Development of Nanofibrous Morphology in LDPE/LLDPE/PP Blends and Its Effect on Mechanical Properties of Blend Films

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ABSTRACT: Nanofibrous morphology has been observed in ternary blends of low density polyethylene (LDPE), linear low density polyethylene (LLDPE), and isotactic polypropylene (PP) when these were melt-extruded via slit die followed by hot stretching. The morphology was dependent on the concentration of the component polymers in ternary blend LDPE/LLDPE/PP. The films were characterized by wide angle X-ray diffraction (XRD), scanning electron microscopy (SEM), and testing of mechanical properties. The XRD patterns reveal that the β phase of PP is obtained in the as-stretched nanofibrillar composites, whose concentration decreases with the increase of LLDPE concentration. The presence of PP nanofibrils shows significant nucleation ability for crystallization of LDPE/LLDPE blend. The SEM observations of etched samples show an isotropic blend of LDPE and LLDPE reinforced with more or less randomly distributed and well-defined nanofibrils of PP, which were generated *in situ*. The tensile modulus and strength of LDPE/LLDPE/PP blends were significantly enhanced in the machine direction than in the transverse direction with increasing LLDPE concentration. The ultimate elongation increased with increasing LLDPE concentration, and there was a critical LLDPE concentration above which it increased considerably. There was a dramatic increase in the falling dart impact strength for films obtained by blow extrusion of these blends. These impressive mechanical properties of extruded samples can be explained on the basis of the formation of PP nanofibrils with high aspect ratio (at least 10), which imparted reinforcement to the LDPE/LLDPE blend. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 4005–4012, 2008

Key words: ternary blends; nanofibrous morphology; polypropylene; low density polyethylene; linear low density polyethylene; mechanical properties; melt-extruded films

INTRODUCTION

Blending and alloying of structurally different polymers offers an opportunity to convert waste plastics into "new" polymeric materials with specific applications. In recent years, there has been a great deal of commercial interest in blends based on polyolefins[1–2] due to several reasons: improvement of processability for certain grades, multilayer films with high barrier properties, recycling of these materials, etc. It is known that development of structure and morphology of the blends depends on the composition, compatibility of the two components, processing parameters, etc.[3] The study of blends in which a component can crystallize is complex because the amorphous component influences the crystallization thermodynamics and kinetics of the other component. Blends in which both components can crystallize are even more complex because the phase separation and crystallization processes can occur simultaneously and/or in competition. Few articles have been published about polyethylene and polypropylene blends, wherein there is a strong influence of one of the components on the crystalline structure of the other.[4] A number of studies are also available on the thermal and mechanical properties of PP blended with polyethylene.[5–7]

It has been long established that the morphology of the dispersed phase in a polymer matrix composite has profound effect on the mechanical properties.[8,9] For example, the fibrous or flaky morphology with high aspect ratio leads to composites having remarkably high stiffness. However, externally adding materials such as carbon, glass fibers, mica, wollastonite, etc. may reduce processability. Therefore, for the aforementioned reasons, extrusion of an immiscible polymer pair in which the dispersed phase forms fibers *in situ* is a practical method to improve the mechanical properties of existing polymers.[10] A typical example is the so-called microfibrillar self-reinforced composite (MFC), which is fabricated by

Material	Supplier	Grade	Melt flow index (g/10 min)	Density (g/cm^3)	T_m (°C) (Melting range)	T_c (°C) (Crystallization temperature)
Low density polyethylene (LDPE)	IPCL[a], India	Indothene (1005FY20)	0.5[b]	0.920	105–110	90
Linear low density polyethylene (LLDPE)	IPCL[a], India	Indothene-LL (20FA010)	1.0[a]	0.920	118–121	104
Isotactic polypropylene (PP)	IPCL[a], India	Koylene (SM100N)	10.0[c]	0.9	165–175	119

[a] IPCL: Indian Petrochemicals, Baroda, India.
[b] 190°C/2.16 Kg.
[c] 200°C/2.16 Kg.

extrusion and subsequent cold or hot drawing of an incompatible polymer pair. This type of material was originally manufactured by the following three processing steps:[11–13] (a) melt-blending of the starting neat polymers and extrusion, (b) cold drawing of the blend, and (c) subsequent annealing of the drawn blend at constant strain and at $T_1 < T < T_2$, where T_1 and T_2 are the melting temperatures of the two components, respectively. The *in situ* microfibrillar blend provides a promising route to enhance the properties of general-purpose polymer-based blends.[14–16] However, the ternary blends have not been studied before for generation of such morphology.

Polyethylene (PE) and isotactic polypropylene (PP) are widely used general-purpose polymers in many fields, especially in packaging and automotive applications.[17–23] The blends of LDPE and LLDPE or HDPE for multilayer packaging have been well established.[24–26] In the present study, the ternary blends, LDPE/LLDPE/PP, have been investigated for the structure development and morphology, and their effect on the mechanical properties of the materials obtained has been examined.

