

# Studies on Mechanical and Thermal Properties of Ternary Blends of Polyethylenes. I

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**ABSTRACT:** Six film samples of varying compositions of linear low-density polyethylene (LLDPE), 10–35 wt %, and high-density polyethylene (HDPE), 40–65 wt %, having a fixed percentage of low-density polyethylene (LDPE) at 25 wt % were extruded by melt blending in a single-screw extruder ( $L/D$  ratio = 20 : 1) of uniform thickness of 2 mil. The tensile strength, elongation at break, and impact strength were found to increase up to 60 wt % HDPE addition, starting from 40 wt % HDPE, in the blends and then decreased. The blend sample B-500 was found to be more

thermally stable than its counterparts. The appearance of a single peak beyond 45 wt % HDPE content in the blend in dynamic DSC scans showed the formation of miscible blend systems and this was further confirmed by scanning electron microscopic analysis. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1691–1698, 2005

**Key words:** blends; polyethylene (PE); differential scanning calorimetry (DSC); mechanical properties; thermal properties

## INTRODUCTION

Polyolefin binary blends have been studied extensively with a view to improving the properties and processability of the homopolymers involved.<sup>1,2</sup> The benefits claimed include, for example, improvements in impact strength,<sup>3–5</sup> optical properties,<sup>6</sup> crystallization rate,<sup>7,8</sup> low-temperature impact strength,<sup>9,10</sup> rheological properties,<sup>11,12</sup> and overall mechanical behavior.<sup>1–5,13,14</sup> A further reason for the study of such blends is that mixtures of such polymers often occur in plastics scrap and waste and affect the possible reuse of such low-cost material.<sup>15–17</sup>

The crystalline morphology of polyolefin blends and its effect upon resultant mechanical properties have also been studied.<sup>13,16,18</sup>

Linear low-density polyethylene (LLDPE) is a very useful material, both as a single component or as a blend with other polymers.<sup>8,19–23</sup> LLDPE cocrystallizes with other grades of polyethylene (PE),<sup>3,8,20,22</sup> thus providing a possibility of improving the mechanical properties of the various grades of PE by blending with LLDPE. Blending high-density polyethylene (HDPE) with LLDPE can increase the susceptibility to bubble instabilities and may cause melt fracture. In addition, high-density applications, in general, require a stiff product that can be enhanced by blending in a

more flexible LLDPE resin, which ultimately increases the output capabilities. Apart from this, LLDPE or HDPE, when added to a low-density polyethylene (LDPE), improves toughness while retaining the processability characteristics<sup>5,6,24</sup> of LDPE. Conversely, LDPE has been blended as the minor component on LLDPE base to improve the optical properties and bubble stability. It has also been concluded from various studies on binary blends that the LDPE/LLDPE and LDPE/HDPE blends are immiscible,<sup>25</sup> whereas HDPE/LLDPE blends are miscible under certain conditions.<sup>20,23,26,27</sup>

The ternary blends<sup>12,28–32</sup> of various PEs, however, have been the subject of far fewer studies with respect to their mechanical, rheological, and thermal properties. Further elucidation of these properties will provide the ability and impetus to tailor such materials to meet specific end uses, cost performance, and so forth. Thus the present investigation focused on preparation of film samples of varying compositions of LLDPE and HDPE, having a fixed amount of LDPE, and to study their mechanical and thermal properties.

## EXPERIMENTAL

Films of varying compositions of LLDPE [M/s Reliance Industries Ltd., Mumbai, India; melt flow index (MFI) = 1.0 g/10 min], 10–35 wt %, and HDPE (M/s Polyolefins Industries Ltd., Mumbai, India; MFI = 3.0 g/10 min), 5–35 wt %, having 25 wt % of fixed amount of LDPE (M/s IPCL, Vadodara, India; MFI = 2.0 g/10 min) were extruded by melt blending in a single-screw extruder ( $L/D$  ratio = 20 : 1) of 2 mil thickness. The

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TABLE I  
Sample Designation

Sample	LLDPE (wt %)	HDPE (wt %)	LDPE (wt %)	Sample code
1	35	40	25	B-100
2	30	45	25	B-200
3	25	50	25	B-300
4	20	55	25	B-400
5	15	60	25	B-500
6	10	65	25	B-600

temperature profile for the barrel (three zones) was taken between 185 and 200°C. The prepared blends were coded as shown in Table I.

Tensile strength and elongation at break of film samples (size 9 × 2 cm) were measured by an automatic tensometer (M/s Prolific Pvt. Ltd., Noida, India) according to ASTM standard D 638 (type IV) test method using dumbbell-shaped samples. The impact strength of the samples was measured by dart impact tester (M/s Prolific Pvt. Ltd.) according to IS 2508-1977 specifications.

