

# Effects of Additions of High-Density Polyethylene on the Processability of Linear Low-Density Polyethylene

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## SYNOPSIS

In considering the processing characteristics of typical linear low-density polyethylenes, it is very likely that the nature and amount of the "high-density" portion of the short chain branching distribution has a strong effect on rheological behavior. In this study, high-density resins of varying molecular weight were blended into a linear low-density polyethylene base resin to determine the effect on viscosity, elasticity, and onset of haze. It was determined that it is not only the high-molecular-weight characteristics of the high-density portion but also the linear nature of the molecules that has a negative effect on processability.

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## INTRODUCTION

Based upon results obtained by the authors in a previous study,<sup>1</sup> indicating that processability is a function of the percent high-density resin in a linear low-density polyethylene (LLDPE), it was decided that a study of LLDPE/high-density PE (HDPE) blends might be useful. A wide range of PE blends has been investigated in the past. LLDPE or HDPE has been added to a low-density PE (LDPE) base to improve toughness while retaining the processability characteristics of the LDPE.<sup>2-4</sup> Conversely, LDPE has been blended as the minor component into an LLDPE base to improve optical properties and enhance bubble stability during tubular film extrusion while taking advantage of the superior physical properties afforded by the use of LLDPE.<sup>5,6</sup>

A number of studies have dealt with the miscibility of various PE-PE blends. The results of these studies suggest that LDPE-LLDPE blends are immiscible, forming two distinct crystalline phases as determined by techniques such as differential scanning calorimetry, X-ray diffraction studies, and Raman spectroscopy.<sup>7</sup> Similar studies on HDPE-

LLDPE blends have shown that these resins are miscible under certain conditions in which component viscosities are well matched and the mixing process is very efficient.<sup>8-11</sup> Solution mixing has been shown to provide intimate mixing; however, melt blending can also yield well-mixed products provided it is done properly.

A study by Vadhar and Kyu indicated that blends produced by sequentially mixing ultrahigh-molecular-weight PE with LLDPE exhibit additive behavior when considering the log viscosity as a function of composition.<sup>9</sup> Similarly, Hu et al. determined that solution-mixed LLDPE-HDPE blends manifest mechanical relaxation behavior that is intermediate between that of the blend components.<sup>10</sup>

The majority of studies on HDPE-LLDPE blends have focused on the miscibility question. Blending HDPE with LLDPE does not offer the same advantages as blending LLDPE with LDPE. LLDPE is difficult to process, HDPE even more so. Blending LLDPE into HDPE can increase susceptibility to bubble instabilities and may cause melt fracture. In addition, high-density applications in general require a stiff product that can be compromised by blending in a more flexible LLDPE resin. One of the few advantages realized in blending LLDPE into HDPE (at approximately 5-10% by weight) is a resulting broader slit/seal temperature range and a decrease in extruder back pressure, resulting in increased output capabilities.<sup>7,12</sup>

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Blending studies were undertaken in this case to confirm observations that increasing levels of high-molecular-weight, linear molecules result in products exhibiting inferior processability. In addition, this study was designed to determine whether the molecular weight of the linear fraction had any effect on the processing characteristics of an LLDPE. A previous study by the authors showed that in comparing resins of similar molecular weight and comonomer content the sample containing 16% high-density molecules processed much better in comparison to a resin containing 25% high-density molecules.<sup>1</sup> Based upon these observations, 90/10 w/w LLDPE-HDPE blends were primarily used in this study.

## EXPERIMENTAL

### Materials

The high-density blend series was formulated from three HDPEs (HD1-3), which ranged in melt index from 6.3 g/10 min–0.07 g/10 min. The blends were formulated at 10 and 20% HDPE by weight. Mixing was accomplished using a twin-screw extruder in a corotating mode with a high mixing configuration as detailed in Figure 1. The configuration included four kneading blocks and a reverse flight to increase back pressure. The remainder of the screw consisted of various low-shear conveying elements. The barrel temperature was maintained at 220°C with a feed rate of 40 g/min and a screw speed of 90 rpm. Barrel residence time was estimated to be approximately 4 min. Blends were processed in the following order:

1. LLDPE B + 10% HD1 (MI = 6.3)
2. LLDPE B + 20% HD1
3. LLDPE B + 10% HD2 (MI = 1)
4. LLDPE B + 20% HD2

5. LLDPE B + 10% HD3 (MI = 0.07)
6. LLDPE B + 20% HD3

This blending sequence ensured that each successive blend was more viscous than the preceding blend. Operating in this manner resulted in a purge that would be viscous enough to flush the barrel before the next lot was collected.

### Size Exclusion Chromatography

Molecular weight measurements were carried out using high-temperature gel permeation chromatography (GPC) with a differential refractometer, low-angle laser light scattering (LALLS) detector, and continuous viscometer, all on-line. Samples were prepared and eluted with 1,2,4-trichlorobenzene containing 0.1% Irganox 1010™ antioxidant. Samples ranged in concentration from 1–2 mg/ml with injection volumes ranging from 175–250 μL. The system was maintained at 145°C throughout all analyses. Sample dissolution was achieved by rotation of samples at 160°C for 24–72 h. Reported molecular weight averages were calculated from continuous viscometer data.