EXPERIMENTAL

Materials

The LDPE, LLDPE, and PP used in this study were commercial grade polymers, and their characteristics properties as provided by the suppliers are listed in Table I. The LDPE grade (Indothene 1005FY20) for liquid packaging applications was used in this study. Film extrusion grade LLDPE (Indothene-LL 20FA010) was used to make a blend with LDPE and PP. The clear extrusion grade PP (Koylene SM100N) was used as the third component in the ternary blend LDPE/LLDPE/PP. All the materials were dried at 60–70°C for at least 6–8 h in an oven before being compounded. No further additives/compatibilizers were used during processing.

Processing of LDPE/LLDPE/PP blends and film preparation

The LDPE, LLDPE, and PP granules were dry-mixed in a tumble jar with the following weight ratios for LD/LLD/PP: 90/00/10, 72/18/10, 63/27/10, 54/36/10, 45/45/10, 36/54/10, 27/63/10, 18/72/10, 00/90/10, respectively. The processing parameters used for the preparation of films by extrusion are explained as follows. These resins for films were made from the melt-blending of LDPE and LLDPE at a fixed amount of PP (10 wt %) in a twin-screw extruder. This melt-mixed blend was then extruded through a slit extrusion die with 50-mm width and 1.0-mm thickness using Haake tape/film extruder (Model PolyLab 4). The temperatures from hopper to die were 150, 170, 190, and 210°C, respectively, and the rotation of the screw was maintained at 40 rpm. The extrudate was hot-stretched by a take-up device with two pinching rolls to facilitate the formation of nanofibrils. The film thickness was controlled to be 80 μm. The blend films were also processed by blow extrusion using a laboratory scale plant with the parameters mentioned in Table II.

Characterization of structure

The extruded films were characterized by using X-ray diffraction (XRD) technique. XRD measurements were

TABLE II
Processing Parameters in Blown Films Extrusion of
LDPE/LLDPE/PP Ternary Blend

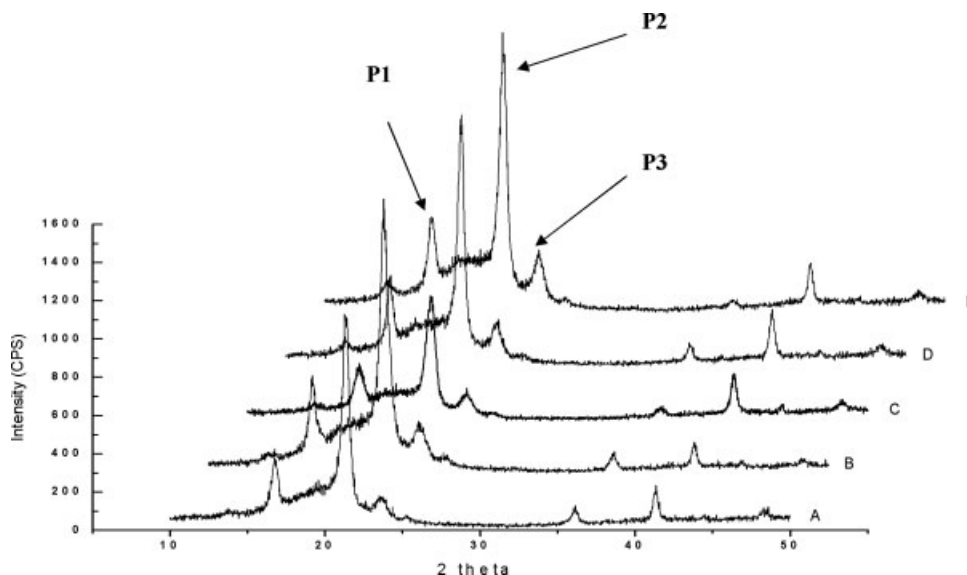| Processing parameter	Value
Screw diameter (mm)	30 mm
Length to diameter ratio for screw	25 : 1
Screw speed (rpm)	40
Extrusion pressure (bar)	5
Blow up ratio	2.5
Extrusion temperature profiles from the feed zone to the die in steps of 10°C	180–210°C

Figure 1 XRD Scans of the LDPE/LLDPE/PP ternary blends at different compositions. (A) LD/LLD/PP (90/00/10), (B) LD/LLD/PP (63/27/10), (C) LD/LLD/PP (45/45/10), (D) LD/LLD/PP (27/63/10), (E) LD/LLD/PP (00/90/10).

carried out on a Phillips diffractometer (CuKα radiation with β-Ni filter, $\lambda = 1.542$ Å) at room temperature. The diffractograms were scanned in a 2θ range of $10\text{–}50°$ at a rate of $4°/\text{min}$. To study crystalline content and phase, the samples were also characterized by differential scanning calorimeter (DSC, Mettler 821E) under nitrogen atmosphere, between 0 and 200°C, at a heating rate of 10°C/min.