A TGA 2950 (TA Instruments, New Castle, DE), equipped with a thermal analyzer 2000 computer control/data-acquisition system, was used to study the thermal stability of the film samples at a heating rate of 10°C/min from 25 to 600°C. The miscibility behavior of the film samples was assessed by the melting endotherms in the differential scanning calorimetric

(DSC) scans of a model 2910 DSC apparatus (TA Instruments), (equipped with a microprocessor TA 2000) at a heating rate of 10°C/min. The morphology of sample B-500 was investigated by Phillips 151 scanning electron microscope (SEM) system. Results of SEM micrographs elucidated the mixing behavior.

## RESULTS AND DISCUSSION

The formation of oxygenated, unsaturated, and hydroperoxide groups, attributed to degradation, thermal or mechanical, during processing of the blend sample B-500, was observed in the IR spectrum of the film sample and reported in a previous article.<sup>31</sup> In the spectrum, the intensities of the peaks related to such groups at different locations of the spectrum were found to be very low and thus was ignored in further studies.

The variation in tensile strength and elongation at break of the blended film samples (B-100 to B-600) are shown in Figures 1 and 2, respectively. It is clear from Figure 1 that the tensile strength of blend samples increased up to 60 wt % HDPE addition, starting from 40 wt % HDPE, and then decreased. The tensile strength of the blend sample containing 25 wt % LDPE, 35 wt % LLDPE, and 40 wt % HDPE (sample B-100) was found to be 15.6 MPa and it increased by 52.2% as the content of HDPE in the blend was increased by a mere 5% (Sample B-200). Figure 1 indicates that the initial increase of tensile strength up to

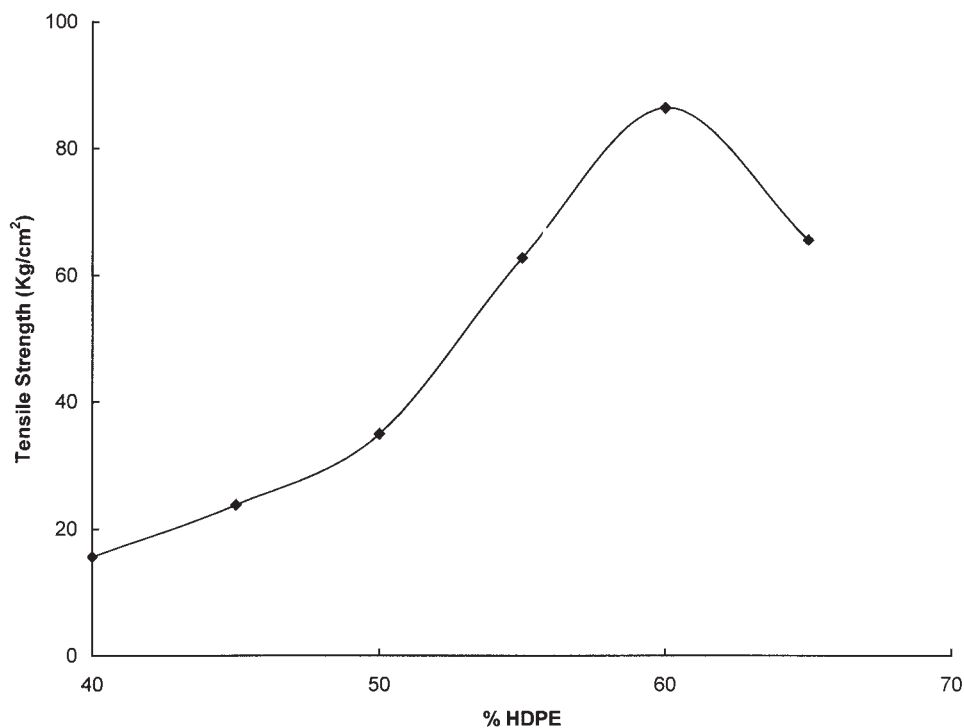


Figure 1 Variation of tensile strength of ternary blends of polyethylenes with HDPE.

