Chapter - 7

Summary & Conclusion
7.0 Summary & Conclusion:

The present dissertation includes blending of polyolefins, primarily polypropylene with two different liquid crystalline polymers, one being an aromatic copolyester, Vectra A950 & the other an aromatic copolyester amide, Vectra B 950. LLDPE, another commodity thermoplastic has also been melt blended with Vectra B 950 only in different proportions as it was done in case of PP.

All these samples were then characterized with respect to their mechanical, thermal, rheological properties and an endeavour has been made to explain these properties on the basis of the morphology developed.

Keeping in mind the factor of incompatibility of the two polymers of quite different nature, the influence of EAA, a co-polymer of ethylene & acrylic acid on the ultimate performance of the PP-TLCP blends was investigated. An attempt was also made to determine the threshold dose of EAA where the properties of the above mentioned blends were optimized.

The mechanical properties such as modulus & UTS of the PP/ Vectra B 950 & PP/ Vectra A 950 whether compatibilized or not found to reach equilibrium values at around (7-8)% of the concerned LCP beyond which there was hardly any change. However the PP/ Vectra B blends always exhibited higher values than the PP/ Vectra A ones. In both the cases the blend containing 5% of LCP and around 3% of EAA showed the peak values when the compatibilizer EAA was incorporated in the said blends. Further the addition of EAA made no great impact in enhancing the modulus or UTS. Both the LCPs behaved in a similar manner in this respect. In both sets of compatibilized blends the peak values of these two mechanical parameters were reached at an early stage of LCP incorporation with respect to the pure blends of PP and LCPs.

The percent elongation at break and the toughness in particular of PP/Vectra B blend samples underwent a sharp decrease compared to the PP/Vectra A blends. The incorporation of EAA into the blends of both the varieties of LCPs made it more ductile & tougher, the extent of which was not realized to the maximum possible extent presumably because of the secondary valence interactions operating between the polar functional groups of LCPs and the polar compatibilizer EAA. The effect of H-bonding on chain stiffening and the consequent reductions in % E.B & toughness were however
more pronounced with PP/Vectra B blend samples as Vectra B at the same doses of its incorporation as with Vectra A system had much more potential sites of interactions with EAA. On comparing the properties of both the blend systems when the content of the compatibilizer was varied keeping the amount of LCP fixed it was observed that the percent elongation at break & toughness of the PP/Vectra A system were much more improved than those of PP/Vectra B system.

The impact properties of the two sets of blends were observed to follow the same pattern as was observed with toughness. The impact strength of the different PP/Vectra B blend samples however showed a slow & steady fall at the initial stages of LCP incorporation followed by a sharp reduction at the later stages while the reverse pattern of changes was exhibited by the PP/Vectra A system. The EAA modified samples however displayed similar pattern of changes in both the cases. At a fixed percent of LCP loading, for both the Vectra B 950 & Vectra A 950 system, the increasing proportions of EAA caused a greater enhancement in impact strength, slightly more in case of the Vectra A system compared to the other one. This difference in behavior can be attributed to the possibility of much lesser extent of hydrogen bonding in case of Vectra A 950 than with the Vectra B 950 system of blend, as has been mentioned earlier.

On comparing the DSC curves of both the blend systems it can be inferred that Vectra A 950, i.e. the only aromatic copolyester type LCP influences the thermal properties, the melting behavior of PP in particular remarkably much more than the Vectra B 950 system. The onset of softening ensues at lower temperature than that of either the pure PP or the PP/Vectra B 950 blends. However the melting endotherms of the various blends of PP/Vectra A 950 are much narrower and the spans over which the phenomenon of melting occurs smaller than the respective characteristics of the PP/Vectra B 950 blend systems. This reflects that the proportions and distributions of the crystalline/amorphous regions developed in the various blend systems of the PP/Vectra A 950 and PP/Vectra B 950 differ quite appreciably.

It is quite interesting to note that, after the addition of the compatibilizer, the two different LCPs impart very little differences in so far as the peak softening temperatures of the different blend systems of identical composition are concerned.
For a fixed LCP content (both Vectra B 950 and Vectra A 950) when the DSC curves of the different blend systems are considered as a function of the compatibilizer EAA content, it can be noted that the peak melting temperature of the PP/Vectra B 950 system samples undergoes an increase with increasing proportions of EAA within the range of EAA content studied. We find the same increasing trend for the PP/Vectra A 950 system up to a certain EAA concentration beyond which the further addition of EAA causes a marginal reduction in peak melting temperature.

