

Studies on Morphology, Mechanical, Thermal, and Rheological Behavior of Extrusion-Blended Polypropylene and Thermotropic Liquid Crystalline Polymer

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ABSTRACT: Polypropylene (PP) was melt-blended in a single-screw extruder with a thermotropic Vectra B-950 liquid crystalline polymer (LCP) in different proportions. The mechanical properties of such blends were compared in respect of their Young's moduli, ultimate tensile strength (UTS), percent elongation at break, and toughness to those of pure PP. The thermal properties of these blends were studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The morphology was studied by using a polarizing light microscope (PLM) and a scanning electron microscope (SEM) while the rheological aspects of the blends and the pure PP were studied by a Haake Rheowin equipment. Mechanical analysis (tensile properties) of the blends showed pronounced improvement in the moduli and the UTS of the PP matrix in the presence of 2–10% of LCP incorporation. TGA of all the blends

showed an increase in the thermal stability for all the blends with respect to the matrix polymer PP, even at a temperature of 410°C, while PP itself undergoes drastic degradation at this temperature. DSC studies indicated an increase in the softening range of the blends over that of PP. Morphological studies showed limited mixing and elongated fibril formation by the dispersed LCP phase within the base matrix (PP) at the lower ranges of LCP incorporation while exhibiting a tendency to undergo gross phase separation at higher concentrations of LCP, which forms mostly agglomerated fibrils and large droplets. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 767–774, 2003

Key words: liquid-crystalline polymers (LCP); mechanical properties; morphology; rheology

INTRODUCTION

Thermotropic main-chain liquid crystalline polymers (LCPs) consist of linear semirigid rodlike molecules that are capable of aligning to a very high degree during melt flow and thus form a highly ordered melt phase. When the polymer melt is cooled, the orientation is retained, which leads to a highly ordered fibrous structure and anisotropic properties. The properties of thermotropic LCPs are based on their oriented structure.^{1–3} The degree of orientation can be influenced by the processing conditions and its environment as well.

LCP moldings can exhibit a layer structure and a skin–core morphology. Near the surface there is a skin layer with extensive highly ordered fibers, while in the core there is less orientation and fiber formation.^{4–8}

LCPs are blended with thermoplastics mainly to reinforce the matrix polymer or to improve its dimen-

sional stability. A small amount of a thermotropic LCP can also make some thermoplastics easier to process due to its relatively low melt viscosity, although a thermotropic LCP and thermoplastics blend consist of two separate phases and are mainly immiscible.^{9,10} A similar skin–core structure can be found in the blends as in pure LCPs. In the skin layer, there are often more oriented fibrous LCP phases, while in the core the LCP phases are less oriented or in spherical form.^{11,12} The LCP content and processing conditions determine whether fibers are formed. The morphology and the resultant properties of the blends are also highly dependent on the composition of the two polymers. The mutual compatibility of the polymers and the interfacial adhesion between them play important roles here. The ratio of the melt viscosities of the polymers affects their miscibility and the fiber formation.^{13,14} In the solid state, blends of LCPs and thermoplastics can exhibit a composite fiber structure if sufficient orientation of the molten LCP phases during processing is achieved.^{15,16}

In the present work, an ester–amide type of LCP was blended with an isotactic stereoregular polypropylene (PP) matrix by a single-screw extruder. The physical, mechanical, and thermal properties of the

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TABLE I
Mechanical Properties for Pure PP and the Blends

Material	Modulus (MPa)	UTS (MPa)	Percent Elongation at Break	Toughness (MPa)	Hardness (Shore D)
Pure PP	596.0	16.0	23	5.0	54
PP + 2% LCP	606.0	24.0	20.0	5.0	56
PP + 5% LCP	703.0	27.0	19.0	4.0	58
PP + 7% LCP	771.0	28.0	18.0	3.0	60
PP + 10% LCP	828.0	29.0	12.0	2.0	63
PP + 15% LCP	640.0	30.0	12.0	1.0	64

blends are discussed here in relation to their morphology and rheology.