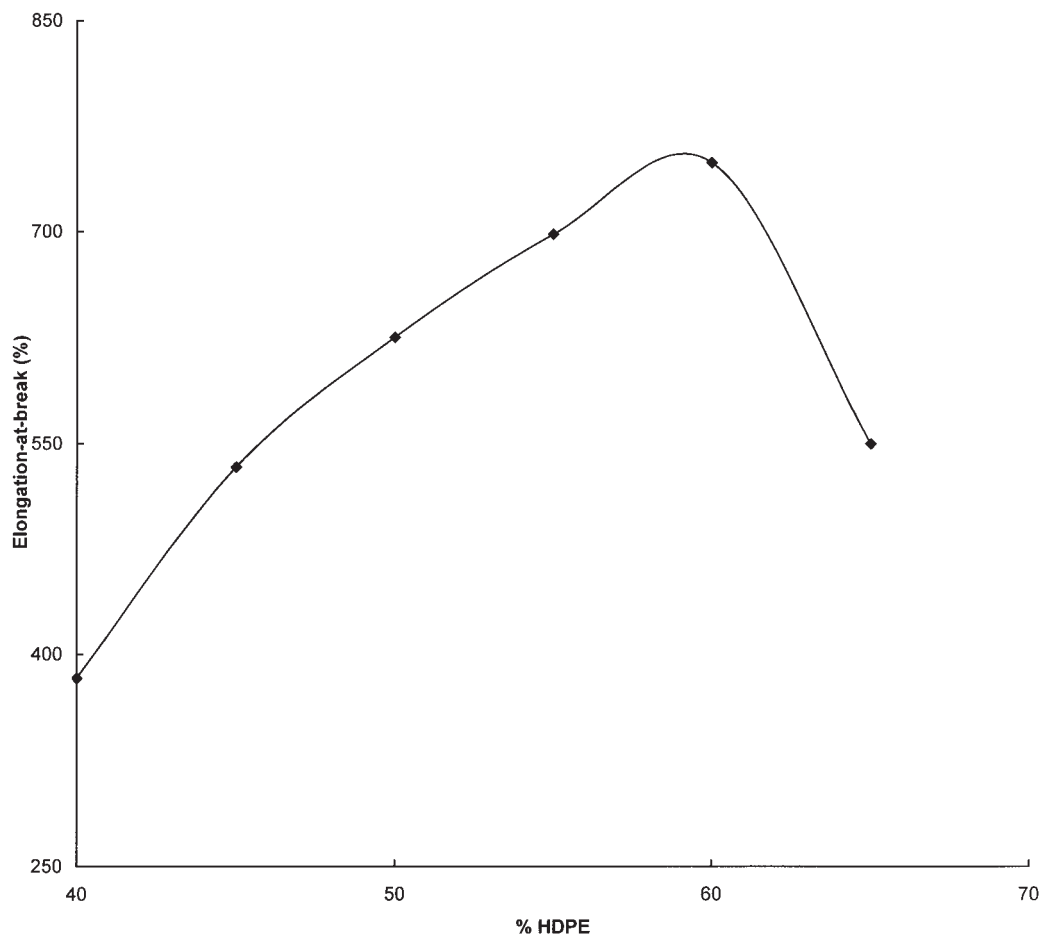
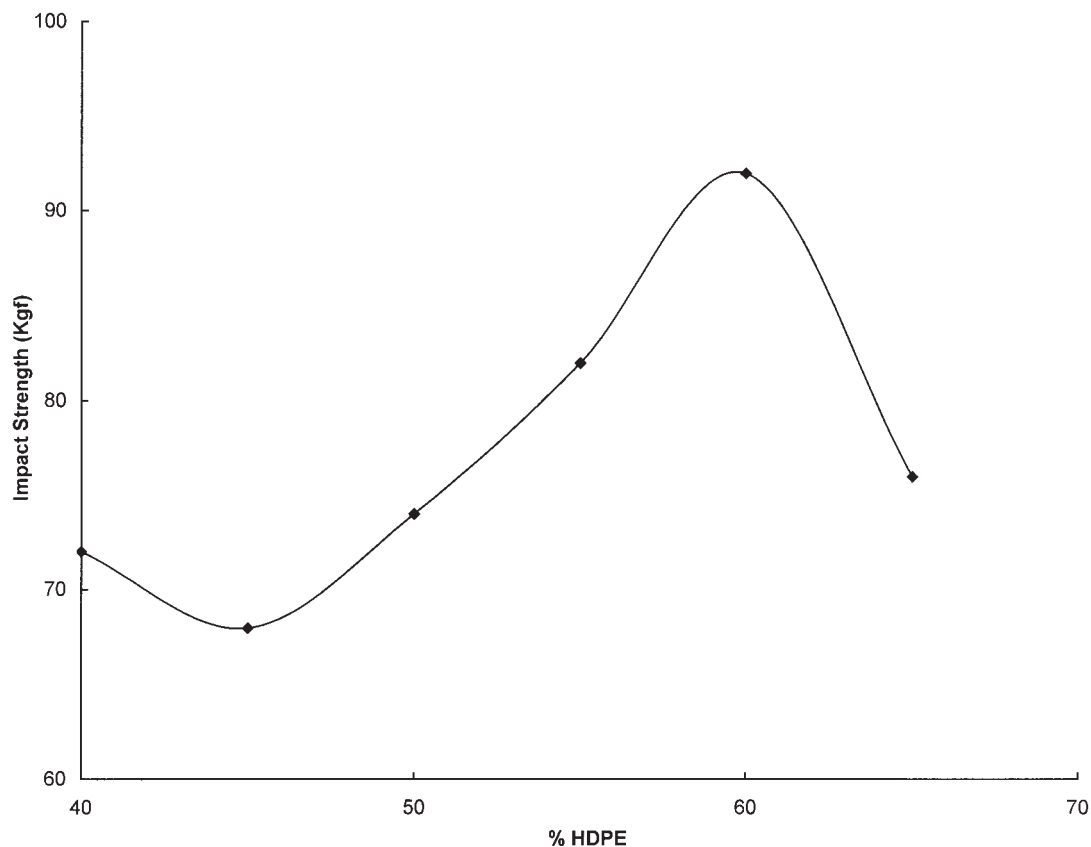


