Influence of molecular weight distribution on low-density polyethylene coating performance

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ABSTRACT: Resin suppliers and processors are trying to correlate resin processing performance to polymer structure in terms of molecular weight distribution and chemical composition distribution. In the past, this has been an involved and tedious procedure. Now there is a better way to correlate laboratory parameters with processing behavior. The optimum resin most appropriate to processing will have molecular weight distribution with a sufficient level of high-molecular-weight molecules along with long-chain branches, preferably skewed toward the larger molecules.

KEYWORDS: Bibliographies, coating, extrusion coating, low density polyethylene, molecular weight distribution, parameters, polyethylene.

Gerhard Luft and other researchers have studied the polymerization of low-density polyethylene (LDPE) and the influence of reactor temperature and reactor pressure in autoclave reactors *(1–5)*. Molecular modeling and prediction of molecular weight distribution and long-chain branching also is common *(6, 7)*. Determination of molecular weight distribution of polyethylenes has been an involved and tedious process due to the complexity of the analytical procedure. With the advent of superior size exclusion packings and new instrumentation, molecular weight characterization of resins dissolved at temperatures above 150°C have become more reliable and reproducible *(8)*.

Long-chain branching analysis of LDPE has been cumbersome because a secondary detection technique (such as light scattering or solution viscometry) must be used in conjunction with differential refractive index (DRI). The universal calibration curve generated from this process is used to obtain the long-chain branching parameters for the LDPE resins *(9–21)*. Recently, qualifying the influence of short-chain branching in polyethylene resins has become easier with the advent of Fourier transform infrared detection (FTIR) used sequentially with GPC–DRI detection *(22–24)*.

Manifestation of the unique molecular characteristics of LDPE can be studied using rheology. Capillary rheology, parallel plate rheology, elongational viscometry, and dynamic mechanical thermal analysis can be used to characterize the solid-state and melt properties of LDPE resins *(24–40)*. These results then can be correlated with LDPE extrusion-coating resin processing characteristics such as "neck-in," "drawdown," and "melt strength" as well as coating end-use properties such as coating density, coating weight, adhesion, heat seal, barrier, and surface characteristics. This understanding can be translated to optimization of polymer processing parameters as well as other LDPE applications *(41–51)*.

One of the simple and informative techniques involves the characterization and predictability of melt tension, or melt strength, of the coating web during processing temperatures as high as 610°F. This method was first introduced by researchers at the Monsanto Research Department

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I. Physical and melt processing characteristics used in the study

Group	Resin	Density, g/10 min	Melt index[a]	Melt tension[b,c]	Total neck-in, in. (610°F)[d]	Drawdown tear-off (610°F mils)
	A	0.9190	6.631	5.25	2.37	0.313
I	B	0.9175	5.495	6.75	1.25	0.526
	C	0.9178	8.147	3.95	1.75	0.366
	D	0.9176	11.018	2.75	3.25	0.149
II	E	0.9174	7.526	4.70	1.50	0.361
	F	0.9178	5.770	5.60	1.88	0.428
	G	0.9180	12.636	1.95	5.75	0.149
III	H	0.9230	4.643	5.55	3.00	0.164
	I	0.9255	4.444	9.25	3.63	0.240

[a]Per ASTM D-1238 at 190°C
[b]See references 52 and 53.
[c]Force required to draw the strand at 5 ft/min
[d]Die width was 33 in.

II. Molecular weight distribution characteristics used in the study

Group	Resin	Mn	Mw	Mz	D	LCB[b]	IV[a] (TCB at 135°C)
	A	17083	151446	592184	8.86	3.7	0.95
I	B	17620	162389	643210	9.22	4.0	1.07
	C	19022	163850	637163	8.61	4.3	1.02
	D	17803	144815	595189	8.13	3.0	0.98
II	E	18306	147405	593184	8.05	4.6	1.05
	F	19125	152383	583750	7.97	3.3	0.95
	G	16190	127222	535006	7.86	3.4	0.96
III	H	18079	125948	16475	6.97	2.4	1.02
	I	15366	120711	534926	7.86	5.2	1.00

[a]Long-chain branching parameter per size exclusion chromatograph used in series with a Viscotek differential viscometer detector
[b]Intrinsic viscosity measured in TCB at 135°C.

at Texas City, TX, in 1965 *(52)*. A variation of this test is used today by most resin manufacturers to monitor polymer molecular-weight-distribution (MWD) uniformity, consistency, and processability. The test involves the measurement of force required to draw molten polymer into a monofilament from a standard melt index orifice at a constant volume extrusion rate and constant temperature. The analysis can be conducted at temperatures between 160°C and 300°C *(53)*.

