

***Blown Film
Characterization
Of Metallocene
Resins Made In
The Phillips Slurry
Loop Process***

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Laboratory Line – The line consists of a 38 mm (1.5 inch) diameter single screw Davis Standard extruder (L/D=24; 2.2:1 compression ratio) fitted with a barrier screw with a Maddock mixing section at the end. The die used was 102 mm (4 inch) in diameter and was fitted with a Dual Lip Air Ring using ambient cooling air. The die gap was 1.52 mm (0.060 inch). The film blowing was done at typical LLDPE conditions as follows: 2.5:1 blow up ratio (BUR), "in-pocket" bubble configuration and 190°C extruder and die set temperatures. The evaluations were made at an output rate of 27.2 kg/hr (60 lb/hr) using a screw speed setting of 115 RPM. These conditions were chosen since the film properties so obtained scale directly with those from larger commercial scale film blowing operations⁽¹⁾.

Commercial Line – This line consists of a 89 mm (3.5 inch) diameter single screw extruder (L/D=24; 2.2:1 compression ratio) fitted with a LLDPE barrier screw. The die used was 203 mm (8 inch) in diameter and was fitted with a Dual Lip Air Ring using chilled air at 15°C (59°F). The die gap was 1.52 mm (0.060 inch). The film blowing was done at typical LLDPE conditions as follows: 2.5:1 blow up ratio (BUR), "in-pocket" bubble configuration and 190°C extruder and die set temperatures. The evaluations on this line were made at an output rate of 113 kg/hr (250 lb/hr or 10 lb/hr/inch of die circumference).

Blown Film Properties

The film properties were measured as follows:

1. Dart impact strength – ASTM D1709 (method A)
2. Machine (MD) and transverse (TD) direction Elmendorf tear strengths – ASTM D1922
3. % Haze was measured in accordance with ASTM D1003 on a XL-211 Hazegard System.
4. Gloss (60°) was measured as per ASTM D2457.

Blown Film Resins

A wide range of metallocene resins, deemed suitable for blown film applications, and ranging in density from 0.905 – 0.942 g/cc and in MI from 0.7 – 3 MI were evaluated using typical LLDPE type film blowing conditions. More fundamental characteristics of these resins are presented in the subsequent sections. For the sake of brevity all Phillips metallocene resins, which were made with a commercial catalyst designated as PA, will be referred to as PPCo-M resins in the remainder of this manuscript.

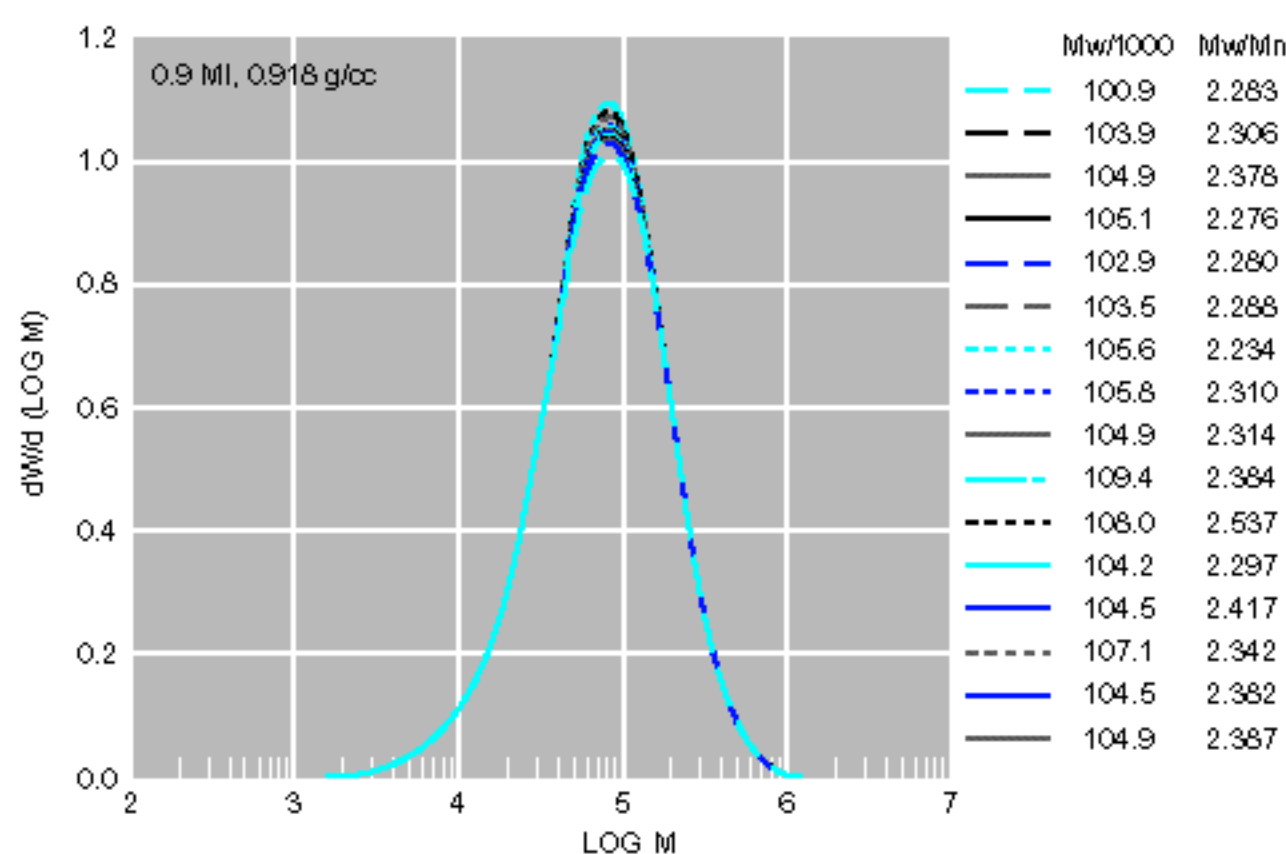
RESULTS AND DISCUSSION

Molecular Characteristics of PPCo-M Resins

Gel permeation chromatography (GPC) traces for sixteen commercial lots of PPCo-M LLDPE resins (0.9 MI, 0.918 g/cc density) are shown in Figure 1. The data indicates that PPCo-M resins are very narrow in molecular weight distribution (MWD) with a polydispersity of between 2.2 – 2.5. Furthermore, the product consistency due to the single-site nature of the metallocene catalyst is obvious from Fig. 1.

FIGURE 1
Gel Permeation Chromatography (GPC) Traces for Sixteen Commercial Lots of PPCo-M Metallocene LLDPE Resins

(Showing Narrow MWD and Good Product Consistency)



The rheology (complex viscosity versus frequency at 190°C) of three representative PPCo-M metallocene resins (0.7 MI, 1.0 MI and 1.5 MI) is shown in Figure 2 along with comparative data for a 1 MI conventional Ziegler-Natta catalyst LLDPE and a commercially available 1 MI metallocene resin (designated as m-LLDPE in Fig. 1) which is believed to contain some level of long chain branching (LCB). Further comparisons of the rheological and molecular characteristics of these polymers are tabulated and shown in Table 1 for a number of PPCo-M resins varying from about 0.7 – 3 MI along with data for a commercial m-LLDPE with LCB, a conventional Ziegler-Natta LLDPE, a chrome catalyst based broad MWD low density linear polyethylene (PC-1) and a conventional high pressure-low density PE (HP-LDPE).

FIGURE 2

Rheology of PPCo-M Metallocene Resins (0.7, 1.0 and 1.5 MI) along with Comparative Data for a 1 MI Conventional Ziegler-Natta (Z-N) LLDPE and a 1 MI m-LLDPE with Long Chain Branching

