

Engineering Properties of Compatibilized Polypropylene/Liquid Crystalline Polymer Blends

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ABSTRACT: Polypropylene (PP) and Vectra A950, a thermotropic liquid crystalline polymer (LCP), blends were prepared in a single-screw extruder with the variation in Vectra A950 content in presence of fixed amount (2%, with respect to PP and LCP mixture as a whole) of ethylene-acrylic acid (EAA) copolymer as a compatibilizer. Mechanical analysis of the compatibilized blends within the range of LCP incorporations under study (2–10%) indicated pronounced improvement in the moduli, ultimate tensile strength (UTS), and hardness. Fourier transform infrared (FTIR) spectroscopy studies revealed the presence of strong interaction through H-bonding between the segments of Vectra A950 and the compatibilizer EAA. Morphological studies performed by scanning electron microscopy (SEM) manifested the development of fine fibrillar morphology in the compatibilized PP/

Vectra A950 blends, which had large influence on the mechanical properties. Differential scanning calorimetry studies showed an initial drop of the melting point of PP in the presence of EAA followed by enhancement of the same in presence of Vectra A950. TGA showed an increase in the thermal stability for all blends with respect to matrix polymer PP. Rheological studies showed that a very small quantity of Vectra A 950 was capable of reducing the melt viscosity of PP particularly in the lower shear rate region and hence facilitated processibility of the blends. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 5279–5285, 2012

Key words: liquid crystalline polymer; compatibility; mechanical properties; spectral properties; morphology; thermal properties

INTRODUCTION

Thermotropic main-chain liquid crystalline polymers (LCPs) consist of linear semi rigid rod-like molecules which 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 concomitant anisotropic properties. The properties of thermotropic LCPs are based on their oriented structure.^{1–3} The processing conditions and its environment as well, can influence the degree of orientation. 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 in the fibers formed.^{4,5}

Considerable interest has been focused on blends and composites based on thermoplastics and LCPs during the last few years for the excellent properties of LCP like high strength, chemical resistance, low

thermal expansion, relatively high melting temperature, and low melt viscosity attributable to its uniform ordered structure.^{6,7} This kind of *in situ* blends is potentially interesting particularly for industrial purposes, since their use may induce simultaneously significant mechanical properties and easier processibility.⁸ A small amount of a thermotropic LCP can also make some thermoplastics easier to process due to its relatively low melt viscosity,^{9,10} although thermotropic LCP and thermoplastics blends consist of two separate phases and are mostly immiscible.^{1,11}

Owing to nonpolar nature of polypropylene (PP) in contrast to the more polar nature of LCP, the lack of compatibility arises which leads to deterioration in mechanical properties, even if fibrils are generated. Therefore, compatibilizations of PP/LCP blends have also been investigated by several researchers.^{12–21} The LCP content, type, and processing conditions as well as the presences of compatibilizers determine the ultimate morphology and hence the properties of such blends.²² All these investigations have enabled us to reach to the conclusion that the addition of compatibilizers to PP/LCP blends leads to an improvement of the dispersion of the LCP fibrils in the PP matrix and to the formation of thinner LCP fibrils than those observed for noncompatibilized blends. The morphology and the resultant properties

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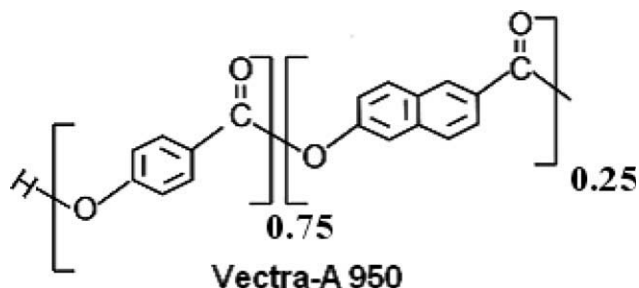
of the blends are also highly dependent on the composition of the same.²³ The mutual compatibility of the polymers and the interfacial adhesion between them of course play an important role here.

