

Studies on the Engineering Properties of LCP-Vectra B 950/PP Blends with the Variations of EAA Content

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ABSTRACT: Polypropylene (PP) was melt blended with Vectra B-950 [a thermotropic liquid crystalline polymer (LCP)], in a single screw extruder in presence of different doses of ethylene acrylic acid (EAA) copolymer, as modifier. The effect of incorporation in different proportions of EAA at a fixed dose of 5% LCP, on mechanical, thermal, morphological, and rheological properties of such blends was studied and the same were compared with that of pure PP and amongst themselves. Mechanical analysis (tensile properties) of the prepared blends exhibited improvements in ultimate tensile strength (UTS), modulus, toughness, hardness, and impact strength of PP matrix with the incorporation of EAA. The improvement in mechanical properties is associated with the formation of

LCP fibrils as evidenced by scanning electron microscopy (SEM). A strong interaction through H-bonding between the segments of Vectra B-950 and EAA was established by FTIR study. Differential scanning calorimetry (DSC) studies indicated substantial increase in melting point of the blends, and thermogravimetric analysis (TGA) showed that the thermal stability of PP was improved with the addition of LCP and EAA. Rheological properties showed that LCP and EAA drop down the melt viscosity of PP and thus facilitate processibility of blends. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 1034–1041, 2011

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

INTRODUCTION

Blending of polymers provides an efficient way of developing new materials with tailored properties and thus has received much attention from academia and industry. However, sometimes the desire to produce improved products by blending a particular pair of polymers is often frustrated by their low compatibility. Hence, there is a strong need to enhance compatibility and the compatibilization of polymer blends becomes an important feature of polymer science and technology.

Main chain liquid crystalline polymers (LCPs) consist of linear semi rigid rod like molecules that are capable of aligning to a very high extent and thus form a highly ordered melt phase. When the polymer melt is cooled, the orientation is retained that leads to a highly ordered fibrillar structures and anisotropic properties. The properties of thermotropic LCPs are based on their oriented structure.^{1–3} The degree of orientation can be influenced by processing conditions and its environment as well.

LCP moulding can exhibit a layered structure with skin and core morphology. Near the surface, there is a skin layer with extensive highly ordered fibrils, whereas in the core, there is lesser extent of fibril orientation and hence less fibre formation.^{4–8}

LCPs are blended with thermoplastics mainly to reinforce the matrix thermoplastics or to improve its dimensional stability. A small amount of LCP can also make viscous thermoplastics (conventional) 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} The blend possesses higher mechanical properties over the thermoplastics and can be processed far more easily than the thermoplastic one. A similar skin core structure can be found in the blends as in pure LCPs. In skin layer, there are often more oriented fibrous LCP phases, whereas in the core, the LCP phases are less oriented or in spherical form.^{11,12}

The mutual compatibility and interfacial adhesion between thermoplastics and LCP can be improved by using EAA as a compatibilizer and that was reflected in the modulus and other mechanical properties of the blends.¹³

The LCP content, type and processing conditions, and the presence of compatibilizers determine the ultimate morphology.^{14–16} The morphology and resultant properties of the blends are also highly dependent on the composition of the blend.

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The ratio of melt viscosity of the polymers affects their miscibility and the mode of fibre formations.^{17,18} In the solid state, blends of LCPs and thermoplastics can exhibit a composite fibre structure if sufficient orientation of the molten LCP phases during processing is achieved.^{19,20}

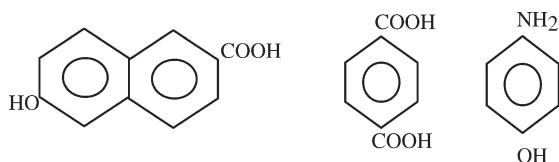
In our earlier report,¹³ PP was melt blended with thermotropic LCP, Vectra B 950 in different proportions in presence of a fixed dose of EAA in which case the level of EAA was kept at 2% and was supposed to function as compatibilizer only. The prepared PP-LCP blends showed improved mechanical properties and thermal stabilities.

