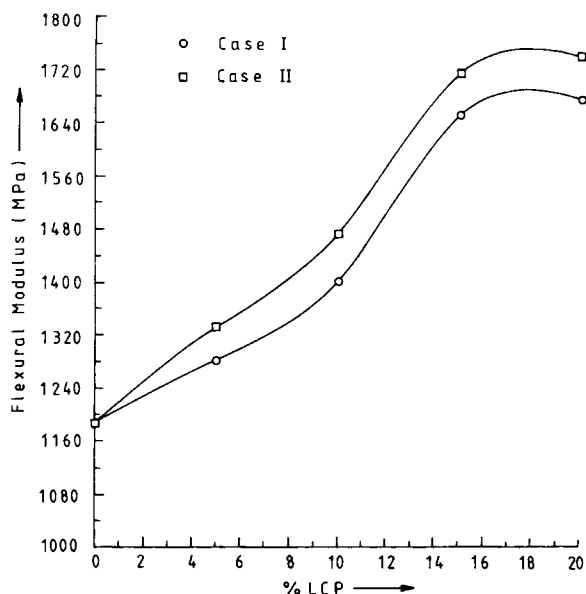


Figure 5 Plot of flexural modulus versus % LCP content in blends of Triax 1180 and Vectra A 950.

individually, the blend with 15% LCP and case II set of processing conditions was taken as the base. Injection molding was carried out by varying one parameter at a time and the corresponding mechanical properties are given in Tables VI through X.

The mechanical properties of the 15% LCP blend injection molded at different barrel temperatures is given in Table VI, keeping in view that the blends could not be injection-molded at temperatures below 255°C. The bar graphs of tensile strength and flexural strength as a function of barrel temperature appear in Figure 6 (a). When the barrel temperature was increased to 265°C the corresponding values of mechanical properties decreased. In case I where a barrel temperature of 280°C was employed, the mechanical properties were the lowest. A lower melt temperature promoted faster solidification, thinner core region, and finer microfibril formation, all favorably contributing to the improvement in mechanical properties. Furthermore, the viscosity of the melt decreases significantly in the case of higher melt temperature which may not allow proper fibrillar formation to take place, hence explaining the superiority of case II over case I. The SEM photomicrographs of cases I and II show that the latter case gave better fibrillar formation than the former, as shown later (Figs. 7 and 8).

Three different mold temperatures were used, i.e., 55, 70, and 80°C. It is seen that the mechanical properties increase with rising mold temperatures. Figure 6 (b) shows the bar graphs of tensile strength