### <sup>13</sup>C Nuclear Magnetic Resonance

<sup>13</sup>C nuclear magnetic resonance (NMR) spectra were obtained on a Bruker AC 300-MHz spectrometer operating at 75.43 MHz. The spectra were recorded at high resolution using inverse gated decoupling conditions and a 90° pulse of 12 μs with a 12-s delay. Samples were run in 1,2,4-trichlorobenzene at 120°C in 10-mm tubes. Sample preparation consisted of swelling the polymer in trichlorobenzene for 0.5 h in the spectrometer. Satisfactory spectra were obtained in approximately 2000 scans. The relative areas of the 3B6-n (long chain branch) peak

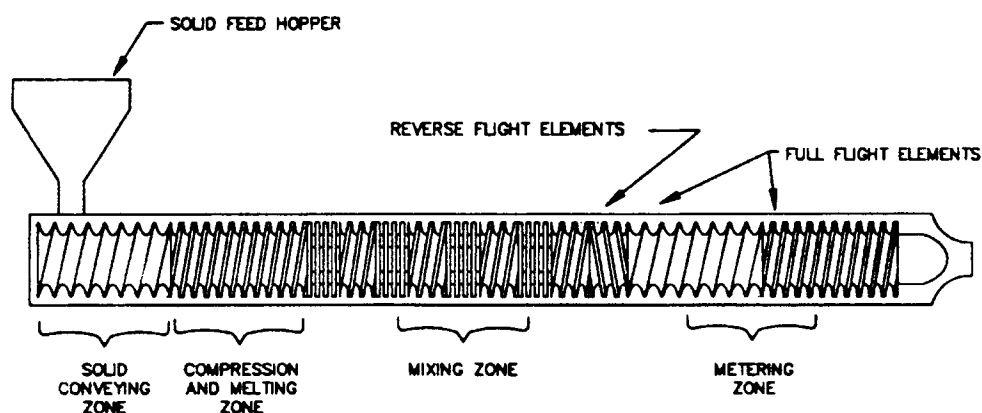


Figure 1 Twin-screw extruder configuration.

**Table I Molecular Weight Data, LLDPE, HD1-HD3, and 10 and 20% Blends**

Resin	Measured ( $\times 10^{-3}$ )		Theoretical ( $\times 10^{-3}$ )	
	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w$
LLDPE	26	95		
HD3 (MI = .07)	13	299		
HD2 (MI = 1)	17	164		
HD1 (MI = 6.3)	19	83		
10% HD3	22	110	24	115
20% HD3	23	119	22	136
10% HD2	25	112	25	102
20% HD2 <sup>a</sup>	33	100	24	109
10% HD1	22	99	25	94
20% HD1	23	95	24	93

<sup>a</sup> SEC injector problem, probably a faulty analysis.

at 32.2 ppm, the 1B2 (ethyl) peak at 11.18 ppm, and the backbone CH<sub>2</sub> peak at 29.99 ppm were determined by planimetry and used to calculate branch frequencies as branches per 1000 backbone carbons.

### Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) measurements were made on a Perkin-Elmer DSC-4 with a TADS software package to collect and analyze the data. Samples ranging in size from 5–10 mg were sealed in aluminum sample pans for analysis. Endotherms were generated at a heating rate of +10°C/h over a range of 40–170°C. An indium standard was used to calibrate the temperature scale and enthalpy of melting calculation.

### Processability Measurements

Capillary flow analysis was used to investigate the flow behavior of the blends because it has the following advantages: good reproducibility, small sample size required, a wide range of strain rates can be investigated, and the property measured can be correlated to extrusion behavior.<sup>13</sup> Constantin suggested that for film applications there is a good correlation between industrial extruder power consumption and apparent viscosity (apparent shear stress/apparent shear rate) as determined by capillary extrusion methods.<sup>14</sup>

Blends were analyzed at 190°C in all cases. A control resin was run daily during the analysis of the blend series. Flow curve reproducibility was good, with an approximately constant 95% confidence limit of  $\pm 0.3$  lb/in<sup>2</sup> over the range of shear rates

investigated. A 1 × 10-mm flat entry cylindrical die was used in the analysis of the blends, resulting in shear rates ranging from 58–576 s<sup>-1</sup>. The 10% high-density blends were also run on a Killion 1.25-in single-screw extruder with a 1.01 × 0.39 × 0.042-in slot die at 212°C. Tape samples were investigated under a microscope to observe surface structure. In addition, photographs were taken of the tape surface at 80× magnification.

In addition to flow curve analyses, extrudate swell ratios were determined by capillary extrusion methods. Four extrudate samples were cut at each shear rate once the force trace exhibited a plateau. A micrometer was used to take two measurements of each sample, approximately 1 cm from the leading end, the measurements being made at right angles to each other. From these eight measurements, the average extrudate diameter was calculated.

## RESULTS

As outlined in the experimental section, capillary extrusion techniques were used to assess the processability of the blends. The capillary rheometer used in this study employed a series of gears that could be changed to alter the crosshead speed of the plunger. As a result, shear rates were limited to preset increments. Shear rates were calculated using the following equation:

$$\text{Shear rate} = \frac{2V_{xh}d_p^2}{15d_c^3} \quad (1)$$

where  $V_{xh}$  is the crosshead velocity in cm/s,  $d_p$  the diameter of the plunger in centimeters, and  $d_c$  the diameter of the capillary in centimeters. The shear stress at a given shear rate was determined as follows:

$$\text{Shear stress} = F/[4Ap(L/d)] \quad (2)$$

where  $A_p$  is the area of the plunger in in<sup>2</sup>,  $L/d$  is the length-to-diameter ratio of the capillary, and the

**Table II Branch Content, HD1-HD3**

Resin	3B <sub>e-n</sub> (long chain)	1B <sub>2</sub> (ethyl)	Total (per 1000 backbone C)
HD3	2.7	2.9	5.6
HD2	1.7	0.3	2.0
HD1	1.6	2.6	4.2

