A Rheological and Morphological Explanation of the Inherent Blocking Force in LLDPE Blown Films

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SYNOPSIS

The inherent film blocking force in linear low-density polyethylene (LLDPE) blown films was studied using several LLDPEs with varying density, molecular weight, and molecular weight distribution (MWD). Melt elasticity, fabrication conditions, and film surface morphology were found to have a significant effect on the inherent film-blocking force in LLDPE blown films. A comprehensive mechanism for the film-blocking force based on molecular weight, rheology, and morphology studies is proposed. LLDPEs with higher density exhibited a lower blocking force. At a constant density, the LLDPEs with higher melt elasticities (slower relaxation rates) exhibited rougher film-surface morphology and produced blown films with lower blocking force. These LLDPEs with an inherent low blocking force are used in grocery sacks, trash bags, and merchandise bag markets where bag openability is a critical performance property. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Films fabricated from linear low-density polyethylene (LLDPE) often have higher coefficients of friction (COF) and exhibit a higher blocking force than that of polyethylene converters and that consumers find acceptable. Polyethylene converters require low COF for their fabrication processes, while consumers desire products exhibiting low blocking force because the grocery sacks, trash bags, merchandise bags, etc., are easier to open. The blocking force is the force necessary to separate two identical, contacting film surfaces from one another as defined by ASTM D 3354, Procedure A. The blocking force of film is generally considered to be unsatisfactory when it is about 20 g or more. To decrease the COF and the blocking force, polyethylene manufacturers incorporate additives into their polymers, which increases their production costs. These additives can adversely affect mechanical properties of the films such as tensile strength, dart impact, and tear strength. In addition, these additives can exude to the surface of the film, causing more problems for converters such as odor and poor adhesion to inks used to print on the surface of the finished product. Commercial producers incorporate additives such as silicon dioxide (SiO_2) as antiblock agents to reduce blocking force and additives such as erucamide as slip agents to reduce COF.[1]

The inherent film-blocking force is strongly dependent on the density of the LLDPE. Generally, higher-density polyethylenes have a lower inherent blocking force and a lower COF. The effect of other fundamental molecular parameters such as molecular weight and molecular weight distribution on the inherent blocking force is not well understood. A number of workers have proposed that polymer melt elasticity is closely related to surface roughness and haze in blown films.[2-4] In this study, the inherent film-blocking force is related to the morphological and rheological properties of the polymers and to blown-film fabrication conditions. In addition, a comprehensive mechanism for the film-blocking force is proposed based on the film-surface morphology, molecular weight distribution, and stress-relaxation studies.

EXPERIMENTAL

Materials Description

Several ethylene–octene copolymerized LLDPEs with varying density, molecular weight, and molecular weight distribution (MWD) were used in this study. Table I illustrates the melt index (I_2, ASTM D 1238, Procedure A, Condition E), melt flow ratio (I_{10}/I_2, ASTM D 1238, Procedure A, Condition F for I_{10}), density, weight-average molecular weight (M_w), and two indices of polydispersity (M_w/M_n and M_z/M_n) for the LLDPEs used in this study. LLDPEs 1–11 do not contain any antiblock additive and LLDPE 12 contains 5000 ppm of silicon dioxide (SiO_2) as the antiblocking agent and 500 ppm erucamide as the slip agent. LLDPEs 1–4 are approximately 0.930 g/cm³ density, LLDPE 5 is approximately 0.925 g/cm³ density, and LLDPEs 6–10 are approximately 0.920 g/cm³ density. LLDPEs 11 and 12 are similar in base density (0.923 g/cm³), melt index, and MWD, but LLDPE 12 contains the antiblocking and slip agent. All densities were measured at 25°C (ASTM D 792, Method B).

Rheological Characterization

All the polymers were characterized using the frequency sweep and step-strain stress-relaxation techniques on a Rheometrics RDA-II dynamic analyzer. The frequency sweep experiments were conducted at 190°C, with 25-mm diameter parallel plates, at 15% strain and the oscillatory rate was incrementally increased from 0.01 to 100 radians/s.