To reveal the microstructure of blends, these were subjected to solvent vapor etching process using xylene. Samples were exposed to xylene vapors for around 4 h at 60–70°C. This type of treatment preferentially etches the less crystalline low-melting-phase LDPE/LLDPE than the crystalline high-melting PP, which leads to bringing up these domains and increasing differentiation in observation. After etching, samples were scanned under scanning electron microscopy. The specimens for morphological observation included the blends of LDPE, LLDPE, and PP at various weight ratios. Before observation, the samples were coated with gold in a vacuum chamber to make them conductive. The morphology was observed by a JEOL JSM-5900LV scanning electron microscope (SEM).

Measurement of properties

The samples were cut from the extruded films in machine and transverse direction and used for mechanical characterization. The tensile properties of the films were measured according to ASTM D882 with on Instron 4204 (INSTRON Series IX Automated Materials Tester: Version 8.30.00) at room temperature. The specimens having dimensions of 15-mm width and 150-mm length were used and the data was recorded at a crosshead speed of 50 mm/min. All specimens were conditioned at room temperature (25°C) for at least 24 h. Five samples were tested, and the average values were reported for each composition. The falling dart impact strength was measured according to ASTM D1709 (Type A). At least four specimens were tested for each composition, and average values have been reported.

RESULTS AND DISCUSSION

The development of various morphological features and also the overall crystallinity in the blends depend on composition, processing conditions, etc. In a blend containing both the components having crystallizing tendency, it is essential to determine the effect of the third component on the crystallinity of the blend at all compositions. This is clearly evidenced in the present studies on LDPE/LLDPE blends containing additional component, i.e., PP, which apparently acts as a nucleating agent. Figure 1 shows the XRD scans of the films extruded using blown film process from the ternary blend of LDPE/LLDPE/PP containing different concentrations of LLDPE with fixed concentration (10%) of PP. Curves A, B, C, D, and E represent the LLDPE content ranging from 0, 27, 45, 63, and 90 wt %, respectively. Other compositions were also studied but the XRD scans are not included in the figure for better clarity. From these scans, it is noticed that two major peaks of PE and two smaller peaks of PP (α-phase) are mainly present in the 2θ range of 10°–30°. The major peaks have been designated as P1, P2, and P3, where P1 and P3 are for PP (α-phase) and P2 for major reflection 110 of PE. The difference occurs in the rel-
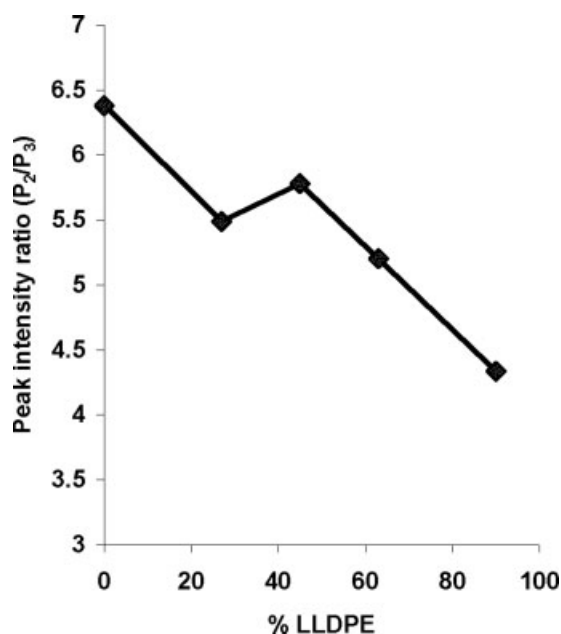
Figure 2 Change in the relative peak intensity for the P_2 and P_3 in the XRD scans of the ternary blends with LLDPE concentration. PP concentration was 10% in all cases.

ative intensities of these peaks with composition, especially the intensity of peak 2 (110 reflection). However, there is no uniform increase in these intensities, since these depend on the relative crystalline growth induced in each component. Figure 2 shows the intensity ratio of peak 2 with respect to peak 3 for different concentrations of LLDPE. It is interesting to note that in the ternary blend, the melting point of PP is the highest, and its crystallization temperature is also much higher than that of the other components (see Table I). Hence, as the melt cools during film processing, PP would crystallize first and become a solid dispersed phase in the molten LDPE/LLDPE blend, which would subsequently crystallize around it. Hence, it is the influence of PP present in the LDPE/LLDPE blend, which has been observed in the present studies. Other authors have studied earlier, the influence of addition of HDPE, LDPE, etc. to the PP and its crystallization behavior, and many have reported contradictory findings.[27–31] In the present findings, concentration of PP was much below 20%, and hence it is unlikely that it will form a continuous phase or it will get nucleated by the polyethylene phase. There is another interesting feature observed from Figure 2, i.e., the peak intensity ratio (P_2/P_3) shows a decreasing trend with the increase of LLDPE content but at certain composition (45–53% of LLDPE), there is a slight increase of P2/P3 seen above the normal trend. This indicates that the crystallization in these ternary blends is governed by the composition, and each component may influence crystallinity of the

