

# Properties of Films Made from Ternary Blends of Metallocene and Conventional Polyolefins

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**ABSTRACT:** Thin films were blown from a composition of 75% linear low density polyethylene (LLDPE) and 25% LDPE. The LLDPE content was made up of different % of metallocene-based and conventional octene-based LLDPE. Tensile strength, dart impact strength, hot tack strength, heat seal strength, and the barrier properties of these films were measured. All the properties showed significant improvement when conventional LLDPE (cLLDPE) was replaced by metallocene-based LLDPE (mLLDPE), even to the extent of only 25%. The blends of 50% mLLDPE and 50% LDPE showed attractive properties. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 53–57, 2001

**Key words:** metallocene LLDPE; conventional LLDPE; LDPE; blends; films; barrier properties

## INTRODUCTION

Linear low density polyethylene (LLDPE) finds its wide applications in packaging films or agricultural thin films. The comonomers used in most commercial LLDPEs are 1-butene, 1-hexene, or 1-octene.<sup>1–5</sup> The conventionally made polyethylenes with the Ziegler–Natta catalyst do not have as uniform comonomer distribution as that using metallocene catalyst.<sup>1,6,7</sup> The molecular weight control is also better for metallocene-based polyethylenes (mPE).<sup>6</sup> Therefore metallocene-based LLDPE (mLLDPE) has superior strength, gloss, and heat sealing properties over conventional LLDPE (cLLDPE) made by the Ziegler–Natta catalyst.<sup>8–11</sup> However, the processability of mLLDPE is not as good as cLLDPE.<sup>8,11</sup> In order to overcome some of the problems of processing and for reducing the cost, blends of mPE with conventional polyethylene or other types of polyethylenes have received much attention, recently.

Munoz et al.<sup>12</sup> have studied the rheological behavior of metallocene-catalyzed high density polyethylene (HDPE) blends. They melt blended mHDPE of varying molecular weights and they have correlated the rheological properties of blends using free volume theory. Rana et al.<sup>13</sup> have studied the blends of mPE with four conventional polyolefins—namely, HDPE, polypropylene (PP), PP copolymer, and PP terpolymer (propylene-*co*-ethylene-*co*-butene). They reported that all the systems are thermodynamically immiscible but mechanically compatible. The degree of compatibility was highest for mPE/HDPE system. They suggested that “like” preferred “like.” Deen Chundury<sup>14</sup> has presented the data on the blend system of mPE/PP for flexible foam application. They observed that properties of the blends were better than those of conventional homopolymers. The blends of metallocene PP and random metallocene ethylene-1-butene have been studied for compatibility between these two by Mader et al.<sup>15</sup> Rana et al.<sup>16</sup> studied the thermal and mechanical properties of blends of ethylene-1-octene copolymers synthesized by conventional Ziegler–Natta catalyst and metallocene catalyst.

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They found that all the blends formed separate crystals in the crystalline state but had limited miscibility in the amorphous regions.

For thin packaging films, the cLLDPE is blended with LDPE up to 30% to improve processability. Shih et al.<sup>17</sup> studied the blend of metallocene polyethylene with conventional LDPE containing 30% LDPE and 70% metallocene PE. They found that the hot tack of the blends to be superior to that of mPE and LDPE. They also observed reduced haze for the films. Thus if small amount of LDPE were blended with mPE, it seemed to improve the hot tack and transparency, due to lower heat seal initiation temperature. However, there are no data on mechanical properties such as dart impact or tensile strength as well as barrier properties of such films made from mLLDPE + LDPE blends. Also, there are no reports on effect of partial replacement of cLLDPE by mLLDPE on the mechanical, barrier, and rheological properties of such films. The partial replacement can help control some of these properties. Also, the recycling of packaging films may involve blends of mLLDPE/cLLDPE/LDPE.

## EXPERIMENTAL

### Materials

Blends were prepared from 75% LLDPE and 25% LDPE. The 75% of LLDPE was made up of different amounts of mLLDPE and cLLDPE. Also, the % of LDPE was varied from 25 to 50% to study the blend properties. The commercially available resins were used. Thus mLLDPE was from Dow Chemicals (Elite melt flow index [MFI] 0.85 g/10 min at 2.16 kg, 190°C); procured from local markets, cLLDPE was from Reliance Industries Ltd. (Reclair 0.9 g/10 min), India; and LDPE was from IPCL (Indothene 4.0 g/10 min), India.

### Compounding and Processing

Table I shows various compositions studied in the present investigation. The blends were prepared by initially dry blending the resins in required proportions and then melt blending using a counter rotating twin screw extruder, Haake Rheocord RC-9000, TW100. The temperature profile was 170, 190, 200, and 210°C for the feed zone, compression zone, metering zone, and die zone respectively. The screw speed was 50 rpm. The extrudates were cooled by water and then

**Table I Blend Compositions of mLLDPE/cLLDPE/LDPE**

Sr. No.	mLLDPE (wt %)	cLLDPE (wt %)	LDPE (wt %)
1	100	0	0
2	0	100	0
3	0	0	100
4	0	75	25
5	18.75 <sup>a</sup>	56.25	25
6	37.5 <sup>b</sup>	37.5	25
7	75 <sup>c</sup>	0	25
8	0	50	50
9	50	0	50

<sup>a</sup> 25% replacement of cLLDPE.