The step-strain stress-relaxation experiments were used to characterize the relaxation times of materials by monitoring the stress relaxation following a single rotation to the selected percent strain. The stress-relaxation experiments were conducted at 190°C and with 25-mm diameter plates at 50% strain.

Blown-film Fabrication Conditions

All the LLDPEs were fabricated on an a 2 in. Egan extruder using a 3 in. blown-film die and 0.76 mm (30 mil) die gap. The blown films were fabricated at 25 rpm extruder speed, 238°C (460°F) melt temperature, 2.7 : 1 blow-up ratio, 32 cm frost line height, and 20 mm (0.8 mil) gauge. The melt temperature was kept constant for different polyethylenes by changing the extruder temperature profile. Frost line height was maintained at 32 cm by adjusting the air-flow rate. In addition, all the 0.920 g/cm³ density LLDPEs were also fabricated with a 2 mm (80 mil) die gap. All the other fabrication conditions were the same as above.

Blocking Force and COF Measurements

All the films were characterized for induced blocking force and COF measurements according to ASTM D 3354, Procedure A, and ASTM D 1894, Procedure A or B, respectively. Table II summarizes the induced blocking force and COF data for the two die gaps studied.

Surface Morphology Characterization

Micrographs at 500X the surface morphology of all the blown films were obtained by using the optical reflectance technique of Nomarski interference

Table I   Polymer Characterization

Polymer	Density (g/cm³)	I_2 (g/10 min)	I_{10}/I_2	M_w	M_z/M_n	M_w/M_n
LLDPE 1	0.9292	0.45	16.27	189,000	38.63	6.24
LLDPE 2	0.9305	0.38	13.45	193,000	29.14	5.71
LLDPE 3	0.9298	0.63	8.24	144,000	12.15	3.87
LLDPE 4	0.9306	0.82	8.33	135,000	11.51	3.53
LLDPE 5	0.9255	0.60	9.82	156,000	19.46	4.88
LLDPE 6	0.9204	0.53	13.53	181,000	36.65	6.20
LLDPE 7	0.9203	0.41	12.37	189,000	30.38	5.83
LLDPE 8	0.9205	0.52	9.27	151,000	13.76	4.42
LLDPE 9	0.9204	0.78	8.87	141,000	14.37	4.16
LLDPE 10	0.9200	1.05	8.00	114,000	9.93	3.55
LLDPE 11	0.9230	0.66	7.14	138,000	7.62	3.36
LLDPE 12[a]	0.9271	0.61	7.23	129,000	8.03	3.33

[a] LLDPE 12 contained 5000 ppm silicone dioxide as an antiblock additive.

Table II   Blocking Force and COF Data for Blown Films

Polymer	Density (g/cm³)	I_2 (dg/min)	I_{10}/I_2	Blocking Force (g) 0.76 mm Die Gap	COF 0.76 mm Die Gap	Blocking Force (g) 2 mm Die Gap	COF 2 mm Die Gap
LLDPE 1	0.9292	0.45	16.27	7.8	0.388	—	—
LLDPE 2	0.9305	0.38	13.45	8.8	0.322	—	—
LLDPE 3	0.9298	0.63	8.24	8.8	0.390	—	—
LLDPE 4	0.9306	0.82	8.33	6.5	0.424	—	—
LLDPE 5	0.9255	0.60	9.82	7.5	0.416	—	—
LLDPE 6	0.9204	0.53	13.53	10.8	0.322	15.0	0.348
LLDPE 7	0.9203	0.41	12.37	16.0	0.366	75.0	0.390
LLDPE 8	0.9205	0.52	9.27	24.3	0.348	70.0	0.296
LLDPE 9	0.9204	0.78	8.87	27.0	0.356	74.0	0.388
LLDPE 10	0.9200	1.05	8.00	46.3	0.822	48.6	0.847
LLDPE 11	0.9230	0.66	7.14	66.5	0.600	—	—
LLDPE 12[a]	0.9271	0.61	7.23	7.5	0.324	—	—

[a] LLDPE 12 contained 5000 ppm silicone dioxide as an antiblock additive.