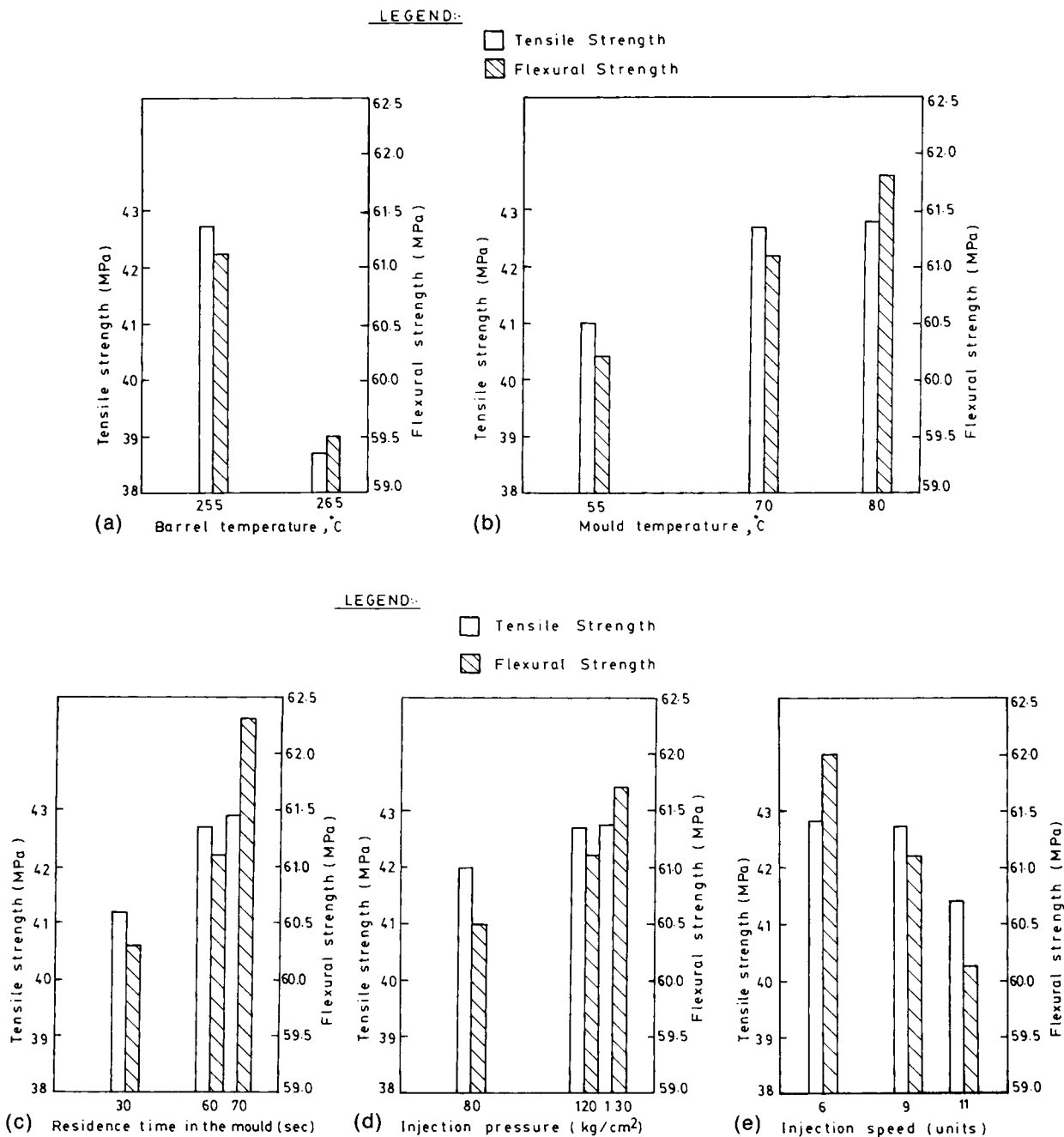
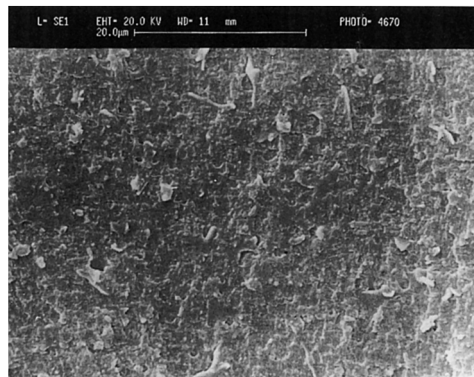


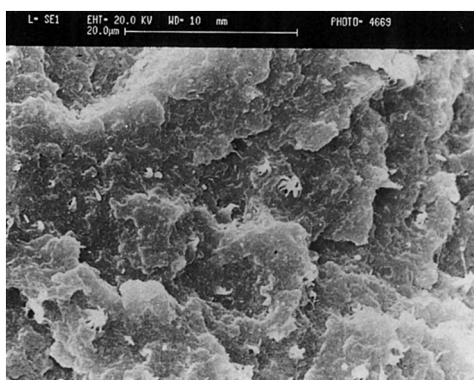
Figure 6 Mechanical properties of the 85/15 blend of Triax 1180 and Vectra A950 with variation in processing parameters, (a) effect of barrel temperature; (b) effect of mold temperature; (c) effect of residence time in the mold; (d) effect of injection pressure; (e) effect of injection speed.

and flexural strength as functions of mold temperature. The use of a heated mold promoted annealing of the specimens, which may result in greater crystallization and hence enhanced mechanical properties. It was seen that the use of a greater residence time in the heated mold was also more favorable, as shown in Figure 6(c).