<sup>b</sup> 50% replacement of cLLDPE.

<sup>c</sup> 100% replacement of cLLDPE.

pelletized. Thin blown films were prepared using a single screw extruder (Dia 45 mm) fitted with vertically upward directed film blowing assembly (Boolani Engineering Ltd., India). The temperature profile was 160, 180, 190, 210, and 230°C for three zones of barrel, die-head, and die respectively. The blow-up ratio was 2.5–2.7 and screw speed was 60 rpm.

### Testing

Dumbbell-shaped specimens (ASTM D882) were punched out from thin films and tensile strength and % elongation at break in machine and transverse directions were determined using the Universal Tensile Testing Machine, LR 50K, Lloyds Instruments Ltd., U.K. Cross-head speed of 100 mm/min was maintained. The dart impact strength was measured as per ASTM D1709, Method A using Falling Dart Impact Machine of International Engineering Ltd., India.

The heat seal initiation temperature, the heat seal strength, and hot tack strength were measured using the Theller Precision Heat Seal Tester.

The water vapor permeability was determined by gravimetric method as per ASTM D895 and Oxygen (O<sub>2</sub>) gas permeability was measured according to ASTM D1434 using the Lyssy Analytic Gas Permeability Fractometer, Model GPM-200, Switzerland, connected with the Dual Column Gas Chromatograph, Gasukuro Kogyo GC 320 and a standard Data Integrator (Oracle-3, Indtech Systems, India) for online recording of the chromatogram and computation of peak area.

**Table II Mechanical Properties of Blown Films of the Blends and Virgin Polymers<sup>a</sup>**

Sr. No.	Blend Composition (wt %)			Tensile Strength at Break (MD) (MPa)	Tensile Strength at Break (TD) (MPa)	Elong. at Break (MD) (%)	Elong. at Break (TD) (%)	Dart Impact Strength (g/ $\mu$ )
	mLLDPE	cLLDPE	LDPE					
1	100	0	0	38.4	38	880	902	14.8
2	0	100	0	27.8	27	630	660	5.12
3	0	0	100	20.20	19.6	820	864	2.12
4	0	75	25	24.4	22.8	770	810	3.44
5	18.75	56.25	25	31	29.60	790	800	12.2
6	37.5	37.5	25	33.56	32.72	800	840	13.4
7	75	0	25	36.84	34	860	960	13.9
8	0	50	50	20.8	20.44	602	668	1.80
9	50	0	50	28.64	26.12	790	820	8.50

<sup>a</sup> MD: machine direction; TD: transverse direction.

MFI values were measured using Davenport Microprocessor based equipment (Model 10) according to the ASTM D1238.

## RESULTS AND DISCUSSION

### Mechanical Properties

Table II depicts the mechanical properties of the films made from various compositions. The temperature profile for mLLDPE was slightly different from that for cLLDPE. The die temperature was 240°C for mLLDPE against 230°C for cLLDPE. Metallocene LLDPE-based films showed superior tensile strength; elongation at break in both machine and transverse directions and higher dart impact strength compared to both virgin cLLDPE and LDPE films. LDPE has lower tensile and dart impact strength than cLLDPE, but it has superior % elongation at break in both machine and transverse directions of the films.

Compositions 4–7 show the effect of replacing cLLDPE by mLLDPE. When only 25% of cLLDPE was replaced by mLLDPE a significantly high dart impact was observed (composition 5). It is interesting to see that by blending even such small amount of mLLDPE, the impact strength increased from 3.44 to 12.2 g/ $\mu$ . This film composition may be more economical than the blend composition containing only mLLDPE and LDPE. Further increase in mLLDPE content has further improved the properties but the improvement is gradual. The increase in dart impact was from 12.2 to 13.9 g/ $\mu$  when replacement of mLLDPE

was from 25 to 100%. Similarly, the tensile strength increased significantly when cLLDPE was replaced by only 25% mLLDPE. Thus both tensile strength and dart impact show improvement, which is much more than linear additivity rule. The % elongation at break also steadily increased when cLLDPE was replaced by mLLDPE. The increase is, however, gradual.

Properties of compositions 4, 8, and 9 compare the effect of LDPE content. It is clear that when LDPE content increased from 25 to 50%, in a blend of cLLDPE + LDPE, the tensile strength, % elongation, and dart impact decreased. However when 50% cLLDPE was replaced completely by mLLDPE, there was a significant increase in dart impact strength as it increased from 1.8 to 8.5 g/ $\mu$ , accompanied by significant increase in tensile strength as well as % elongation at break. Thus even smaller replacement of cLLDPE by mLLDPE improves the mechanical properties.