In the present work, isotactic stereo-regular polypropylene (PP) was melt blended with an ester amide type of LCP (a fixed dose) in presence of different proportions of EAA using single screw extruder. The object of our present work is to study the effect of incorporation of modifier (EAA) on PP-LCP blend. The physical, mechanical, spectral, and thermal properties of the blends are discussed here in relation to their morphological and rheological properties.

EXPERIMENTAL

Materials

The LCP used in this work was Vectra B-950 supplied by Ticona, USA. It is an aromatic copolyester amide comprising 60 mole % Hydroxynaphthoic acid (HNA), 20 mole % Terephthalic acid (TA), and 20 mole % *p*-aminophenol (AP). The structures of HNA, TA, AP are as follows:



The typical properties of the LCP include melting point $\sim 280^\circ\text{C}$, tensile strength ~ 165 MPa, and elongation at break $\sim 3.0\%$. The matrix polymer used was PP homopolymer [Repol HO 30SG having an MFI of 3.0 g/10 min] supplied by M/s. Reliance Industries Limited, Mumbai, India. EAA obtained from Du-Pont, USA, is a copolymer of ethylene and acrylic acid, which has been used here as a modifier. The co monomer content and the MFI are 6% and 3.0 g/10 min, respectively.

Blending

The fixed doses LCP (5%) was first manually mixed with the matrix thermoplastic PP as dry pellets. The variable amounts of EAA used in the blends were 2, 5, 7, and 10% by weight, respectively, as shown in Table I. The LCP was dried by keeping it in the oven

TABLE I
Different Composition of Blends

Blends	Weight percent of component		
	PP	Vectra B 950	EAA as % of mixture PP and Vectra B 950
A	100	0	0
B	95	5	2
C	95	5	5
D	95	5	7
E	95	5	10

maintained at $110 \pm 5^\circ\text{C}$ till the time it reached a constant weight, which was checked intermittently.

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

Processing

Both the blends and the Pure PP matrix polymer were compression moulded in the form of a rectangular sheet in a Moor Press (temperature 285°C and pressure 0.098 MPa). As similar conditions as possible were maintained for the preparation of all blends. The processing conditions were optimised by trial and error and kept constant for all the blend compositions.

Characterization

Tensile properties were measured according to ASTM using universal testing machine Instron, Model 4302. The samples were punched from a compression-moulded 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 itself. All testing were carried out at room temperature. The data reported were averages of at least six measurements and typical scattering range of the results were $\pm 5\%$. FTIR-spectra were obtained using Parkin Elmer RX-I, FTIR spectrophotometer. The thin film samples were used for this study. The Differential scanning calorimetry (DSC) measurements were carried out from Shimadzu (DSC-50) in an inert atmosphere of nitrogen at a heating rate of $10^\circ\text{C}/\text{min}$. Thermogravimetric analysis (TGA) of various samples was carried out in a Perkin Elmer Delta series TGA-7 under nitrogen atmosphere at a heating rate of $20^\circ\text{C}/\text{min}$. The scanning electron micrographs for gold-coated samples were obtained on a Hitachi (S415A) microscope. The melt rheological properties of different blends 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 blends of PP-LCP with variation in content of EAA as modifier have been shown graphically in Figure 1–3. The mechanical properties of only PP (modulus: 596.0 MPa, UTS: 16.0 MPa, %EB: 23.0, toughness: 5.0 MPa, hardness: 54.0 shore D, impact strength: 20.1 J/m) and its blend with LCP have already been reported in detail in our previous article.²¹

Both, the moduli and ultimate tensile strength (UTS) of the PP-LCP blends undergo a steady increase upto the loading of (5–7%) EAA as shown in Figure 1. The same parameters for PP-LCP blends (without EAA) were less than that of EAA-modified PP-LCP blends. The overall increase in modulus and UTS may be attributed to a unique combination of the following factors. On blending PP with LCP, immediate loss in symmetry to some extent and the consequent loss in crystallinity of the PP chains (because of incorporation of LCP and EAA) is more than compensated by the presence of linear relatively more rigid, stiff and oriented LCP molecules, which have reasonably high aspect ratios and hence in turn form composites of high modulus and high tensile strength.

