Studies on Morphology, Mechanical, Thermal, and Dynamic Mechanical Behavior of Extrusion Blended Polypropylene and Thermotropic Liquid Crystalline Polymer in Presence of Compatibilizer

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ABSTRACT: Polypropylene was melt blended in a single screw extruder with thermo tropic Vectra B-950 liquid crystalline polymer (copolyester amide) in different proportions in presence of 2% of EAA ,ethylene-acrylic acid copolymer (based on PP) as a compatibilizer. The mechanical properties of such compatibilized blends were evaluated and compared in respect of their Young's Modulii, Ultimate tensile strength, percent elongation at break, and toughness to those of Pure PP. The Morphology was studied by using a polarizing light microscope (PLM) and Scanning electron microscope (SEM). The Thermal characterization of these blends were carried out by differential scanning calorimeter (DSC).The mechanical properties under dynamic conditions of such compatibilized blends and pure PP were studied by dynamic mechanical analyzer (DMA). Mechanical analysis (Tensile properties) of the compatibilized blends displayed improvements in Modulii and ultimate tensile strength (UTS) of PP matrix with the incorporation of 2–10% of LCP incorporation. The development of fine fibrillar morphology in the compatibilized PP/LCP blends had large influence on the mechanical properties. Differential scanning calorimeter (DSC) studies indicated no remarkable changes in the crystalline melting temperature of the blends with respect to that of pure PP. However, an increase in the softening range of the blends over that of PP was observed. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 2345–2352, 2009

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

INTRODUCTION

Main chain liquid crystalline polymers (MCLCPs) 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 which leads to a highly ordered fibrous structures and anisotropic properties. The properties of thermotropic LCPs (TLCPs) are based on their oriented structure.[1–3] The degree of orientation can be influenced by processing conditions and its environment as well.

LCP molding can exhibit a layered structure with skin and core morphology. Near the surface there is a skin layer with extensively high ordered fibers, while in the core there is less orientation and consequently less fiber 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 consists 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 while in the core the LCP phases are less oriented or in spherical form.[11,12]

The LCP content, type and processing conditions as well as the presence of compatibilizers determine the ultimate morphology.[13–15] The morphology and resultant properties of the blends are also highly dependent on the composition of the blend.

The mutual compatibility and interfacial adhesion is expected to be improved by using EAA as a compatibilizer and that was reflected in the modulus and other mechanical properties of the blends.

The ratio of melt viscosity of the polymers affects their miscibility and the mode of fiber formations.[16,17] In the solid state, blends of LCPs and

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thermoplastics can exhibit a composite fiber structure if sufficient orientation of the molten LCP phases during processing is achieved.[18,19]

In the present work ester amide type of LCP was blended with isotactic stereo regular polypropylene (PP) by a single extruder.

The physical, mechanical, and thermal properties of the blends are discussed here in relation to their morphology and rheology.

EXPERIMENTAL

Materials

The Liquid Crystalline Polymer used in Vectra B-950 produced by Ticona. It is an aromatic Copolyesteramide comprising 60 mol %, Hydroxy naphthoic acid (HNA), 20 mol %, Terephthalic acid (TA), and 20 mol % p-aminophenol (AP). The structures of HNA, TA, and AP are as follows
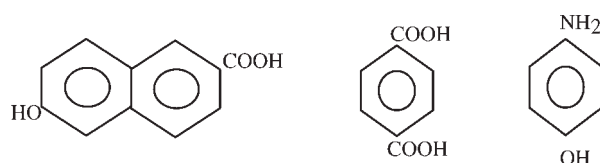
The typical properties of the LCP include: Melting point $\sim$ 280°C, tensile strength $\sim$ 165 MPa and elongation at break $\sim$ 3.0%.

The matrix polymer used was polypropylene homopolymer (Repol HO 30SG having an MFI of 3.0 and a general purpose type) 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 the MFI are 6 and 3%, respectively.

Blending

The LCP was first manually mixed with PP. The variable amounts of LCP used in the blends were 2, 5, 7, and 10% by weight (of PP), respectively. The wt % of EAA was kept constant at 2 with respect to the weight of PP for each composition of blends.

The melt blending of the materials was performed by a single screw extruder at a temperature 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 testing.