### Heat Sealing Properties

Table III shows the heat seal and hot tack strength properties of various films. For all the films, thickness was 60  $\mu$  and heat seal temperature was 115°C. The heat seal initiation temperature is lowest for LDPE. As the amount of mLLDPE increased, the heat initiation temperature decreased, and heat sealing strength and hot tack strength increased steadily. Results of Shih et al.<sup>17</sup> also support our findings. The increase in heat sealing and hot tack strength was very significant when 50% of cLLDPE was replaced by mLLDPE (composition 6).

**Table III Heat Seal Initiation Temperature, Heat Sealing Strength, and Hot Tack Strength of the Blown Films<sup>a</sup>**

Sr. No.	Blend Composition (wt %)			Heat Seal Initiation Temperature (°C)	Heat Sealing Strength (g)	Hot Tack Strength (g)
	mLLDPE	cLLDPE	LDPE			
1	100	0	0	104	2660	204
2	0	100	0	111	2314	178
3	0	0	100	98	1280	84
4	0	75	25	110	1642	150
5	18.75	56.25	25	108	1684	164
6	37.5	37.5	25	108	2210	194
7	75	0	25	103	2340	200
8	0	50	50	109	1436	126
9	50	0	50	104	1920	168

<sup>a</sup> Film thickness = 60  $\mu$ ; heat sealing temperature = 115°C.

Composition 4, 8, and 9 show the effect of LDPE content. The heat seal initiation temperature was not affected to any extent, but heat sealing and hot tack strength decreased considerably. When cLLDPE is replaced by mLLDPE, there is noticeable improvement in the heat sealing strength as well as hot tack strength, while the heat seal initiation temperature reduced to 104°C, matching it with that for mLLDPE. The improved heat seal properties can be attributed to lowering of heat seal temperature as suggested by Shih et al.<sup>17</sup>

#### Barrier Properties

Table IV shows the permeability of water vapor and O<sub>2</sub> gas for different films. Properties of compositions 4–7 show the effect of replacement of cLLDPE by mLLDPE. It is very clear that the water permeability as well as O<sub>2</sub> gas permeability for the films

decreased to large extent when mLLDPE replaced cLLDPE. The reduction in O<sub>2</sub> gas permeability is almost by 50% when only 25% of cLLDPE was replaced by mLLDPE. Properties of compositions 4, 8, and 9 show the effect of increasing LDPE from 25 to 50%. The O<sub>2</sub> gas permeability was not seriously influenced while water vapor permeability increased substantially. When cLLDPE was replaced by mLLDPE, there was a sizable decrease in permeability of O<sub>2</sub> gas and water vapor.

#### MFI Values

Table V depicts the variation of MFI for various compositions. The MFI of mLLDPE is slightly less than that of cLLDPE but the difference is marginal, while MFI for LDPE is much higher than that for both grades of LLDPE. The MFI values seem to be closely linked with the compositions. Thus as the %

**Table IV Water Vapor and O<sub>2</sub> Gas Permeability of the Blown Films at Room Temperature**

Sr. No.	Blend Composition (wt %)			Water Vapor Permeability ( $P_{H_2O}$ ) $\times 10^{10}$ (cc mm/cm <sup>2</sup> s cmHg)	Oxygen Gas Permeability ( $P_{O_2}$ ) $\times 10^{10}$ (cc mm/cm <sup>2</sup> s cmHg)
	mLLDPE	cLLDPE	LDPE		
1	100	0	0	164	7.92
2	0	100	0	240	36.4
3	0	0	100	660	24.92
4	0	75	25	320	28.9
5	18.75	56.25	25	252	13.5
6	37.5	37.5	25	226	12.04
7	75	0	25	190	8.72
8	0	50	50	410	26.92
9	50	0	50	330	16.38

**Table V MFI Values of Different Blend Compositions at 190°C**

Sr. No.	Blend Composition (wt %)			MFI Values (g/10 min)		Ratio of MFI at 5 kg and MFI at 2.16 kg
	mLLDPE	cLLDPE	LDPE	At 2.16 kg	At 5 kg	
1	100	0	0	0.798	2.486	3.15
2	0	100	0	0.914	2.834	3.1005
3	0	0	100	3.7902	11.8214	3.118
4	0	75	25	0.9417	2.9384	3.125
5	18.75	56.25	25	0.8967	2.7979	3.1202
6	37.5	37.5	25	0.8728	2.7232	3.119
7	75	0	25	0.8256	2.5741	3.117
8	0	50	50	1.3402	4.183	3.121
9	50	0	50	1.2268	3.8200	3.113

of mLLDPE has increased, the MFI values decreased slightly. Similarly, as the amount of LDPE increased, MFI increased proportionately. Most interestingly, all the three grades that are blended and also the different blend compositions show a very comparable ratio of MFI values at 5 and 2.16 kg loads. This indicates that the molecular weight distributions show a similar pattern for all the compositions and individual polymers.

## CONCLUSIONS

In a film produced from blend composition of 75% LLDPE and 25% LDPE, replacement of octene-based cLLDPE by even 25% of mLLDPE, there is very significant improvement in mechanical and heat sealing properties. The barrier properties also show good improvement. Considering all the properties replacing cLLDPE by mLLDPE in the range of 25–50% is adequate in getting superior properties.

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