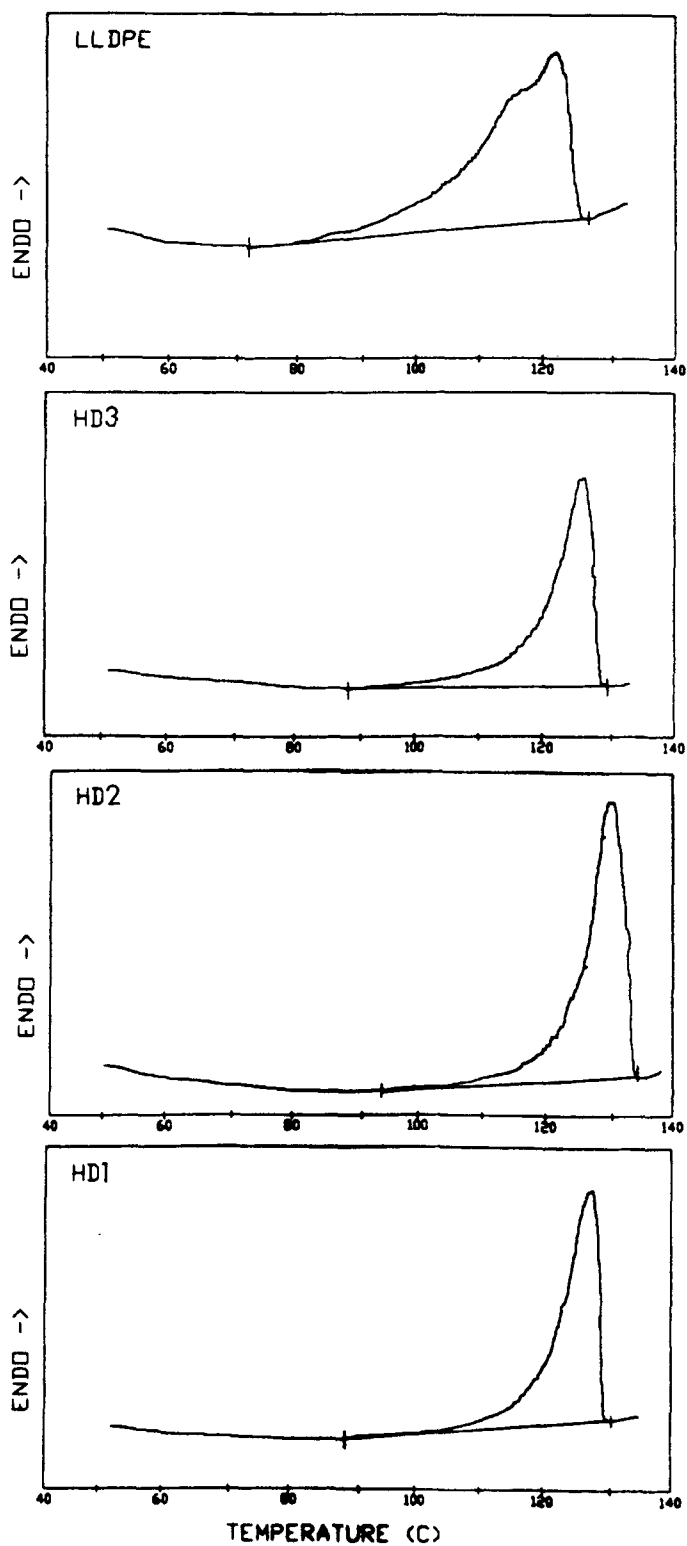


Figure 2 DSC melting endotherms, LLDPE base resin, HD1-3.

force in pounds is determined from the response of a calibrated pressure transducer interfaced with a chart recorder.

The high-density resins used in formulating the blends were analyzed in terms of molecular weight by size exclusion chromatography (SEC). As ex-

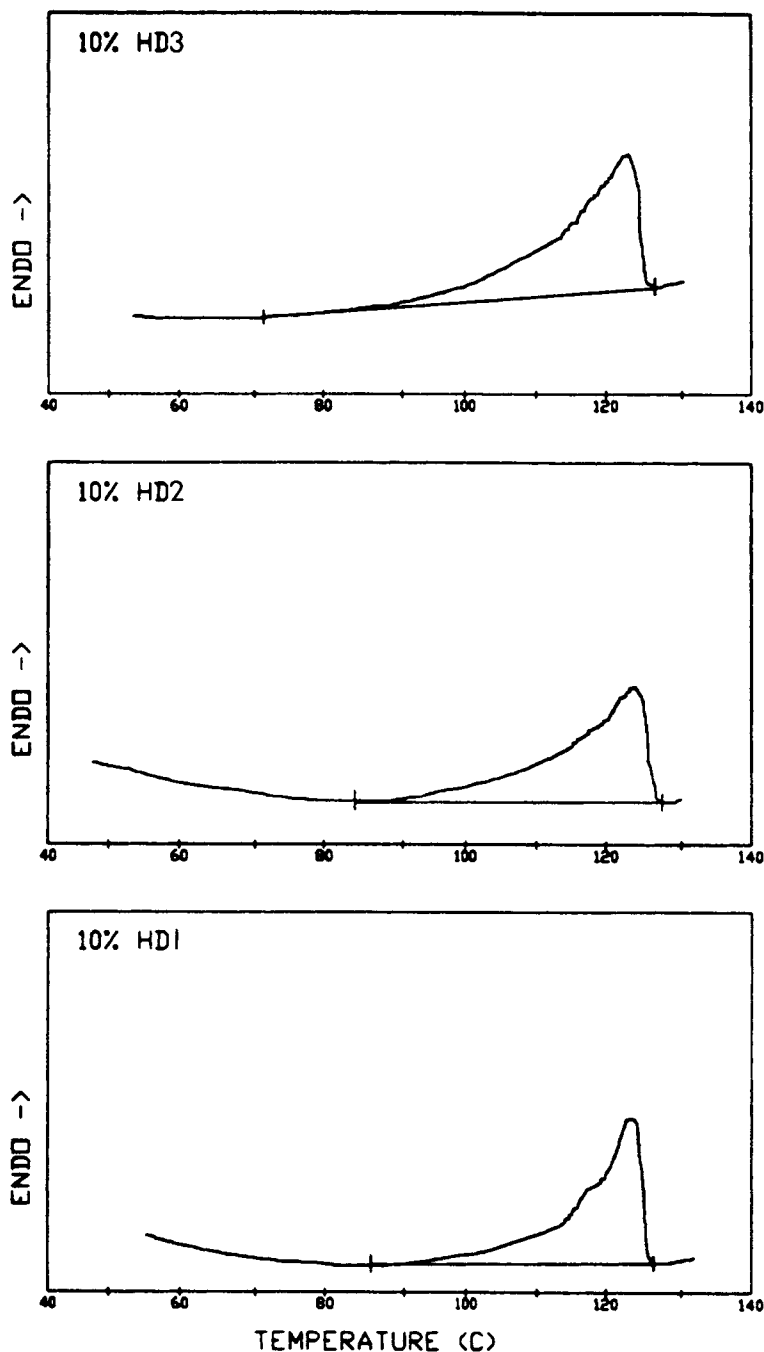


Figure 3 DSC melting endotherms, 10% HDPE blends.