Processing

Both the blends and the Pure PP were compression molded in the form of a rectangular thin sheet in a

Moore Press (temperature 285°C and pressure, 10 tons). As similar conditions as possible were maintained for all the blends. The processing conditions were optimized by trial and error and kept constant for all the blend compositions.

Testing

Tensile properties were measured according to ASTM 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 and the toughness was determined from the stress-strain curves itself.

The differential scanning calorimeter (DSC) measurements were carried out by using DSC-apparatus from SHIMADZU (Model No. DSC-50) in an inert atmosphere of nitrogen.

The studies on dynamic mechanical behavior were carried out by dynamic mechanical analyzer (DMA 983) in presence of nitrogen atmosphere.

Mechanical properties

The mechanical properties of the various blends of PP and LCP in presence of compatibilizer have been shown graphically in Figures 1–5 where the different mechanical parameters shown at the line $X = 0$, represent the values of the EAA modified PP (i.e., without any LCP) only.

The mechanicals of only PP and its blends with LCP have already been reported in our previous work.[20]

Both, the moduli, and ultimate tensile strength of the PP matrix undergo a steady increase with increasing proportions of thermo tropic liquid crystalline polymer in presence of EAA as a compatibilizer. However, the same parameters for EAA modified PP were less than that of pure PP (without LCP). Thus, there was some plasticization effect on PP in presence of EAA.

On blending with LCP, the immediate loss in symmetry to some extent and the consequent loss in crystallinity of the PP chains (because of the incorporation of the compitibilizer 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.

Moreover, EAA is a copolymer of ethylene and acrylic acid. The acidic group in the polymer is being assumed to interact with the various functional groups present in Vectra B-950 molecules and acts as a compatibilizer in the blends of TLCP (Vectra B-950) and PP. It has been found that in presence
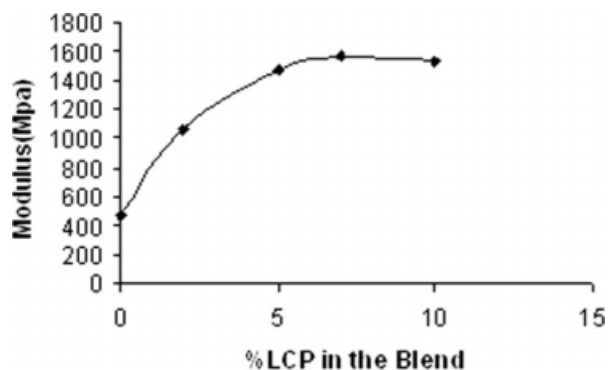
Figure 1 Variation of Modulus versus Blend Composition for PP + 2%EAA and its blends with LCP in different proportions.

of compatibilizer the modulus is much more than, that was observed with only PP and TLCP blend.[19]

During the melt blending, the LCP molecules align to very high degrees and thus form highly ordered and oriented melt phase. When the polymer melt is cooled, the orientation is retained within the blend and hence the improvements in properties.[21]

It was reported that the graft side chain liquid crystalline copolymer based upon acrylic acid functionalized polypropylene (PP-AA) acted as compatibilizer for polypropylene/Liquid crystalline polymer(LCP) polyblend and enhanced physical properties were obtained.[22]

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 absorptive forces exerted over long area of the fibrils which is responsible for the observed increases in mechanical properties. These results are very much in agreement with the findings reported for the systems based on blends of PE and LCP.[2]

It may however be noted that the initial steep rise in these two parameters with respect to Virgin PP appears to be corroborated by scanning electron microscope (SEM) and polarizing light micrographs
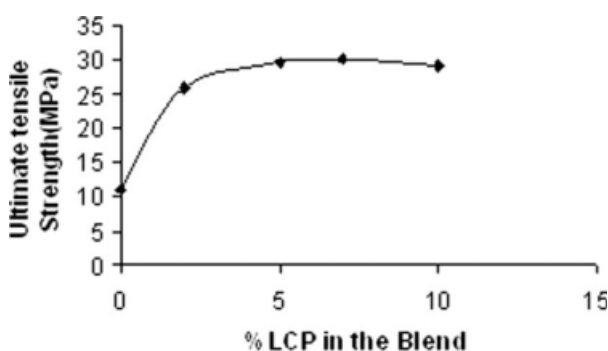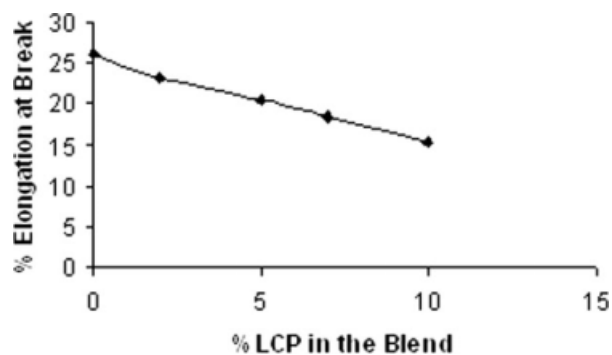