EAA being a copolymer of ethylene and acrylic acid, the acidic group in the polymer is assumed to be involved in secondary interaction with the various functional groups present in Vectra B-950 molecules by virtue of being a well-balanced modifier in the present blends. During the melt blending by extrusion, the LCP molecules align to very high degrees and thus form highly ordered and oriented

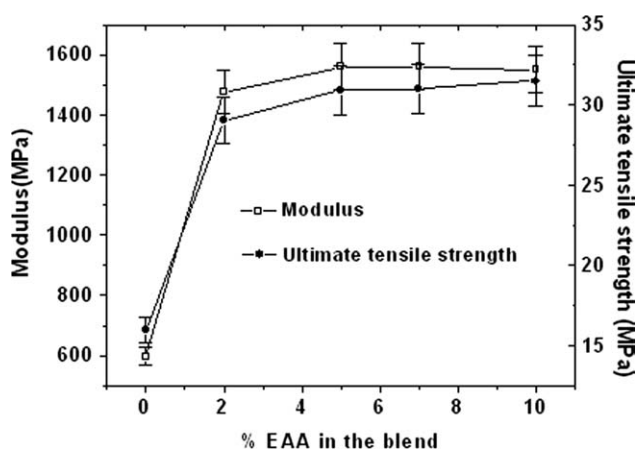


Figure 1 Variation of modulus and UTS vs. blend composition as a function of variation in EAA content at a fixed dose of (5%) LCP incorporation.

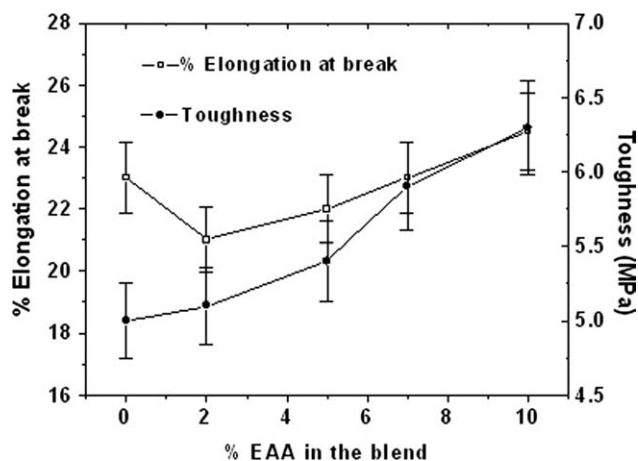


Figure 2 Variation of % elongation at break and toughness vs. blend composition as a function of variation in EAA content at a fixed dose of (5%) LCP incorporation.

phase. When the polymer melt is cooled, the orientation is supposed to be still retained within the blend and hence the improvements in properties.²² The properties were anisotropic as the orientation was more in the machine direction than in transverse direction. During compression moulding at a later stage, multidirectional flow destroyed the orientation somewhat and some isotropicity in properties developed because of redistribution of oriented molecules in both directions.

It was reported that the graft side chain liquid crystalline copolymer based upon acrylic acid functionalised PP (PP-AA) acted as compatibilizer for PP-LCP polyblend and enhanced physical properties.²³ It might be assumed that though the matrix and the reinforcing components are widely different in nature and have little affinity for each other, it is the surface adsorptive forces exerted over long area of the fibrils, which is responsible for the observed increases in mechanical properties.

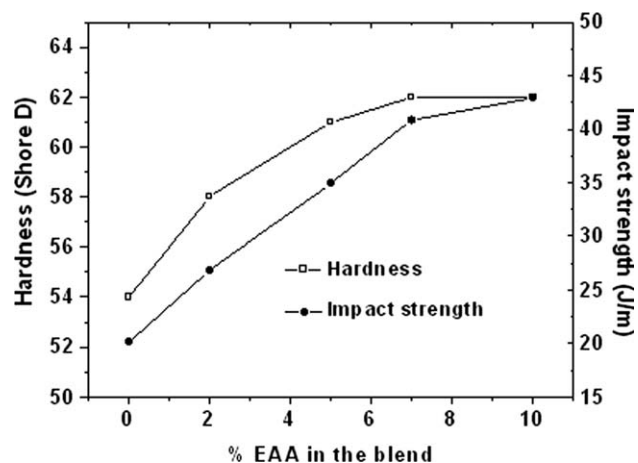


Figure 3 Variation of hardness and izod impact strength vs. blend composition as a function of variation in EAA content at a fixed dose of (5%) LCP incorporation.