pected from the reported range in melt flow index values, the weight average molecular weights were determined to be significantly different for all three resins. Table I lists the molecular weight data for the base LLDPE resin, the three high-density resins, and the 10 and 20% blends. The theoretical number average molecular weight of the mixture was calculated as follows:

$$(\bar{M}_n)_{\text{mixture}} = 1 / \sum w_i / (\bar{M}_n) \quad (3)$$

The theoretical weight average molecular weight of the mixture was calculated according to eq. (15):

$$(\bar{M}_w)_{\text{mixture}} = \sum w_i (\bar{M}_w)_i \quad (4)$$

The theoretical values appear to match the measured values reasonably well, suggesting that no great amount of chain scission occurred during the blending operation. One exception to this appears to be the 20% HD4 blend, which exhibits a high  $\bar{M}_n$  and

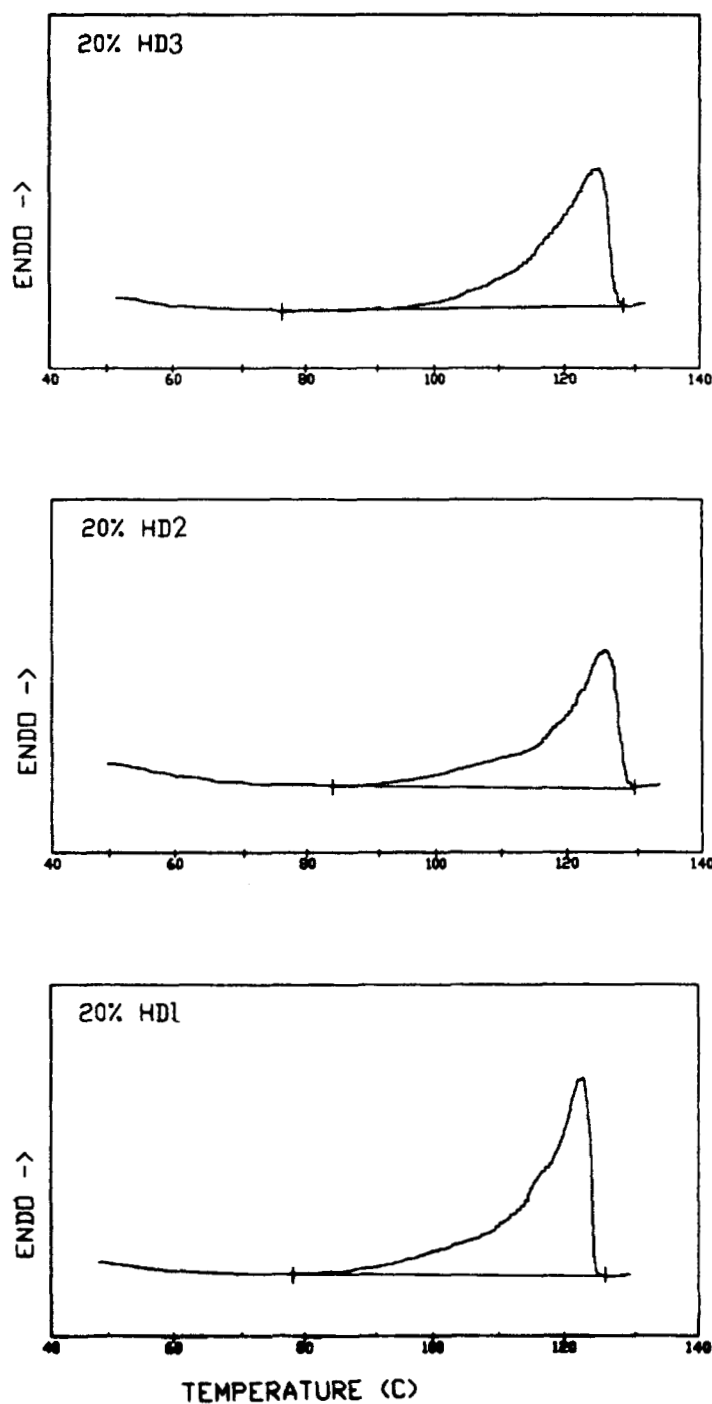
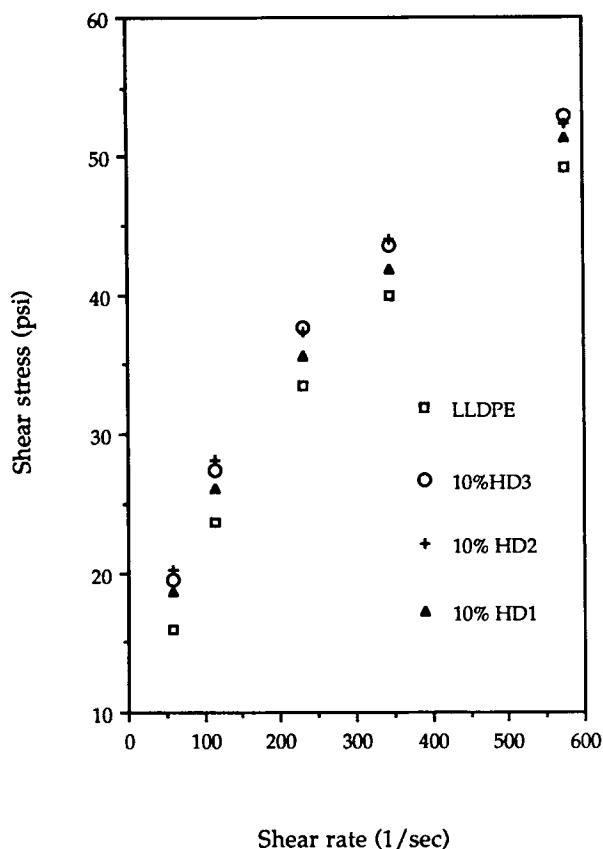


Figure 4 DSC melting endotherms, 20% HDPE blends.

low  $\bar{M}_w$ . Upon reviewing the original SEC data, it was evident that there was an injector problem resulting in an incorrect amount of solution being injected. As a result, the viscometer averages were abnormally high and the LALLS numbers low. The universal calibration is not affected in this case and,

indeed, the original data shows that these numbers fall in line with the rest of the series.