Figure 2 Variation of percentage elongation at break of ternary blends of polyethylenes with HDPE.

50 wt % was slow, but beyond 50 wt % and up to 60 wt %, it increased sharply, thereafter decreasing up to 65 wt % HDPE addition in the blend. The elongation at break increased linearly with increasing HDPE content (Fig. 2) with a slight scatter of data points up to 55 wt % HDPE addition in the blend. It then increased slowly on further addition of HDPE, up to 60 wt % HDPE content, thereafter decreasing very sharply up to 65 wt % HDPE addition in the blend.

The initial increase in tensile strength and elongation at break might be ascribed to the formation of multiple entanglements and the cocrystallization process. Initially, dissolution and cocrystallization between LLDPE and HDPE chain molecules might occur. This might be possible given that the structural differences on a molecular level would be at a minimum and the crystal structure of the cocrystallized HDPE and LLDPE could contain only PE-type linear sequences of both components. This would allow the molecules of these two components to mix together, leaving the side group, comonomer segments of LLDPE, outside the cocrystalline regions (i.e., in the amorphous phase). These molecular segments at the boundary of the crystallites would

differ from those of HDPE and LLDPE in their mobility and thus they would exert different type of forces on the crystalline region. These forces, attributed to segmental mobility at the boundary of the crystallites, could cause fluctuations and could result in multiple entanglements, that is, physical crosslinking with the molecules of LDPE present in the amorphous region, and thus might create a pseudo-rubberlike network in amorphous phase.<sup>11,14,33</sup> The rubberlike elasticity accounted for the increase in tensile strength and elongation at break up to 60 wt % addition of HDPE in the blends. Beyond 60 wt % addition, the LLDPE molecules might also participate in the formation of cocrystal, thus decreasing the entanglements; in turn this would decrease the tensile strength and elongation at break. Gupta et al.,<sup>3,4</sup> Tincer et al.,<sup>11</sup> and Bhateja et al.<sup>14</sup> proposed a similar concept in their studies of the binary blends of PEs. At high fractions of HDPE, segregated molecules of cocrystallized LLDPE/HDPE molecules might also be present, which would produce a particle effect<sup>11</sup> in the blend, rather than complete incorporation, and thus a decrease in the tensile strength. The decrease in elongation at

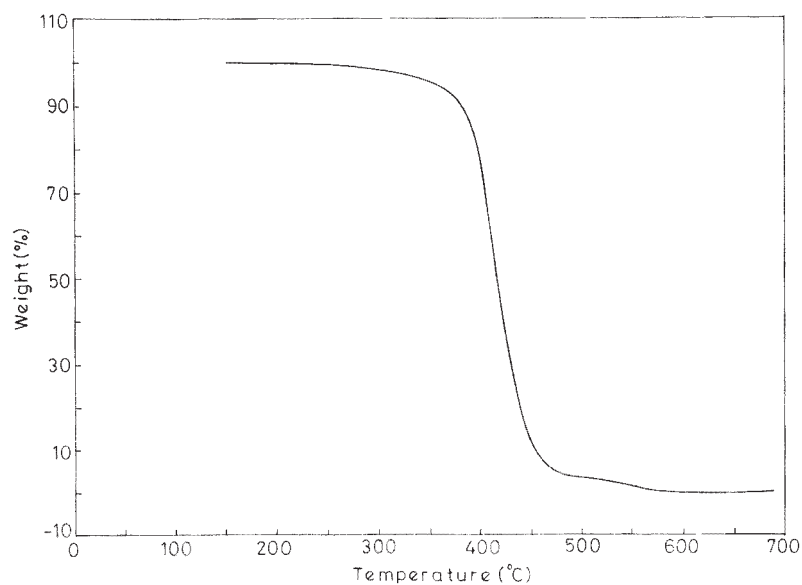


**Figure 3** Variation of impact strength of ternary blends of polyethylenes with HDPE.

break might also be attributable to shortening of the amorphous regions<sup>34</sup> present in the ternary blend systems.

