Rheological Indicators of LDPE to Predict Processing Performance in Extrusion Coating

Claes Oveby

Tetra Pak Carton Ambient AB, Lund, Sweden

ABSTRACT

Various LDPE grades behave differently in the coating process due to different rheological properties. This paper presents how these differences in both level and consistency of the rheological properties will influence the performance in the coating process.

INTRODUCTION

In extrusion coating a thin molten film of low density polyethylene (LDPE) is extruded onto a substrate. LDPEs from high-pressure autoclave reactors for extrusion coating with a Melt Flow Rate (MFR) range from 6 to 9 g/10 min and with a density of 917-921 kg/m^3 have been considered for a long time as a uniform commodity.

However, as evolution goes towards faster coating lines, differences in processing performance between various LDPE grades have been observed (e.g. web break and edge instabilities causing manufacturing defects).

MATERIALS AND METHODS

Rheological measurements

The rheological measurements were performed on a StressTech controlled stress melt rheometer. Polymer pellets were melted, compressed and stamped into discs with a diameter of 25 mm and a thickness of 1 mm. Parallel plates were used and measurements were done under nitrogen atmosphere to prevent thermal degradation of the sample. Oscillatory measurements were performed at 170 °C in the linear viscoelastic region with a frequency sweep between 20 and 0.01 Hz.

When a material undergoes oscillatory stress with frequency, the response can be expressed in terms of a storage modulus, G’ a loss modulus, G’’ and a complex viscosity, η^*.

Extrusion coating trials

Thirteen grades of autoclave LDPE from different suppliers were tested in two pilot extrusion coating lines at three different occasions. All grades had MFR between 7 and 9 g/10 min and densities of 918-920 kg/m^3. The melt temperature was monitored to 295-305 °C, by means of an infrared camera and air gap was between 180-300 mm.

The methodology was in principle the following. Extruder screw rpm (revolution per minute) was set to give 10 g/m^2 at 150 m/min in order to obtain stable processing conditions. The line speed was then increased in steps of 50 m/min until the web broke. The line speed at which the web broke (draw-down speed) and the neck-in (reduction of web width) were reported. This was made in duplicate for each grade of LDPE.

G’ and η_0 monitoring of LDPE

In order to determine the differences in G’, η_0 and product consistency, LDPE suppliers were selected to send samples from at least 50 batches to Tetra Pak during a period of 4-8 months for G’ and η_0 measurements.

RESULTS AND DISCUSSION

Rheological indicators

From the frequency sweep two rheological indicators are found. G’ is determined at G’’ equal to 500 Pa by the use of a Cole-Cole[1] plot (Fig. 1). The log G’’ is plotted versus the log G’ in the range of 200-900 Pa of the G’’. A linear relation is obtained and the G’ can be determined at G’’ equal to 500 Pa (log 500 = 2.7).

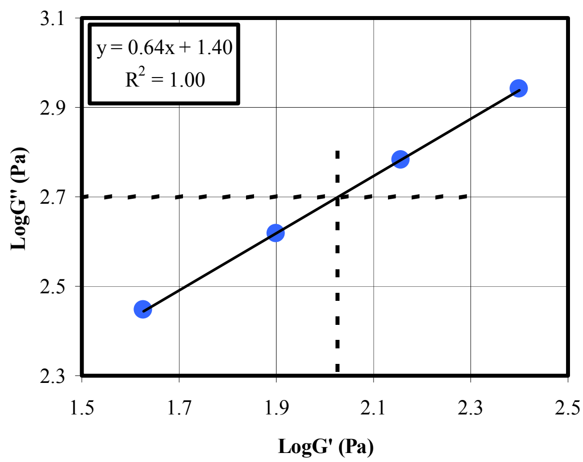

Figure 1. The log loss modulus (G’’) versus log storage modulus (G’) for the determination of the G’ at G’’ equal to 500 Pa. Modulus measured at 170 °C in a frequency sweep between 20 and 0.01 Hz.

Zero shear viscosity, η_0 is determined by extrapolation by the use of a 3 parameters Cross equation:

$$\eta^* = \frac{\eta_0}{(1+(\lambda\omega)^n)} \qquad (1)$$

where

η_0 is the zero shear viscosity,
λ a characteristic relaxation time and
n is the power law index.

The curve fit calculation is preferably done with the Microsoft Excel solver[2].

Rheological model

The results from the extrusion coating trials were analysed by the use of a multivariate data analysis software[3]. G’ and η_0 were set as variables and observed draw-down (DD) as the response (17 observations).

The model diagnostics evaluation gave the following results:

R^2 = 0.76 (estimates goodness of fit)
Q^2 = 0.72 (estimates goodness of prediction)

From the multivariate data analysis the following relationship was found:

$$DD=1311-7.55G'-0.022\eta_0 \,(m/min) \qquad (2)$$

In Fig. 2 the observed draw-down is plotted versus the predicted draw-down.