In addition to molecular weight analysis, average long chain and short chain branch content was determined by  $^{13}\text{C}$  NMR analysis. Table II lists the branching data for the three HDPE resins under



**Figure 5** Flow curve from capillary extrusion, LLDPE base resin, 10% blends.

consideration. HD3 has a slightly higher average long chain branch content compared to HD1 and HD2. These small differences are not, however, expected to affect the processability characteristics of the blends. In terms of short chain branch content, HD2 is a virtually linear resin with 0.3 short chain branches per 1000 backbone carbons compared to 2.6 and 2.9 short chain branches per 1000 backbone carbons for HD1 and HD3, respectively.

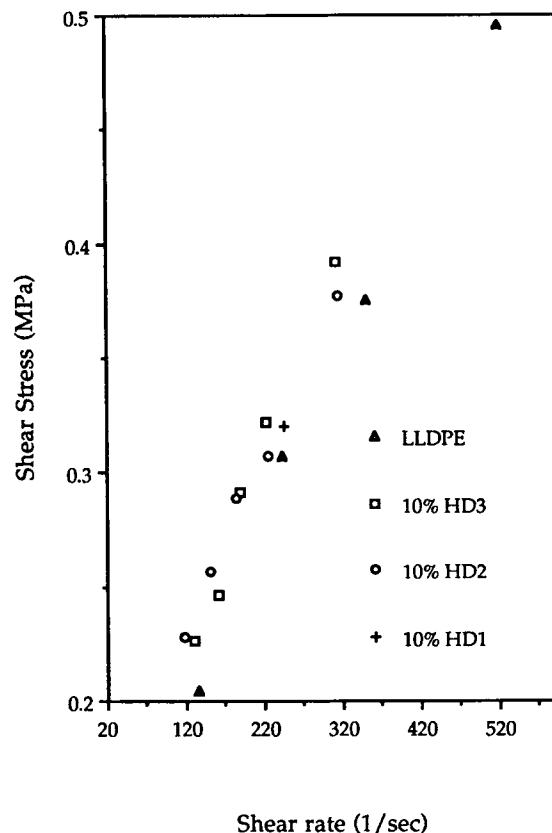
**Table III** Flow Curve Data, LLDPE Base Resin, HD1-HD3

Shear Rate (s <sup>-1</sup> )	Shear Stress (lb/in <sup>2</sup> )			
	LLDPE	HD3	HD2	HD1
58	15.9	30.5	12.9	4.8
115	23.7	38.1	18.3	7.9
230	33.5	46.7	25.7	12.4
346	39.9	52.4	31	16.2
576	49.2	—	38.1	21.4

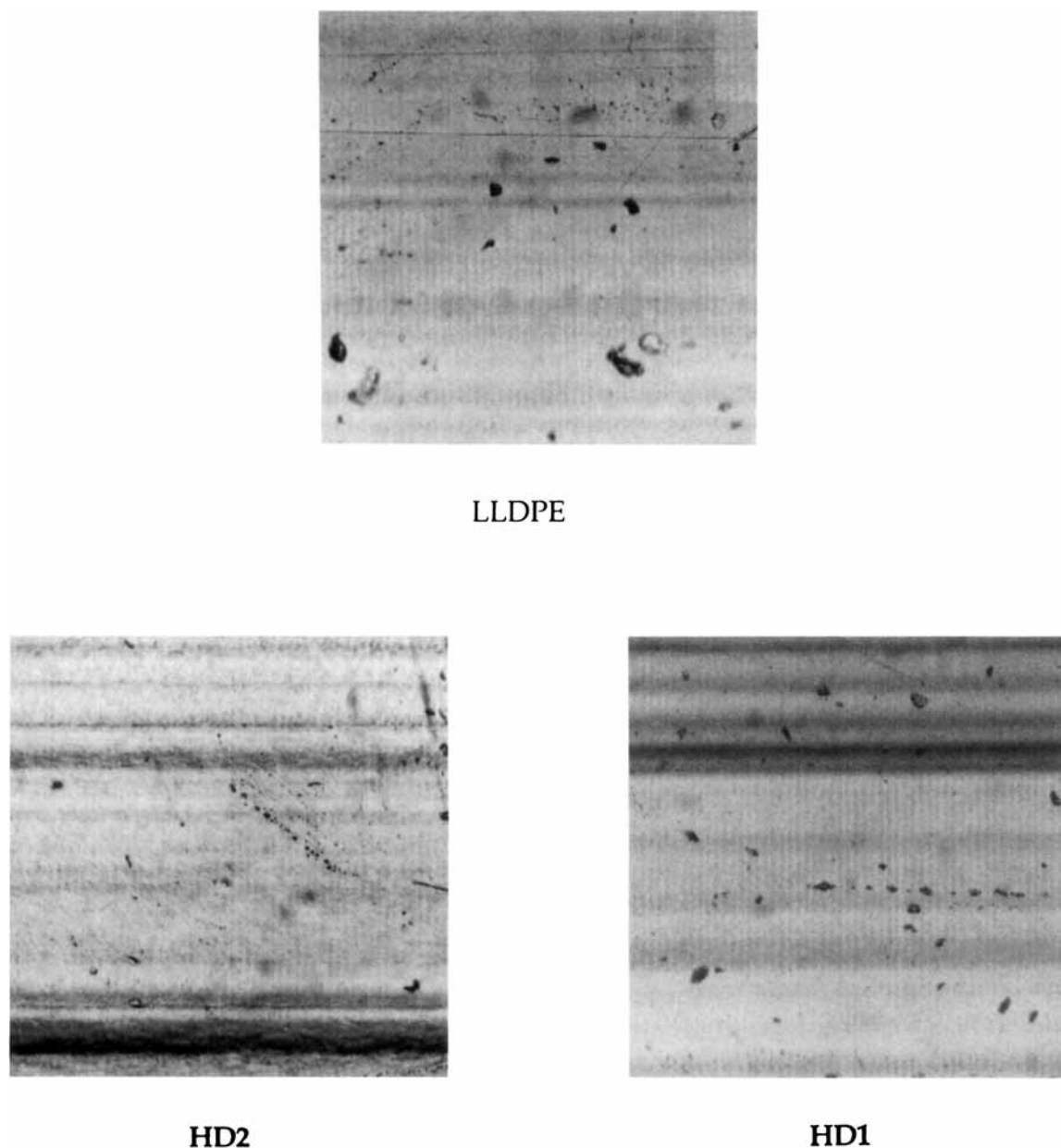
**Table IV** Flow Curve Data, 10 and 20% HDPE Blends