Vectra A950, a thermotropic ester type LCP was utilized to improve overall engineering properties particularly mechanical properties of different thermoplastics by several researchers.^{1,8,14,24–26} In our earlier investigation,²⁷ PP was melt blended with thermotropic LCP, Vectra A 950 in different proportions without using any compatibilizer. The prepared PP/LCP blends containing very small amount (2–10%) Vectra A950 showed improved mechanical properties and thermal stabilities. We have extended this study and different PP/Vectra A 950 blends are prepared in presence of a compatibilizer ethylene-acrylic acid (EAA) copolymer under melt condition. The physical, mechanical, spectral, and thermal properties of the prepared compatibilized blends are discussed here in relation to their morphology and rheology.

EXPERIMENTAL

Materials

The LCPs used in this work was Vectra A-950 produced by Ticona, U.S.A. This is aromatic copolyester comprising 25 mol percent of 2, 6-hydroxynaphthoic acid (HNA) and 75 mol percent of para hydroxybenzoic acid. (The typical properties of the Vectra A 950 are melting point $\sim 280^\circ\text{C}$, tensile strength ~ 165 MPa, and elongation at break $\sim 3.0\%$). The chemical structure of Vectra A 950 is shown below.



The matrix thermoplastic used in this study was PP homopolymer (Repol HO 30SG, having an MFI of 3.0 g/10 min) supplied by M/S Reliance industries (Mumbai, India).

EAA is a copolymer of ethylene and acrylic acid which has been used here as a compatibilizer. The comonomer content and MFI are 6% and 3.0 g/min, respectively. It was supplied by Dow Chemicals, USA.

Blending

The LCP (Vectra A 950) and EAA copolymer were first manually mixed with PP. The compositions of

TABLE I
Compositions of Different PP-Vectra A 950 (LCP) Blends in Presence of Compatibilizer

Blends	Weight percent of components		
	PP	Vectra A 950 (LCP)	EAA (as % of mixture of PP and Vectra A)
A	100	0	0
B	100	0	2
C	98	2	2
D	95	5	2
E	93	7	2
F	90	10	2

the different PP/Vectra A 950 blends are given in the following Table I. The blends were prepared under molten condition 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 in a subsequent operation. These were dried before the subsequent processing and characterization. The extruder had an L/D ratio of 28:1 and the screw had nearly equal three zones of feeding, compression, and metering.

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 and pressure 15 tons). As similar conditions as possible was maintained for the preparation of all blends. The processing conditions were optimized by trial and error and kept constant for all the blends compositions.

Characterization

Tensile properties such as modulus, ultimate tensile strength (UTS), percent elongation at break (EB%), and toughness were measured according to ASTM D 638 using 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. All testings were carried out at room temperature. The data reported were averages of at least six measurements and typical scattering range of the results were $\pm 5\%$. The hardness was determined by means of durometer in shore D Scale following ASTM D-2240-64T. Impact strength was measured by Izod Impact Machine (Model No. Win PEN CEAST S.P.A. Italy) following ASTM D256 having 3 mm sample thickness.

Fourier transform infrared (FTIR) spectra were obtained using Perkin-Elmer RX-I, FTIR spectrophotometer. The thin film samples were used for this

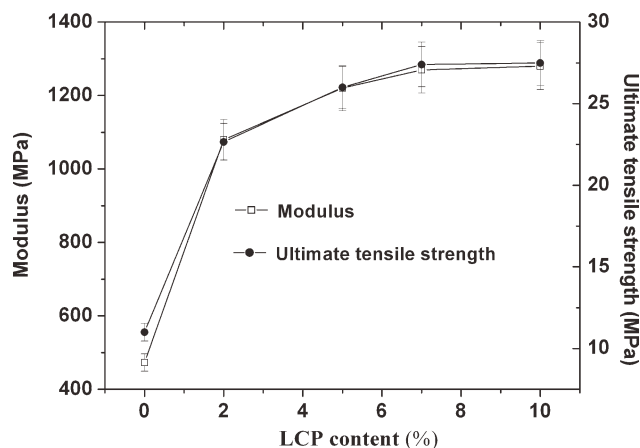


Figure 1 Plots of different modulus and ultimate tensile strength values of PP/Vectra A950 blends with the variation of LCP contents in presence of fixed dose of compatibilizer (EAA).