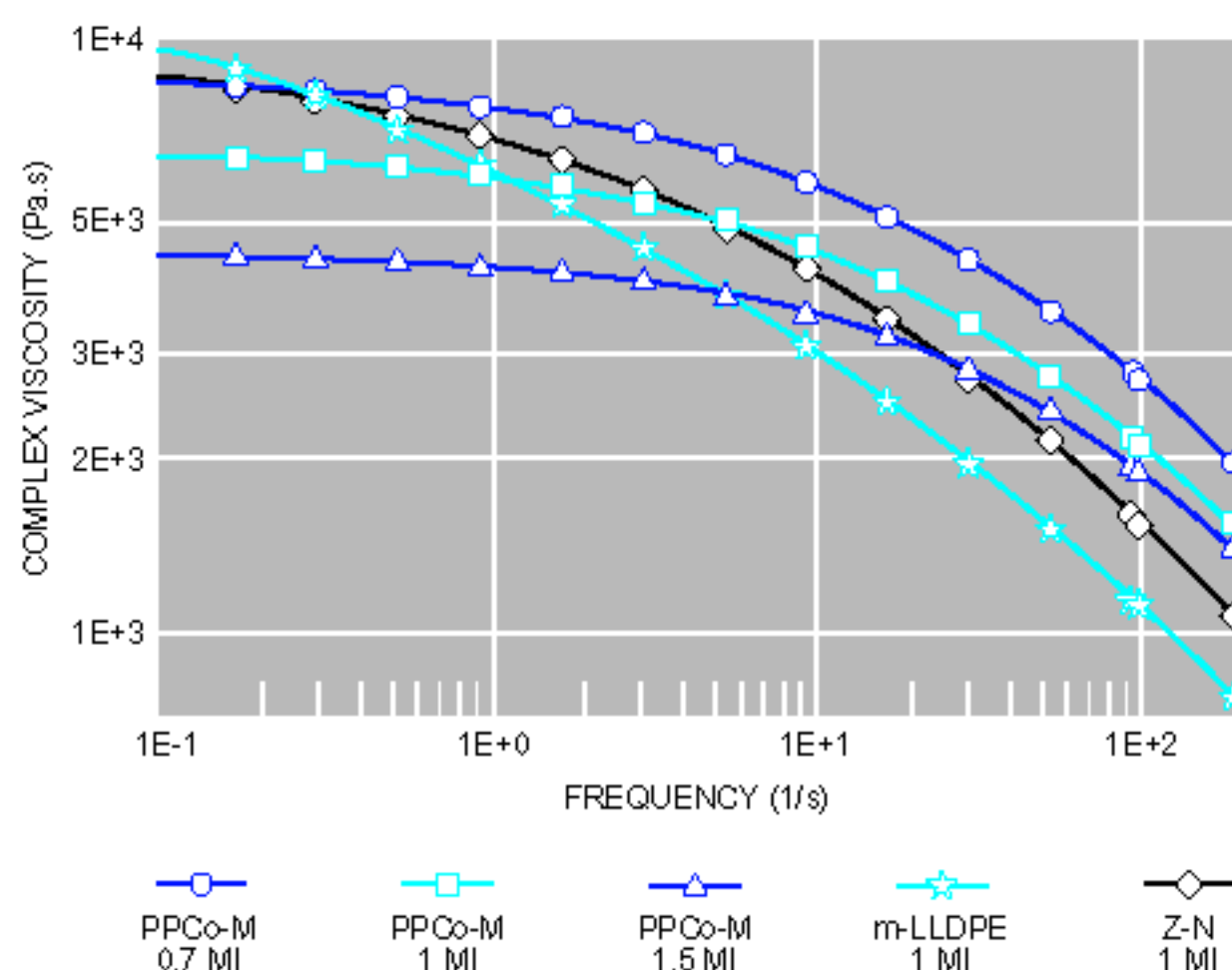


TABLE 1

Rheological and Molecular Characteristics of Several PPCo-M Metallocene Resins Along with Comparative Data for Several Other Resin Types

RESIN	Ea (kJ/mol)	MI (g/10 min)	Mw (kg/mol)	Mn (kg/mol)	Mw/Mn
PA-1	21.7	0.72	107.32	48.27	2.22
PA-2	23.3	1.00	95.49	44.50	2.15
PA-3	23.7	1.36	87.09	38.42	2.24
PA-4	23.7	1.89	80.37	36.44	2.21
PA-5	22.1	2.80	73.36	31.77	2.31
Ziegler-Natta LLDPE	23.9	1.00	108.11	26.45	4.08
m-LLDPE	41.0	1.00	83.29	36.07	2.36
PC-1	33.9	0.24	215.68	12.65	17.04
HP-LDPE	44.5	1.81	73.47	23.33	3.36

Examination of the flow activation energies, E_a , shows that the PPCo-M metallocene resins exhibit the lowest E_a values of about 24 kJ/mol similar to that for the Ziegler-Natta LLDPE. In contrast, the chrome catalyst resin PC-1 has a higher E_a value of about 34 kJ/mol, the commercial m-LLDPE with LCB still higher at 41 kJ/mol and the HP-LDPE with the highest E_a value at 44.5 kJ/mol. It is well known in the literature that the E_a value is indicative of the level of long chain branching, increasing as the level of LCB increases^[4]. Thus the data in Table 1 clearly suggests an absence of any LCB in the PPCo-M resins.

With reference to Fig. 2 again, the PPCo-M metallocene resins exhibit a lower degree of shear thinning than either the Ziegler-Natta LLDPE or the m-LLDPE. This is attributed to the fact that PPCo-M resins are narrower in MWD than the conventional Ziegler-Natta LLDPE and furthermore do not contain any long chain branching as shown in Table 1.

Lastly, it should also be mentioned that the short chain branching distribution (SCBD) or comonomer distribution in the PPCo-M resins has been shown to be extremely homogeneous across the entire molecular weight distribution due to a unique self-induced short chain branching mechanism that occurs with this particular catalyst during polymerization of ethylene^[4]. The ramifications of this homogeneous SCBD will be discussed further in a later section.

Blown Film Properties

Effects of Resin Density and Molecular Weight –

The dart impact strength, MD tear strength and TD tear strength of 25 micron (1 mil) blown films as a function of resin density are shown in Figures 3, 4 and 5, respectively. It should be noted that these resins were processed without any slip/antiblock agents and without a processing aid. From Figure 3, it is observed that the dart impact strength increases, as expected, as resin density decreases following a nearly exponential relationship. At 0.910 g/cc density, no breaks were observed up to the maximum dart weight tested which was 1400 g. Dart impact strengths of about 425 g were obtained at 0.918 g/cc density and of about 100 g at 0.930 g/cc density.

The MD and TD tear strengths showed a somewhat different dependence on resin density than the dart impact strength. As can be seen from Figs. 4 and 5, the MD and TD tear strengths are both roughly constant up to a resin density of 0.925 g/cc exhibiting values of about 225 g and 450 g, respectively. Above 0.925 g/cc density, a steady decline in both tear properties with increasing density can be readily seen.

FIGURE 3
Effect of Resin Density on Dart Impact Strength
25 Micron (1 mil) PPCo-M Metallocene Blown Films

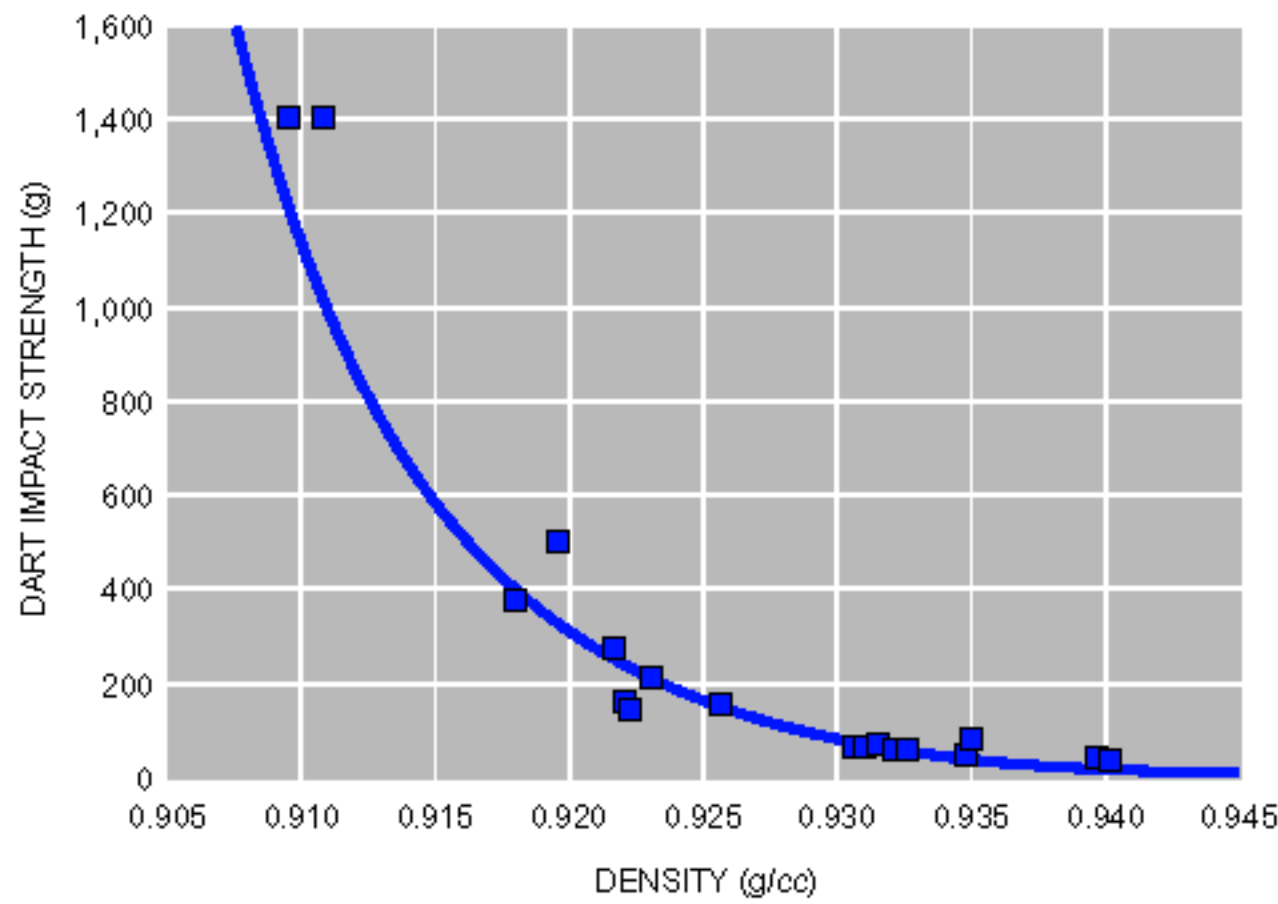
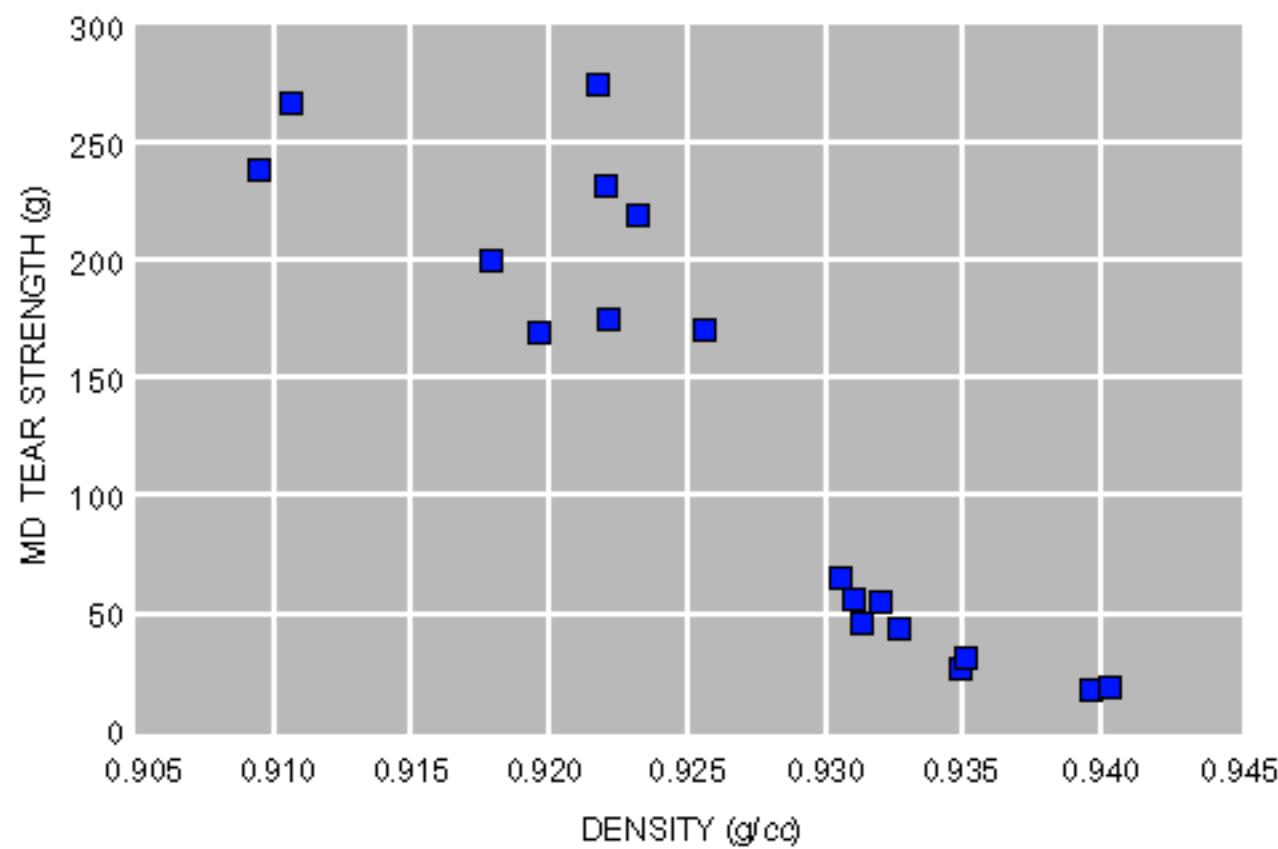