Figure 3 Variation of % Elongation at Break versus Blend composition for PP + 2%EAA and its blends with LCP in different proportions.

(PLM) (Figs. 8 and 7), where the LCP phase seems to be elongated exhibiting a tendency towards fibril formation particularly at higher doses of TLCP in presence of the compatibilizer. The aspect ratios of these fibrils are found to be much higher than those observed with PP-LCP blend without any compatibilizer.[19]

The percent elongation at break and toughness values of this compatibilized blends undergo steady decrease as expected and thus leading to a stiffer and brittle matrices. 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 Young's modulii and UTS, i.e., they exhibit a steady increase with increasing proportions of LCP (Fig. 5). 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. This may possibly be explained by the fact that the hardness being a surface property might
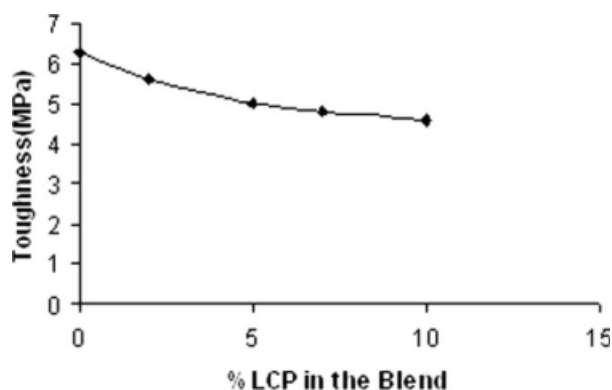

Figure 2 Variation of Ultimate Tensile Strength versus Blend Composition for PP + 2%EAA and its blends with LCP in different proportions.

Figure 4 Variation of Toughness versus Blend Composition for PP + 2%EAA and its blends with LCP in different proportions.
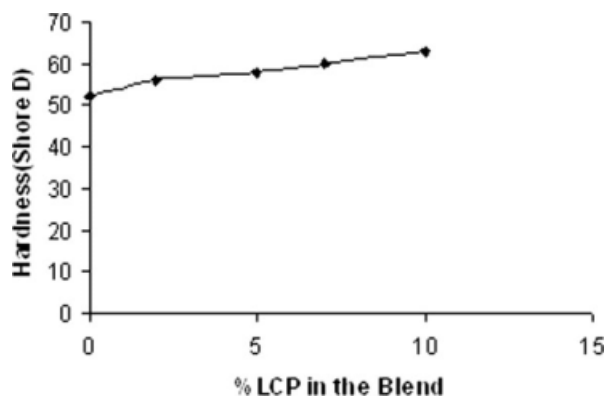
Figure 5 Variation of Hardness versus Blend Composition for PP + 2%EAA and its blends with LCP in different proportions.

be controlled by the diffusing conglomerated phases of LCP domains towards the surface.

Thermal properties: Differential scanning calorimetry

The DSC tracings of Pure PP and its various blends with LCPS in presence of EAA as a compatibilizer are depicted in (Fig. 6). Similar DSC studies with pure PP and PP-LCP in various proportions in absence of any compatibilizer were reported in our previous work.[20] It is quite interesting to note that the incorporation of EAA as a compatibilizer (to the extent of 2%) appears to have very little influence on the crystalline melting temperature of isotactic PP and its various blends with LCPs. The presence of 2% of relatively softer EAA although homogenizes quite well with PP (as evidenced from the micrographs) and hastens the incipience of PP softening towards lower temperature, the ultimate crystalline melting temperature of PP remains almost unaltered.