From the TG analysis it is quite apparent that the TLCP, Vectra B 950 gives higher thermal stability to PP than the Vectra A 950, as the former delays the onset temperature of PP degradation much more than the latter. The aromatic co-polyester TLCP, i.e., the Vectra A 950 however causes the degradation, (after the onset) to occur at a much slower rate than that obtained with the blend of PP & aromatic copolyester amide TLCP Vectra B 950.

With the incorporation of 2% EAA as compatibilizer in the various blend compositions of the PP-Vectra B 950 system it can be noted that, although the blends have still higher onset temperature of degradation than both the pure PP & EAA modified PP, the influences of increasing LCP addition are somewhat reduced as the differences in the incipience of degradation differ very little. They appear to degrade at almost the same rate within themselves. The EAA modified PP/Vectra A 950 blend samples of different composition follow the similar trend with respect to their onset temperature of degradation as that of the unmodified ones. There are hardly any differences in their onset values. Although the rates of degradation of the different blend composition appear to remain unaffected they however undergo a relatively slower rate with respect to both PP & EAA modified PP. The marginal increase in thermal stability with increasing amounts of Vectra A 950 is quite apparent at higher temperatures when they exhibit higher fragments of residues & sluggish rate of degradation according to the % LCP present in the blends.

On increasing the proportions of EAA, the compatibilizer in a blend of PP/LCP (containing 5% LCP) it is revealed that in case of PP/Vectra B 950 system, the addition of EAA beyond 2% has very little influence on the overall thermal stability of the various blends, but it is obvious that the addition of Vectra B 950 up to an optimum concentration of 2% increases the thermal stability to a great extent. In
case of PP/Vectra A 950 system, the same conclusion can be drawn as the addition of more & more EAA has no impact in modifying the overall thermal stability of the PP/Vectra A 950 blends.

While considering the morphology developed in the different sets of blends of PP/Vectra A 950 & PP/Vectra B 950 it is observed that while in case of Vectra B 950, right from the beginning of its incorporation in the PP matrix there is a tendency towards fibril formation, the aspect ratio of which decreases continually with increasing LCP content. PP/Vectra A system however demonstrates a lesser tendency towards such fibril formation & further more the aspect ratio of it hardly changes as the Vectra A content increases within the range under study. However in such cases the number of phase separated fibrils per unit area of the matrix increases.

With the incorporation of 2% EAA as compatibilizer in the PP matrix we can see dramatic changes in the morphology. The formation of short fibril is initiated at the initial stages of Vectra B incorporation and the morphology is governed by somewhat random distribution of short fibrils accompanied by irregularly shaped and sized droplets of LCPs. However at higher doses of Vectra B 950 some oriented long fibrils having relatively higher aspect ratio pervade the matrix.

On the contrary, somewhat reverse picture is observed with EAA compatibilized Vectra A samples, while being compared to the non-modified PP/Vectra A 950 samples. Thin and long fibrils with high aspect ratios are formed almost from initial stages of blending of LCPs, the concentration of which goes through a maximum at around 7% of Vectra A 950 and then starts diminishing.

When the proportion of EAA is varied in a blend of PP/ Vectra B 950 LCP (5%) having a constant quantity of LCP, we find the morphology to be dominated by spherical droplets of the LCP phase instead of a fibrillar morpholology as encountered in a PP/Vectra B sample without any compatibilizer. The fibrils appear to be broken and discontinuous. Furthermore with increasing proportion of EAA, the droplets seem to be gradually dissolved and the distinct sharp interfaces between the fibrils and the matrix is gradually replaced by the indistinct and diffused interfaces between either the remaining fibrils or the droplets and the continuous phase of PP matrix. A more of less identical morphology is observed with PP/Vectra A (5%) LCP containing various proportions of EAA.
Both the virgin LCPs, namely Vectra B 950 and Vectra A 950 when blended with isotactic PP in various proportions reduce the melt viscosity of PP remarkably. The aromatic copolyester amide Vectra B 950 is found to be much more efficient in reducing the viscosity compared to vectra A 950.