FIGURE 4
Effect of Resin Density on Machine Direction (MD) Elmendorf Tear Strength
25 Micron (1 mil) PPCo-M Metallocene Blown Films



The film properties were found to be essentially independent of molecular weight (inverse MI) for the range of resins examined. This independence may be seen from Figure 6 where the TD tear strength is shown as a function of resin MI. It is quite clear that there is no effect of molecular weight on TD tear. The dart impact and MD tear strength properties were similarly independent of molecular weight as well.

FIGURE 5
Effect of Resin Density on Transverse Direction (TD) Elmendorf Tear Strength
25 Micron (1 mil) PPCo-M Metallocene Blown Films

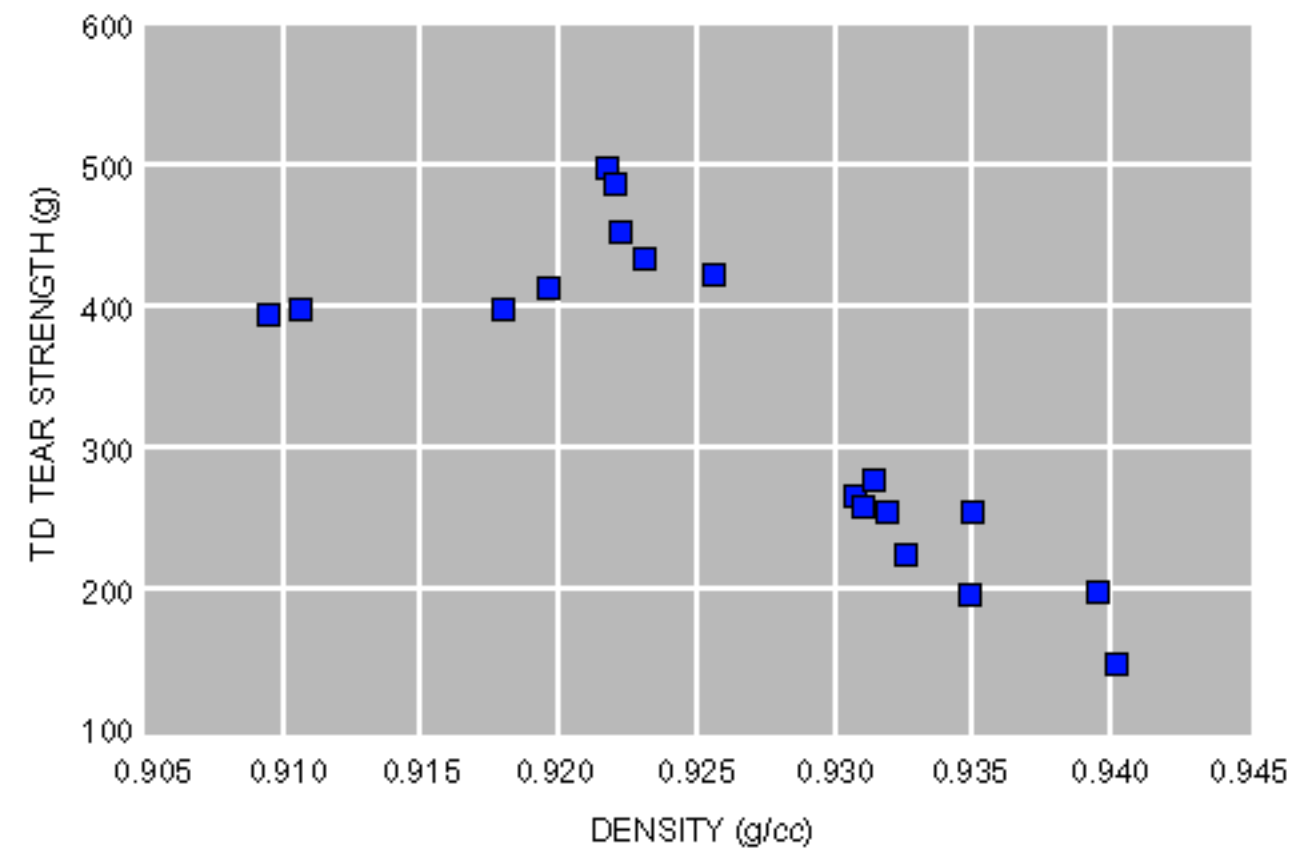
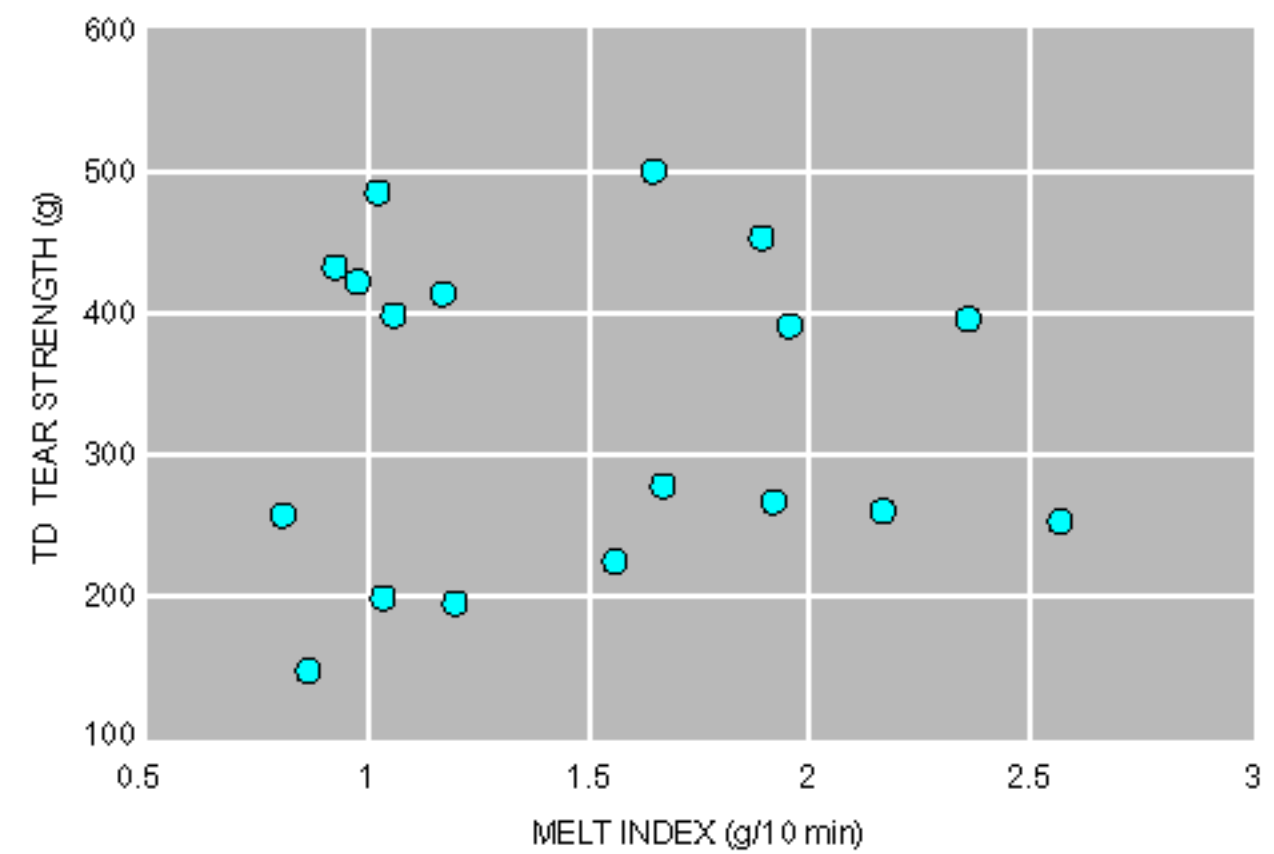