It may be assumed that the relatively more amorphous EAA present in the PP matrix to the extent of 2% hardly affects the T_m of the matrix polymer. The breakdown of the crystal structure of PP and the consequent reduction in T_m on its incorporation is almost immediately compensated by the high melting LCP phases which now are relatively more homogeneously mixed with LCP as can be seen from the scanning electron micrograph. The increasing LCP content is also found to have little or no influence on the crystalline melting temperature of PP matrix in the blends with higher proportions of LCP within the range of LCP content under study. However, there was a gradual, slow, and steady increase in the softening ranges of the various blends of EAA modified PP with LCP.

MORPHOLOGY

Polarizing light micrographs

The micrographs of the various PP modified with EAA and LCP blend samples have been shown pictorially (Fig. 7).

The PLM (Fig. 7), clearly indicate the long thread like structure which are typical of the texture of nematic phase.[23,24] In presence of EAA, the LCP mixes quite well with thermoplastic (PP) and gives a homogeneous mix and adhesion between the two phase are improved as is evident from the mechanical properties of the blends. The rigid rod like structure of LCP into the PP matrix in presence of EAA as a compatibilizer improves the mechanical properties of these various compatibilized blends. The blends behave as high performance composite where the LCP fibrils are randomly distributed and encapsulated by the PP resin matrix.

The fractured surfaces of the melt blended samples obtained by extrusion show an increasing tendency of the LCP fibrils to grow in thickness and to get oriented or aligned with the PP matrix with increase in LCP content in the blend. However, in all the blends there is always a statistical distribution of the LCP fibrils, the thicker ones being more predominant in blends having higher percentage of LCP. In our present study, the influence of decreasing aspect ratio (as manifested by increasing fibril diameter) on different mechanical parameters at
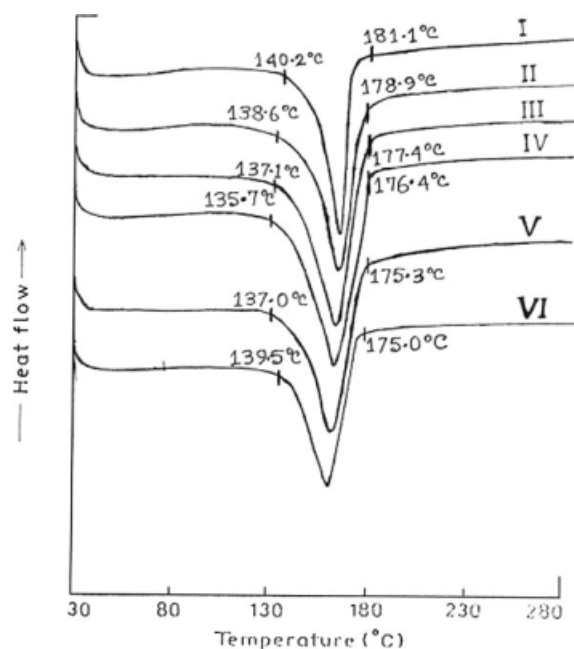