The variation in the impact strength of the blended film samples (B-100 to B-600) with HDPE content in

the blend composition is shown in Figure 3. It is clear from Figure 3 that the impact strength showed a non-linear variation, such that on initial addition of up to 45 wt % HDPE, starting with 40 wt % HDPE content in LLDPE and LDPE (fixed at 25 wt % in all blend



**Figure 4** TGA curve of blend sample B-500.

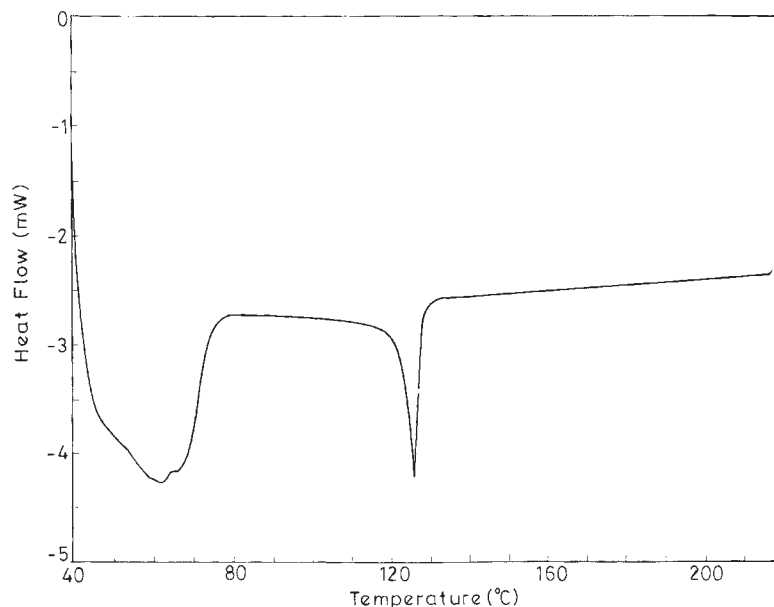


Figure 5 DSC scan of blend sample B-100.

samples), it decreased and then increased on further addition of HDPE up to 60 wt % in the blend, thereafter decreasing up to 65 wt % HDPE addition in the blend composition. The impact strength of the blend composition did not produce much impact modification with the addition of HDPE in the blend, but showed only a systematic variation with blend composition. This might be a consequence of the cocrystallization behavior of the blend. A similar concept was reported by Gupta and coworkers<sup>4</sup> in their study of the impact modification of the blends of LLDPE/

HDPE. They found that the variation of impact strength with blend composition showed a variation similar to that of crystallization behavior<sup>35</sup> of the blends.

The loss in weight with temperatures of the blend sample B-500 is shown by dynamic TGA curve in Figure 4. From this figure, it can be observed that the initial degradation temperature (IDT) and final degradation temperature (FDT) are 323.7 and 526.7°C, respectively, whereas the temperature of 50 wt % loss ( $T_{50}$ ) of the sample is 413.7°C. From these data, it may

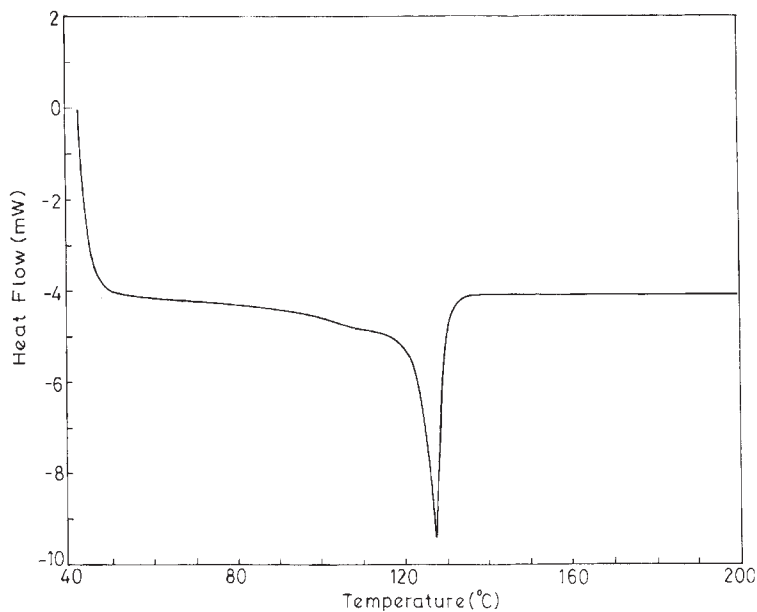


Figure 6 DSC scan of blend sample B-200.