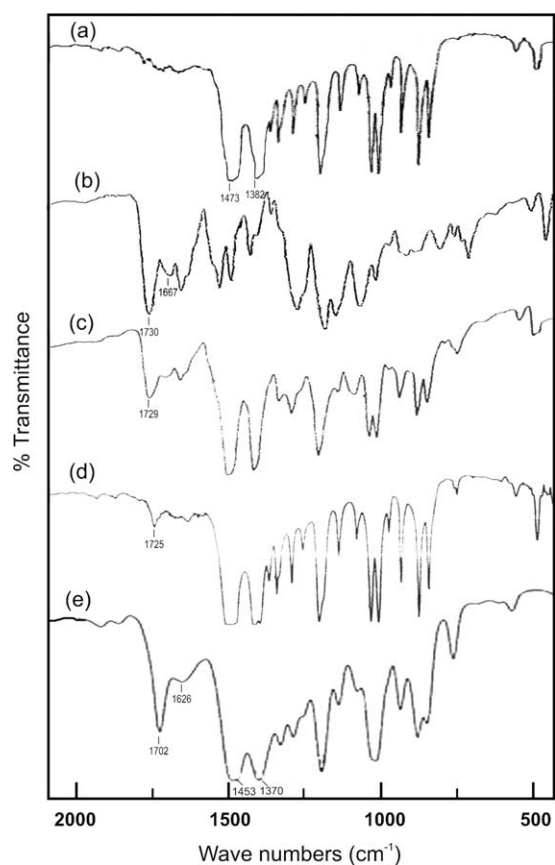


Figure 4 FTIR-spectra of (a) PP, (b) LCP (Vectra B 950), (c) PP+5% LCP, (d) PP+ 5% EAA, and (e) PP+5% EAA+5% LCP.

It may, however, be noted that the initial rise in these two parameters with respect to virgin PP appears to be corroborated by SEM (Fig. 7), where the LCP phase seems to be elongated exhibiting a tendency towards fibril formation of LCP in presence of the EAA. The aspect ratios of these fibrils are found to be much higher than those observed with PP-LCP blend without any modifier.

The Figure 2, displays the percent elongation at break (EB) and toughness values of various PP-LCP blends with the variation of EAA content. The crystalline isotactic PP has in general poor elongation characteristics. On melting under shear, the crystallinity is expected to be reduced to a greater extent. However, on cooling in presence of more rigid linear fibrils of LCP, the growth of crystallinity is disturbed. But strong adsorptive forces of these fibrils appear to immobilize the chains and arrest its slippage preventing orientation. Thus as expected, the EB values of the LCP modified PP is reduced to some extent. This study was explained in detail in our earlier article.²¹ The initial drop of EB value is due to the presence of higher amount (5%) of rigid LCP moieties compared to the lower amount (2%) of softer EAA moieties. However, as the EAA content increases, the blend systems become more and more

plasticized and even in spite of the secondary interaction of EAA with equivalent proportions of the functional groups present in LCP, the plasticizing action is more predominant and enables the blend to exhibit an increasing trend in the EB characteristic.

The variation of toughness as a function of EAA for fixed quantity of LCP (5%) of PP-LCP blends (Fig. 2) exhibits a continuous upward swing manifesting the influence of presence of relatively more tough and rubbery EAA.

The hardness values of the various blends of PP-LCP also exhibit a steady increase with increasing proportions of EAA (Fig. 3). This may possibly be explained by the fact that the hardness being a surface property might be controlled by the diffusing conglomerated phases of EAA domains towards the surface. The interesting feature in this particular mechanical parameter is that the increasing trend remains unabated even at higher proportions of LCP under study, although the other mechanicals tend to undergo decrease in this region.^{13,21} It may possibly be due to more and more chemisorptions of EAA near the surface of the blends.