Figure 6 DSC Plots. I–Pure PP, II–PP + 2%EAA, III–PP + 2%EAA + 2% LCP, IV–PP + 2%EAA + 5% LCP, V– PP + 2%EAA + 7% LCP, VI–PP + 2%EAA + 10% LCP.
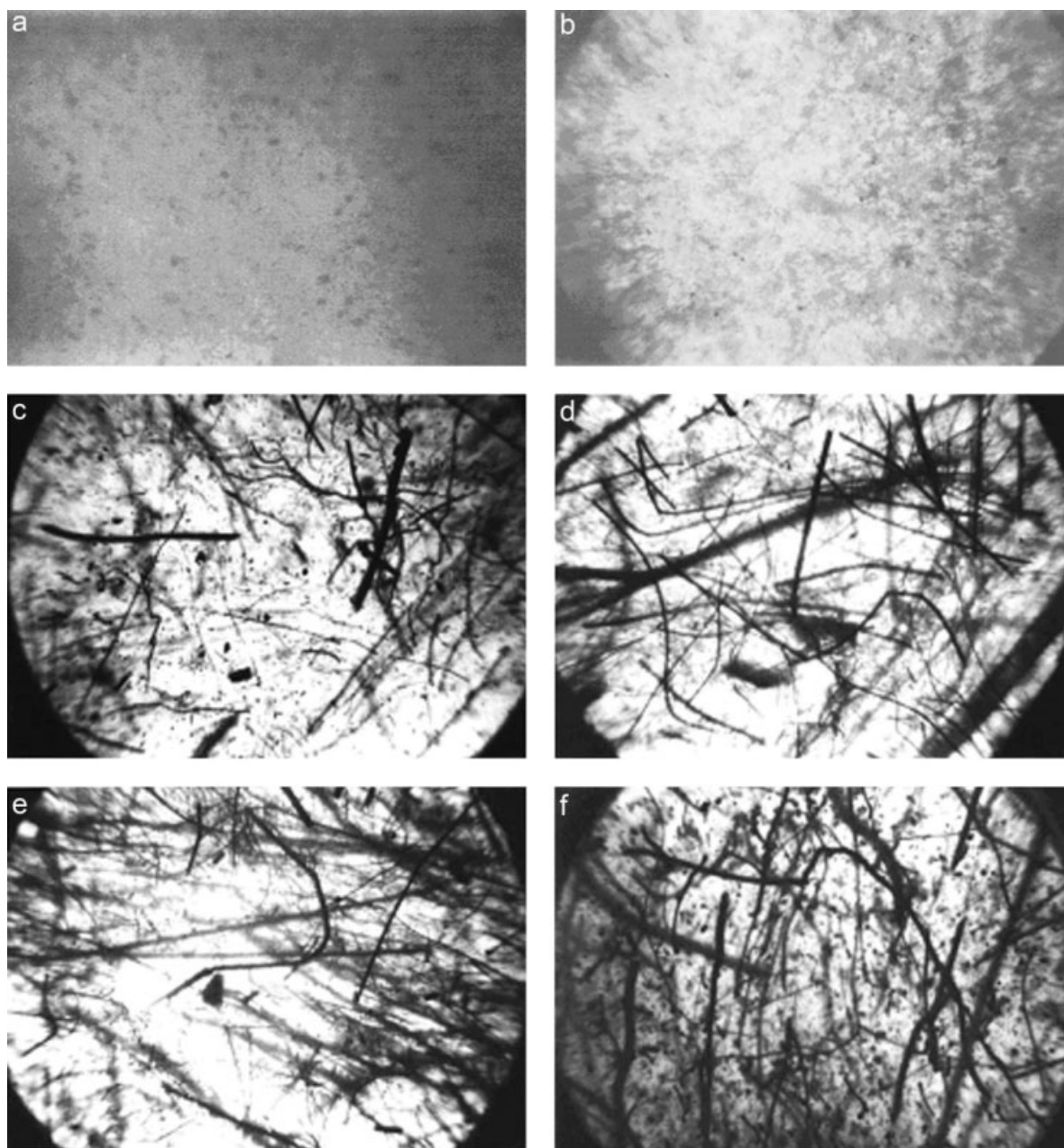
Figure 7 Polarizing Light Micrographs. (a) Pure–PP, (b) PP + 2%EAA, (c) PP + 2%EAA + 2%LCP, (d) PP + 2%EAA + 5%LCP, (e) PP + 2%EAA + 7% LCP, (f) PP + 2%EAA + 10% LCP.

higher percentage of LCP concentration has been depicted.

Over the entire range of LCP under study, the LCP phase appears to form elongated fibrils into the PP matrix in presence of EAA as compatibilizer. The LCP phase appears in the matrix in the form of small spheres or thick fibers depending on the LCP content and the orientation during processing.[7,21,25–27] 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 UTS.

Scanning electron microscope

The formation of fine fibrillar structures and the consequent enhancement in mechanical properties in the direction of flow as has been encountered in our case are highly dependent on the processing conditions employed.[28]