other. Figure 3 shows the variation of crystallinity as a function of LLDPE concentration determined from the XRD scans. The degree of crystallinity was estimated by measuring the area under the all the crystalline peaks and overall amorphous region in the XRD scans in the same manner as reported elsewhere.[32–34] It is observed that the crystallinity is much higher in the presence of 10% of PP than the original binary blend, and the difference increases for higher LLDPE content above 60%. Since LDPE has low crystallinity, this enhancement of crystallinity value must originate from preferential nucleation of LLDPE on the surface of PP, which was maintained at 10%. The DSC thermograms (first heating cycle) of these ternary blend films are shown in Figure 4. It is interesting to observe that as the concentration of PP is increased, there are not only multiple melting peaks observed in the region of 150–160°C but also the melting endotherm (123°C) of LLDPE becomes more intense and sharp. This suggests that PP is crystallized in two crystalline forms (α and β), and also LLDPE has higher crystallinity when PP is present in the LDPE/LLDPE blends. These are in agreement with the findings from XRD, i.e., the crystallinity in these blends is affected by the presence of PP. Further, PP is found to crystallize in two phases, which is in keeping with the earlier reports that PP when subjected to shear deformation and orientation during crystallization can exist in two phases.[5] Figure 5 shows the SEM micrographs, recorded at 25K× magnification, of these ternary blend films at different compositions: (A), (B), and (C)
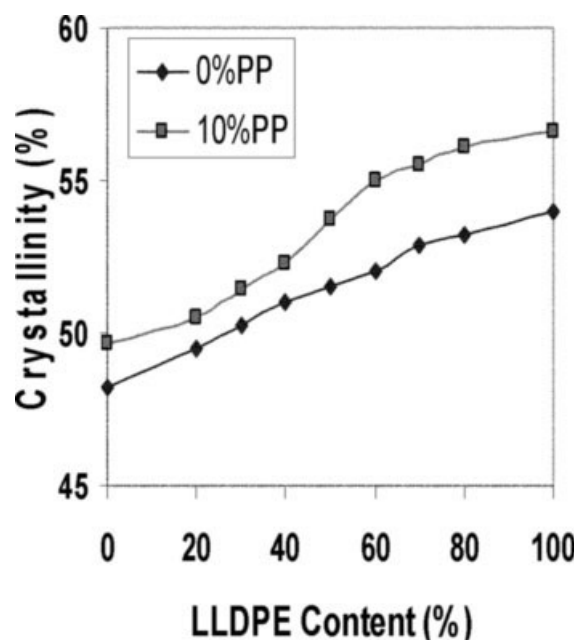

Figure 3 Variation of crystallinity in the LDPE/LLDPE/PP ternary blends with LLDPE concentration at fixed PP content (10%) compared to original (0% PP).
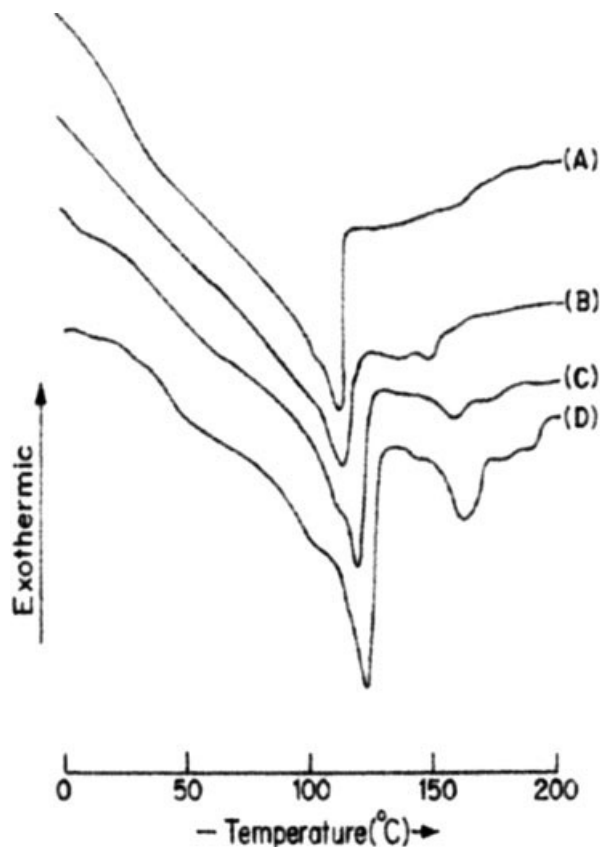
Figure 4 DSC first heating scans of the ternary blend films of LDPE/LLDPE/PP with varying concentrations of PP at fixed LDPE/LLDPE composition of 20/80. (A) PP = 0 wt %, (B) PP = 5 wt %, (C) PP = 10 wt %, (D) PP = 15 wt %.