Experimental

Melt flow index. The analysis was performed at 190°C per American Society for Testing and Materials (ASTM) method D-1238.

Density. Density was measured on pieces of resin cut from compression molded discs fused at 190°C. The pieces were placed in density columns calibrated by glass floats and secondary standards.

Melt tension (MT). This analysis is performed using a procedure similar to those outlined in references 52 and 53. The equipment used was a modified melt-flow index extrudate plastometer with additional pulley and draw-off attachment; a force measuring device then indicates the force induced at the standard extrusion flow rate.

Size exclusion chromatography. Three milligrams of each resin were dissolved with slight agitation in 1,2,4 trichlorobenzene (TCB) heated to 160°C for 2 h. The polymer solution was transferred to a Waters 150°C instrument, which had two mixed bed "B" columns and a precolumn manufactured by Polymer Laboratories (PL). Column calibration was performed using fixed concentrations of narrow polystyrene standards (Easical–PL) with peak molecular weights ranging from 8.5 x 10^6 to 580. Polyethylene resins were analyzed by fitting the linear polystyrene calibration with a broad polyethylene secondary standard resin. The calibration was linear through the range of the standards used for this analysis and extrapolated beyond this range using a first-order polynomial function.

Processing parameters. All resins were run on a commercial coater at various temperatures, including 610°F. For all runs, the die gap used was 0.028 in.

Results

Tables I and II provide the physical and melt processing characteristics of the resins used in this study. They are broadly classified into three groups: I, II, and III.

Figure 1 shows the linear calibration obtained for the MWD analysis of all resins. This calibration range covered calibration limits of 8.5 x 10^6 to 580 Mp as indicated by polystyrene narrow standards. The resins were characterized for their long-chain branching distribution using a differential refractive index detector as well as a differential viscometer detector.

Figure 2 compares the MWD of a representative resin from each

group. Notice the differences in the shape of the low-molecular-weight tail as well as the high-molecular-weight peak of the distribution. A combination of these two aspects of the distribution and the long-chain branching composition distribution influences the MT and, thus, the processing behavior of these resins.

Group I resins show the highest average molecular weight (Mw) of the total class of resins studied here. In general, they have the broadest dispersity, and the highest peak intensity of the high-molecular-weight part of the MWD. They also have an inward tail on the low-molecular-weight tail side of the distribution.

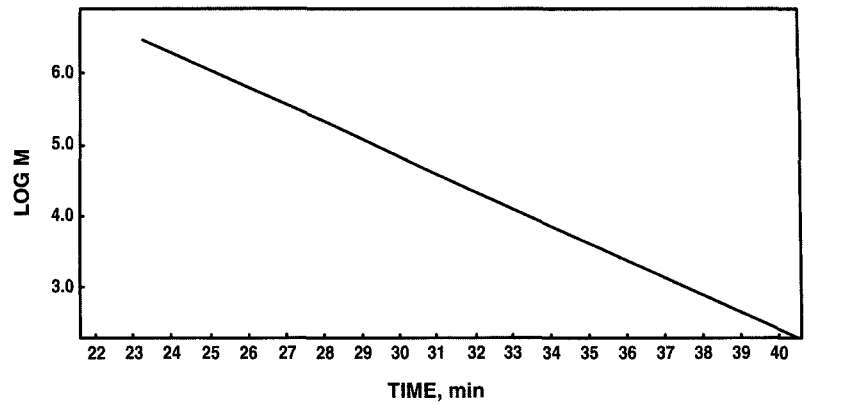
Group II resins show a medium Mw of the group of resins studied here. In general, they have medium dispersity and medium peak intensity of the high-molecular-weight peak of the MWD. Their melt tension properties are slightly lower than the polymers in Group I.