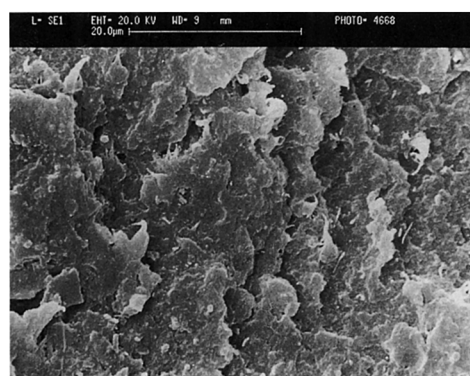
Figure 6(d) shows the bar graph of mechanical properties of the 15% LCP blend at injection pressures of 80, 120, and 130 kg/cm². There is no significant enhancement in mechanical properties with increasing injection pressure. This suggests that injection pressure is not a critical parameter but implies that a minimum injection pressure is required



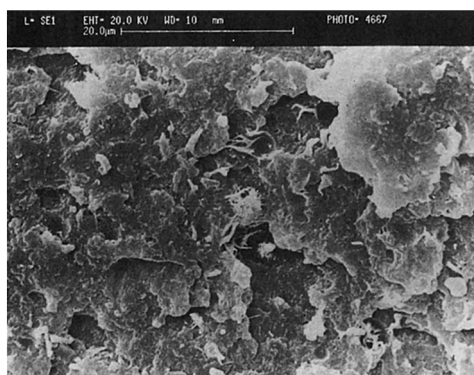
(a). Pure Triax



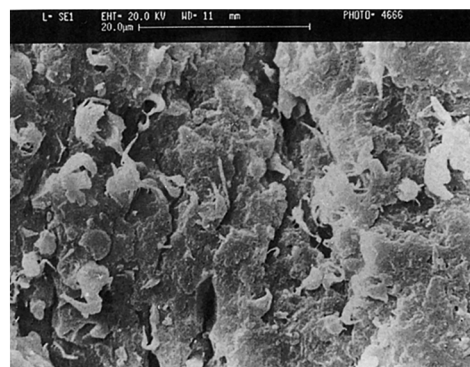
(b). 5 % LCP



(c). 10 % LCP



(d). 15 % LCP

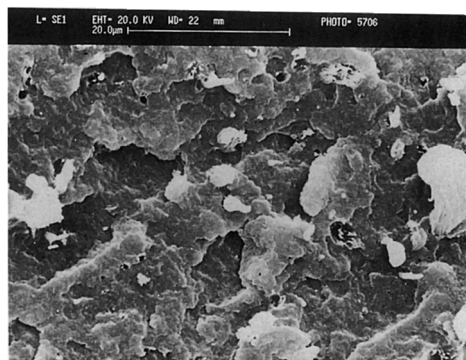


(e). 20 % LCP

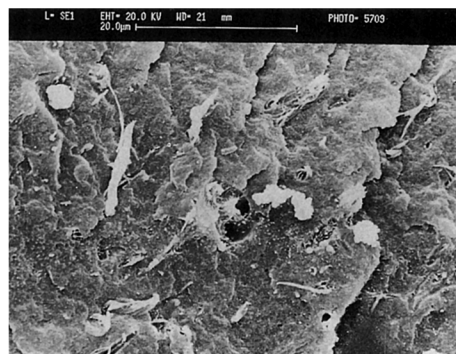
Figure 7 Scanning electron micrographs of fractured flexural bars of blends of Triax 1180 and Vectra A 950. (a) Pure Triax. (b) 5% LCP case I, core region. (c) 10% LCP case I, core region. (d) 15% LCP case I, core region. (e) 20% LCP case I, core region.

for complete filling of the mold to take place during injection molding. Further increase in injection pressure does not have a significant effect on the mechanical properties of the blend.