EXPERIMENTAL

Materials

The LCP used in this work was Vectra B-950 produced by Ticona (Summit, NJ). It is a totally aromatic extrusion-grade copolyesteramide comprising 60 mol % hydroxynaphthoic acid (HNA), 20 mol % terephthalic acid (TA), and 20 mol % *p*-aminophenol (AP). (The typical properties of the LCP are a melting point $\sim 280^\circ\text{C}$, tensile strength ~ 165 MPa, and elongation at break $\sim 3.0\%$.) The matrix polymer used was the PP homopolymer (Repol HO30SG, having an MFI of 3.0 and which is used for general purposes) supplied by M/S Reliance Industries Ltd. (Mumbai, India).

Blending

The LCP was first manually mixed with the matrix thermoplastic PP as dry pellets. The amount of LCP used in the blends were 2, 5, 7, 10, and 15% by weight.

The melt blending of the materials was performed by a single-screw extruder at temperatures ranging from 285 to 310°C. The extrudates in the form of thin ribbon were immediately quenched in a water bath and repelletized and dried before subsequent processing and testing.

Processing

Both the blends and the pure PP matrix polymer were compression-molded in the form of a rectangular sheet in a Moore Press (temperature, 285°C; pressure, 15 tons). As similar conditions as possible were chosen for the blends as for the matrices. The processing conditions were not optimized for every individual blend composition.

Testing

Tensile properties were measured according to ASTM D 638 using a universal testing machine, Instron

Model 4302. The samples were punched from a compression-molded sheet and inspected for pores and nicks before being subjected to testing. The strain rate was 5.0 mm/min and the toughness was determined from the stress-strain curves themselves.

The hardness was determined by a Shore D durometer. The specific gravities of the samples were inspected by following the conventional principle of Archimedes.

The differential scanning calorimetry (DSC) measurements were carried out using a DSC-7 of Perkin-Elmer in an inert atmosphere of nitrogen. The heating rate was maintained at 10°C/min.

Thermogravimetric analysis (TGA) was carried out using a TGA apparatus from the Perkin-Elmer TGA7 Delta Series. The testing was carried out in an atmosphere of nitrogen and the heating rate was maintained at 20°C/min.

The morphology was determined by a Krüss Tri-nocolour polarizing microscope and a scanning electron microscope (SEM). The rheological studies were carried out in a Haake Rheowin equipment.

RESULTS AND DISCUSSION

Mechanical properties in relation to morphology

Table I shows the mechanical properties of the various blends of PP-LCP. These results indicate that the tensile strength and the Young's moduli of the thermoplastic PP matrix underwent a steady increase with an increasing LCP content. This can possibly be related to an effective heterogeneous phase nucleating action in the form of fibrils exerted by the LCP moieties during the crystalline growth of the stereoregular PP melt during cooling and leading to an LCP fibril-reinforced PP-LCP composite. It may, however, be noted that the initial steep rise in these two parameters with respect to virgin PP (to $\sim 8\%$ LCP incorporation) was not observed at the later stages of LCP incorporation. This appears to be corroborated by the SEM and polarizing micrographs (Figs. 1 and 2), where the LCP phase appears to be elongated, exhibiting a tendency toward fiber formation, particularly at low concentrations. PP, an absolutely nonpolar hydrocarbon homopolymer

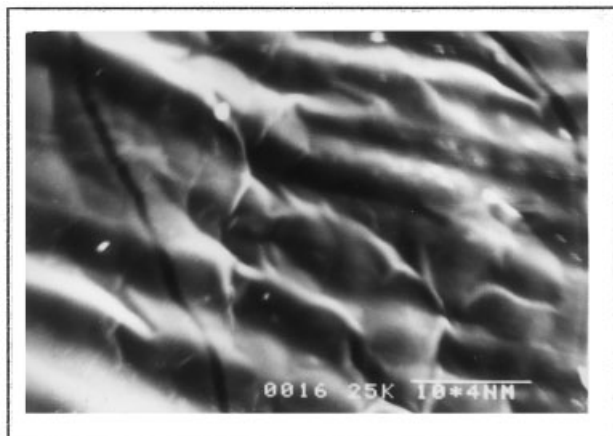


Fig 1(a)

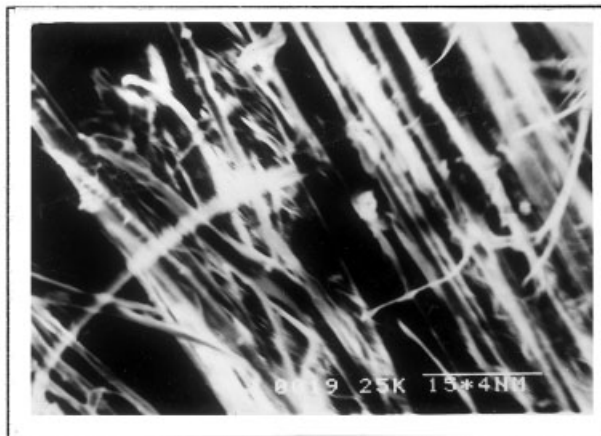


Fig 1(b)