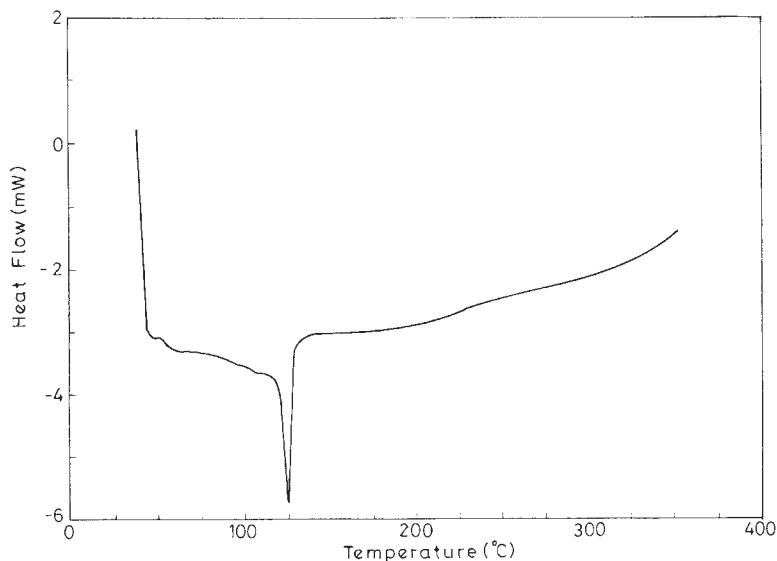


Figure 7 DSC scan of blend sample B-300.

be concluded that the thermal stability of the blend sample was improved over that of the individual components, as reported elsewhere<sup>13</sup> in a previous article. This might be a result of the dissolution and cocrystallization of LLDPE chain molecules into HDPE chain molecules. These cocrystallized chain molecules, no doubt, would degrade at higher temperatures.

Figures 5–10 illustrate the fusion endotherms of various compositions of LDPE/LLDPE/HDPE blend systems. The melting peak temperatures for LDPE, LLDPE, and HDPE were 106, 126, and 131°C, respectively (manufacturer-supplied values). The DSC

curves of pure materials are given in a previous work.<sup>30</sup> The DSC curves of blend samples containing 40 wt % (B-100) (Fig. 5) and 45 wt % (B-200) (Fig. 6) content show two endotherms, one at a shoulder of the other. The first broad peak at the lower side of the temperature scale (Figs. 5 and 6) might be attributable to LDPE and the second sharp peak might be attributable to the melting of the cocrystals resulting from the initial dissolution of HDPE chain molecules into the LLDPE chain molecules.<sup>22</sup> As the content of the HDPE was increased to 65 wt % in the blend, there appeared only a single endotherm in the DSC thermo-

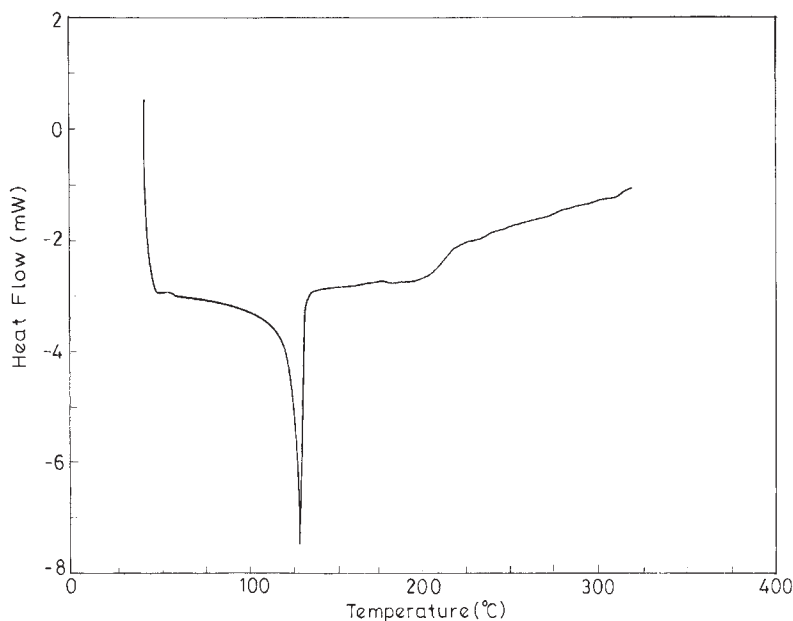


Figure 8 DSC scan of blend sample B-400.