Shear Rate (s <sup>-1</sup> )	Shear Stress (lb/in <sup>2</sup> )					
	10% HD3	10% HD2	10% HD1	20% HD3	20% HD2	20% HD1
58	19.5	20.2	18.6	19.3	19.3	17.1
115	27.5	28.1	26.2	27.1	27.1	24.3
230	37.6	37.4	35.7	36.7	36.7	33.1
346	43.6	44.0	41.9	42.9	43.1	39.0
576	52.9	52.4	51.4	51.4	51.4	47.6

DSC studies were carried out on the blends to determine whether intimate mixing was achieved during the blending process. Figure 2 shows the melting endotherms of the virgin LLDPE and the HDPE additives. Figures 3 and 4 display the melting endotherms of the 10 and 20% HD1-HD3 blends, respectively. It appears from these traces that the blending operation was successful because there ap-



**Figure 6** Flow curve from single-screw extrusion, LLDPE base resin, 10% blends.



**Figure 7** Photographs of tape surfaces, 80 $\times$  magnification, 2.5 rpm.

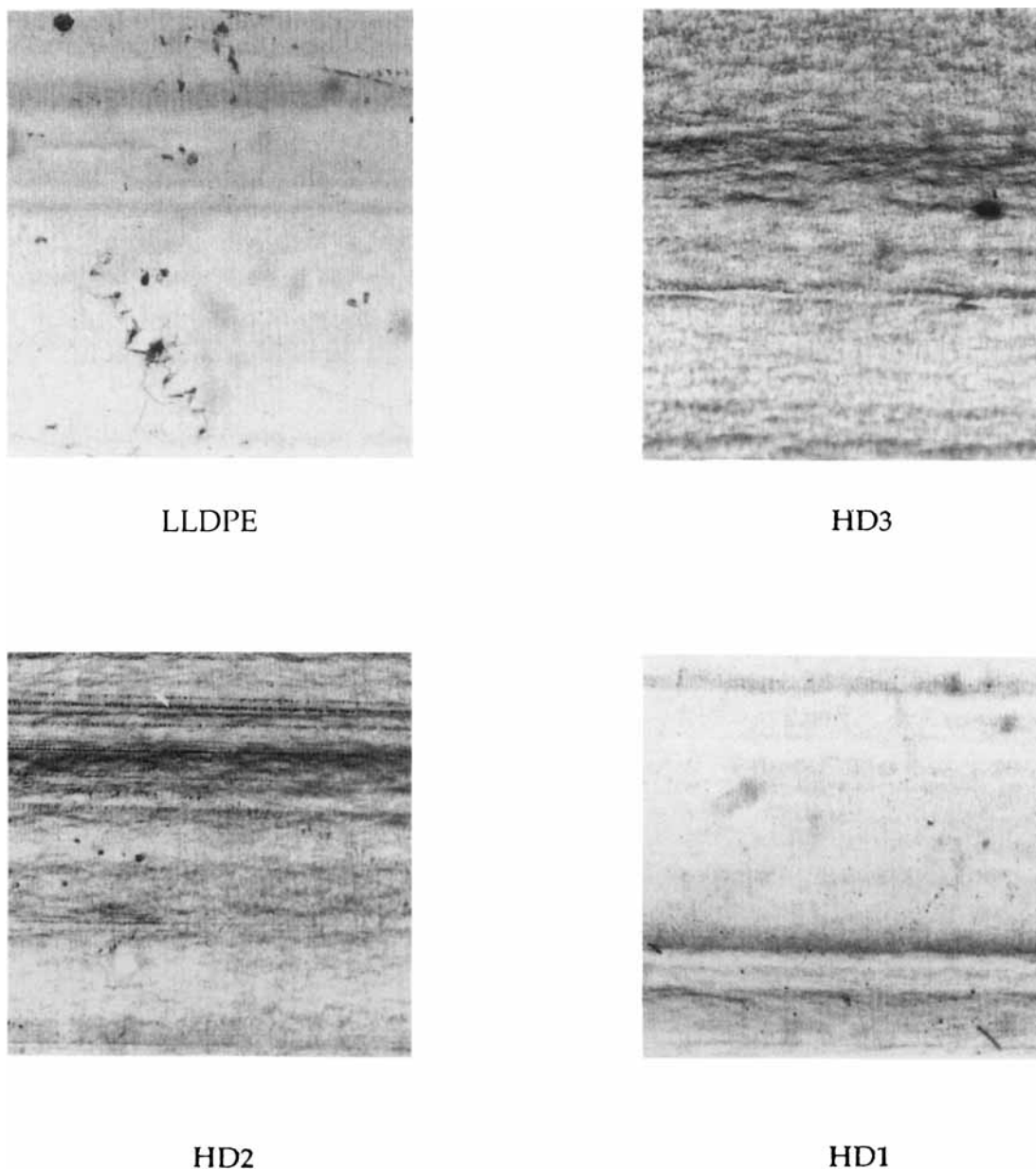
pears to be only one “crystalline” peak in evidence in addition to the lower melting component of the LLDPE base resin. However, because the high-density peak of the LLDPE component and the HDPE peak melt over very similar ranges, any phase segregation at 10 or 20% HDPE would be very difficult to detect.