study. The scanning electron micrographs for gold-coated samples were obtained on a Hitachi (S415A) microscope. All the samples under testing for scanning electron microscopy (SEM) were tensile fractured surfaces that were used directly without any solvent etching. Differential scanning calorimetry (DSC) measurements were carried out from Shimadzu (DSC-50) in an inert atmosphere of nitrogen at a heating rate of 10°C/min. TGA of various samples was carried out in a Perkin–Elmer Delta series TGA-7 under nitrogen atmosphere at a heating rate of 20°C/min. The melt rheological properties of different composites were evaluated employing a constant shear rate plate and cone (3° angle), rotational viscometer (Rheotron 2744E from Brabender, Germany) at 200°C.

RESULTS AND DISCUSSION

Mechanical properties

The mechanical properties of the various compatibilized PP-LCP blends as a function of variation in LCP (Vectra A950) in presence of fixed proportion of compatibilizer have been shown in Figures 1–3.

Figure 1 shows the plots of different moduli and UTS values of PP/LCP blends as a function of LCP contents. Both the values undergo a steady increase with the increase in LCP content. The immediate loss in symmetry imparted by PP alone due to blend formation and the consequent loss in crystallinity of the PP chains is more than compensated by the presence of linear, relatively more rigid, stiff, and oriented LCP molecules which have reasonably high aspect ratio. As a result high modulus and high tensile strength values have been achieved. Similar observation was made with PP/LCP blends in absence of compatibilizer in our earlier study²⁷ and was

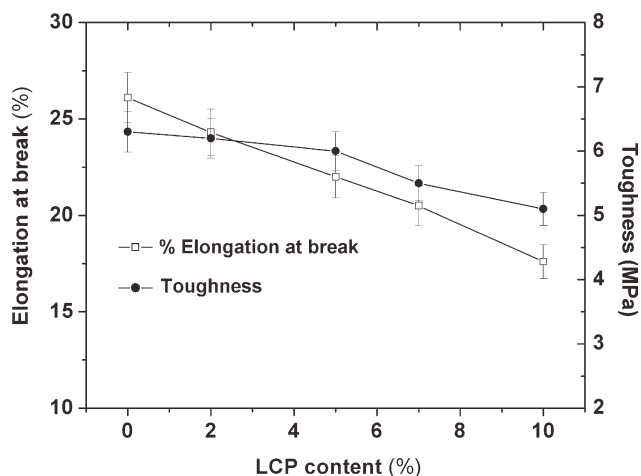


Figure 2 Plots of different EB% and toughness values of PP/Vectra A950 blends with the variation of LCP contents in presence of fixed dose of compatibilizer (EAA).

ascribed to only surface adsorptive forces extended over the extensive increase in fibrillar surface areas of LCPs.

Moreover, EAA is a copolymer of ethylene and acrylic acid. The acidic group in the compatibilizer is being assumed to be involved in interaction with the ester group present in Vectra A-950 molecules through intermolecular H-bonding. It has been schematically represented in Scheme 1 and thus EAA acts as a compatibilizer in the blends under study. Again it has been found that in presence of compatibilizer the modulus is much more enhanced than what was obtained with the blend of PP and LCP alone.²⁸ Under melting condition, the LCP molecules align to very high degrees and thus form highly ordered and oriented melt phase causing an enhancement in the probability of H-bonding. When the polymer melt is cooled, the orientation is retained