corresponding to films containing LLDPE concentration of 56, 63, and 72 wt %, respectively, at fixed weight ratio of PP (10 wt %). In all cases, *in situ* generated nanofibrillar morphology is clearly noticed. When the concentration of LLDPE was increased from 56 to 72 wt %, the shape of the dispersed phase (PP) underwent significant changes: at low concentration of LLDPE (56 wt %), the dispersed PP phase is rod-like particles with a low aspect ratio while at high concentration of LLDPE, the PP particles are almost deformed into nanofibrils of length equal to 300 nm and width equal to 30 nm [see Fig. 5(C) with scale bar of 300 nm]. The smallest size which could be detected at higher magnification (35K×) was 5 nm, but because these micrographs could not give good quality prints, these have not been included here. The blends with LLDPE (56 wt %) addition have shorter fibrils, because the LLDPE forms a thin shell around the PP spheres and does not allow their coalescence. Thus, these ternary blends exhibit *in situ* fiber formation of PP dispersed phase, which goes to nanofibrillar stage at higher concentration of LLDPE. Other authors who studied the LCP/thermoplastics *in situ* composite also found that under same process-
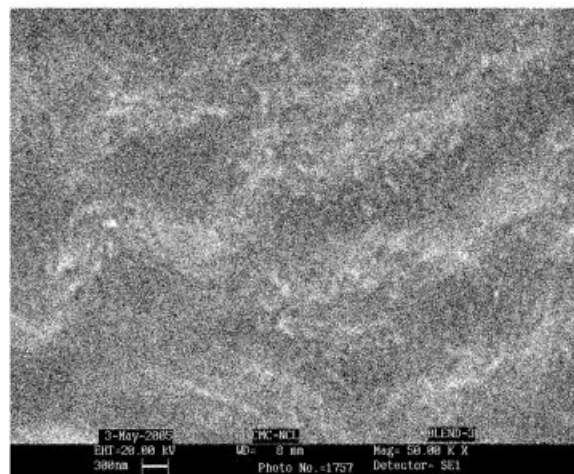
ing parameters there is a minimum concentration below which the droplet–fiber transition is difficult to take place.[35,36]
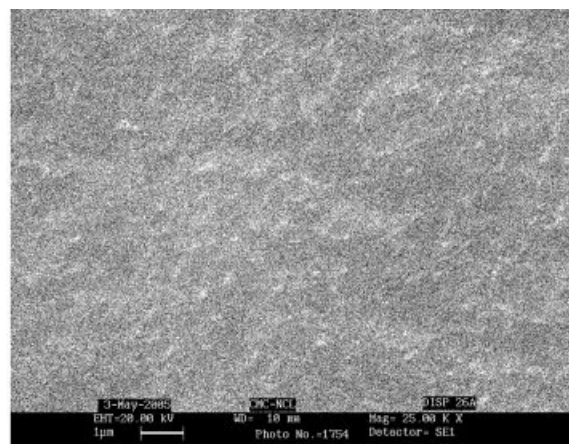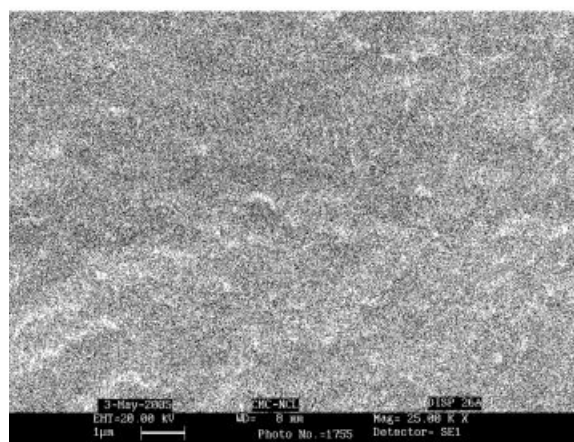
Figure 5 SEM micrograph of the LDPE/LLDPE/PP ternary blends at different weight ratios. (A) LDPE/LLDPE/PP (34/56/10), (B) LDPE/LLDPE/PP (27/63/10), (C) LDPE/LLDPE/PP (18/72/10). SEM taken after solvent vapor etching.
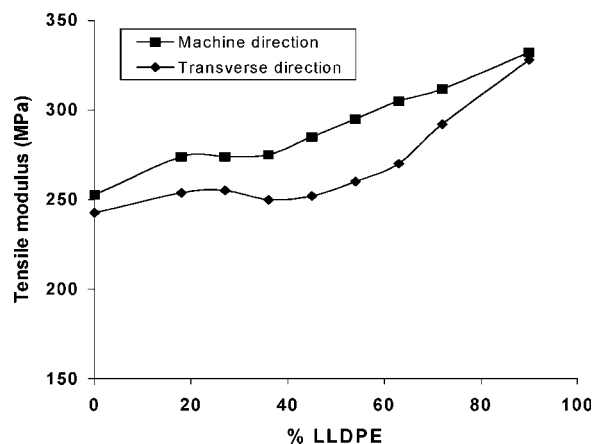
Figure 6 Tensile modulus of the ternary blends of LDPE/LLDPE/PP at fixed concentration of PP (10%) and varying percentage of LLDPE.