The SEM Micrographs (Fig. 8) appear to indicate much more fine and uniform distribution of the LCP fibrils within the PP matrix in presence of compatibilizer in comparison to the PP/LCP blend without any compatibilizer.[20] Although the irregularly
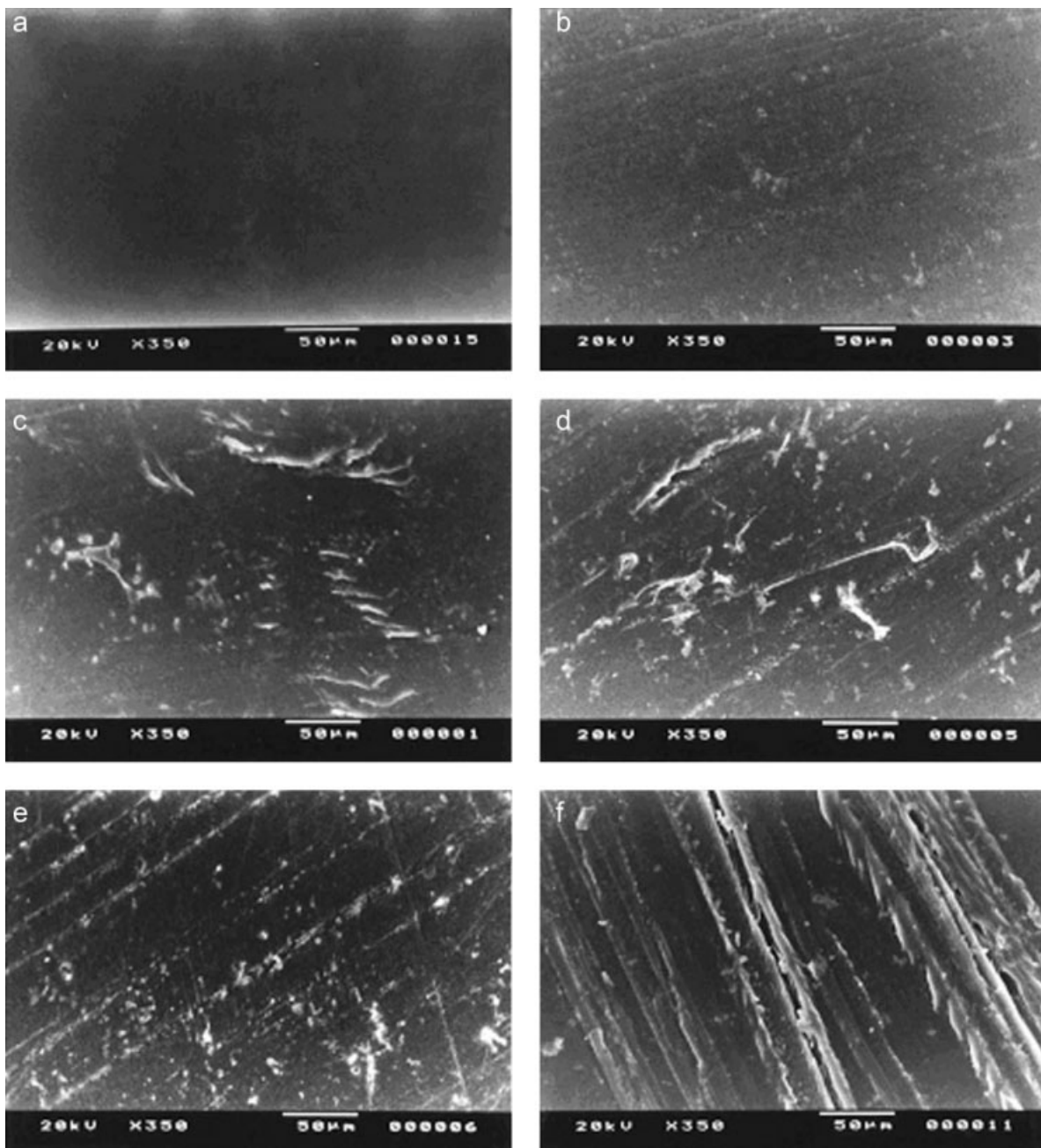
Figure 8 Scanning electron micrographs. (a) Pure PP, (b) PP + 2%EAA, (c) PP + 2%EAA + 2% LCP, (d) PP + 2%EAA + 5% LCP, (e) PP + 2%EAA + 7% LCP, (f) PP + 2%EAA + 10% LCP.

shaped discrete dispersed phases of the LCP in the form of thick fibrils with low aspect ratios are much more prevalent in systems without any compatibilizers, the addition of EAA as compatibilizer dramatically reduces the interfacial tension and the anisotropic LCP phases exhibits some what diffusing fibril-matrix interfaces.