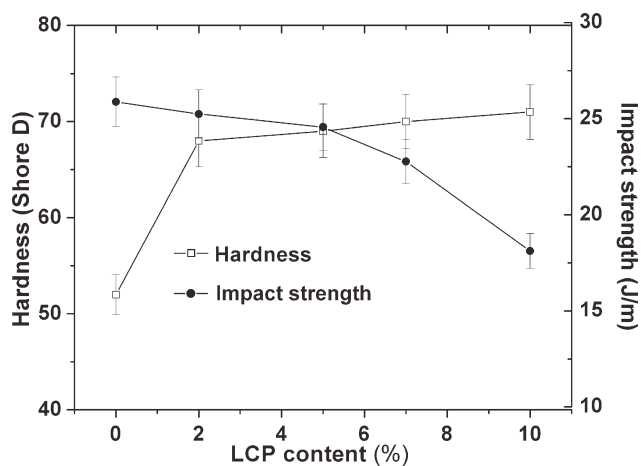
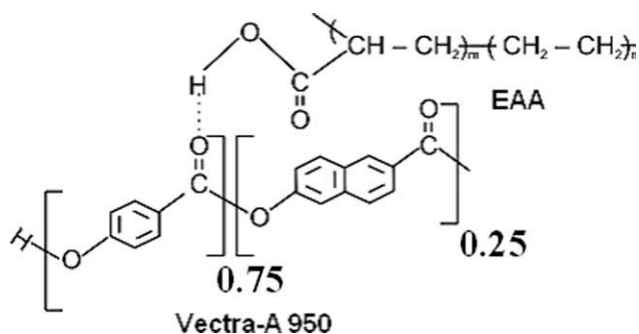


Figure 3 Plots of different hardness and impact strength values of PP/Vectra A950 blends with the variation of LCP contents in presence of fixed dose of compatibilizer (EAA).



Scheme 1 Intermolecular H-bonding between segments of EAA and Vectra-A950.

within the blends and hence the improvements in properties.

Figure 2 shows the plots of percent elongation at break (%EB) and toughness values of PP/LCP blends with the variation in LCP contents. Both the 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 with PP. The impact properties of virgin PP are somewhat destroyed by intermolecular chain stiffening due to H-bonding also.

The hardness values of the various PP/LCP blends also show increasing trend with the increase in proportions of LCP (Fig. 3), a phenomenon of normal expectations where moduli increases and % EB decreases. It may possibly be explained by the fact that the hardness, being a surface property might be controlled by the defusing 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 stiff and brittle blends. The decreasing trend of the impact values is observed with the increasing LCP content for PP/LCP blends in presence of a fixed amount of compatibilizer (Fig. 3). It can be explained that with the increase in LCP content in the blends, the stiffer and brittle characteristics of the same increases and hence the impact values also show decreasing trend.

FTIR spectra

FTIR spectra of PP, Vectra-A950 and the blends of PP/VectraA950, PP/EAA, and PP/EAA/Vectra-A950 are shown in Figure 4. PP shows its characteristic absorption bands for the deformation vibration of methyl ($-\text{CH}_3$) and methylene ($-\text{CH}_2-$) groups at 1473 cm^{-1} and 1382 cm^{-1} , respectively,²⁹ and they get much subdued and shift to somewhat lower frequency regions, at 1453 cm^{-1} and 1370 cm^{-1} , respec-

tively, in the PP/EAA/Vectra-A950 blends as a result of structural modification. The peak at 1725 cm^{-1} attributed to carbonyl stretching of EAA³⁰ in PP/EAA blends shifts to 1700 cm^{-1} in the PP/EAA/Vectra-A950 blends owing to the strong interaction via intermolecular H-bonding with Vectra-A950. The band for the ester carbonyl stretching frequency appearing at 1736 cm^{-1} for Vectra-A950³¹ also shifts to lower frequency regions at 1700 cm^{-1} in the PP/EAA/Vectra-A950 blends and thus further lend support to strong H-bonding. In comparison, the FTIR spectra of only PP, only Vectra-A950 and PP/Vectra-A950 blends, there was no such shifting in the aforementioned peaks (ester carbonyl) indicating absence of any interaction, as expected. Probable interactions through intermolecular H-bonding between EAA and Vectra-A950 are shown in Scheme I.