The increasing trend of the impact values as the EAA content is progressively increased in the blends having fixed LCP content (5%) is quite obvious (Fig. 3). The plasticizing influences exerted by soft rubbery EAA enables the LCP chains to relax comfortably in the empty holes generated due to the presence of EAA.

FTIR-spectra

FTIR spectra of PP, LCP (Vectra-B950) and the blends of PP-LCP (VectraB950), PP-EAA and PP-EAA-Vectra-B950 are shown in Figure 4. PP shows its characteristic absorption peaks for the deformation vibration of methyl ($-\text{CH}_3$) and methylene ($-\text{CH}_2-$) groups at 1473 cm^{-1} and 1382 cm^{-1} , respectively,²⁴ and they get much subdued and shift to somewhat lower frequency regions, at 1453 cm^{-1} and 1370 cm^{-1} , respectively, in the PP-EAA-Vectra-B950 blends as a result of structural modification. The peak at 1725 cm^{-1} attributed to carbonyl stretching of EAA²⁵ in PP-EAA blends shifts to 1702 cm^{-1} in the PP-EAA-Vectra-B950 blends owing to the strong interaction via intermolecular H-bonding with Vectra-B950. The bands for the ester carbonyl and amide carbonyl stretching frequencies appearing at 1730 cm^{-1} and 1667 cm^{-1} for Vectra-B950²⁶ also shift to lower frequencies regions at 1702 cm^{-1} and 1626 cm^{-1} , respectively, in the PP-EAA-Vectra-B950 blends and thus further lend support to strong H-bonding. In comparison, the FTIR spectra of only PP, only Vectra-B950 and PP-Vectra-B950 blend, there was no such shifting in afore mentioned peaks

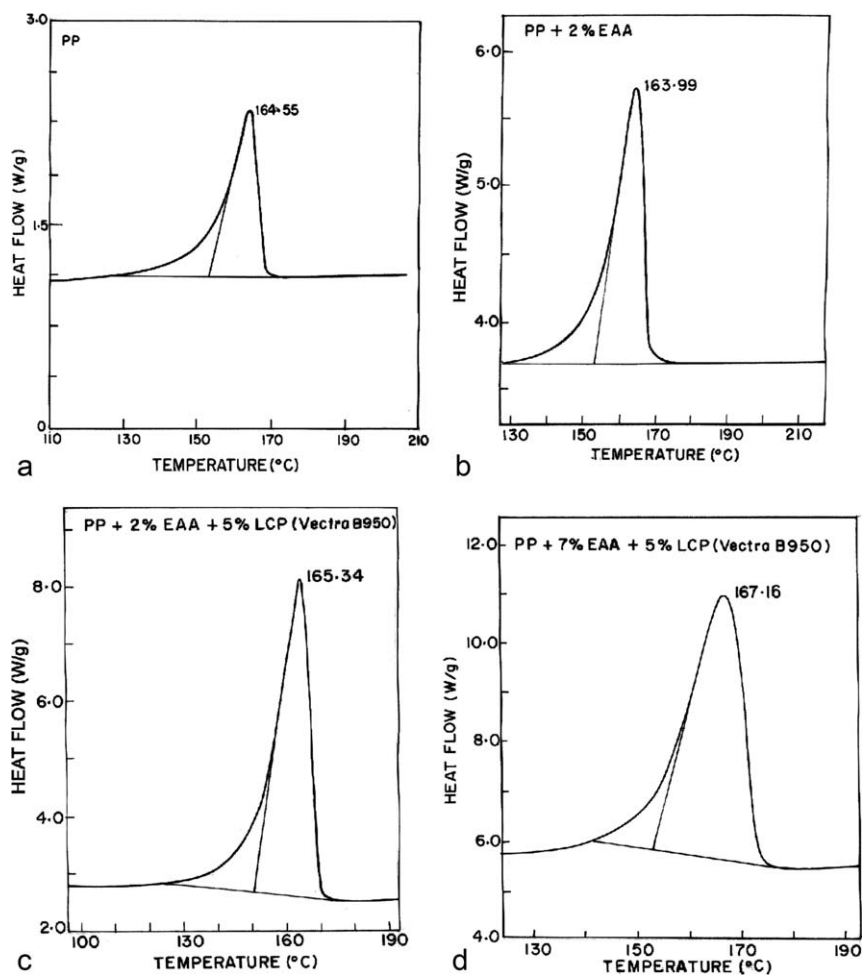
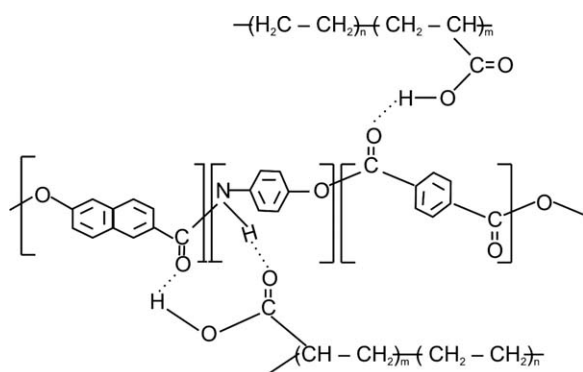