FIGURE 6
Effect of Resin Melt Index (Inverse Molecular Weight) on Transverse Direction (TD) Elmendorf Tear Strength
25 Micron (1 mil) PPCo-M Metallocene Blown Films

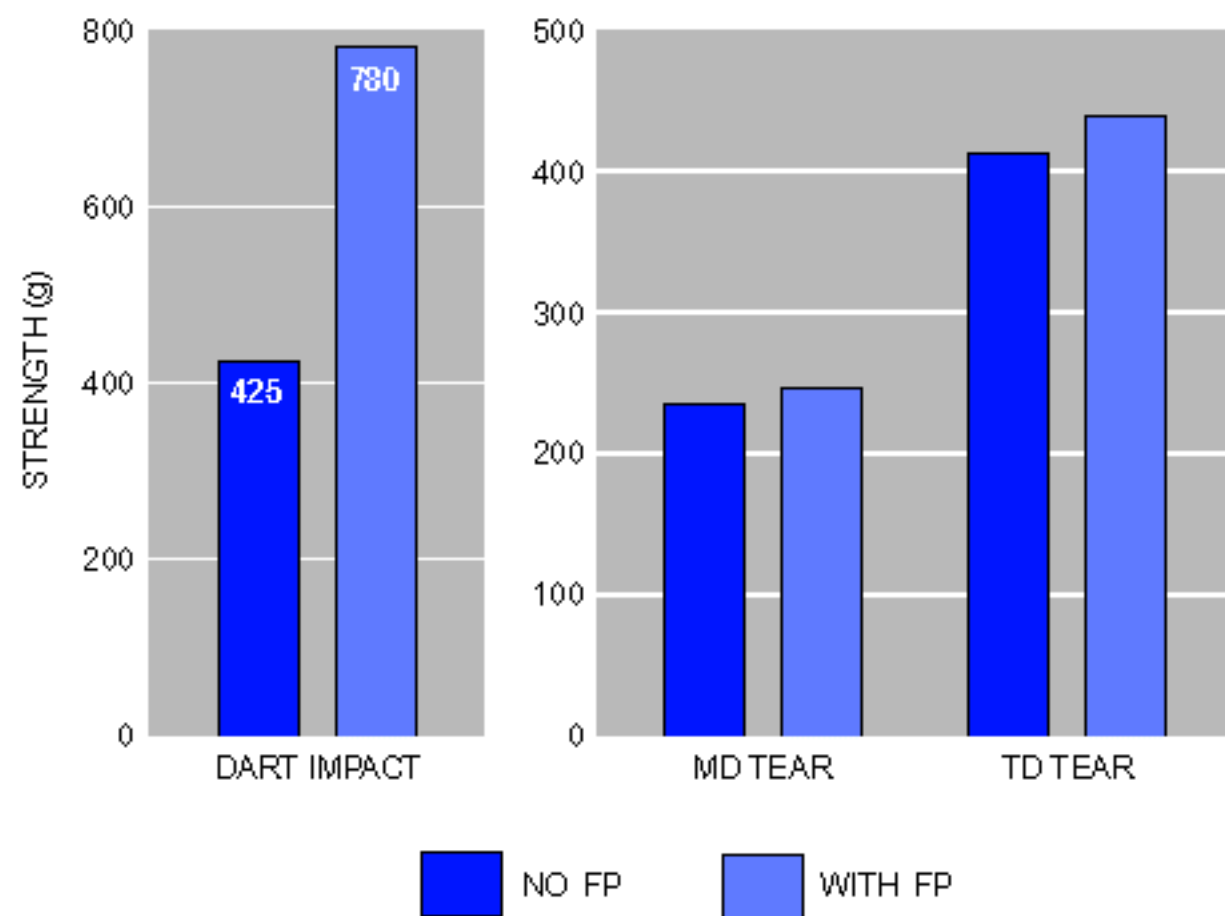


Effect of Processing Aid – Fluoropolymer processing (FP) aid (Dynamar FX-9613 from Dyneon), which is normally incorporated into LLDPE resins to improve processability and prevent melt fracture, was found to have a positive effect on the impact strength of PPCo-M blown films as shown in Figure 7. The dart impact strength increases from 425 g to 780 g upon addition of a low level of FX-9613. Interestingly, no change in either of the tear properties is observed in Fig. 7.

FIGURE 7

Effect of Fluoropolymer (FP) Processing Aid on Blown Film Properties

25 Micron (1 mil) PPCo-M Metallocene LLDPE Resin (0.9 MI, 0.918 g/cc)

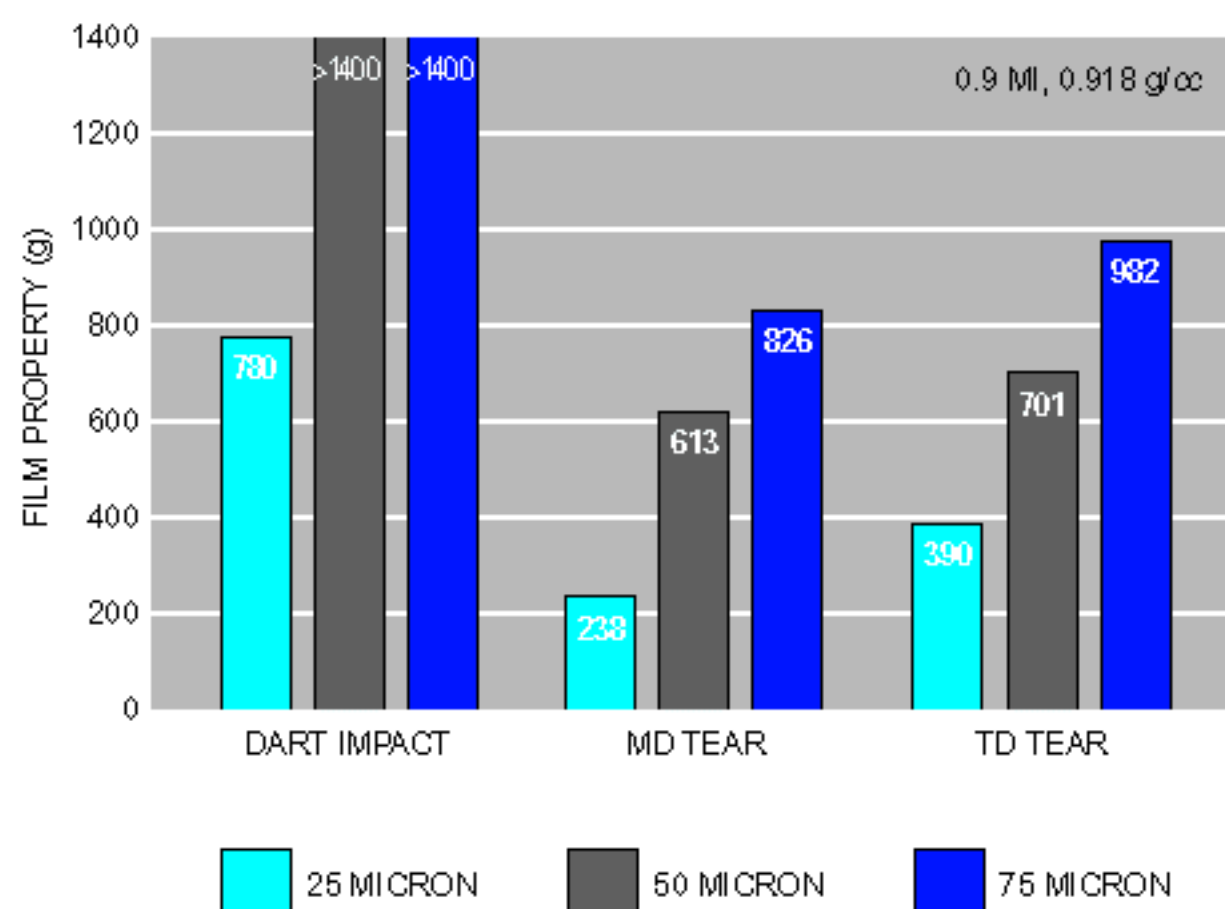


impact strength of 780 g for the 1 mil blown film and greater than 1400 g for the 2 and 3 mil films. The MD tear strength increases more than proportionally with film gauge i.e. a doubling of thickness results in more than a doubling of the MD tear strength. In contrast, the TD tear strength increases but less than proportionally with thickness. Thus as the film gauge increases, the lower drawdown ratios required to obtain thicker films results in films with more balanced film properties as can be seen from the TD/MD tear strength ratio from Fig. 8 which decreases from 1.6 to 1.2 for the 1 mil and 3 mil films, respectively.

Clarity of Metallocene Blown Films – One of the more unusual and unique features of the PPCo-M resins was the excellent clarity exhibited in blown films for resins ranging in density from as low as 0.905 g/cc to as high as 0.942 g/cc which is well into the high density regime. Good clarity is typified by low % haze and high % gloss. In Figure 9 are shown graphically the effects of both resin density and film thickness or gauge on % haze. It is seen that the % haze for the 25 micron or 1 mil blown films shows a largely linear dependence on resin density and furthermore ranged from only 3 – 8 % for this entire density range of 0.905 – 0.942 g/cc. Furthermore, it should be noted that the gloss (60°) for these films ranged from about 110 – 135 %. The excellent clarity of these blown films even for resin densities above 0.925 g/cc was surprising and largely unexpected. This is currently thought to be a consequence of two main factors. First, as was mentioned earlier, the current commercial PPCo-M catalyst has been shown to provide an extremely homogeneous short chain branching distribution across the entire molecular weight spectrum^[9]. This uniform SCBD (both intermolecular and intramolecular) is expected to result in small and uniformly sized crystallites which inhibit any significant scattering of transmitted light. Secondly, the narrow MWD and the absence of any LCB (as shown earlier) in these resins results in very low polymer melt elasticity. The low melt elasticity results in a very smooth film surface which minimizes any scattering of reflected light. A combination of these two factors provides for blown films (and expectedly cast films as well) with low % haze and high % gloss, resulting in unusually superior clarity at low and high densities. The clarity at medium to high densities provides the potential of an unusually good balance of film clarity and stiffness properties.