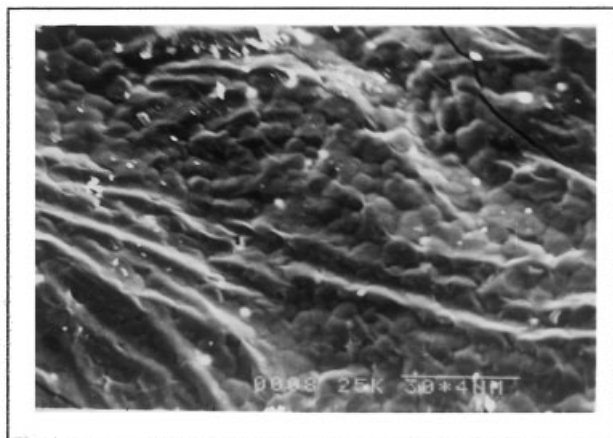


Fig 1(c)

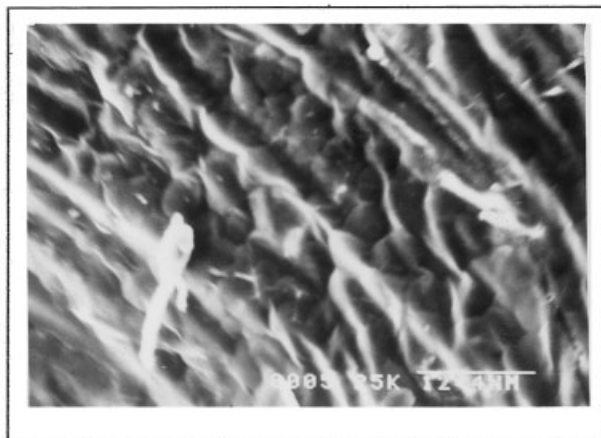


Fig 1(d)

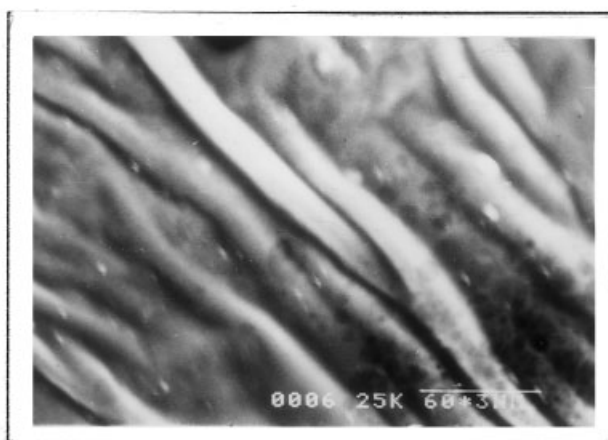


Fig 1(e)

Figure 1 Scanning electron micrographs: (a) pure PP; (b) pure LCP; (c) PP + 5% LCP blend; (d) PP + 10% LCP blend; (e) PP + 15% LCP blend.

having high order of tacticity (isotactic), has very little affinity toward an extensively polar LCP. As the polymers under study are not miscible, the adhesion be-

tween the two separate phases affects the properties of the blend. LCP does not normally mix well with thermoplastics and thus the blends consisted of two sep-

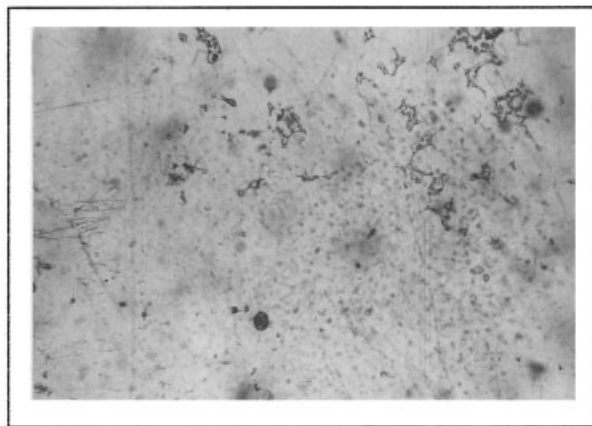


Fig 2(a)