Figure 5 DSC plots of (a) PP, (b) PP+2%EAA, (c) PP+2%EAA+5%LCP, and (d) PP+7%EAA+5%LCP.

(both ester carbonyl and amide carbonyl) indicating absence of any interaction as expected.

It was reported earlier that the ester carbonyl stretching frequency of Vectra-A950 appearing at 1731 cm^{-1} gets shifted in the lower frequency region of 1720 cm^{-1} in the polystyrene-Vectra-A950-silicone rubber blend owing to strong interfacial interaction.²⁷ A schematic presentation of the possible interaction in conformity with this observation for the present system is given below.



THERMAL PROPERTIES

Differential scanning calorimetry (DSC)

The DSC curves of PP and its blend with LCP Vectra B 950 as a function of variation in modifier EAA

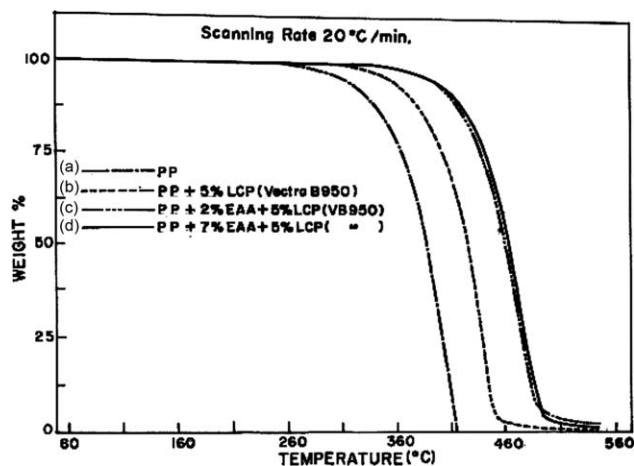


Figure 6 Thermogravimetric analysis of PP-Vectra B blends (5% LCP) in presence of varying doses of EAA: (a) PP, (b) PP+5%LCP, (c) PP+2%EAA+5%LCP, and (d) PP+7%EAA+5%LCP.