contrast.[5] The blown-film samples were prepared for analysis in the same manner as would be used for electron microscopy, i.e., coating with a thin layer of gold.

the lowest block and LLDPE 11 exhibited the highest block with LLDPE 8 in between the two samples (16.0, 24.3, and 66.5 g of blocking force, respectively). Figure 4 shows the effect of fabrication for

RESULTS AND DISCUSSION

Optical Micrographs

The density is a major predictive factor for the film-blocking force, as can be seen in Table II. Higher-density LLDPEs gave blown films with a low blocking force. A more critical evaluation of the blocking force data led to the tentative conclusion that a blocking force of approximately 7 or 8 g represented essentially a lower limiting value. This hypothesis was supported by the fact that LLDPE 11, which did not contain the antiblock agent SiO_2, had a blocking force of 66.5 g, whereas the LLDPE 12, which had the same weight-average molecular weight, M_w/M_n, and density, but contained SiO_2 additive, had a blocking force of 7.5 g.

The optical micrographs in Figures 1–5 dramatically illustrates the important role of surface morphology in determining the observed level of blocking force. In general, the roughness of the surface was deemed to correlate directly with the blocking force, even though no rigorous quantitative relationship was established. Comparing the surface micrographs of LLDPEs 7, 8, and 11 (Figs. 1–3), LLDPE 7 exhibited the roughest and LLDPE 11 exhibited the smoothest surface with LLDPE 8 in between the two samples. LLDPE 7 also exhibited

Figure 1   LLDPE 7, Blocking Force = 16.0 g. Blown films fabricated with 0.76 mm (30 mil) die gap.
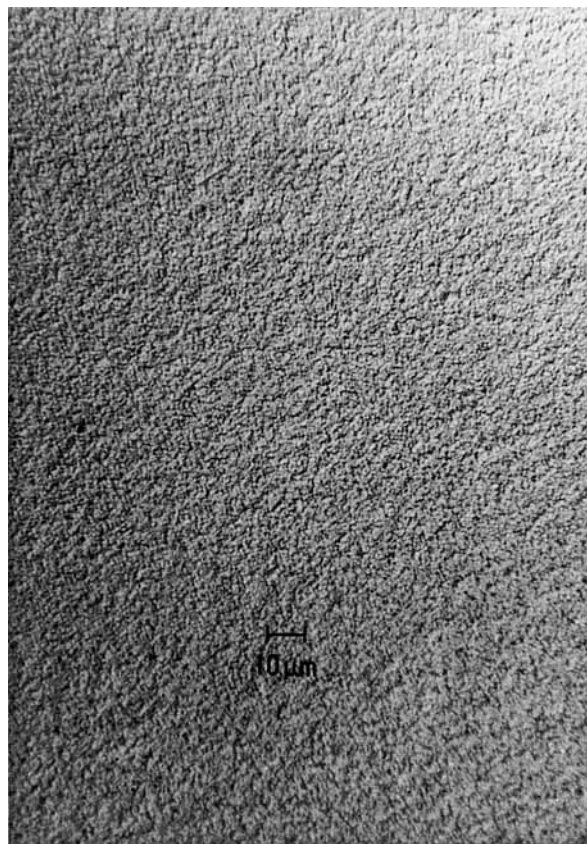
Figure 2 LLDPE 8, Blocking Force = 24.3 g. Blown films fabricated with 0.76 mm (30 mil) die gap.

LLDPE 8 utilizing a wider die gap (2 mm) compared to Figure 2, which was fabricated with a 0.76 mm die gap for the same polymer. Figure 5 illustrates the micrograph for LLDPE 12 that contained an antiblock agent and the rougher surface is due to the SiO_2 particles present in the film. Therefore, from the above micrographs, we concluded that the films with rougher surface morphology exhibited lower induced blocking-force values and films fabricated with a wider die gap exhibited higher blocking force and smoother surface morphology.