To study the effect of these morphological features on the mechanical properties, the films were tested for tensile, elongation, and falling dart impact measurements. The tensile strength, tensile modulus, and elongation at break as a function of LLDPE concentration are shown in Figures 6–8, respectively. Significant increases in tensile modulus and tensile strength are observed with increasing LLDPE content, while above the LLDPE content of 45%, the tensile modulus and tensile strength were considerably increased. This can be associated with the corresponding increase in the overall crystallinity observed in these blends. On the other hand, the elongation at break of these *in situ* fibrous composites, as shown in Figure 8, shows increasing trend with the LLDPE content initially, but remains same in the mid region and again increases at high LLDPE content. This trend is not in keeping with the expectations from crystallinity, which is found to increase at such compositions and would lead to decrease in the elongation/flexibility.

Most interesting features of the films made from these ternary blends were observed in their falling dart impact properties. In Figure 9(A), the impact strengths of the films of these blends are shown with the increase of LLDPE content at same PP content (10%), and Figure 9(B) indicates the dart impact values of the ternary blend films made by lab-scale blown film extruder, which have biaxial orientation with blow ratio of 2.5 as a function of PP content at same LDPE/LLDPE concentration of 20/80, respectively. The tremendous increase in the impact strength is seen in these blends, which is unusual for LDPE/LLDPE films. These findings can be explained only on the basis of reinforcing effects of the PP fibers generated *in situ* during processing. There appears to be an optimum composition at which all the mechanical properties are maximum.
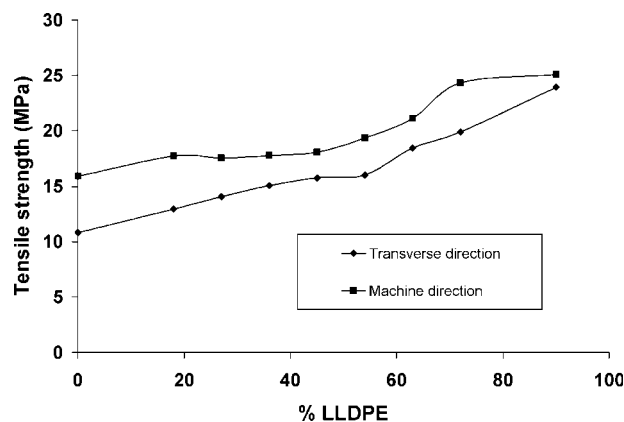
Figure 7 Tensile strength of the ternary blends of LDPE/LLDPE/PP at fixed concentration of PP (10%) and varying percentage of LLDPE.

The phenomenon of self reinforcement has been observed in thermoplastic/LCP-based composites,[37–40] where *in situ* fiber formation has been reported. Similar phenomenon may be present in the ternary blends of LDPE/LLDPE/PP wherein the PP fibers having much higher modulus than the LDPE/LLDPE can give the reinforcement. Since there is no particular orientation of these fibers in the films made from these blends, there is overlap of the fibers giving crisscross effect, similar to cross-ply composites.[41] This can lead to increase in the strength, modulus as well as impact strength of the product. Thus, fibrillar structure is a key step in achieving reinforcement. However, the generation of the microfibrils or nanofibrils is a complex rheological as well as thermal process, in which the dispersed phase is first deformed into fibers under an appropriate flow field and then frozen into the solid state before it could relax back to the spherical form or into larger particles. Hence, it is necessary to optimize proper processing conditions and composition of the blend during processing to obtain *in situ* composite with different micro or nanofibrillar struc-
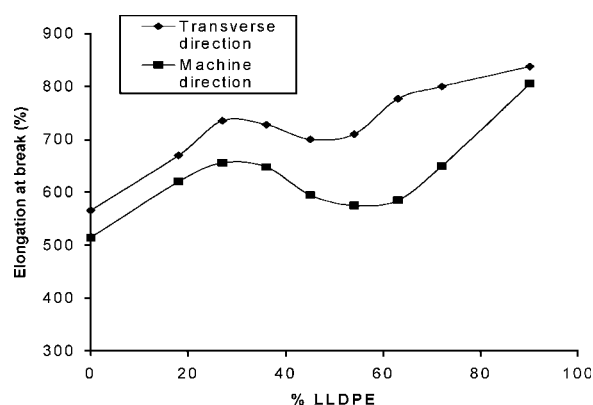