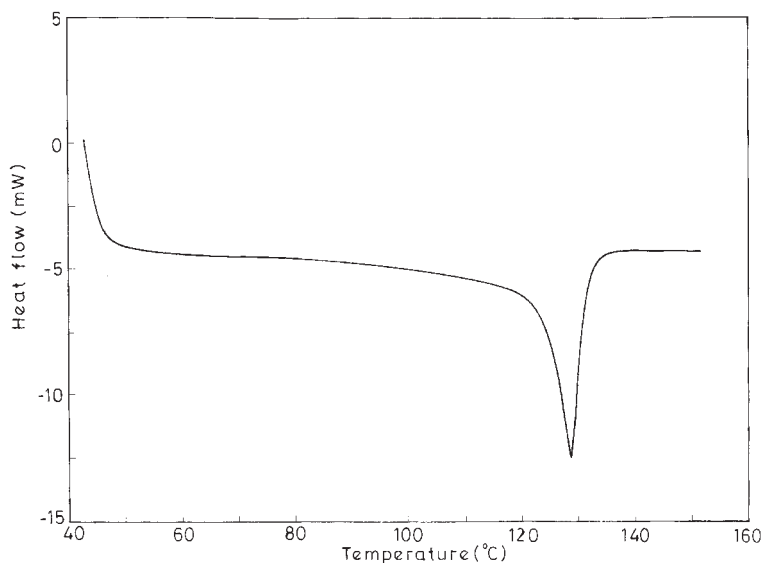


Figure 9 DSC scan of blend sample B-500.

gram for blend samples B-300 (Fig. 7), B-400 (Fig. 8), B-500 (Fig. 9), and B-600 (Fig. 10), suggesting that cocrystallization occurred between all the components of the blend samples. It seemed that LLDPE and HDPE, in particular, had an ability to crystallize together with LDPE and formed cocrystals. The increase of all mechanical properties up to 60 wt % HDPE addition in the blends supported this. Other workers,<sup>3,7,9,11,14,20,22</sup> while studying the crystallization of binary blends of HDPE/LLDPE and UHMWPE/LLDPE, also proposed a similar concept of cocrystallization. In other words, one could conclude that the miscible blend resulted while blending

LDPE, LLDPE, and HDPE beyond 45 wt % HDPE addition in the blend. Further, this was confirmed by SEM analysis of the tensile fractured surface of the blended film sample B-500. From the SEM microphotographs (Fig. 11) at two magnifications, it is clear that there appeared a fibrillar structure along with some transverse striations of the fibrils and formed transverse connections between the fibrils. These transverse connections were apparently attributable to the intercrystalline LLDPE phase, thus suggesting that the components of the blends LDPE, LLDPE, and HDPE resulted in a miscible blend.<sup>23</sup>

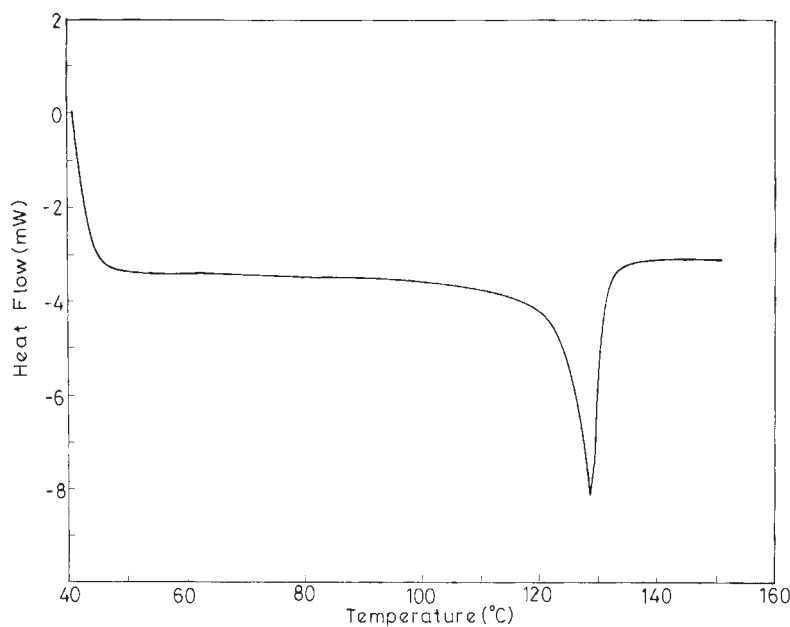


Figure 10 DSC scan of blend sample B-600.

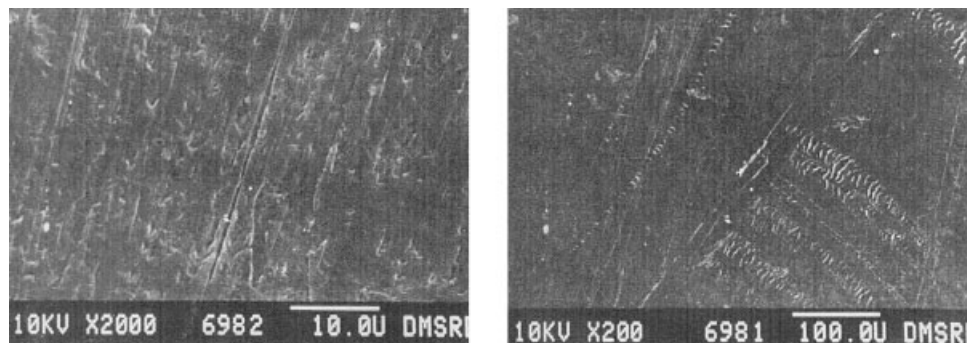


Figure 11 SEM microphotographs of blend sample B-500 at two magnifications.