Morphology

Scanning electron microscopy

The scanning electron micrographs of PP and two of its blends in presence of a fixed amount (2%) of compatibilizer are shown in Figure 5. Fine and uniform distribution of the LCP fibrils within the PP matrix in presence of compatibilizer is observed. It is noted that the proportions of the irregularly

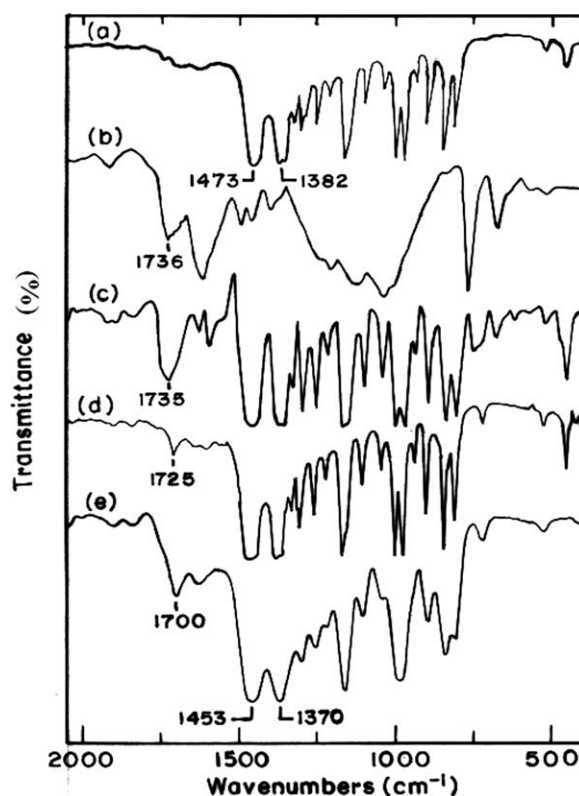
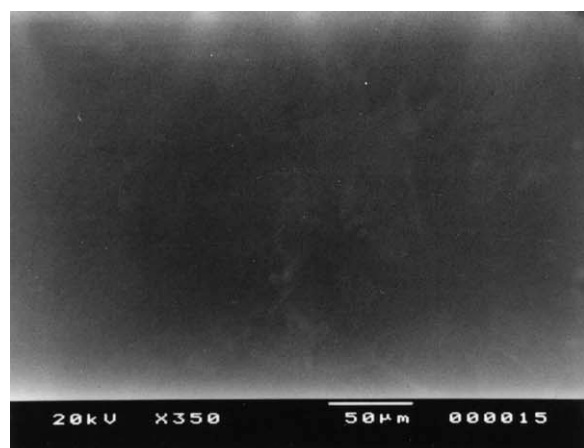
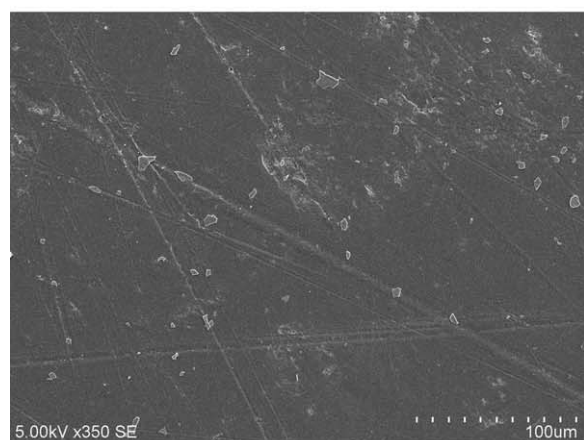


Figure 4 FTIR spectra of: (a) PP, (b) Vectra A950, (c) PP + Vectra A950 (5%), (d) PP + EAA (5%), and (e) PP + EAA (5%) + Vectra A950 (5%).



(a)



(b)



(c)

Figure 5 Scanning electron micrographs of (a) PP, (b) PP + EAA (2%)+Vectra A950 (5%), and (c) PP + EAA (2%) + Vectra A950 (7%).

shaped droplets (sometimes elongated) increase with simultaneous formation of fibrils, which appeared to be dissolved in the matrix in considerable proportions. The tendency toward formation of more and more thin fibrils that can enhance the mechanical properties (as observed earlier) by exerting adsorp-

tive forces over a wide surface area is noted as the LCP content increases. Toughness and EB (%) are the two properties, which bear an inverse relationship with modulus and UTS. The strong adsorptive force on the surface of thin fibril as has been manifested in the scanning electron micrographs of the blends remarkably reduces the chain flexibility of PP and not allowing to be extended under the application of tensile load. This leads to a reduction in EB% and consequently augments the concentration of stresses, which lead to brittle fracture and thus lowering the toughness and also impact strength values. Compatibilization has also been noted to have dramatic effects on morphology, with the LCP being dispersed more effectively, creating smaller fibrils with high aspect ratios, yielding smoother surfaces and allowing less fiber pullout. A more fibrillar structure has been observed with the increase in LCP dispersion, thereby improving the ability of the LCP to reinforce the matrix. The interfacial tension between the nonpolar PP matrix and the polar LCP fibrils is greatly reduced by the presence of EAA.