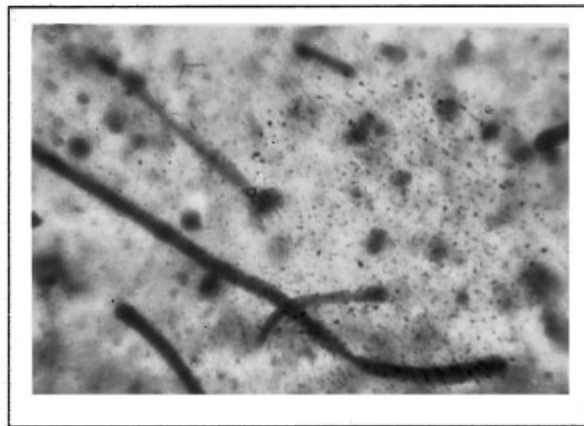


Fig 2(b)

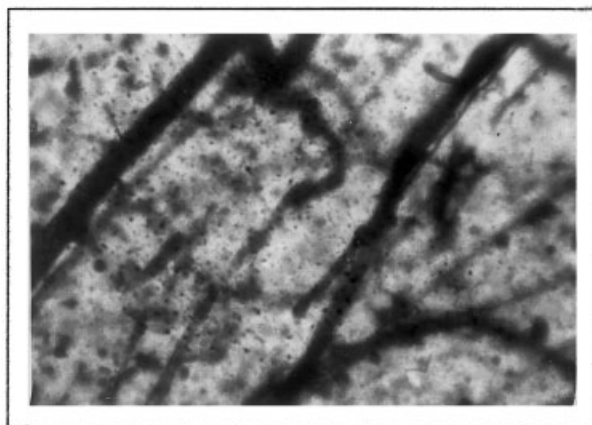


Fig 2(c)



Fig 2(d)

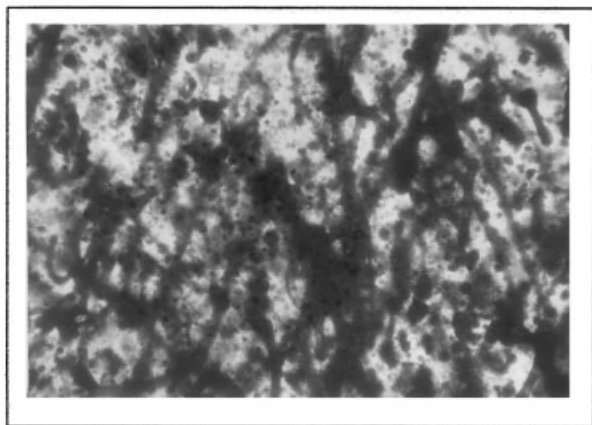


Fig 2(e)

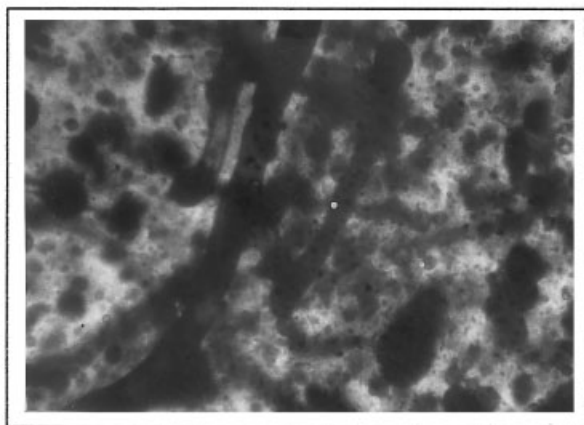


Fig 2(f)

Magnification: 40X

Figure 2 Polarizing light micrographs: (a) pure PP; (b) PP + 2% LCP blend; (c) PP + 5% LCP blend; (d) PP + 7% LCP blend; (e) PP + 10% LCP blend; (f) PP + 15% LCP blend.