Molecular Weight and Molecular Weight Distribution

To begin to understand the role of molecular weight and MWD in the determination of the observed blocking force, various attempts were made to find relationships with numerous statistics and features of the individual MWDs as measured by gel permeation chromatography (GPC). Figure 6 shows the relationship of blocking force and M_w. The relationship (higher M_w leading to lower blocking

force) appears to break down for LLDPEs 10 and 11 relative to the other LLDPEs since the former has lower blocking force and lower M_w, whereas the latter has a higher blocking force and higher M_w. This is especially surprising since LLDPE 11 is higher in density than is LLDPE 10. Figures 7 and 8 show the relationship between the blocking force and the polydispersity indices, M_w/M_n and M_z/M_n, respectively. The relationship of high polydispersity with low blocking force suggests that a minimum fraction of high molecular weight molecules (e.g., M_w's above 1 million) must be present in order for a reduction in blocking force to be observed, but that this fraction of high molecular weight molecules cannot be increased without bound, as the ultimate composition must still be fabricated into film at reasonable fabrication conditions. The differentiation of the blocking force behavior for these LLDPEs as a function of density is most apparent when considering M_z/M_n (Fig. 8), which is more highly weighted by the higher molecular fraction in the MWD. For polyethylenes with a density of 0.920 g/cm^3, a clear dependence of blocking force and surface roughness

Figure 3 LLDPE 11. Blocking force = 66.5 g. Blown films fabricated with 0.76 mm (30 mil) die gap.
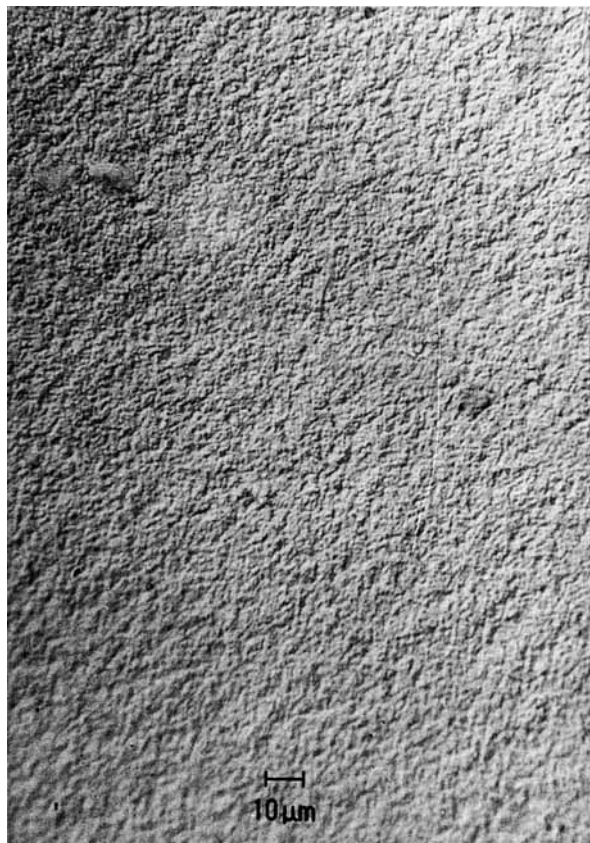
Figure 4   LLDPE 8. Blocking force = 70.0 g. Blown films fabricated with 2.0 mm (80 mil) die gap.
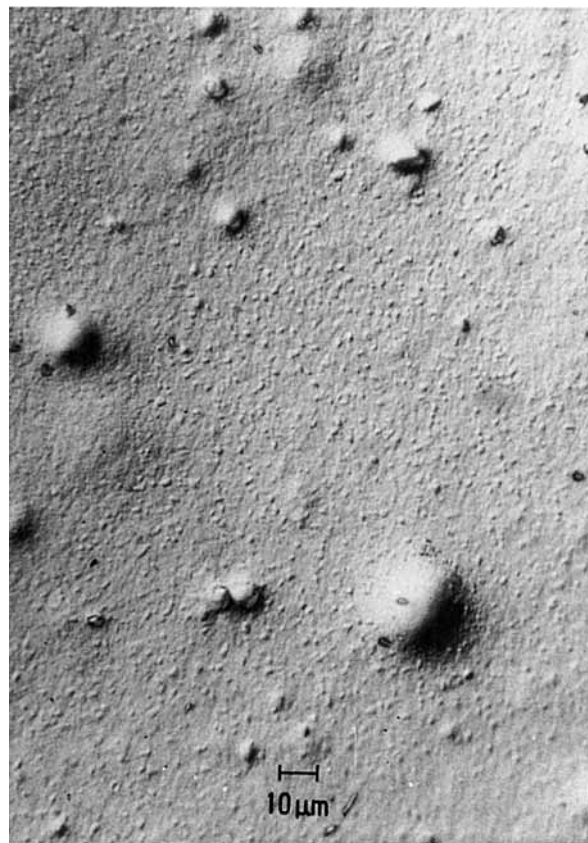
Figure 5   LLDPE 12 (with 5000 ppm antiblock agent). Blocking force = 7.5 g. Blown films fabricated with 0.76 mm (30 mil) die gap.