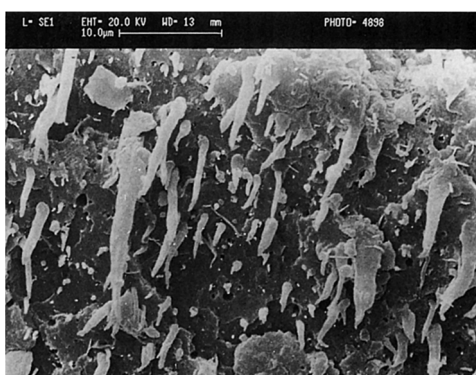
Figure 6(e) shows that the mechanical properties decrease with a rise in injection speed. This can be explained by the work of Bailey and Rzepka,²¹ who discovered that changes in skin-core thickness arise



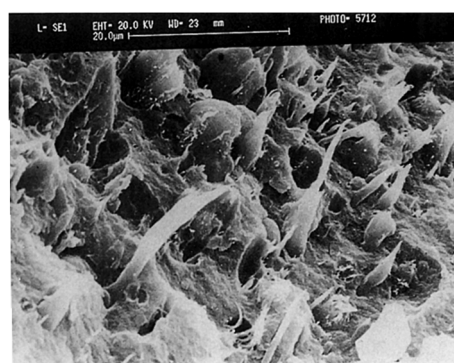
(a). 5 % LCP



(b). 10 % LCP



(c). 15 % LCP



(d). 20 % LCP

Figure 8 Scanning electron micrographs of fractured flexural bars of blends of Triax 1180 and Vectra A 950. (a) 5% LCP case II, core region. (b) 10% LCP case II, core region. (c) 15% LCP case II, core region. (d) 20% LCP case II, core region.

as a result of the transition in shear force field from a more Newtonian flow at lower injection speeds to one of increasingly non-Newtonian and pseudo-plastic flow at higher injection speeds. High injection speeds increase the shear rate of only a very narrow region close to the wall and gives rise to aligned fibers in a more local zone surrounding a much thicker core section. Hence, a lower injection speed is more conducive to the formation of a thicker, highly aligned skin layer leading to better mechanical properties. Thus an injection speed of 6 units was the best, compared with speeds of 9 and 11. The maximum injection speed permissible is 12 units, and the molding would not be carried out at injection speeds less than 6 units.

Thus it is seen that the process variables were very important in determining the final properties of the blends and it was confirmed that a lower barrel

temperature, higher mold temperature, greater injection pressure, lower injection speed, and greater residence time in the mold were favorable for the enhancement of mechanical properties in the self-reinforced blends of Triax/LCP with the LCP as the minor component. The effect of processing conditions on morphology is discussed in the following section.

Morphologic Studies

Scanning Electron Microscopy

Figures 7, 8, and 9 show the SEM photomicrographs of pure Triax and its blends with LCP. The fractured surface of pure Triax [Fig. 7(a)] shows a homogeneous, smooth surface characteristic of a compatibilized blend. Figure 7(b-e) shows the SEM pho-

tomicrographs of blends with 5, 10, 15, and 20% LCP processed under the first set of processing conditions (Case I). These show very little microfibril formation because they were processed at very high temperatures, and homogeneous mixing of Triax and LCP takes place due to a drop in the melt viscosity of the system. These blends did not show much enhancement in mechanical properties.

Figure 8 (a–c) shows the SEM photomicrographs of the core regions of the blends of Triax and LCP at compositions of 5, 10, 15, and 20% LCP processed under the second set of conditions (case II). The blends with 15 and 20% LCP show a fibrillar morphology, as is reflected in their superior mechanical properties.