The thin long fibrils having relatively high aspects ratios get involved in some sort of interaction over greater surface area and improve the mechanical properties. However, at the later stages of the LCP incorporation, the number of oriented fibrils increases in number with an increasing extent of orderliness and thus leading to somewhat brittle crystalline structure.

Dynamic mechanical analysis

Storage modulus

The variations of storage modulii with temperature within the range of (35–180°C) in case of PP-EAA-LCP blends and also PP-EAA blend are shown in Figure 9(a). It is found that the low temperature
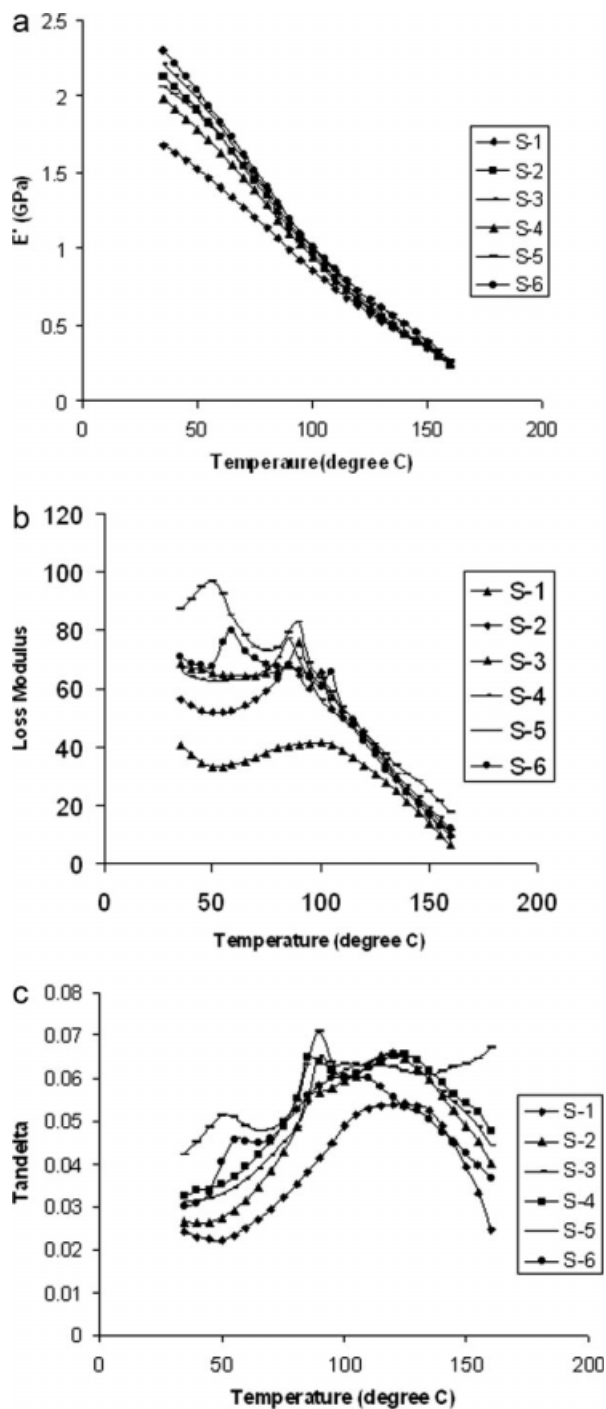
Figure 9 (a) Variation of storage modulus with temperature for Pure PP, PP + 2%EAA and its blends with LCP in different proportions. S-1 Pure PP, S-2 PP + 2%EAA, S-3 PP + 2%EAA + 2%LCP, S-4 PP + 2%EAA + 5% LCP, S-5 PP + 2%EAA + 7% LCP, S-6 PP + 2%EAA + 10% LCP. (b) Variation of Loss Modulus with temperature for Pure PP, PP + 2% EAA and its blends with LCP in different proportions. S-1 Pure PP, S-2 PP + 2%EAA, S-3 PP + 2%EAA + 2%LCP, S-4 PP + 2%EAA + 5% LCP, S-5 PP + 2%EAA + 7% LCP, S-6 PP + 2%EAA + 10% LCP. (c) Variation of Tan delta with temperature for Pure PP, PP + 2% EAA and its blends with LCP in different proportions. S-1 PurePP, S-2 PP + 2%EAA, S-3 PP + 2%EAA + 2%LCP,S-4 PP + 2%EAA + 5% LCP, S-5 PP + 2%EAA + 7% LCP, S-6 PP + 2%EAA + 10% LCP.

value (up to about 60°C) for the storage modulus progressively increases in case of LCP blends, although within narrow limits, as the percentage of LCP increases in the blends. The storage modulii of all the samples including the PP however decrease with increase in temperature.