Group III resins show the lowest Mw and the smallest peak intensity of the high-molecular-weight peak of the MWD. Their melt tension properties are the lowest of all polymers, except resin "I".

Closer analysis of the molecular composition and processing behavior of these resins shows some interesting trends:

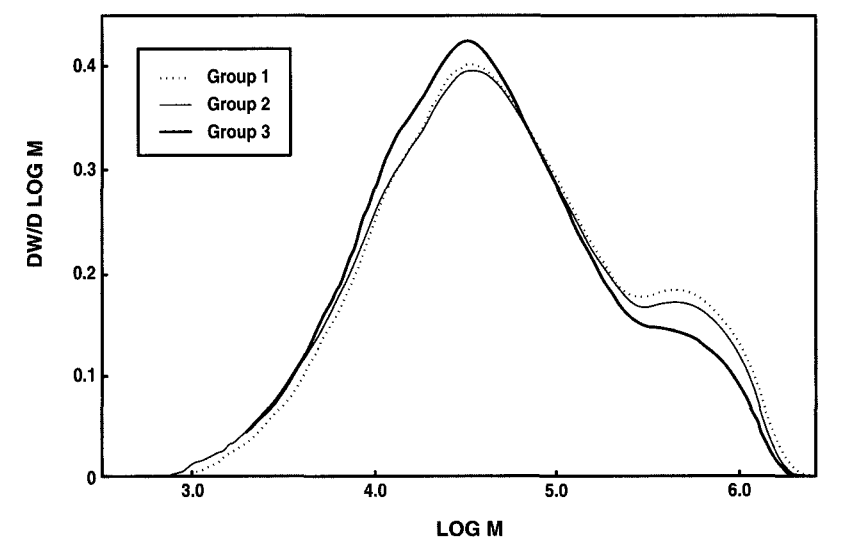
- The wider the distribution, the lower the rate of neck-in; this is complemented by the fact that these resins also have higher levels of long-chain branching.
- The level of long-chain branching and their distribution are controlled by the pressure and temperature of the autoclave reactors used to manufacture these resins. Therefore, the key is to develop well characterized resins manufactured under tightly controlled conditions and to use them as benchmarks to meet exact needs of specific customers.
- Changes in melt viscosity are minimal, but the spread in long-chain

1. Linear calibration for the MWD analysis



Polynomial coefficients: Log (M) = A + BT
A = 1.21358e + 001, B = −2.431759e − 001

2. Molecular weight distribution of each group



K value *10e5: 14.1000 Alpha value: 0.7000
Flow rate marker: BHT Flow rate marker retention time: 42.15

Point	*Name*	*RT, min*	*Mol. wt.*	*Log M*	*Fit ratio*	*Used*
1	PS	23.22	8500000	6.929	1.001	Yes
2	PS	24.90	3040000	6.483	1.000	Yes
3	PS	26.67	1030000	6.013	1.000	Yes
4	PS	28.55	330000	5.519	1.000	Yes
5	PS	29.78	156000	5.193	1.000	Yes
6	PS	31.18	66000	4.820	0.999	Yes
7	PS	32.58	28500	4.455	1.000	Yes
8	PS	34.45	9200	3.964	1.001	Yes
9	PS	36.15	3250	3.512	1.000	Yes
10	PS	39.00	580	2.763	1.001	Yes
11	BHT	42.15	100	2.000	1.037	No

branching levels, as well as the dispersity of the MWD, is significant enough to produce a wide range of processing behavior for these resins.

- Although the trends observed are not earth shattering, a couple of areas that may be addressed in the future are:

1. New capillary rheometers with a specific option called "thrust" *(54)* may be used to obtain pressure coefficient of viscosity parameter of resins; this parameter can be obtained to determine viscosity behavior of resins at high pressures, such as those observed during commercial processes (up to 30,000 psi).
2. Another attachment that can be fitted to a high-pressure capillary rheometer is a slit flow monitor *(55)*. This device is used to obtain true shear stress as a function of volume throughput without having to correct for entrance effects using the Bagley or orifice die methods. The device comes attached with several pressure transducers, and, by positioning one of the pressure transducers away from the plane of the die, hole pressures can be measured as a function of shear rate. From these hole pressures, elastic response (first normal stress differences) can be calculated.