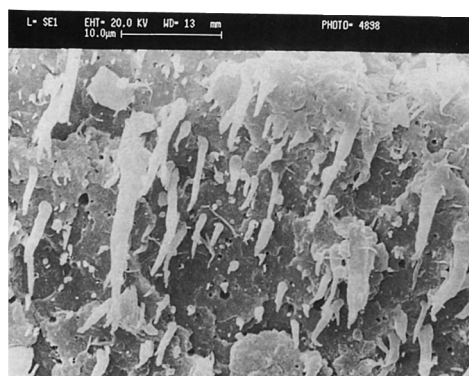
Figures 9(a) to 9(d) represent the core and skin regions of the blends with 15% and 20% LCP processed under the second set of processing conditions (Case II). These show a typical skin–core morphology with elongated fibrils constituting the skin

layer which are shorter in length and reduce to ellipsoidal globules in the core region. Thus it is seen that the processing conditions play a vital role in determining the morphology of these blends.

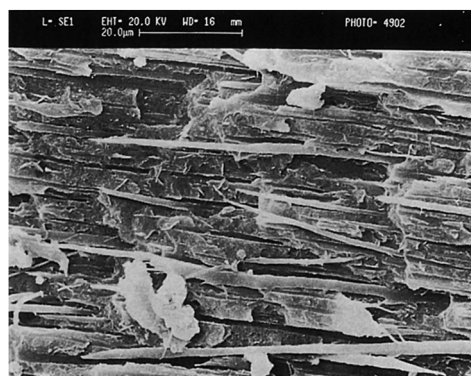
CONCLUSIONS

An alloy of polyamide 6 and ABS has been melt-blended with a thermotropic LCP and it was found that the mechanical properties were enhanced by the incorporation of LCP. The blend composition with 15% LCP gave the highest tensile strength with an increase of 40% over that of the base polymer in case II. The blend with 20% LCP showed the highest tensile modulus and an increase of 38% over that of the base polymer.

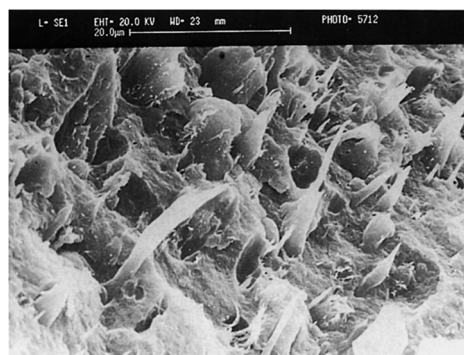
The flexural strength and modulus gave a steady increase with a rise in LCP concentration, with the 20% LCP showing the highest values. It is seen that



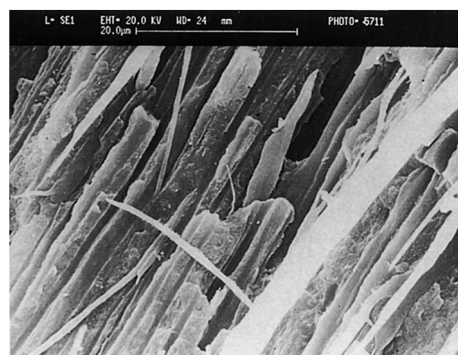
(a). 15 % LCP Core Region



(b). 15 % LCP Skin Region



(c). 20% LCP Core Region



(d). 20 % LCP Skin Region

Figure 9 Scanning electron micrographs of fractured flexural bars of blends of Triax 1180 and Vectra A 950. (a) 15% LCP case II, core region. (b) 15% LCP case II, skin region. (c) 20% LCP case II, core region. (d) 20% LCP case II, skin region.

at the same LCP content, the mechanical properties of the blends increased with a lower melt temperature, lower injection speed, higher mold temperature, higher injection pressure, and maintenance of a longer pressure time as well as residence time in the mold during injection molding.

The LCP phase appeared in the matrix in the form of fibrils or globules, depending upon the processing conditions and composition of the blend. The molded specimens have a distinct skin-core morphology with elongated fibrils constituting the skin layer. This was reflected in the superior mechanical properties of these blends. It was concluded that 15 to 20 wt % of LCP in the blend would be the appropriate LCP level for self-reinforcing blends. It was found that the processing conditions play a vital role in determining the mechanical properties and morphology of the polyblends and need to be optimized.

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