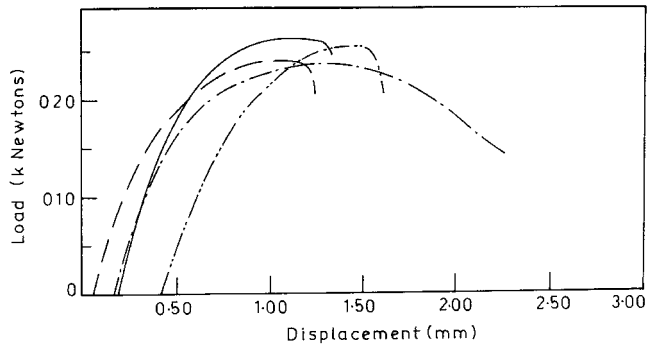


Figure 3 Stress versus strain plots: (— — —) pure PP; (— · —) PP + 5% LCP; (—) PP + 10% LCP; (— — —) PP + 15% LCP.

arate phases. The LCP phase appeared in the matrix in the form of small spheres or fibers depending on the LCP content and the orientation during processing.^{9,17-20}

At the lower level of LCP incorporation, where no gross phase separation occurs, the elongated and oriented crystalline fiber of LCP, as mentioned above, acts as fibers for the formation of a somewhat LCP fiber-reinforced PP composite. The polarizing micrographs of the various blends of PP-LCP (Fig. 2) appear to corroborate the mechanical properties as discussed above. At lower concentrations of LCP incorporation, the LCP phase appears to form elongated fibrils, the diameters and concentrations of which gradually increase with increase in its doses, that is, there is probably a gradual drop in the aspect ratio. Because of the high surface energy at the interfaces of the fibrils, the preferential adsorptive forces exerted by the elongated fibril surface might be expected to enhance the tensile modulus and the ultimate tensile strength (UTS). At the initial stages, the formation of small nuclei, which gradually grow and elongate, is also quite discernible.

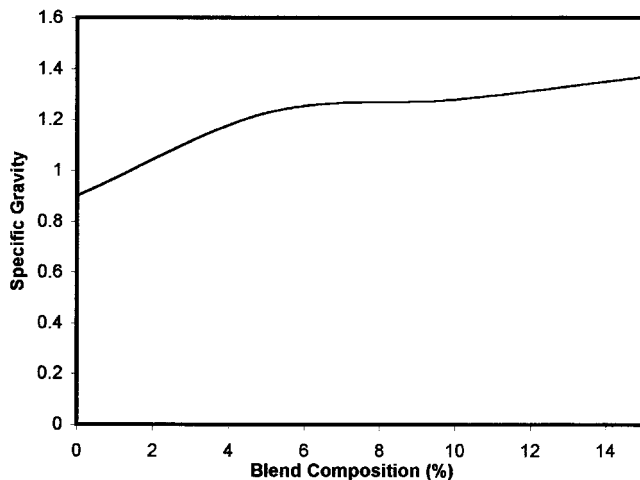


Figure 4 Variation of specific gravity with blend composition for pure PP and the blends.

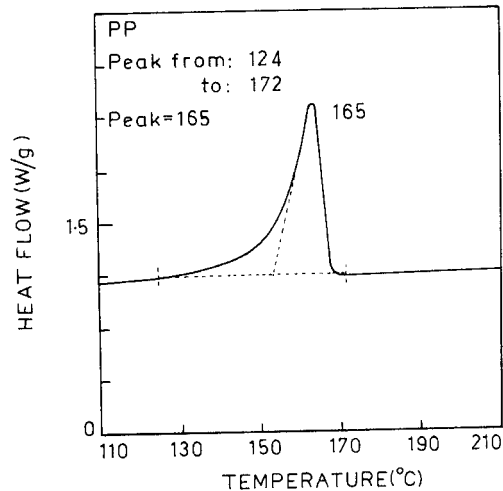


Fig 5(a)

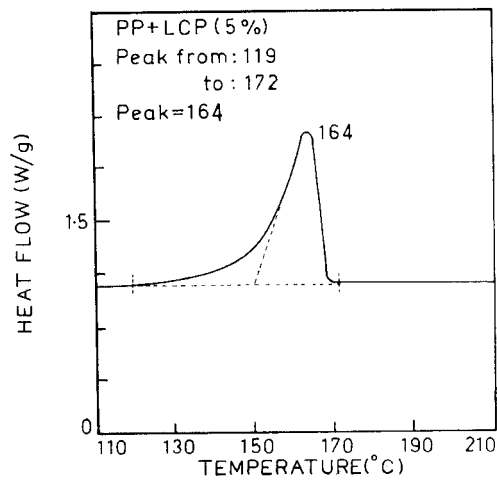


Fig 5(b)