In case of EAA modified LCPs where the EAA content has been kept constant at 2% it is noted that with the incorporation of 2% of Vectra A 950, the melt viscosity is reduced quite appreciably even below that of EAA modified PP in spite of the stiffening action due to the H-bond formation between the LCP and the EAA modifier. However on further addition of LCP (5%) Vectra A 950 the viscosity increases over that of the blend containing 2% LCP but still lies below the viscosity of EAA modified PP. With Vectra B 950, the blend of 2% LCP with EAA modified PP the initial melt viscosity almost closely matches that of the PP because of extensive H-bonding between EAA and the ester/amide groups of LCP. As the EAA content is fixed, further incorporation of Vectra B 950 experiences lesser extent of H-bond and the melt viscosity falls.

When the compatibilizer (EAA) content is varied with a particular PP/Vectra B (5%) blend, there are hardly any differences in melt viscosities between the various blend compositions, and all of them exhibit melt viscosities lower than the PP itself. In case of the blends with Vectra A 950, the increasing proportions of EAA lead to more and more decreasing melt viscosities.

The influence of Vectra B 950 in modifying the properties of LLDPE has been studied as an isolated piece of work after being inspired to see the reinforcing action of the said LCP in crystalline isotactic PP. In this case also a phase separated composite is observed. Vectra B improves the mechanicals like modulus, UTS and hardness etc up to a level of 6-7% of its incorporation in the blend beyond which either the mechanicals suffer deterioration or remain static in equilibrium. Consequently the % EB, toughness and izod impact strength undergo decreases with increasing percentages of Vectra B 950.

From the DSC tracings it is revealed that although the peak softening or melting temperature of LLDPE almost remains constant even on increasing the LCP content in the blend, both the onset temperature of melting and the energy required for melting the crystallites developed in blends of different composition undergo changes.
The LCP change by virtue of their orienting and decreasing influence develop crystallite of equal sizes which melt vary sharply and cause melting endotherms narrower with increasing LLDP contents. The TGA thermogram exhibits increasing thermal stability of the blends with increasing Vectra B content as expected. The melt viscosity on the other hand decreases as the proportion of Vectra B 950 increases.

It can thus be concluded that,

1. Both the thermotropic liquid crystalline polymers (TLCPs) namely Vectra B 950 and Vectra A 950 irrespective of their chemical nature are capable of reinforcing relatively weaker polylefins like PP and LLDPE upto an optimum level of their incorporation.

2. Properties based on ductility, e.g. toughness, impact strength etc. however undergo substantial decreases.

3. The presence of a suitable compatibilizer EAA in the present case improves the degree of compatibility of both the types of LCPs with the polyolefins.

4. The compatibilizer helps to improve mechanicals further over those obtained earlier in absence of it and the peak values of these mechanicals are achieved at lower doses of LCP incorporation.

5. The compatibilizer being relatively elastomeric and soft in nature the ductility based properties are affected less and marginal improvement is observed in all of them.

6. Both the LCPs contain functional groups which are capable of interacting with the acidic part of the compatibilizer by way of hydrogen bond formation, which causes chain stiffening to some extent and thus prevent the toughening action of EAA from being exploited to the fullest possible extent.
7. The possibility of H-bond formation is more with Vectra B 950 as it contains both ester and amide functional groups in contrast to Vectra A 950 which bears only the ester groups. Thus Vectra B 950 is more efficient in its reinforcement action.

8. The LCPs, both Vectra A and Vectra B 950 increase the thermal stability of PP, Vectra B, 950 being more effective than Vectra A 950 in this respect, as it increases both the onset temperature of degradation and the percent residue left within the range of temperature studied. The rate of degradation in case of composites with Vectra A 950 is relatively slower than that of Vectra B 950. The thermal stability of LLDPE is also increased by Vectra B, 950.

9. The incorporation of LCP, both Vectra A 950 and B 950 in PP reduces the melt viscosity and hence facilitates processing.

10. Irrespective of the presence or absence of compatibilizer phase separated blends always appear in both cases of TLCPs.