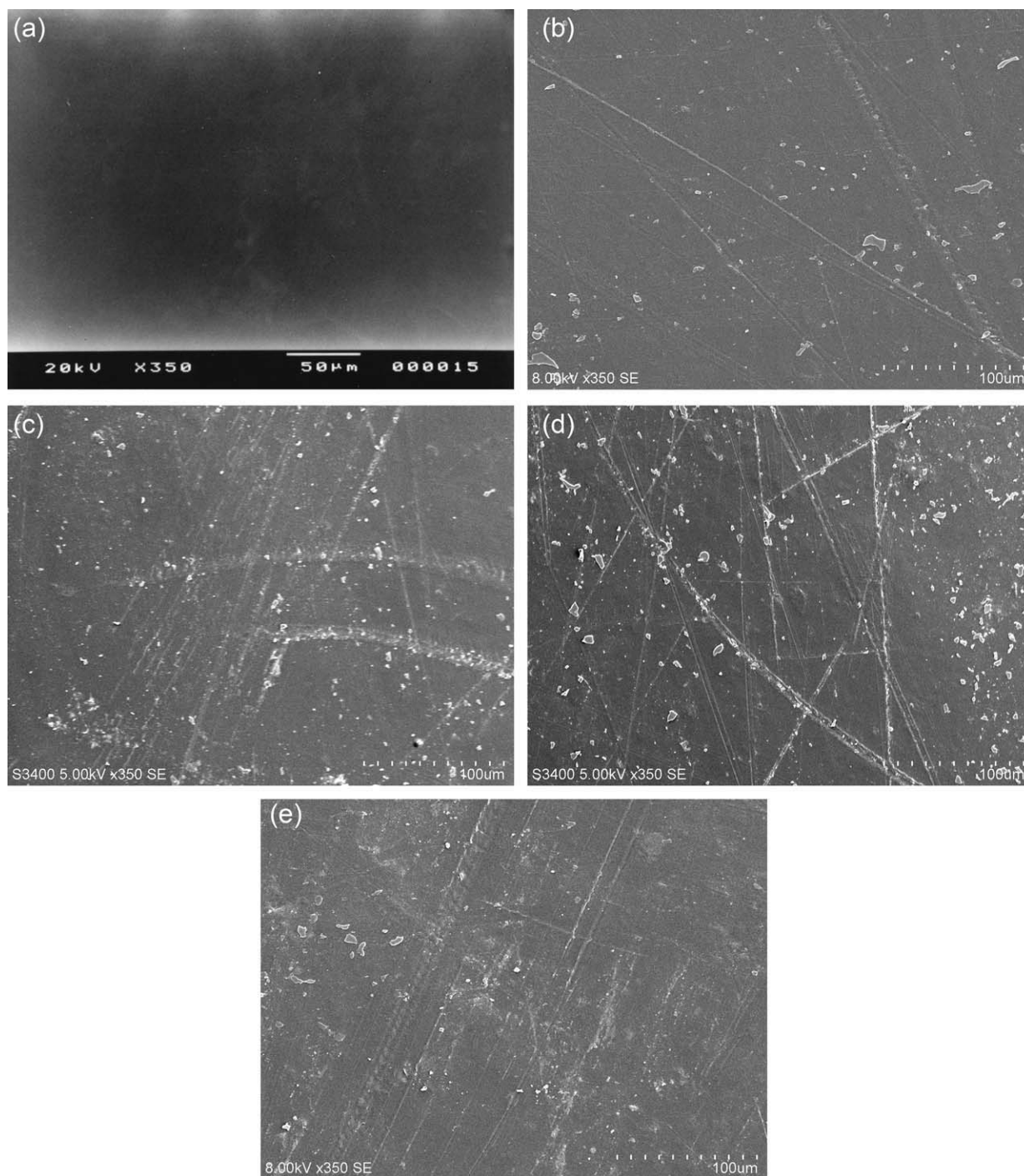


Figure 7 Scanning electron micrographs of PP-LCP Vectra B950 blends (5% LCP) in presence of varying doses of EAA: (a) PP, (b) PP+ 5%LCP, (c) PP+2%EAA+5% LCP, (d) PP+5%EAA+5% LCP, and (e) PP+7%EAA+5% LCP,.

content have shown in Figure 5. The incorporation of the modifier (2% EAA), a softer ingredient with much lower softening temperature (86–88°C) plasticizes the PP matrix marginally and thus lowers the peak melting temperature of PP-EAA blend slightly, Figure 5(b) as reported in our previous work.¹³ When LCP (5%) is incorporated into the PP-EAA blend (2% EAA), the melting point of the blend

increases. Further increase in EAA content (from 2 to 7%) at a fixed dose of LCP (5%) leads to relatively substantial enhancement in the melting point. This can only be accounted for the more and more secondary valence forces (higher extent of H-bond formation) generated between the polar groups of LCP and the acidic groups of EAA as have been reflected in FTIR studies.