on the MWD is evident. When the LLDPEs with a density of approximately 0.925 g/cm^3 were considered, it was suggested that a series of curves might exist, each based upon density. However, the lower limitation in the value of the blocking force obscured the role of density since the LLDPEs with a density of 0.930 g/cm^3 all showed essentially the same blocking force.

Rheological Properties

When the 0.920 g/cm^3 density LLDPEs were fabricated using a 2 mm (80 mil) die gap, the observed increase in blocking force suggested that another important factor was fabrication conditions. Table II summarizes the blocking-force data for films fabricated with a 2 mm die gap. To understand the role of fabrication conditions, the rheological properties of the polymers were analyzed.

Complex viscosity and tan delta data were obtained at a constant temperature (190°C) and at frequencies of 0.01–100 radians/s. Figure 9 shows the complex viscosity and tan delta data plotted vs.

frequency for LLDPEs 7, 8, and 11. The complex viscosity vs. frequency curve gives the characteristic viscosity vs. shear rate data. The tan delta versus frequency curve is characteristic of the elasticity of
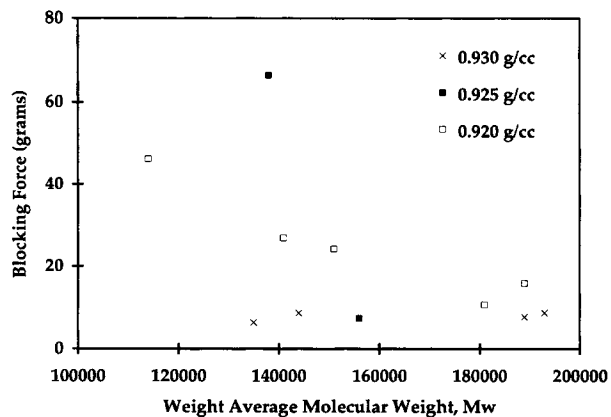
Figure 6   Relationship between blocking force and weight average molecular weight.
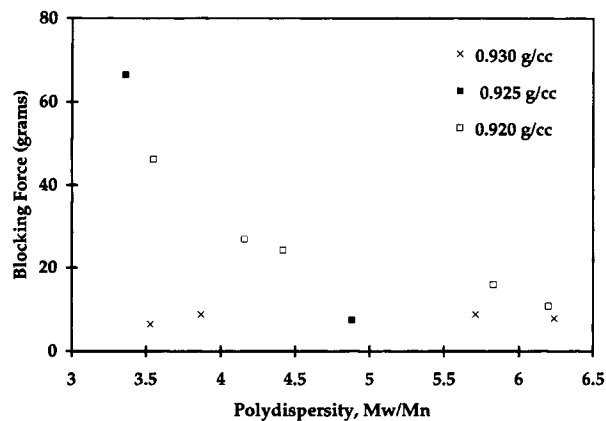
Figure 7 Relationship between blocking force and M_w / M_n.