Conclusions

Several parameters and their influence on processing of low-density polyethylene are discussed in light of correlating these laboratory parameters with processing behavior.

The key parameters are melt tension, molecular weight, molecular weight distribution, and long-chain branching distribution. The optimum resin (which balances neck-in and drawdown behavior) most appropriate to processing will have molecular weight distribution with a sufficient level of high-molecular-weight molecules along with long-chain branches, preferably skewed toward the larger molecules.

Autoclave reactor temperatures and pressures are used to optimize the balance between the high-molecular-weight shoulder and the low-molecular-weight section of the distribution in coating resins. The long-chain branches act as anchors to reduce the viscosity of the melt at high processing temperatures while maintaining resin flow integrity with lower neck-in behavior, assuming the molecular weight distribution is wider than that of regular coating-grade resins. Further work on melt elasticity and long-chain branching distribution measurements obtained at extrusion conditions (temperature and pressure) will be crucial to completely understand molecular properties and their influence on coating extrusion behavior. TJ

Literature cited

1. Feucht, P., Tilger, B., and Luft, G., *Chem. Eng. Sci.* 40(10): 1935(1985).
2. Luft, G. and Dorn, M., *Die Angew. Makromol. Chemie* 147: 119(1990).
3. Luft, G. and Dorn, M., *Die Angew. Makromol. Chemie* 188: 177(1991).
4. Tilger, B. and Luft, G., *TAH* 84: 335(1987).
5. Luft, G., Kaempf, R., and Seidl, H., *Die Angew. Makromol. Chemie* 111: 133(1983).
6. Kotliar, A. M., *J. Polym. Sci.* (Part A) 2: 4327(1964).
7. Wu, P. C., Howell, J. A., and Ehrlich, P., *J. Appl. Polym. Sci.* 85: 603(1963).
8. Gel Permeation Chromatography Columns and Polymer Calibration Narrow Dispersity Standards, Polymer Laboratories Inc. Brochure, Amherst, MA, 1992.
9. Yau, W. W. and Rementer, S. W., *J. Liquid Chrom.* 13(4): 627(1990).
10. Moldavan, D. G. and Polemenakos, S. C., *GPC Symposium Proceedings*, Waters, Inc., Milford, CT, 1989, p. 129.
11. Haney, M., First International Conference on Molecular Mass Characterization of Polymers, University of Bradford, England, 1989.
12. Strazielle, C., IUPAC, 1990.
13. Nordmeier, E., Lanver, U., and Lechner, M. D., *Maromolecules* 23: 1072(1990).
14. Accession, D. E. and Knapp, W. C., *J. Appl. Polym. Sci.* 25: 119(1980).
15. Drott, E. E. and Mendelson, R. A., *J. Polym. Sci.* (Part A-2) 8: 1361(1970).
16. Miltz, J. and Ram, A., *J. Polym. Sci.* 9: 685(1971).
17. Scholte, T. G., *Developments in Polymer Characterization* (J. V. Dawkins, Ed.), Vol. 4, Applied Science, Barking, 1983, pp. 1–36.
18. Rudin, A., Grinshpun, V., and O'Driscoll, K. F., *J. Liquid Chrom.* 7: 1809(1984).
19. Otocka, E. P., Roe, R. J., Hellman, M. Y., *et al., Macromolecules* 4(4): 507(1971).
20. Graessley, W. W., *Developments in Polymer Characterization* (D. V. Dawkins, Ed.), Vol. 4, Applied Science, Barking, 1985, pp. 371–388.
21. *123rd National Meeting of American Chemical Society Proceedings*, ACS, Washington, D.C., 1953, p. 6127.
22. Markovich, R. P., Smith, L., and Hazlitt, L. G., *ANTEC 1987 Proceedings*, SPE, Brookfield, CT, p. 98.
23. Nishikida, K., "GPC-FTIR applications," internal report, Perkin Elmer Corp., Norwalk, CT, 1992.
24. Stryker, H. H., "Relating SCB and LCB in selected LDPE resins," internal report, Chevron Chemical Co., Orange, TX, 1971.
25. Pohrt, V. J., *Kunststoffe* 66: 481(1986).
26. Schott, W. R., Bezigian, T. A., and Mamish, A. L., *TAPPI 1991 Polymers, Laminations and Coatings Conference Proceedings*, TAPPI PRESS, Atlanta, p. 353.
27. Martin, L. D., Dark, W. A., and Crawford, D. C., "The effect of temperature and draw distance of coating extrudates," internal report, Chevron Chemical Co., Orange, TX, 1967.
28. Roth, C. E., "Effect of high extrusion coating temperatures on the melt index of LDPE resins," internal report, Chevron Chemical Co., Orange, TX, 1972.
29. Crawford, D. C., "Effect of extrusion temperature and Corona treatment on the surface of LDPE," internal report, Chevron Chemical Co., Orange, TX, 1974.
30. Roos, F. H., "Characterization of low pressure LDPE resins," internal report, Chevron Chemical Co., Orange, TX, 1975.
31. Crawford, D. C. and Dark, W. A., "The relationship between crystallinity and physical properties in LDPE," internal report, Chevron Chemical Co., Orange, TX, 1976.
32. La Mantia, F. P., Valenza, A., and Acierno, D., *Polym. Eng. Sci.* 28(2): 90(1988).
33. Ultracki, L. A. and Schlund, B., *ANTEC 1986 Proceedings*, SPE, Brookfield, CT, p. 737.
34. Siegmann, A. and Nir, Y., *Polym. Eng. Sci.* 27(15): 1182(1987).
35. Morese-Seguela, B. and Constatin, D., *ANTEC 1985 Proceedings*, SPE, Brookfield, CT, p. 616.
36. Kalyon, D. M., Tan, V., Bhakuni, S., *et al., ANTEC 1986 Proceedings*, SPE, Brookfield, CT, p. 741.
37. Winter, H. H. and Holly, E., *ANTEC 1985 Proceedings*, SPE, Brookfield, CT, p. 613.
38. Zimm, B. H. and Stockmayer, W. H., *J. Chem. Phys.* 17(12): 1301(1949).
39. Minoshima, W. and White, J. L., *J. Non-Newtonian Fluid Mechanics* 19: 275(1986).
40. Leblans, P.J.R. and Bastiaansen, C., *Macromolecules* 22: 3312(1989).
41. Karszes, W. M., *TAPPI 1990 Polymers, Laminations and Coatings Conference*