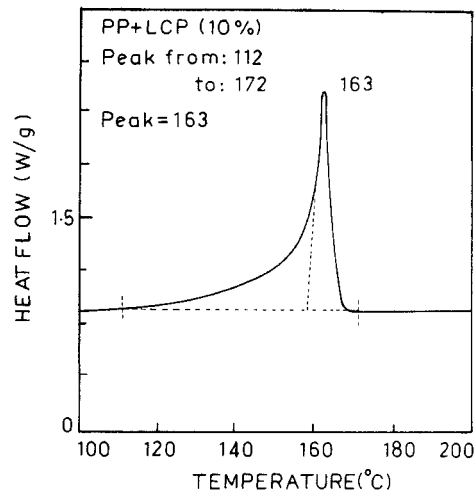


Fig 5(c)

Figure 5 DSC plots: (a) pure PP; (b) PP + 5% LCP blend; (c) PP + 10% LCP blend.

Now, with a further increase in the proportion of LCP beyond the optimum, gross phase separation might be expected to be responsible for little or no increase in these two mechanical aspects. The SEM/polarizing micrographs exhibited an aggregated disposition of fibrils having a comparatively lower aspect ratio compared to the earlier reinforcing ones ob-

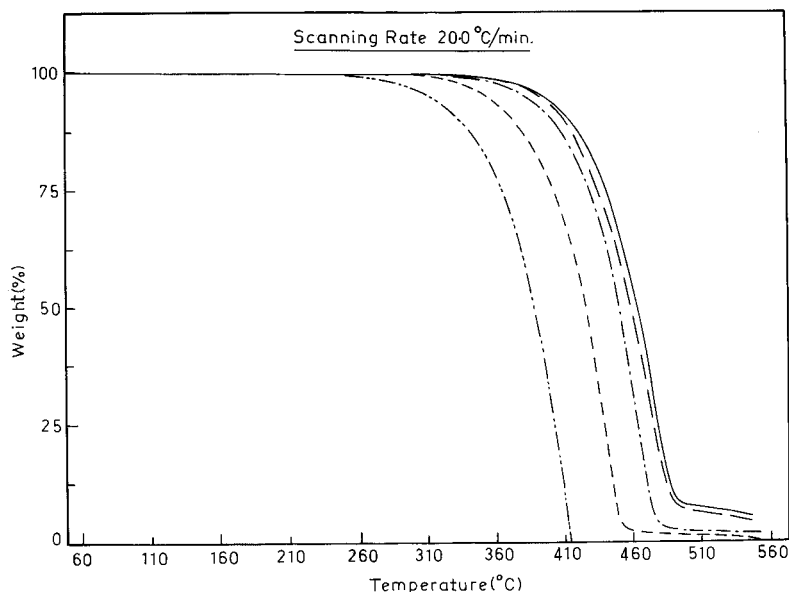


Figure 6 TGA plots: (---) pure PP; (- - -) PP + 5% LCP; (—) PP + 10% LCP; (—) PP + 15% LCP.

served at low concentrations of LCP and a spherical or droplet disposition of the incompatible LCP phases within the PP matrix as well instead of long elongated fibrils (high aspect ratio) and thus offering very little contribution toward reinforcement of the matrix. Thus, it may be assumed that, beyond an optimum LCP content, a dual combination of thick fibrils and droplet phases of LCP appear, the latter being little effective in modifying the mechanicals. At higher doses of LCP, particularly beyond ~7–8%, the thin elongated fibrils are found to disappear while aggregates of LCP fibrils appear along with spherical droplets.

The SEM micrographs clearly corroborate the above observations (Fig. 1). A layered structure of blend moldings is quite apparent.^{5–8} The phase boundaries in blends containing lower percentages of LCPs appear to be somewhat indistinct and diffusing, which presumably indicates limited mixing at the interfaces. In blends containing higher percentages of LCPs, the phase boundaries appear to be sharp and indicative of improper mixing.

The percent elongation at break and the toughness values of the blends undergo a steady decrease as expected and thus lead to a stiffer and brittle matrix. The poor ductility of the blends can be ascribed to the inability to transfer the fracture energy through the transcrystalline regions between the phases, causing debonding at the interfaces and rupture at earlier stages compared to PP.