Figure 5 is a plot of apparent shear stress as a function of apparent shear rate for the base LLDPE resin (as received) and the 90/10 LLDPE–HD1–3 blends. All three blends exhibit higher shear stresses at a given shear rate as compared to the base

LLDPE. Table III lists the shear stress as a function of shear rate for the three high-density resins and the linear low-density base resin. HD1 and HD2 have lower apparent viscosities in comparison to the base LLDPE resin, yet all six blends show an increase in apparent viscosity relative to the base LLDPE (Table IV). It is interesting to note that the higher-molecular weight HD2 and HD3 blends yield approximately equivalent flow curves.

Single-screw tape extrusion of the 90/10 LLDPE–HDPE blends yields the same information with the HD2 and HD3 blends exhibiting similar,



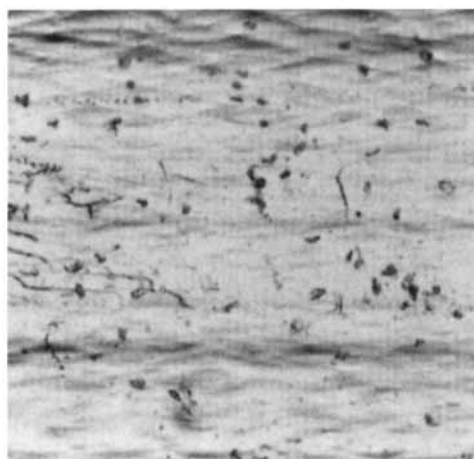


**Figure 8** Photographs of tape surfaces, 80 $\times$  magnification, 4 rpm.

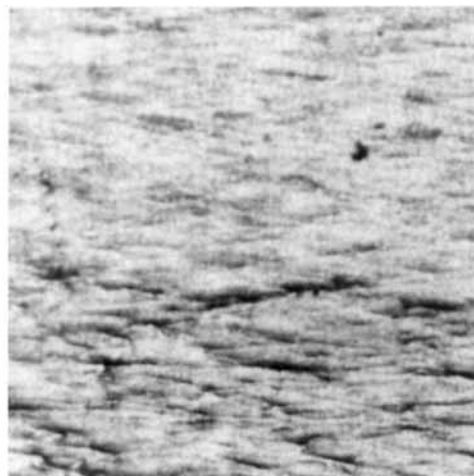
higher shear stresses at a given shear rate as compared to the base resin (Fig. 6). As noted above in the capillary extrusion trials, the HD1 blend exhibits a flow curve that is shifted upward relative to the base LLDPE resin but not to the same extent as the HD2 and HD3 blends. Analysis of extrudate samples at progressively increasing shear rates indicates that the HD2 and HD3 blends exhibit haze at lower shear rates compared to the base resin and the HD1 blend. Figures 7–9 show a series of photographs of tape surfaces at progressively increasing screw speeds. All four samples display smooth, glossy surfaces at

the lowest screw speeds with the HD2 and HD3 blends exhibiting haze at 2.5 rpm (no photograph of HD3 blend at 2.5 rpm available) compared to the observation of haze at 4 rpm for the HD1 blend (Fig. 8) and 6 rpm for the base LLDPE resin (no photographs available at 6 rpm). At 8 rpm (Fig. 9), all four resins exhibit fully developed haze.

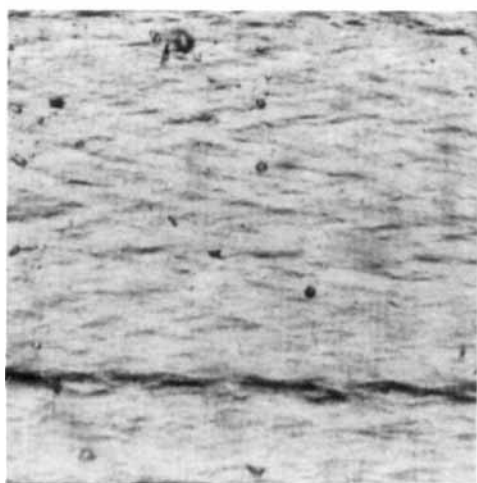
The flow curve data as listed in Table IV (plotted in Fig. 10) indicates that for the blends composed of 20% HDPE in LLDPE B the flow curves follow the same order as the 10% blends but are shifted slightly downward in comparison. Because the HD1