Figure 9 Tan delta and complex viscosity vs. frequency.

a given polymer. Lower tan delta values at frequencies of less than 1 s^{-1} are characteristic of a polymer that relaxes slowly (longer relaxation times). Therefore, a low slope in the lower frequency range of the tan delta vs. frequency curve can be interpreted as a more elastic melt for a given polymer. It was observed that, in general, broader MWD indicates slower relaxation. As seen in Figure 9, comparing LLDPEs 7, 8, and 11, the rate of change of the tan delta curve at lower frequencies is higher for LLDPE 11 and the blocking force for LLDPE 11 is much larger than for LLDPEs 7 and 8 (66.5, 24.3, and 16.0 g blocking force, respectively). The rheological data show that the observed melt behaviors cover a range of elasticities and viscosities and are related to the variation in blocking force and surface roughness. Therefore, mechanisms explaining blocking force, surface roughness, or both should be based firmly upon the viscoelastic behavior of the polymers.
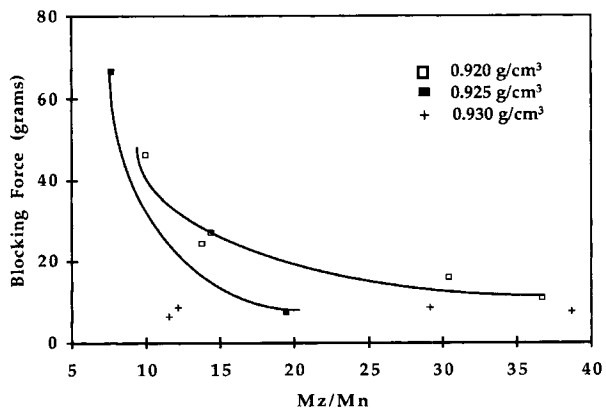
The actual measurement of relaxation rates from the step-strain stress relaxation experiments confirmed the general relationship of MWD to the relaxation rate. The LLDPEs with the broadest MWD and the lowest tan delta curve exhibited the slowest relaxation rates. Figure 10 shows the torque response to the step strain plotted vs. time at 50% strain for LLDPEs 7, 8, and 11. The slopes of these curves characterize the relaxation rates of the polymer in that the steepest slopes were associated with the greatest relaxation rates and the highest blocking force.

Proposed Mechanism for Blocking Force

A mechanism for the film-blocking force based upon the surface morphology, polymer structure, and viscoelastic behavior can now be derived, incorporating the surface morphology into a more general theory of molecular behavior arising to varying degrees as
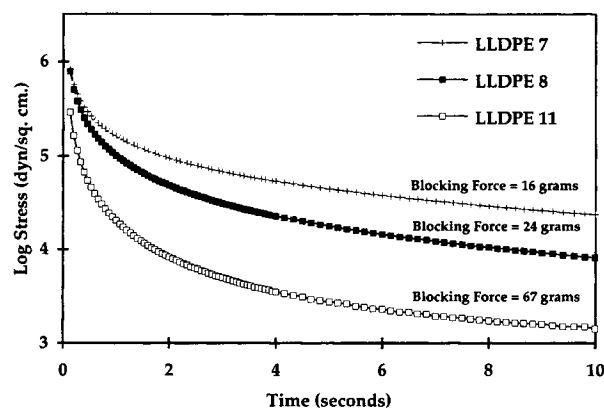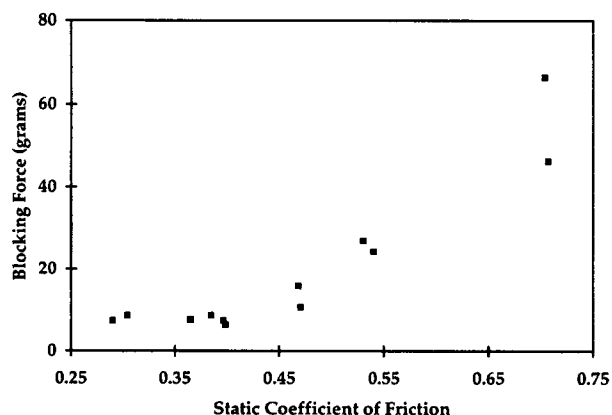

Figure 8 Relationship between blocking force and M_z / M_n

Figure 10 Step-strain stress-relaxation (strain = 50%, test temperature = 190°C).

a result of the differences in chain structure. Two fundamental postulates for the proposed mechanism are:

1. The blocking force is the direct result of molecular interactions such as chain entanglements and/or van der Waals forces between the surfaces of two films (such interactions would also produce cling in cast and blown films, since the presence of a low molecular weight, highly short-chain branched fraction in the polymer has been proposed as giving rise to cling.[6]

2. The occurrence of surface roughness on a microscopic scale, which can attenuate these intrinsic molecular forces, results in lower observed blocking forces.