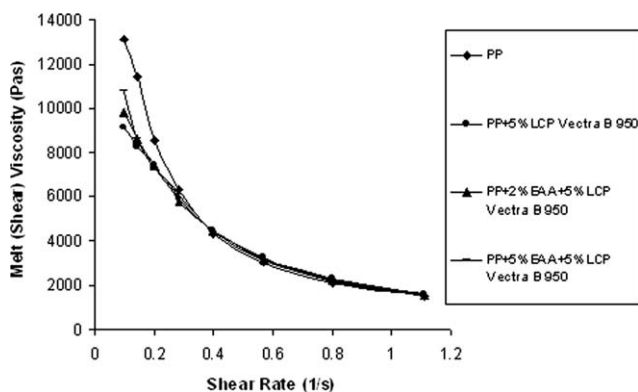


Figure 8 Plots of melt viscosity vs. shear rate of PP-LCP Vectra B950 blends (5% LCP) in presence of varying doses of EAA.

Thermogravimetric analysis (TGA)

The TGA thermograms of PP and of various blends of PP-LCP are shown in Figure 6. From the thermograms, it can be noted that the onset temperature of degradation of PP increases (260–310°C) with the incorporation of 5% LCP VectraB 950. There is a further enhancement of onset temperature of degradation of PP (340°C) on addition of 2% EAA as modifier. It indicates that both LCP & EAA enhance overall thermal stability of PP-LCP blends. Further addition of EAA (2–7%), there is no substantial change in degradation temperature, i.e., they have almost identical onset temperature of degradation, identical rate of degradation and leave behind residues having marginal differences in their contents.

MORPHOLOGY

Scanning electron microscopy (SEM)

The scanning electron micrographs of PP and its various blends with LCP as a function of EAA as modifier are shown in Figure 7. The phase boundaries in PP-LCP blends containing 5% LCP (without any EAA), appear to some extent indistinct and diffusing indicating limited mixing at the interface. In presence of 2% EAA, the SEM micrograph appears to indicate fine and uniform distribution of the LCP fibrils within the PP matrix in comparison to the PP/LCP blend without any modifier, Figure 7(b).

The increasing level of EAA (2–7%) has a profound influence on the morphology of PP-LCP blend as shown in Figure 7 (c–e). The gradual transmission of spherical droplets or small fibrillar LCP into more and more elongated thinner fibrils in the direction of extrusion brings about tremendous changes in the properties as reported earlier.¹³ The conversion of thick fibrils with lower aspect ratio into thinner fibrils with higher aspect ratios with the increasing doses of EAA content is more distinct and promi-

nent. The gradual increase in indistinctiveness at the PP-LCP interfaces is a direct consequence of influence of EAA in imparting modification at the interfaces and reducing the fragile characteristics of the various blends.

Rheology

The Figure 8 displays the influence of varying the EAA content (at a fixed level of LCP incorporation, 5%) on the melt viscosity of the blends. The isotactic PP used in the present study, as expected maintains high melt viscosities with respect to the blends in the region of shear rate under study. Vectra B950, being a copolymer of ester and amide 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. There is a marginal enhancement of the melt viscosity of PP-LCP blends with the incorporation of the EAA (2–5%). It can possibly be assumed that EAA has been involved in some sort of interaction through H-bonding with the ester, amide groups present in the LCP, and thus some stiffening action has been imparted.

CONCLUSION

This study has revealed the effect of incorporation of EAA as modifier in the PP-LCP (a fixed dose of 5% LCP used) blends. The prepared PP-LCP blends showed substantial improvement in mechanical properties like UTS, modulus, toughness, hardness, and also thermal stabilities with the incorporation of vary low doses (2–7%) of EAA. FTIR results confirmed the existence of strong interaction between EAA and LCP Vectra B 950 through intermolecular H-bonding in the blends.

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