FIGURE 8

Effect of Film Thickness on Blown Film Properties of PPCo-M Metallocene LLDPE Resin



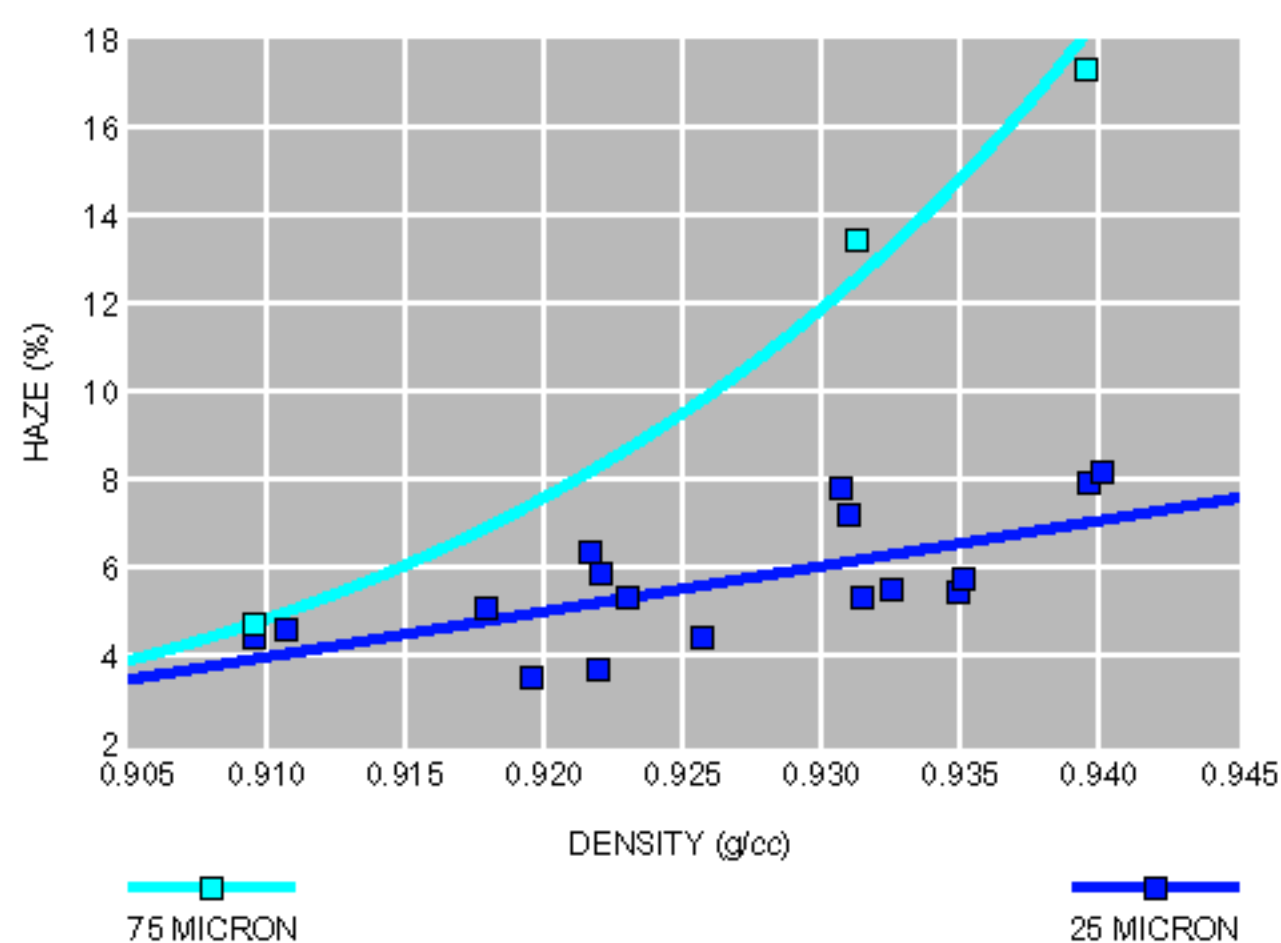
Effect of Film Thickness – The effect of film thickness on film properties was explored by making higher gauge (2 mil and 3 mil) blown films. A representative example of this type of data is shown for a 0.9 MI, 0.918 PPCo-M metallocene LLDPE resin (with FP) in Figure 8. Note that the properties for the higher gauges are reported as measured and are not normalized per unit thickness. The dart impact strength increases roughly proportionally with thickness with an

As may be seen from Fig. 9, at higher gauges (75 micron or 3 mils) the clarity of the films shows a much more exponential dependence on resin density. At low densities (for example 0.910 g/cc), there is virtually no change in % haze between the 25 micron and 75 micron films. As resin density increases, the % haze of the 75 micron films increases exponentially. Even so,

it can be seen from Fig. 9 that even a 75 micron film of a 0.939 g/cc density resin has a haze value of only about 18 % haze which for this density and film gauge is considered to be exceptionally good. Benchmarking comparisons given later in this report will show that even 25 micron blown films from conventional LLDPE (~0.918 g/cc) resins routinely exhibit 15 – 20% haze.

FIGURE 9
Effects of Film Thickness and Resin Density on Clarity of PPCo-M Metallocene Blown Films

As Measured by % Haze. Low % Haze Indicates High Clarity

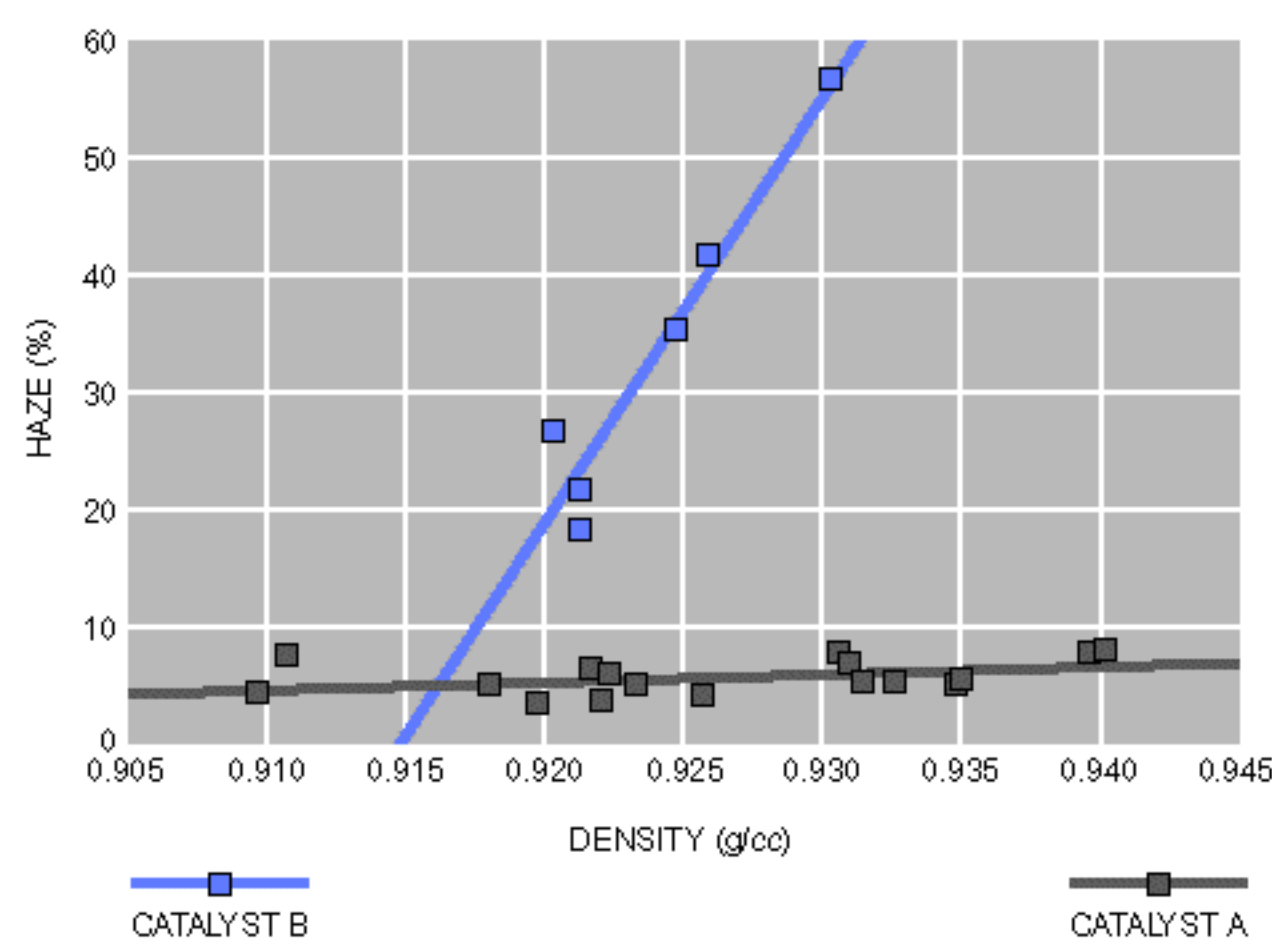


In the course of the development of a commercially viable metallocene catalyst, it was learned that contrary to popular perception today not all metallocene catalysts give resins that exhibit good clarity. A clear example of that is demonstrated in Figure 10 where the % haze of 1 mil blown films made from resins of similar MI and density from two different catalysts, PA and PB, is shown as a function of resin density. Catalyst PA (as discussed above) provides excellent clarity in the entire density regime investigated. However, and quite dramatically, catalyst PB yields resins that exhibit very poor clarity as evidenced by the much higher haze at comparable densities. In addition, it is also noteworthy that the slope of change in % haze as a function of density for resins from catalyst PB is significantly higher than for resins from catalyst PA. It is currently believed that this considerable difference in film clarity stems, at least in large part, due to differences in the short chain branching distribution. Preliminary results suggest that while catalyst PA gives resins with a very homogeneous SCBD, resins from catalyst PB in fact exhibit a heterogeneous SCBD [13]. The above data strongly suggests that good clarity of

metallocene based resins depends on some very fundamental molecular characteristics and therefore should not be considered a given for resins made with all metallocene catalysts.