This indicates that the extent of stored elastic energy in PP undergoes an increase in presence of LCP within a certain low temperature range. The (glassy) crystalline PP thus appears to be reinforced over this low temperature region in this way, although the reinforcing influence almost levels off in case of blends with high % of LCP incorporation under study particularly at high temperature region. The extended fibrillar morphology of the *in situ* generated LCP increases the in phase shock absorbing capacity of the blend. However, the rate of reduction of E' i.e., dE'/dt with increase in temperature is maximum in case of the blend with the highest % of LCP. In pure PP three transitions can be distinguished in the E'/T curve. The beta (β) transition or glass transition at 25.1°C for the amorphous parts of the semi crystalline PP[29] has almost merged with our starting temperature of analysis. The characteristic transition temperature appears to be shifted gradually to higher temperatures for the various blends. At the higher temperatures the alpha (α) transition for PP occurs at 87.0°C which is related to the crystalline fractions present in EAA modified PP. The corresponding temperatures for its various mixtures with LCPs' however increase with increasing doses of LCP within a very narrow range. Although the regular structure of PP breaks down more and more with the incorporation of LCP, the increasing crystalline structure of LCP helps to modify the storage modulus characteristic of PP.

Loss modulus

The effect of LCP loading on the loss modulii of EAA modified PP/LCP, EAA modified PP, and of PP itself at a constant frequency of loading are shown in Figure 9(b). Three different transitions for the out of phase energy dissipation, characteristic of these samples were recorded in this figure. The beta transition or glass transition normally observed with PP at 25.1°C[29,30] attributed to the amorphous parts of the semi crystalline PP is missing in our case as the take off temperature in our experiments was higher than the said temperature. On the higher temperature scale the alpha transition for PP at 87°C was observed and this related to the crystallites.

Here, in case of pure PP only alpha transition at 87°C was evident due to the chosen temperature range. But for modified PP (in blends with EAA), two closely spaced peaks were visible one of which occurs at a relatively lower temperature than that of

pure PP and the other resembling that of PP. EAA is more amorphous than PP. The low temperature peak possibly arises due to the fringed amorphous phase within the crystallite and the subsequent high temperature peak for the remaining crystallites of PP. It is interesting to note that the α-transition peak of the PP-EAA blend spanned over a wide range of temperature and this shows the immense compatibility of EAA and PP crystallites undergoing breakage at this temperature.

It is observed that the blends of EAA modified PP and LCP have higher loss modulus peaks which are possibly sharper than the PP-EAA blend system or even PP alone due to more and more increases in crystallinity and orientability of the fibrils of LCP incorporated. This can be well explained by SEM. As LCP does not normally mix well with thermoplastics, EAA as a compatibilizer in the present work seems to have played its role efficiently at lower doses of its incorporation. It is clear that up to 5% of LCP loading, the fibrillar structure of LCP is not so distinct but diffused where as at higher LCP loading though each fibril of LCP is assumed to be properly wetted by the EAA modified PP, the individual LCP fibril exerts its orienting influence over the PP matrix in such a manner that they appear as aggregates of blends of rigid chains and exhibits brittle character.

In case of LCP blends again two peaks were prominent but they were appreciably separated. The two separated peaks in case of LCP blend samples with higher LCP loading may be attributed to varying relaxation period of two different phases.

Tan δ

The modifying influence of comptibilizer on the damping parameters of the various EAA modified PP-LCP blends is presented in Figure 9(c). As expected the dampening properties of the EAA modified PP are better than that of PP alone. Two closely spaced peaks for PP-EAA, and for 5, 7, and 10% LCP loaded blends are indicative of pronounced energy dissipation due to better interaction in between the two components and that the mobilities of polymer chains were somehow restricted. Tan δ, the ratio of E''/E' goes through a series of maxima like that of E''; the tan δ maximum appearing at several degrees centigrade higher than those for the E'' peak.

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