### CONCLUSION

It is concluded from the preceding results and discussion that the tensile strength, elongation at break, and impact strength of the blended film samples first increased up to 60 wt % addition of HDPE in the ternary blends of polyethylene having a fixed amount of LDPE. The blended film sample B-500 was found to be more thermally stable than its counterparts. DSC analysis showed the formation of a homogeneous blend system, which was further confirmed by SEM analysis.

### References

- Paul, D. R.; Newman, S. Eds. *Polymer Blends*; Academic Press: New York, 1978.
- Manson, J. A.; Sperling, L. H. *Polymer Blends and Composites*; Plenum Press: New York, 1976.
- Gupta, A. K.; Rana, S. K.; Deopura, B. L. *J Appl Polym Sci* 1992, 44, 719.
- Gupta, A. K.; Rana, S. K.; Deopura, B. L. *J Appl Polym Sci* 1993, 49, 477.
- Yilmazer, U. *J Appl Polym Sci* 1991, 42, 2379.
- Speed, C. S. *Plast Eng* 1982, 7, 39.
- Kyu, T.; Vadhar, P. *J Appl Polym Sci* 1986, 32, 5575.
- Shishesaz, M. R.; Donatelli, A. A. *J Appl Polym Sci* 1981, 21, 869.
- Laguna, O.; Collar, E. P.; Taranco, J. *J Polym Eng* 1987, 7, 169.
- Weng, W. *Angew Makromol Chem* 1978, 74, 147.
- Tincer, T.; Coskun, M. *Polym Eng Sci* 1993, 33, 1243.
- Han, C. D.; Yu, T. C. *Polym Eng Sci* 1972, 12, 81.
- Srivastava, D. *Polym Plast Technol Eng* 2003, 42, 229.
- Bhateja, S. K.; Andrews, E. H. *Polym Eng Sci* 1983, 23, 888.
- Robertson, R.; Paul, D. R. *J Appl Polym Sci* 1992, 17, 2579.
- Lindsay, C. R.; Barlow, J. W.; Paul, D. R. *J Appl Polym Sci* 1981, 26, 9.
- Laguna, O.; Collar, E. P.; Taranco, J.; Vigo, J. P. *J Polym Mater* 1987, 4, 195.
- Deanim, R. D.; Sansone, M. F. *Polym Prepr (Am Chem Soc Div Polym Chem)* 1978, 19, 211.
- Sakellarides, S. L.; Mchaugh, A. V. *Polym Eng Sci* 1988, 25, 1179.
- Hu, S. R.; Kyu, T.; Stein, R. S. *J Polym Eng Polym Phys* 1987, 25, 71.
- Farr, M. P.; Harrison, I. R. *Polym Prepr (Am Chem Soc Div Polym Chem)* 1990, 31, 257.
- Donatelli, A. A. *J Appl Polym Sci* 1979, 23, 3071.
- Vadhar, P.; Kyu, T. *Polym Eng Sci* 1987, 27, 202.
- Hadjiandreou, P.; Baker, M.; Harrats, C. *SPE ANTEC Proc* 1987, 45, 1427.
- Schlund, B.; Utracki, L. A. *Polym Eng Sci* 1987, 27, 1524.
- Edward, G. H. *Br Polym J* 1986, 18, 88.
- Pracella, M.; Penedetti, E.; Galleschi, F. *Thermochim Acta* 1990, 162, 163.
- Srivastava, D.; Nagpal, A. K.; Mathur, G. N. *J Polym Mater* 1997, 13, 1102.
- Highhat, S.; Birley, A. W. *Adv Polym Technol* 1990, 10, 143.
- Srivastava, D.; Garg, R.; Kumar, P.; Saxena, D. C.; Mathur, G. N. *Macromol Mater Eng* 2000, 283, 81.
- Srivastava, D.; Kumar, P.; Mathur, G. N. *Mater Manuf Process* 2001, 16, 419.
- Srivastava, D. *J Polym Env*, to appear.
- Zhao, Y.; Luo, Y.; Jiang, B. *J Appl Polym Sci* 1993, 50, 1797.
- McHerron, D. C.; Wilkes, G. L. *Polymer* 1993, 34, 915.
- Ree, T.; Eyring, H. *J Appl Phys* 1955, 26, 793.