FIGURE 10
Effect of Metallocene Catalyst Type on Clarity of Blown Films as Determined by % Haze Measurements

25 Micron (1 mil) Film. Low % Haze Indicates High Clarity



Blown Film Processability

The blown film processability of PPCo-M metallocene resins using typical LLDPE film blowing conditions was observed to be very good, requiring no modifications of existing LLDPE film blowing equipment. A dual lip air ring, as is standard in all LLDPE set-ups, is however required due to the inherently poor melt strength of all LLDPE type resins. Some processability limitations were encountered with these resins due to their unique molecular characteristics and these factors are outlined below along with a discussion of the common means to overcome them.

Blocking Behavior – It was observed that for metallocene resins lower than roughly 0.925 g/cc density, the bubble exhibited considerable friction with the wooden collapsing tower and nip rolls. In addition, these films also tended to block or consolidate on the take-up rolls after being allowed to sit for 24 – 48 hours. Such blocking behavior is typical of LLDPE resins resulting in very high coefficients of friction (COF) as has been noted in the literature [14, 15, 16, 17]. Furthermore, the blocking behavior has been noted to be strongly dependent on the resin density, increasing as the density decreases [14].

The degree of blocking was assessed through the measurement of the COF (static) and data for 25 micron (1 mil) PPCo-M blown film resins of various densities is shown in Figure 11. The data in Fig. 11 is for resins with (a) no slip/antiblock and no fluoropolymer (FP) processing aid (b) no SA but with FP (c) with SA and no FP and (d) with SA and with FP. The data reveals some interesting trends. First, resins with no SA and no FP (diamond symbols) do show high COF values of about 1. Perhaps surprisingly, the same resins with no SA but with FP (square symbols) show even higher COF or blocking. This is thought to be a consequence of the fact that the FP processing aid results in a very smooth, almost glass-like film surface which serves to promote greater surface contact between the two film surfaces in the blown tube resulting in higher degree of blocking. Upon addition of 3 wt % (based on total polymer) of a commercially available LLDPE slip/antiblock concentrate (Ampacet 10430 AB PE MB from AMPACET Corp. which itself contains 5 wt % slip, 25 wt % antiblock and 70 wt % of a LLDPE carrier resin) to the resins below 0.925 g/cc density, the COF is significantly reduced to about 0.15 – 0.25 which brings the COF into a more appropriate range for ease of processing and film handling. It should be added here that the 3 wt % level was not optimized in any way but rather was thought to be more than sufficient to overcome the processing and blocking difficulties encountered in the whole density range studied between 0.900 – 0.925 g/cc.

FIGURE 11
Effect of Slip/Antiblock (SA) and Fluoropolymer (FP) Processing Aid on Coefficient of Friction-Static

25 Micron (1 mil) PPCo-M Metallocene Blown Films

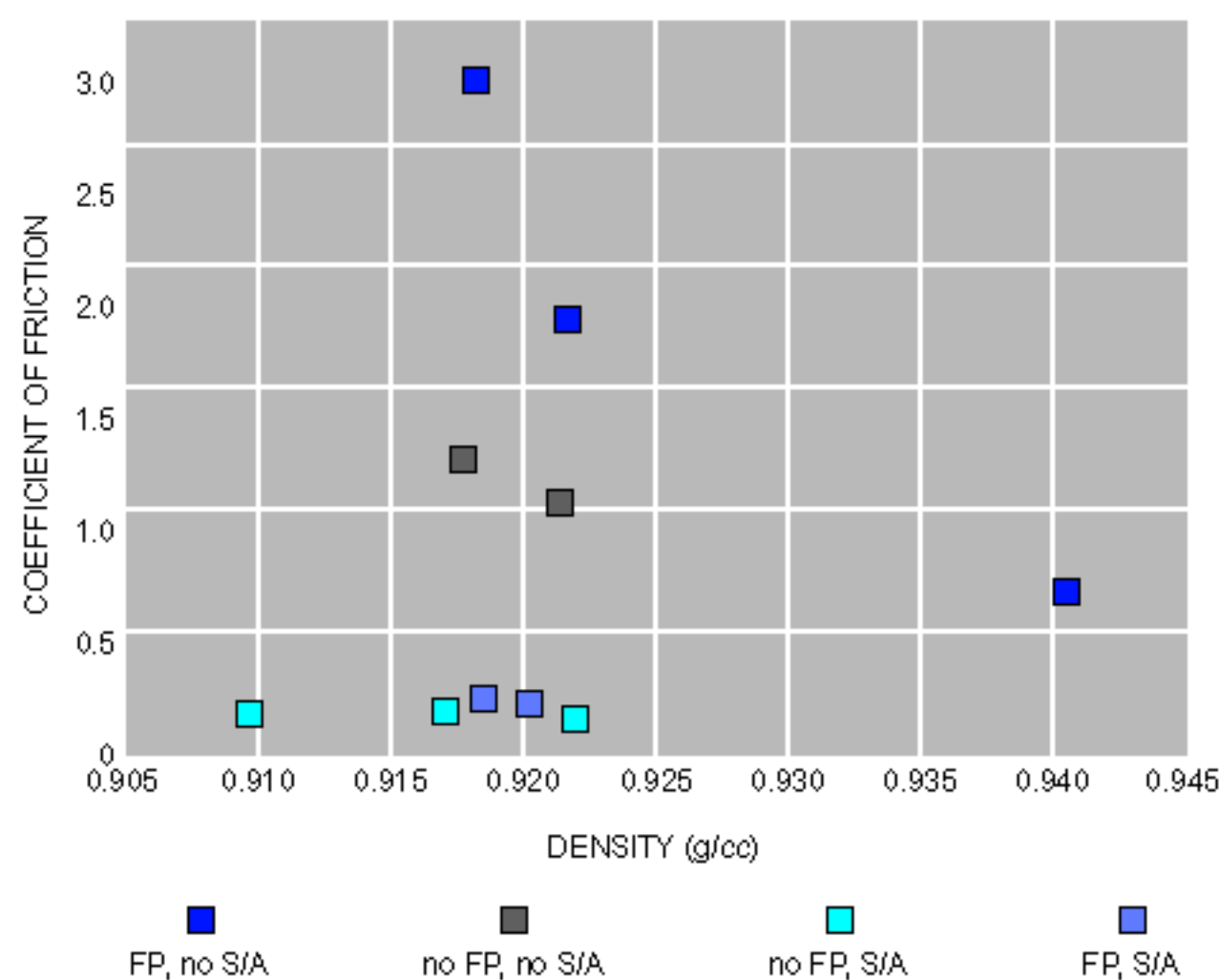
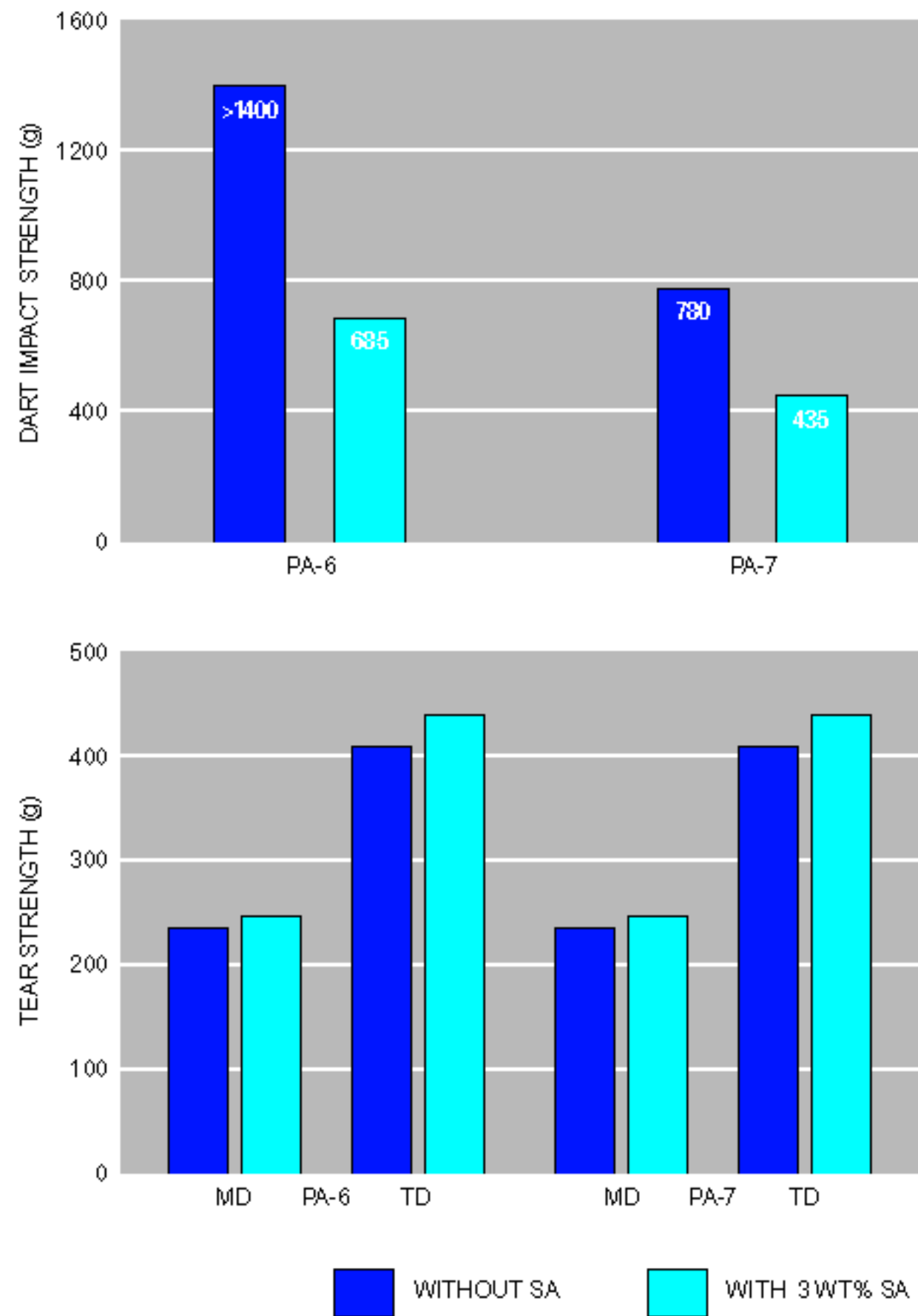