Figure 8 Variation of elongation at break with LLDPE content for the ternary blends of LDPE/LLDPE/PP at fixed concentration of PP (10%).
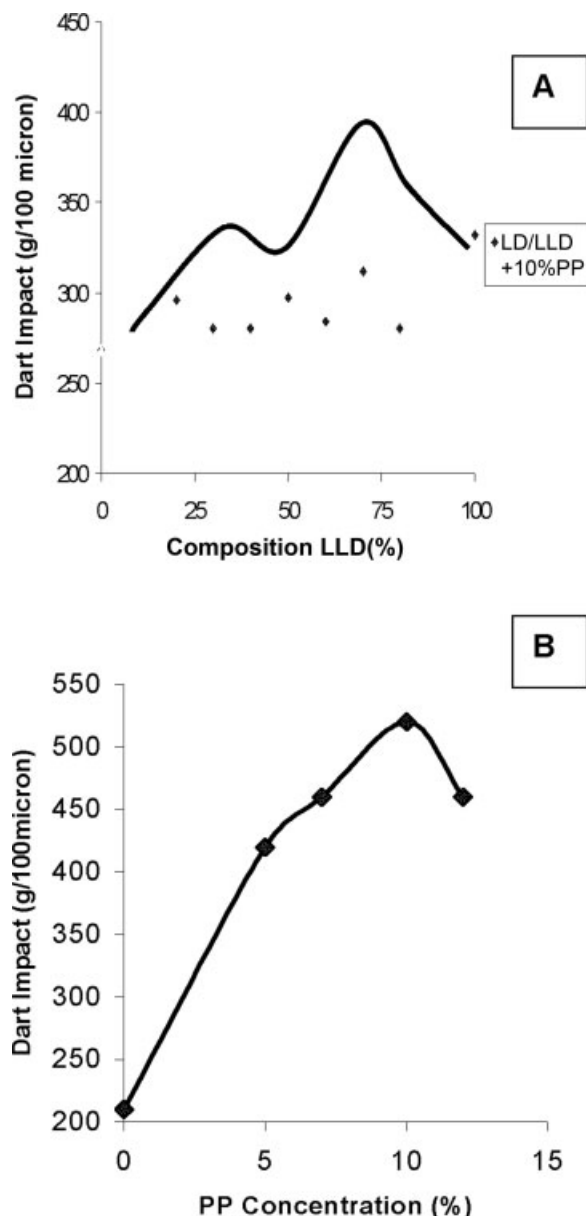
Figure 9 Falling dart impact strength of the ternary blends of LDPE/LLDPE/PP at (A) fixed concentration of PP (10%) and varying concentration of LLDPE made from slit die. (B) Films with different concentration of PP at fixed LDPE/LLDPE composition of 20/80 made from lab-scale blown film extruder with blow up ratio of 2.5.

tures, giving large improvements in the properties using commonly available materials. Further studies are underway to investigate melt flow behavior and structure development of these ternary blends with a whole range of compositions with various grades of polymers having different melt flow index values. These results being much more exhaustive will be presented in later publications.

CONCLUSION

It has been shown that by processing the ternary blends of LDPE/LLDPE/PP, *in situ* nanofibrillar

morphology can be generated, which has been confirmed from WAXRD and SEM observations. These show high level of orientation and nanofibrillar morphology with a small diameter of the fibrils (10–5 nm). The effect of the LLDPE concentration upon the distribution and the size of the dispersed PP phase, as well as on fibrils has been brought out. The tensile modulus and strength of LDPE/LLDPE/PP blends were significantly enhanced with increasing LLDPE concentration in machine as well as transverse directions, indicating that the *in situ* generated nanofibrils of PP have good reinforcement in the LDPE/LLDPE blend. Ultimate elongation increased with increasing LLDPE concentration in both the directions because of reinforcement and higher degree of downgauging of the films extruded from the LDPE/LLDPE/PP blend.