The hardness values of the various blends of PP–LCP show a similar trend as those of the Young's moduli and the UTS, that is, they exhibit a steady increase with increasing proportions of LCP. The interesting feature in this particular mechanical param-

eter is that the increasing trend remains unabated even at higher proportions of LCP where gross phase separation of the LCP domains from the PP matrix appears to have occurred. This may possibly be explained by the fact that the hardness, being a surface property, might be controlled by the diffusing conglomerated phase-separated LCP domains toward the surface. It may thus be assumed that the incorporation of even a low amount of LCP in PP leads to the formation of a stiff and brittle composite.²¹

The stiffer but brittle characteristics of the various PP–LCP blends may be observed in their corresponding stress–strain diagram (Fig. 3). It may be observed that the area under the stress–strain diagram decreases continuously with increasing proportions of LCP.

Figure 4 shows the variation of specific gravities of the blends in relation to their compositions. This, of course, is as per our expectation, as the incorporation of denser LCP moieties into the comparatively less dense PP matrix might be expected to lead to an increase in density.

Thermal properties

The DSC curves of pure PP and two of its blends (5 and 10%) with LCP are shown in Figure 5(a–c). The melting temperature of the PP matrix appears to remain almost unaffected by the incorporation of LCP, and there is only a marginal drop by one or two degrees within the range of concentrations studied. One more salient feature of these DSC tracings is the gradual and steady broadening of the softening ranges of the blends as compared to those of pure PP. An

inward shift of the onset temperature of softening is quite discernible.

This sort of melting behavior may possibly be explained by a combination of two opposing factors contributing simultaneously within the range of concentration studied. The breakdown of the crystal structure of PP and the consequent reduction in the melting temperature is almost immediately compensated by the high melting LCP phases stimulating a range of crystalline structures (heterogeneous phase nucleation) of different sizes and shapes of the PP-included phase. The broadening of the softening range may possibly be due to a range of widely different sizes of the crystal structures, which increase with increasing proportions of LCP. Thus, it may be assumed that the effect of crystallinity in the ultimate blends remains almost identical to that of the virgin PP,¹⁷ which, in effect, might have compensated the high melting point of stereoregular isotactic PP.²²

The TGA of the blend samples and that of pure PP (Fig. 6) provides us with information about the stability of the blends. It is found that, while PP becomes completely degraded, leaving no residues within the range of temperatures studied, the blends leave residues which increase in amount with increasing proportions of the LCP. The increase in the thermal stability of the PP matrix by the LCP phase is quite evident from the thermograms which exhibit an increased onset temperature of degradation and a delayed (sluggish) rate of degradation of the various blends compared to that of pure PP.

Rheology

The rheological aspects are shown in Figure 7(a–c). These clearly indicate that blending LCP to the extent of 5% with PP facilitates the processing of comparatively viscous PP melts. Although at lower shear-rate regions ($\dot{\gamma} < 10 \text{ s}^{-1}$) there is little difference in the shear stress developed in the PP + 5% LCP blend and pure PP itself, at the higher shear-rate regions ($\dot{\gamma} > 10 \text{ s}^{-1}$), the shear stress developed by the blend (PP + 5% LCP) is much less compared to pure PP. This is quite apparent from the τ (shear stress) versus $\dot{\gamma}$ (shear rate) plot [Fig. 7(b)] of the blend and virgin PP at a temperature of 285°C.

A representative plot of the melt (shear) viscosity (η) versus the shear rate ($\dot{\gamma}$) at 285°C for PP and its blend with 5% LCP is shown in Figure 7(a). There is a drop in the melt viscosity for the PP + 5% LCP blend with respect to pure PP over the entire range of the shear rate studied.^{9,10} At higher shear rates, beyond 20 s^{-1} , however, the difference between the shear melt viscosities of the PP + 5% LCP blend and that of pure PP is narrowed. The shear melt viscosity of the blend, after undergoing a sharp decrease at the low shear-rate region ($< 10 \text{ s}^{-1}$), is reduced at a considerably