Thermal Analysis

Differential scanning calorimetry

The DSC curves of pure PP, PP + 2% EAA and its one of blends with LCP (to the extent of 5% of PP present) in presence of 2% EAA are shown in Figure 6. The pure isotactic PP exhibits a melting range, 125–172°C, the majority of the crystallites melting at the peak temperature, ~ 164°C. EAA being compatible with PP, plasticizes the matrix resulting in somewhat decrease in the peak temperature of melting (163°C). The notable feature is that in presence of Vectra A 950, there is a rise in the peak temperature for melting which even surpasses that of the PP alone. This can possibly be ascribed to the fact that

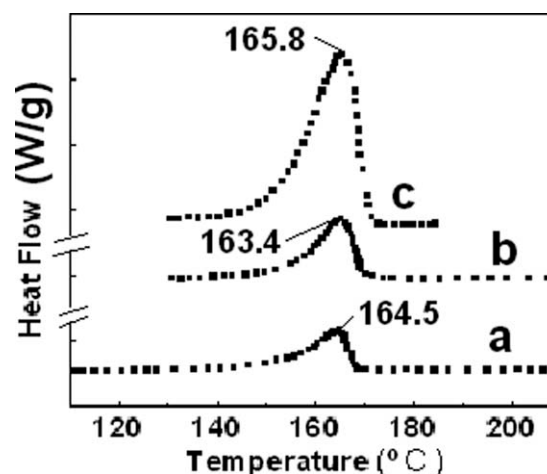


Figure 6 DSC thermograms of: (a) PP, (b) PP+EAA (2%), and (c) PP + EAA (2%) + Vectra A950 (5%).

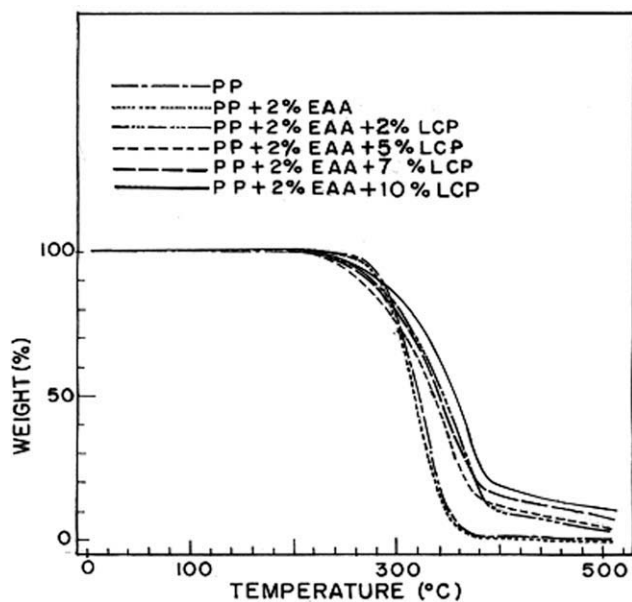


Figure 7 TGA of PP, PP + EAA (2%) and PP + EAA (2%) + Vectra A950 blends containing different Vectra A950 content.

the aromatic polyester in LCP undergoes secondary interaction with the acid group of EAA as shown in FTIR study. The incorporation of EAA breaks down the regular crystal structure of PP and increases its amorphicity. This is evident from the relatively lower peak crystalline melting point in its DSC tracing. The linear aromatic ring structure of LCP further breaks down the crystal structure but the combined effect of secondary interaction through H-bonding and the high melting point of LCP raises the melting temperature of the blends even beyond that of pure PP.