Proceedings, TAPPI PRESS, Atlanta, p. 621.
42. Ultracki, L. A. and Schlund, B., *Polym. Eng. Sci.* 27(5): 367(1987).
43. La Mantia, F. P. and Accierno, D., *Eur. Polym. J.* 21(9): 811(1985).
44. Furuta, M., Hosoda, S., and Kojima, K., *J. Appl. Polym. Sci.* 33: 401(1987).
45. Braselmann, H. and Nurse, R. H., *Modern Plastics* 10: 78(1983).
46. Lee, C., Peat, I., Wild, L., *et al., ANTEC 1988 Proceedings*, SPE, Brookfield, CT, p. 591.
47. Datta, N. K. and Birley, A. W., *Plastics & Rubber Processing and Applications* 3: 237(1983).
48. Kanai, T. and White, J. L., *Polym. Eng. Sci.* 24(15): 1185(1984).
49. Speed, C. S., *ANTEC 1986 Proceedings*, SPE, Brookfield, CT, p. 214.
50. Hadjiandreou, P., Bakar, M., and Harrats, C., *ANTEC 1987 Proceedings*, SPE, Brookfield, CT, p. 1427.
51. Lee, C., Peat, I., Wild, L., *et al., ANTEC 1988 Proceedings*, SPE, Brookfield, CT, p. 183.
52. Kaltenbacher, E. J., Howard, C. B., and Parson, H. D., *Tappi* 50(1): 20(1967).
53. *Measurement of Melt Strength Parameter of LDPE Resins*, standard test procedure, Chevron Chemical Co., Orange, TX, 1975.
54. Advanced Capillary Extrusion Rheometer (ACER) with Thrust option, Polymer Laboratories Inc., Piscataway, NJ.
55. Advanced Capillary Extrusion Rheometer (ACER) with Slit Flow Monitor option, Polymer Laboratories Inc., Piscataway, NJ.

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