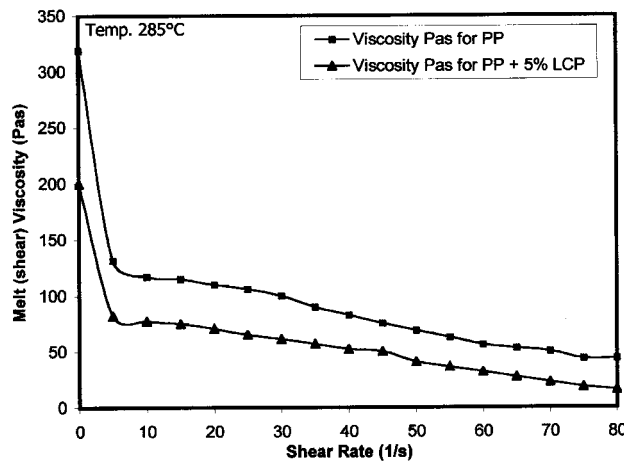


Fig 7 (a)

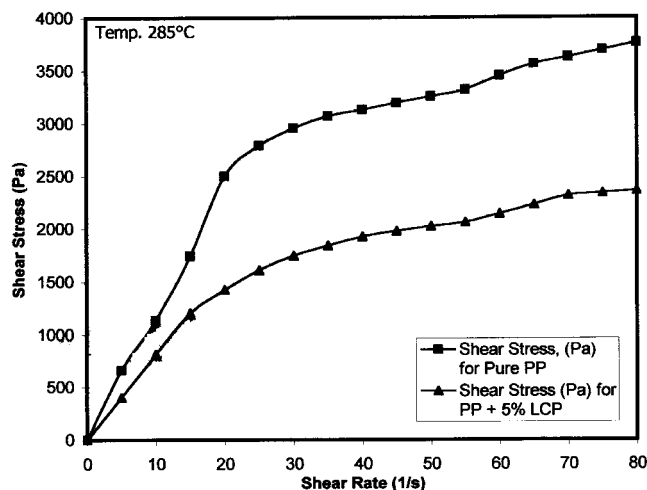


Fig 7 (b)

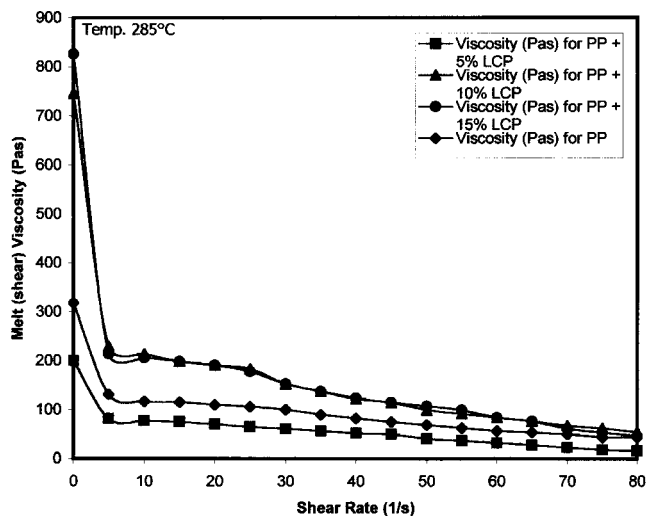


Fig 7 (c)

Figure 7 Rheological plots: (a) Variation of shear (melt) viscosity with shear rate for pure PP and PP + 5% LCP blend; (b) variation of shear stress with shear rate for pure PP and PP + 5% LCP blend; (c) variation of shear (melt) viscosity with shear rate for pure PP, PP + 5%, PP + 10%, and PP + 15% LCP blends.

lower rate while that of pure PP follows a gradual, steady rate which is also remarkably less in comparison to its own steep fall at the initial stages.

It may possibly be assumed that the LCP, by virtue of its unique characteristics of low melt viscosity, has brought forth an overall decrease in the melt viscosity over the entire range of the shear rate studied for this blend in particular. Furthermore, the crystallinities of the LCP at the melt stage might have reduced the rate of structure breakdown of the PP matrix at the higher shear-rate region, while the structure breakdown of virgin PP goes on unabated at a much faster rate compared to the blends.

The rheological patterns of the blends containing 10 and 15% LCPs are different in nature and appear to pose difficulties during processing as they all exhibit higher melt viscosities (shear) compared to pure PP within the range of the shear rate studied [Fig. 7(c)]. The shear-stress values also follow the same pattern. The crystallinity of the phase-separated LCP phase appears to offer more resistance to flow. There is hardly any difference in the melt behavior of the PP + 10% LCP and PP + 15% LCP blends, respectively.

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