Thermogravimetric analysis (TGA)

The Figure 7 gives an idea of the relative thermal stabilities of PP, PP + EAA (2%) and of its various blends with Vectra A 950 in presence of 2% EAA. The thermograms of PP and its blends with 2% of EAA almost closely match each other although the blend has marginally lower thermal stability than that of PP (because of the presence of softer EAA) both in terms of marginal earlier onset and a fast rate of degradation. The thermal stability of PP/Vectra-A 950 blends containing 2% EAA as a compatibilizer show an increasing trend with the increase of Vectra-A 950 contents. Isotactic PP used in our study is a highly crystalline polyolefin. It can be assumed that while preparing the blend, the crystallinity of PP is broken up to provide interstices the LCP guest molecules. The major matrix being PP the initial decomposition temperature of the host and guest blend is reduced. The overall gain in thermal stabil-

TABLE II
Thermogravimetric Analysis

Materials	Temperature of 5 wt % loss (°C)	Residues at 500°C (%)
PP	281	0
PP + EAA (2%)	279.5	0
PP + EAA (2%) + LCP (2%)	256	3.5
PP + EAA (2%) + LCP (5%)	250	5
PP + EAA (2%) + LCP (7%)	254	8
PP + EAA (2%) + LCP (10%)	260	12

ity particularly toward the higher temperature range is attributed to the high thermal stability of LCP, which of course increases with increasing LCP content. The temperature of 5 wt % loss and the residues left at 500°C for different blends are tabulated in Table II.

Rheology

The melt viscosity of PP in presence of compatibilizer decreases, Figure 8, as expected than that of the PP alone only because of the presence of low temperature softening EAA copolymer. The distinctive feature in this plot is that when LCP is incorporated, there is further progressive decrease in melt viscosity with progressive increase in LCP content particularly in the lower region of shear rate under study. Vectra A950, being a copolymer ester by virtue of its having a linear rigid structure, on its incorporation into PP breaks down the crystalline lattice of the PP matrix and also lowers its melt viscosity substantially by enforcing the PP chain to flow in the flow direction of linear LCP chain. Thus, it can be concluded that LCP facilitates processing in presence of

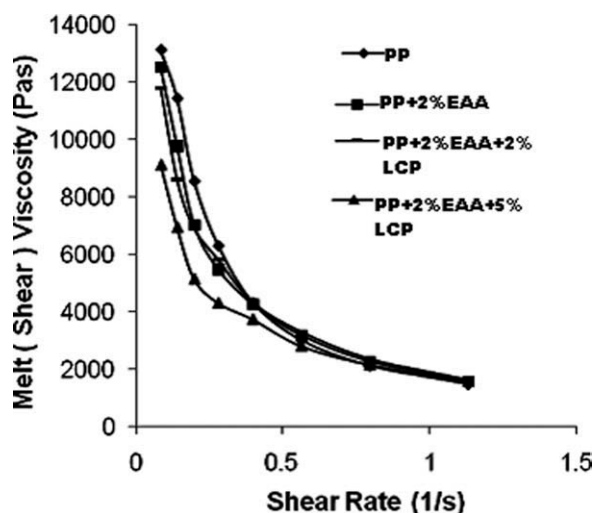


Figure 8 Plots of melt viscosity versus shear rate of PP and different blends in presence of fixed dose of compatibilizer (EAA).

compatibilizer, EAA by lowering the well-known high melt viscosity of PP.

CONCLUSIONS

This study has revealed that the prepared PP/Vectra A950 blends in presence of a compatibilizer (EAA) show substantial improvement in mechanical properties like modulus, UTS, hardness, and also thermal stabilities with the incorporation of very low doses (2–7%) of Vectra-a 950. FTIR results confirmed the existence of strong interaction between the segments of EAA and LCP Vectra A 950 through intermolecular H-bonding in the blends. The development of fibrillar morphology in the compatibilized PP/Vectra A950 blends was established by SEM study. This investigation demonstrates that the preferential alignment of Vectra A950 during melt blending as well as the enhanced interfacial adhesion between Vectra A950 and the compatibilizer EAA play the key role in improving the mechanical properties of the blends.

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