References

1. Han, J. H.; Chin, C. F.; Li, D. J.; Han, C. D. Polymer 1995, 36, 2451.
2. Leclair, A.; Favis, B. D. Polymer 1996, 37, 4723.
3. Utracki, L. A. Two Phase Polymer Systems, Vol. 2; Hanser Verlag: Munich, 1991.
4. Tervoort-Engelen, Y.; van Gisbergen, J. Polym Commun 1991, 32, 261.
5. Krager-Kocsis, J. Polypropylene Structure Blends and Composites, Vol. 1/2; Chapman Hall: London, 1995.
6. Kim, W. N.; Hong, S.-I.; Choi, J. S.; Lee, K. H. J Appl Polym Sci 1994, 54, 1741–1750.
7. Martinelli, A.; de Souza, C. D.; Nicole, R. In Proceedings of 58th Antech Conference, Vol. 2; Drinan, J., Ed; Society of Plastics Engineers, 2000; p 2443.
8. Machiels, A. G. C.; Dam, J. V.; Boer, A. P. D.; Norder, B. Polym Eng Sci 1997, 37, 1512.
9. Evstatiev, M.; Fakirov, S. Polymer 1992, 33, 877.
10. Fakirov, S.; Evstatiev, M.; Petrovich, S. Macromolecules 1993, 26, 5219.
11. Fakirov, S.; Evstatiev, M. Adv Mater 1994, 6, 395.
12. Fakirov, S.; Evstatiev, M.; Friedrich, K. In Polymer Blends, Vol. 2: Performance; Paul, D. R., Bucknall, C. B., Eds.; Wiley: New York, 1999; p 455.
13. Fakirov, S.; Evstatiev, M.; Petrovich, S. Macromolecules 1993, 26, 5219.
14. Favis, B. D. In Polymer Blends, Vol. 1: Formulation; Paul, D. R.; Bucknall, C. D., Eds.; Wiley: New York, 2000; p 502.
15. Monticciolo, A.; Cassagnau, P.; Michel, A. Polym Eng Sci 1998, 38, 1882.
16. Evstatiev, M.; Fakirov, S.; Krasteva, B.; Friedrich, K.; Covas, J. A.; Cunha, A. M. Polym Eng Sci 2002, 42, 826.
17. Del Nobile, M. A.; Licciardello, F.; Scrocco, C.; Muratore, G.; Tappa, M. J Food Eng 2007, 79, 217.
18. Kartalis, C. N.; Papaspyrides, C. D.; Pfaendner, R. Polym Degrad Stab 2000, 70, 189.
19. Stewart, R.; Goodship, V.; Guild, F.; Green, M.; Farrow, J. Int J Adhes Adhes 2005, 25, 93.
20. Brandl, W.; Marginean, G.; Chirila, V.; Warschewski, W. Carbon 2004, 42, 5.
21. Robinson, S.; Goodhead, T. C. J Mater Process Technol 2003, 139, 327.
22. Jacobasch, H. J.; Grundke, K.; St Schneider, Simon, F. Prog Org Coat 1995, 26, 131.

23. Lync, J. C. J Compos Technol Res 1990, 12, 229.
24. Lu, J.; Sue, H. J. J Polym Sci Part B: Polym Phys 2002, 40, 507.
25. Yilmazer, U. J Appl Polym Sci 1991, 42, 2379.
26. Field, G. J.; Micic, P.; Bhattacharya, S. N. Polym Int 1999, 48, 461.
27. Li, J.; Wang, Q.; Chan, C. M.; Wu, J. Polymer 2004, 45, 5719.
28. Zhang, X. M.; Ajji, A. Polymer 2005, 46, 3385.
29. Poon, B. C.; Chum, S. P.; Hiltner, A.; Baer, E. Polymer 2004, 45, 893.
30. Li, J.; Shanks, R. A.; Olley, R. H.; Greenway, G. R. Polymer 2001, 42, 7685.
31. Li, J.; Shanks, R. A.; Long, Y. Polymer 2001, 42, 1941.
32. Radhakrishnan, S.; Sonawane, P. J Appl Polym Sci 2003, 89, 2994.
33. Radhakrishnan, S.; Soujanya, C. J Mater Sci 1998, 33, 1069.
34. Radhakrishnan, S.; Soujanya, C. Polymer 2001, 42, 6723.
35. Michiels, A. G. C.; Denys, K. F. C.; Vandom, J.; Boer, A. P. D. Polym Eng Sci 1996, 36, 2451.
36. Machiels, A. G. C.; Denys, K. F. J.; Vandom, J.; Boer, A. P. D. Polym Eng Sci 1997, 37, 1512.
37. Lin, Q. H.; Yec, A. F. Polym Eng Sci 1993, 33, 789.
38. Kurauchi, T.; Ohta, T. J Mater Sci 1984, 19, 1699.
39. Koo, K. K.; Inoue, T.; Miyasaka, K. Polym Eng Sci 1985, 25, 741.
40. Li, Z. M.; Yang, M. B.; Haung, R.; Feng, J. M. J Mater Sci 2001, 36, 2003.
41. Hull, D.; Clyne, T. W. An Introduction of Composite Materials; Cambridge University Press: Cambridge, 1996; Chapter 2.