FIGURE 12
Effect of Slip/Antiblock (SA) on Blown Film Performance

PPCo-M Metallocene Resins:
 PA-6 (2MI, 0.910 g/cc), PA-7 (0.9 MI, 0.918 g/cc)



Besides the intended effect of the SA, which was to reduce the COF, some unintended and undesirable effects on blown film performance were also observed. The effects of addition of 3 wt % SA on film properties is shown in Figure 12 for two resins, PA-6 (2 MI, 0.910 g/cc) and PA-7 (0.9 MI, 0.918 g/cc). The dart impact strength for both resins reduces upon addition of the SA concentrate. However, there is essentially no effect of the SA on either of the tear strengths. This reduction in impact strength is unexpected and reasons for it are not fully known at this time. However, it is likely due to poor interfacial adhesion of the antiblock (believed to be non surface-treated silica) with the polymer matrix. A reduction in impact strength of high density polyethylene (HDPE) using unmodified calcium carbonate has been observed recently [9]. In that same study, it was further shown that using modified

calcium carbonate instead actually reversed that trend and resulted in an increase in the impact strength of the HDPE. Lastly, the clarity of the blown films as measured by haze did decrease (haze increased roughly by a factor of 2) upon addition of this level of SA. Therefore, some penalty in clarity should be expected with the addition of any particulate (silica here) agent, even at low levels.

Melt Fracture – Another common problem in the blown film processing of LLDPE type resins is the occurrence of sharkskin or surface melt fracture (SSMF) as noted in the literature ^[19, 20, 21]. The occurrence of SSMF is dependent on output rate, die geometry (gap), temperature and melt viscosity as well as other factors. It is well understood in the literature that SSMF occurs at a critical shear stress, although this stress level can vary with polymer structure (Mw, MWD, LCB, etc.). For the metallocenes resins of interest here, it was observed that the critical shear stress in the blown film die was of the order of 0.2 MPa. In resins which did exhibit melt fracture, addition of 0.07 wt % fluoropolymer processing aid (Dynamar FX-9613 from Dyneon) completely eliminated the SSMF. It is important to clarify that the need for fluoropolymer to prevent SSMF in these resins will depend on a variety of processing factors mentioned above and thus cannot be generalized here. In addition, it should be recalled that the use of processing aid also resulted in an improvement in the dart impact strength of the blown film as shown in an earlier section.

Bubble Stability – While no quantitative measure of bubble stability of the PPCo-M metallocene resins during film blowing was performed in this study, some comment about the general processability of these resins is appropriate. As is now widely recognized and well understood, metallocene resins are typically characterized by their narrow MWD and virtually no long chain branching (Dow CGCT resins are exceptions since they do contain some long chain branching ^[21]). These molecular characteristics, while responsible for the improved metallocene properties such as clarity, toughness, low heat sealing, etc., also result in lower melt strength than conventional Ziegler LLDPE resins ^[22]. In addition, metallocene resins tend to run hotter than Ziegler LLDPEs (due to more viscous heating in the extruder – a consequence of higher high shear rate viscosities), thereby requiring more cooling. These general metallocene processing characteristics were found to be applicable to the PPCo-M resins as well. Thus PPCo-M metallocene resins exhibit comparable bubble stability to other metallocene resins but decreased bubble stability compared to Ziegler LLDPEs. However, it should be reemphasized that PPCo-M resins ran very well on standard LLDPE/LDPE equipment and required no modifications whatsoever.

BENCHMARKING STUDIES

In an effort to gain a comprehensive understanding of the processing-property tradeoffs with PPCo-M metallocene resins compared to other metallocene and Ziegler LLDPE resins, a number of benchmarking studies were performed in-house on a commercial scale blown film line described in the experimental section. The results of these studies are summarized in Tables 2 – 4.

In Table 2, the performance properties of a 50 micron (2 mil) blown film made from a 2 MI, 0.910 g/cc PPCo-M metallocene resin are compared to data for several commercial metallocene resins taken directly from the resin manufacturer's data sheets. While some differences in the film performance are no doubt attributable to the differences in film blowing, the main point of the data is to show that PPCo-M metallocene resins provide equal or better film properties compared to currently available metallocenes.

TABLE 2
Comparison of Blown Film Performance of PPCo-M Metallocene Resin with Commercial Metallocenes

PROPERTY	X*	Y*	Z*	PPCo-M
Catalyst	Metallocene	Metallocene	Metallocene	Metallocene
MI (g/10 min)	1	1	1	2
Density (g/cc)	0.902	0.908	0.915	0.910
Gauge (microns)	50	50	50	50
Dart Impact (g)	>830	>830	550	>1400
MD Tear (g)	355	480	360	613
TD Tear (g)	500	650	760	701
Gloss, 60° (%)	90	85	78	98
Haze (%)	1.1	3.0	4.9	4.4

* All data for resins X, Y and Z is taken from the manufacturer's data sheets.

In Table 3, a PPCo-M metallocene LLDPE resin (0.9 MI, 0.918 g/cc) is compared to three other commercially available metallocenes. All the data in Table 3 was obtained by blowing the various resins under identical film blowing conditions. Resins L and M, due to their much lower densities, were processed with slip/antiblock concentrate whereas resin N and the PPCo-M resin were processed without SA. Resins L and M show lower dart impact strength than the other

two resins despite their lower densities due to the negative effect of antiblock on impact strength shown earlier. A comparison of resin N with the PPCo-M resin shows that while the film properties are mostly comparable, the PPCo-M film exhibits superior clarity as evidenced by the significantly lower haze and much higher gloss values for the PPCo-M film. This data is further indication, as suggested earlier with reference to Fig. 10 as well, that not all metallocene resin films exhibit good clarity.

TABLE 3
Comparison of Blown Film Performance of PPCo-M Metallocene LLDPE with Several Commercial Metallocenes Resins

PROPERTY	L	M	N	PPCo-M
Catalyst	Metallocene	Metallocene	Metallocene	Metallocene
MI (g/10 min)	1	1.5	1	0.9
Density (g/cc)	0.902	0.905	0.917	0.918
Slip and Antiblock	yes	yes	no	no
Gauge (microns)	25	25	25	25
Dart Impact (g)	646	618	>810	>810
MD Tear (g)	157	104	211	209
TD Tear (g)	321	238	331	419
Gloss, 60° (%)	87	-	96	133
Haze (%)	10.7	-	32.1	4.0

All data obtained on 8 inch die, 0.060" gap, 2.5:1 BUR, 250 lb/hr

Lastly, a comparison of a PPCo-M metallocene LLDPE resin with three commercially available Ziegler LLDPE resins of similar MI and density is shown in Table 4. Once again, the data in Table 4 was obtained by blowing all resins at identical conditions on the commercial scale line. The resins were all processed without any slip/antiblock. The clear advantage of metallocene resins relative to conventional Ziegler LLDPE resins is evident from this table which shows significantly higher impact strength and superior clarity for the PPCo-M resin compared to the Ziegler resins. Dart impact strengths for the PPCo-M resin are higher than the comparable Ziegler resins by a factor of about 8 – 15 times. Furthermore, the clarity of the PPCo-M film is clearly superior to any of the Ziegler LLDPEs. The tear strength properties of the PPCo-M resin show a mixed picture, with equivalence to resins R and T but lower tear strengths compared to resin S. Finally, the

TABLE 4
Comparison of Blown Film Performance of PPCo-M Metallocene LLDPE with Several Commercial Ziegler-Natta (Z-N) LLDPEs

PROPERTY	R	S	T	PPCo-M	PPCo-M
Catalyst	Z-N	Z-N	Z-N	Metallocene	Metallocene
MI (g/10 min)	1	0.7	1	0.9	0.9
Density (g/cc)	0.920	0.923	0.918	0.918	0.918
Slip and Antiblock	no	no	no	no	no
Gauge (microns)	25	25	25	25	12.5
Dart Impact (g)	120	116	62	>810	446
MD Tear (g)	277	385	114	209	93
TD Tear (g)	475	561	509	419	271
Gloss, 60° (%)	62	68	95	133	121
Haze (%)	18.4	19.5	12.2	4.0	5.0

All data obtained on 8 inch die, 0.060" gap, 2.5:1 BUR, 250 lb/hr

additional data in Table 4 for the 12.5 micron (0.5 mil) PPCo-M blown film shows the potential to downgauge these resins and yet maintain a good balance of performance characteristics. It can be easily seen from Table 4 that the dart impact strength of the 12.5 micron PPCo-M film is still considerably higher than any of the 25 micron conventional LLDPE resins and continues to show good clarity as well, although at some expense of the tear strengths.