The relationship between surface roughness and blocking force is supported by the data in Figure 11 where a clear relationship between blocking force and COF is evident. One would expect that, at least to a first approximation, COF would be a function of surface roughness. The surface roughness occurs primarily as a result of the interaction among density, melt rheology, and the variables controlling film fabrication. The overriding variable in determining the surface morphology, the observed blocking force, and the COF appears to be density. The decrease in blocking force and increase in surface roughness and COF as density increases suggests that in crystallization, crystallization rates play a central role in the mechanism, since they tend to trend with density. The variation in blocking force at a constant density must be primarily the direct result of surface roughness as manifested on a scale comparable to

Figure 11 Relationship between blocking force and static COF.

the above micrographs. A comparison of the surface morphology of LLDPE 11 (without antiblock, Fig. 3) to that of LLDPE 12 (with SiO_2 antiblock, Fig. 5) clearly demonstrates that the observed blocking force and surface morphology are not intrinsic properties, controlled primarily by molecular weight and MWD. However, the combination of the surface morphology and intrinsic attractive forces specific to a given LLDPE structure intuitively suggests that producing a rougher surface (during the fabrication of any particular LLDPE) should result in greatly reduced film-to-film contact, which, in turn, would be manifested in an apparent reduction in the blocking force. Now what is needed is an explanation for the observed surface roughness.

In the cases of the majority of films produced from the polyethylenes described herein, the origins of the rough surfaces appear to be a complex function of the chemical structure (i.e., molecular weight, MWD, and additives such as SiO_2) and film fabrication conditions (die gap, output rate, etc.). Under the right fabrication conditions with the appropriate melt behavior, such as a highly shear-stressed melt exiting a narrow die gap coupled with a relaxation time of sufficient duration, the relaxation of the residual stresses in the amorphous phase *after* crystallization could produce an indented surface topography, whereas a more complete relaxation prior to crystallization could result in a smoother surface. As the density is increased and the crystallization rate increases, the tendency for crystallization prior to relaxation would be increased. The relaxation rates reported in Figure 10 are in agreement with such a mechanism, since the time it takes the melt to exit the die and reach the frost line is on the same order of magnitude ($\sim$ 1 s), at least on the fabrication equipment used in this experiment. By widening the die gap, the shear stress of the melt as it exits the die is reduced (lower shear rate) so that less of the initial stress needs to relax prior to crystallization, resulting in a lower level of surface roughness. The relationship of this relaxation mechanism to the extensional forces arising from the inflation of the bubble and the nip roll speed are not as easily understood, since the observed orientation of crystalline domains would be expected to increase, not decrease with a wider die gap. However, if the above mechanism is valid, one might expect to find a higher degree of amorphous orientation in those films with low blocking force fabricated at the narrower die gap when compared to the same polyethylene fabricated into blown film at the wider die gap. The amorphous orientation as well as the effect of other fabrication variables such as blow-up ratio

and frost line height will be analyzed at a future date.

CONCLUSIONS

There exists a clear inverse relationship between LLDPE blown film-surface roughness and blocking force (at constant density). The surface roughness in blown films is a function of fabrication conditions, polymer structure, and additives, such as SiO_2. For constant molecular structures (similar density, short-chain branching distribution, and MWD, etc.), LLDPE blown films exhibiting a rougher surface morphology will provide a lower blocking force. Rougher surface morphology and lower blocking force at similar fabrication conditions result from high melt elasticity (slower relaxation time) of the LLDPE copolymers. LLDPE copolymers with the higher fraction of a very high molecular weight species exhibit higher melt elasticity. These relationships are the basis for a comprehensive mechanism for the film-blocking force.

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