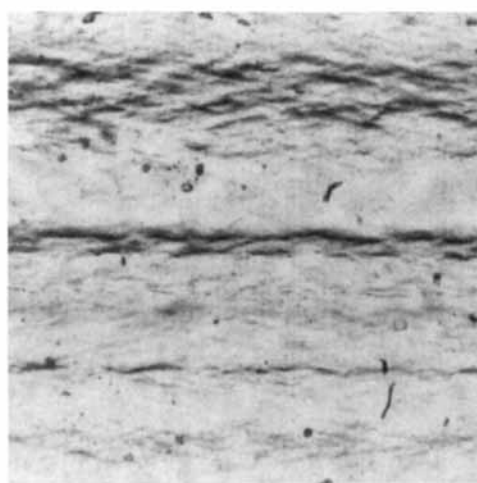
LLDPE



HD3



HD2



HD1

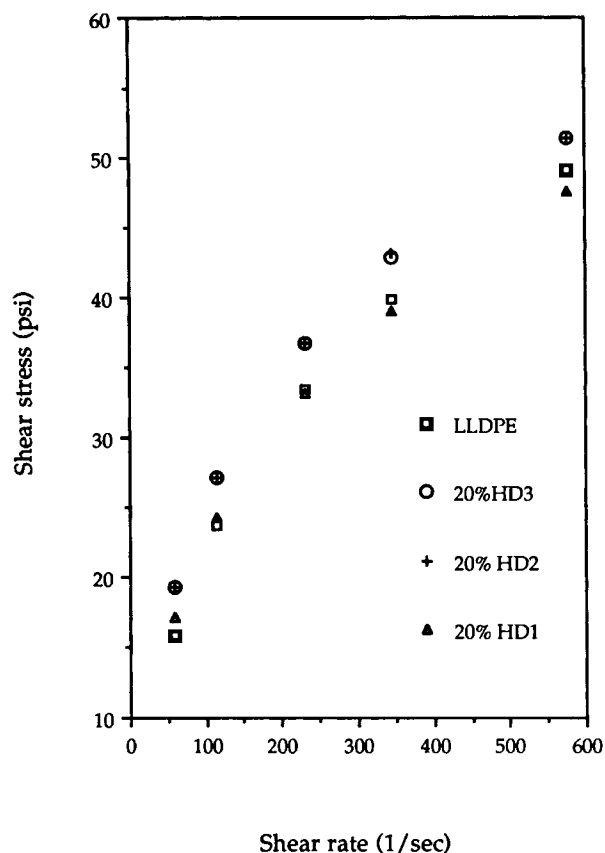
**Figure 9** Photographs of tape surfaces, 80× magnification, 8 rpm.

and HD2 resins are less viscous than the LLDPE base resin, this downward shift in going from 10 to 20% HDPE is not surprising.

Upon considering the relative viscosities of the blend components, it is very likely that the HD3 resin is not mixing into the base LLDPE because its melt index is approximately 1/14 that of the major blend component. As stated previously, viscosities must be well matched to achieve effective mixing. A likely situation in this case is that the more viscous minor component is "swimming" in the less viscous major component, which is absorbing all the

shearing during mixing. The more viscous component functions as a filler because molecules of the two polymers are not dispersed uniformly. This may account for the fact that the HD3 flow curve is not shifted upward relative to the HD2 curve as might be expected given the much higher weight of the HD3 resin.

In addition to flow curve analysis, extrudate swell was determined as a function of shear rate (Table V). In all cases, the blends exhibited higher extrudate swell ratios compared to the base LLDPE. Blends with HD3 (highest molecular weight addi-



**Figure 10** Flow curve from capillary extrusion, LLDPE base resin, 20% blends.

tive) exhibited the greatest increase in extrudate swell at both 10 and 20% by weight. This is not surprising because melt elasticity is expected to increase as the molecular weight distribution is broadened, as the average molecular weight is increased, and also with increasing numbers of linear molecules. Cogswell<sup>13</sup> suggested that in a melt with a broad molecular weight distribution the long molecules form a network around the shorter molecules. As the melt is stressed, the long chains accept a

disproportionately large amount of stress, leading to an above-average elastic response. At 10% by weight, the HD1 and HD2 blends exhibit approximately equivalent swelling behavior. At 20% by weight, HD1 exhibits slightly greater extrudate swell ratios compared to the 20% HD2 blend. An increase in melt elasticity as determined by extrudate swell measurements is likely to contribute to the development of melt defects, thereby having a negative effect on processability.

In considering the above results, it is evident that the linear character of the high-density portion of the distribution has a large effect on processability. It could be argued that the increase in average molecular weight that results from blending the higher-molecular-weight HD2 and HD3 resins into the LLDPE base resin is the cause of the observed processability differences. However, the addition of a high-density component of lower average molecular weight (HD1) than the base resin also causes an upward shift in the flow curve, an increase in extrudate swell, and a lower critical shear rate at the onset of haze. These results cannot be attributed to molecular weight effects.

## CONCLUSIONS

In this type of study, there are a number of variables to consider. To investigate high-density additives with sufficiently different molecular weights, it is unavoidable that the melt indices be vastly different. Mixing is a critical step. Vadhar and Kyu demonstrated that blends exhibited positive or negative deviations from additive rheological behavior, depending upon the mixing technique.<sup>9</sup> Given the broad range of melt indices exhibited by the high-density resins used in this study, it was difficult to ensure that the blends had similar degrees of mixing. In addition, flow curve analysis is not extremely enlightening although it does have the advantage of

**Table V** Extrudate Swell Ratios, LLDPE Base Resin, 10 and 20% HDPE Blends

Shear Rate (s <sup>-1</sup> )	Extrudate Swell Ratio						
	LLDPE Base	10% HD3	10% HD2	10% HD1	20% HD3	20% HD2	20% HD1
58	1.47	1.66	1.53	1.54	1.70	1.55	1.59
115	1.51	1.71	1.59	1.60	1.76	1.60	1.63
230	1.61	1.81	1.65	1.66	1.79	1.63	1.70
346	1.67	1.83	1.70	1.74	1.80	1.69	1.73
576	1.73	1.90	1.79	1.81	1.87	1.79	1.78

requiring small sample sizes and offers the possibility for melt elasticity analysis because extrudate swell measurements can be performed.

Given these limitations, the blending study detailed above led to the following conclusions. In the case of blends of linear low density with HDPE, it appears that the molecular weight of the linear fraction has some effect. Blends formulated with HD2 showed an upward shift in the flow curve that was greater than that caused by the addition of the lower-molecular-weight HD1. It is likely that the very high viscosity of HD3 prevented complete mixing, resulting in a poorly dispersed blend.

In terms of melt elasticity, the addition of HDPE to an LLDPE base resulted in increased extrudate swell ratios regardless of the molecular weight of the high-density component. It is evident from this study that it is not only the high-molecular-weight characteristics of the linear fraction of a pure LLDPE but also the linear nature that affects processability. It was observed that addition of 10% HD1 resulted in lower shear rates at the onset of haze, an increase in extrudate swell, and an upward shift in the apparent viscosity compared to the LLDPE base resin despite the fact that the average molecular weight of the blend was slightly lower than that of the base resin.

These results support the conclusions outlined in a previous study by the authors,<sup>1</sup> suggesting that an increase in the fraction of high-density molecules results in a decrease in processability both in terms of viscosity and melt elasticity. These effects result in a lower critical shear rate at the onset of melt defects such as haze and sharkskin.

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