CONCLUSIONS

A wide range of metallocene resins ranging in MI from 0.7 – 3 g/10 min and in density from 0.905 – 0.942 g/cc made in the Phillips slurry loop process were evaluated for blown film applications at typical LLDPE type processing conditions. These metallocene resins were characterized to be narrow in molecular weight distribution (2.2 – 2.5 polydispersity) and free of any long chain branching. Blown films from these resins exhibited an excellent balance of film properties such as dart impact and tear strengths, clarity and processability. The impact and tear strengths were observed to depend primarily on resin density, increasing as the density decreased. No dependence of film properties on molecular weight (inverse MI) was observed in the range investigated. A low level of

fluoropolymer processing aid was found to result in a significant improvement in impact strength but no change in tear strengths. The dart impact and MD tear strength properties of higher gauge films (2 mil and 3 mil) increased roughly proportionally with thickness while the TD tear strength increased less than proportionally with thickness resulting in an improved TD/MD tear balance at higher gauges. The clarity, as measured by haze and gloss, of all blown films ranging from 0.905 – 0.942 g/cc was found to be excellent and unusual. Resins in the entire density range from the low density range of 0.905 g/cc to the high density range of 0.942 g/cc exhibited haze in range of 3 – 8 % haze and gloss (60°) in the range of 110 – 135 %. This unusually high clarity, particularly at densities above 0.925 g/cc is currently believed to be due to a combination of two factors – homogeneous short chain branching distribution at both the intermolecular and intramolecular levels and low polymer melt elasticity.

Significant blocking (high COF) was observed in blown films especially below 0.925 g/cc density. However, addition of a slip/antiblock concentrate helped reduce the COF considerable for all densities down to 0.905 g/cc. The presence of slip/antiblock was further observed to result in a sharp drop in impact strength and a decrease in film clarity but no change in the tear properties. The reduction in impact strength is believed to be due to poor interfacial adhesion between the antiblock agent and the polymer matrix. Sharkskin or surface melt fracture was observed with some of these resins under particular film blowing conditions. However, addition of a small level of a fluoropolymer processing aid completely eliminated the melt fracture. The bubble stability of these PPCo-M metallocene resins was found to be quite comparable with other metallocene resins but lower than conventional Ziegler LLDPE resins. This was expected due to the narrow MWD and the complete absence of any long chain branching.

Benchmarking comparisons of the PPCo-M metallocene blown films with other commercial metallocene and Ziegler LLDPE resins shows clearly that PPCo-M resins show equal or better film property performance balance than current LLDPE resins. In particular, better clarity compared to other metallocenes and better clarity and considerably higher impact strength compared to other Ziegler LLDPE resins was consistently observed in this study.

Finally, it is concluded that metallocene resins produced in the Phillips slurry loop process will offer a very good balance of processability and performance characteristics, which can be optimized for various applications by appropriate choice of resin and processing conditions.

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Laboratory Line – The line consists of a 38 mm (1.5 inch) diameter single screw Davis Standard extruder (L/D=24; 2.2:1 compression ratio) fitted with a barrier screw with a Maddock mixing section at the end. The die used was 102 mm (4 inch) in diameter and was fitted with a Dual Lip Air Ring using ambient cooling air. The die gap was 1.52 mm (0.060 inch). The film blowing was done at typical LLDPE conditions as follows: 2.5:1 blow up ratio (BUR), "in-pocket" bubble configuration and 190°C extruder and die set temperatures. The evaluations were made at an output rate of 27.2 kg/hr (60 lb/hr) using a screw speed setting of 115 RPM. These conditions were chosen since the film properties so obtained scale directly with those from larger commercial scale film blowing operations⁽¹⁾.

Commercial Line – This line consists of a 89 mm (3.5 inch) diameter single screw extruder (L/D=24; 2.2:1 compression ratio) fitted with a LLDPE barrier screw. The die used was 203 mm (8 inch) in diameter and was fitted with a Dual Lip Air Ring using chilled air at 15°C (59°F). The die gap was 1.52 mm (0.060 inch). The film blowing was done at typical LLDPE conditions as follows: 2.5:1 blow up ratio (BUR), "in-pocket" bubble configuration and 190°C extruder and die set temperatures. The evaluations on this line were made at an output rate of 113 kg/hr (250 lb/hr or 10 lb/hr/inch of die circumference).

Blown Film Properties

The film properties were measured as follows:

1. Dart impact strength – ASTM D1709 (method A)
2. Machine (MD) and transverse (TD) direction Elmendorf tear strengths – ASTM D1922
3. % Haze was measured in accordance with ASTM D1003 on a XL-211 Hazegard System.
4. Gloss (60°) was measured as per ASTM D2457.

Blown Film Resins

A wide range of metallocene resins, deemed suitable for blown film applications, and ranging in density from 0.905 – 0.942 g/cc and in MI from 0.7 – 3 MI were evaluated using typical LLDPE type film blowing conditions. More fundamental characteristics of these resins are presented in the subsequent sections. For the sake of brevity all Phillips metallocene resins, which were made with a commercial catalyst designated as PA, will be referred to as PPCo-M resins in the remainder of this manuscript.

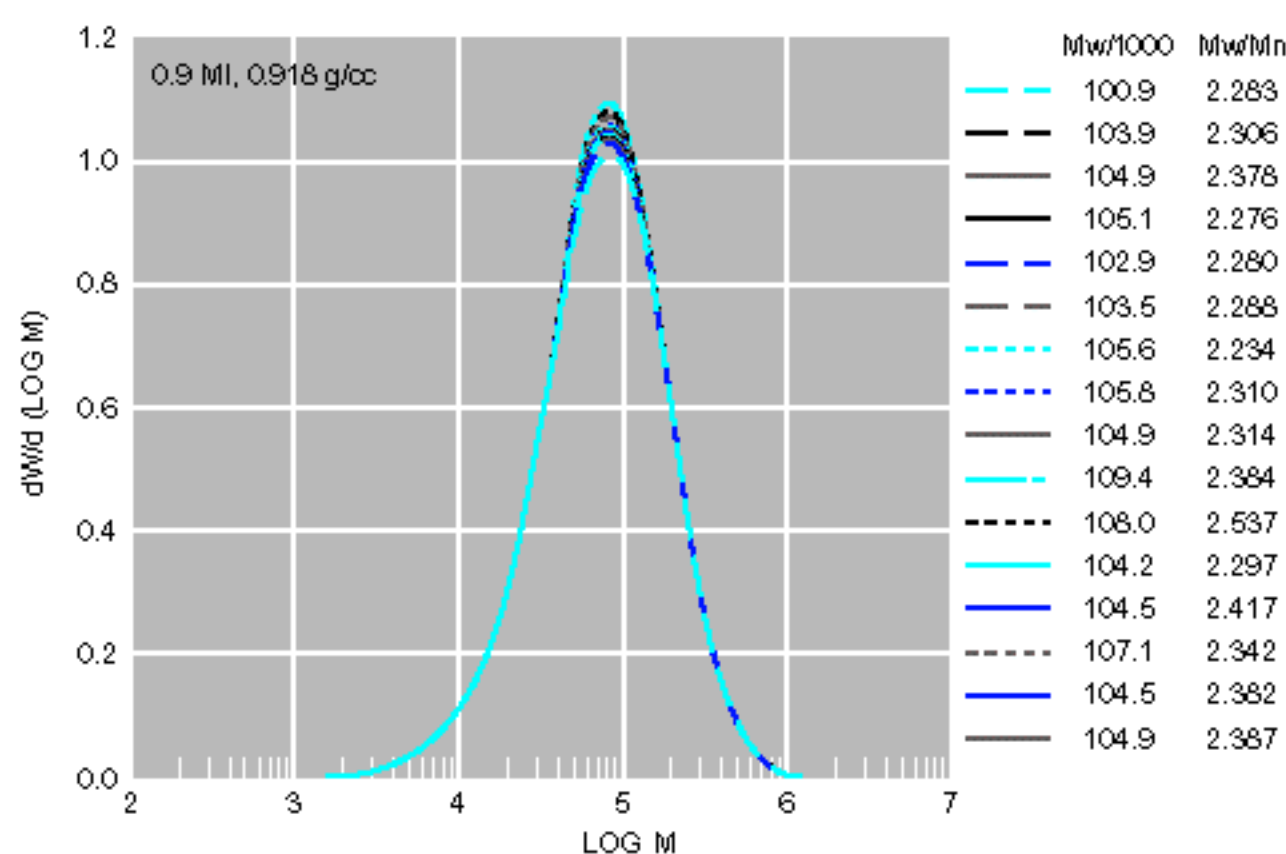
RESULTS AND DISCUSSION

Molecular Characteristics of PPCo-M Resins

Gel permeation chromatography (GPC) traces for sixteen commercial lots of PPCo-M LLDPE resins (0.9 MI, 0.918 g/cc density) are shown in Figure 1. The data indicates that PPCo-M resins are very narrow in molecular weight distribution (MWD) with a polydispersity of between 2.2 – 2.5. Furthermore, the product consistency due to the single-site nature of the metallocene catalyst is obvious from Fig. 1.

FIGURE 1
Gel Permeation Chromatography (GPC) Traces for Sixteen Commercial Lots of PPCo-M Metallocene LLDPE Resins

(Showing Narrow MWD and Good Product Consistency)



The rheology (complex viscosity versus frequency at 190°C) of three representative PPCo-M metallocene resins (0.7 MI, 1.0 MI and 1.5 MI) is shown in Figure 2 along with comparative data for a 1 MI conventional Ziegler-Natta catalyst LLDPE and a commercially available 1 MI metallocene resin (designated as m-LLDPE in Fig. 1) which is believed to contain some level of long chain branching (LCB). Further comparisons of the rheological and molecular characteristics of these polymers are tabulated and shown in Table 1 for a number of PPCo-M resins varying from about 0.7 – 3 MI along with data for a commercial m-LLDPE with LCB, a conventional Ziegler-Natta LLDPE, a chrome catalyst based broad MWD low density linear polyethylene (PC-1) and a conventional high pressure-low density PE (HP-LDPE).



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