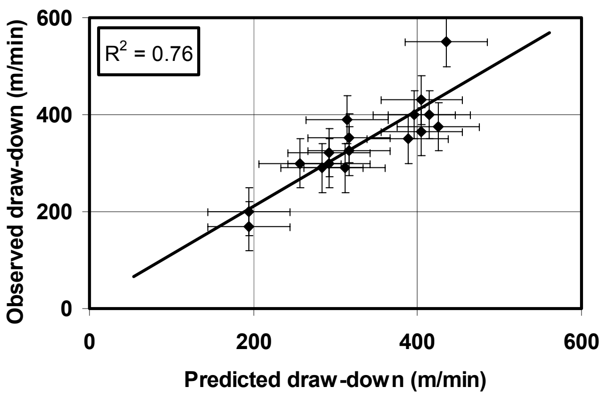

Figure 2. Observed versus predicted draw-down for all the 17 observations from the extrusion coating trials. The predicted draw-down is calculated from Eq. 2.

A linear relationship between draw-down and neck-in (NI), with an R^2 of 0.93, was also found:

$$NI=0.13DD+44 \text{ (mm)} \tag{3}$$

MFR showed much poorer correlation to observed draw-down. An R^2 of 0.37 was achieved when observed draw-down was plotted versus measured MFR (Fig. 3)

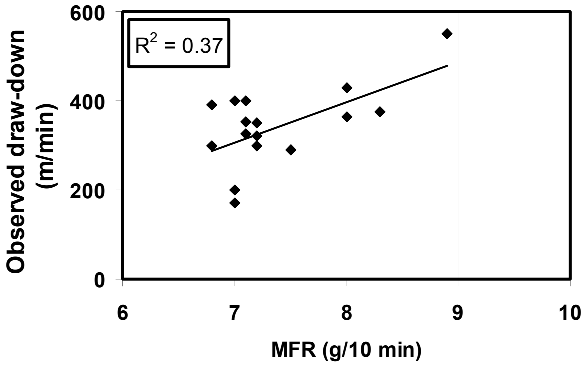

Figure 3. Observed draw-down versus Melt Flow Rate.

The results from the oscillatory measurements, the pilot extrusion coating trials and the results from the predictions are given in Table 1. MFR is given in g/10 min, G' in Pa, η_0 in Pas, p-DD (predicted draw-down) in m/min, o-DD (observed draw-down) in m/min and o-NI (observed neck-in) in mm.

Table 1. Summary of the data measured and generated at the pilot extrusion coating trials.

LDPE	MFR	G'	η_0	p-DD	o-DD and o-NI	
1	7.1	105.1	4220	414	400	99
2	7.0	132.7	4640	194	200	71
3	8.0	108.2	3580	405	365	91
4	6.8	123.4	5000	257	300	87
5	7.2	120.9	4280	292	300	84
6	7.1	117.2	4420	317	325	85
7	7.5	118.5	4280	311	290	80
8	7.2	108.5	4230	388	350	88
9	8.9	105.2	3220	435	550	-
10	7.0	132.7	4640	194	170	-
11	8.0	108.2	3580	405	430	-
12	6.8	116.3	4900	314	390	-
13	7.2	120.9	4280	292	322	-
14	7.1	117.2	4420	317	352	-
15	7.0	106.5	4575	396	400	-
16	7.5	118.3	5565	284	290	-
17	8.3	105.4	3635	425	375	-

Consistency of LDPE

Process capability is defined as the 6σ interval that defines a statistically controlled process. An index of capability is C_p where:

$$C_p = \frac{USL - LSL}{6\sigma} \tag{4}$$

where

USL and LSL are the upper and lower specification limits, respectively.

This is an indicator of what the process could do if properly centered. A similar index, C_{pk}, indicates the capability of the process as it is currently centered.
C_{pk} is the smallest of:

$$C_{pu} = \frac{USL - \overline{X}}{3\sigma} \tag{5}$$

or

$$C_{pl} = \frac{\overline{X} - LSL}{3\sigma} \tag{6}$$

where

$\overline{X}$ is the average value of the population.

The process capability, P_{pk}, is defined in the same way as C_{pk} but takes also the process variation into consideration. P_{pk} is calculated using the overall variation. Both the between-subgroup and within-subgroup contribute to the overall variation. C_{pk} is calculated using the within-subgroup variation, but not the shift and drift between subgroups.

The mean of G' and η_0 and the P_{pk} for G' and η_0 for the different LDPE grades are shown in Table 2.
The tolerances (USL – LSL) for G' is set to 10 Pa and for η_0 to 800 Pas.

Table 2. Results from monitoring of LDPE.

LDPE	G' (Pa)	P_{pk} (G')	η_0 (Pas)	P_{pk} (η_0)
A	116	1.11	4300	0.86
B	108	0.73	4350	0.69
C	122	0.60	4650	0.80
D	107	0.81	3500	1.02
E	106	0.81	3500	0.77
F	120	0.66	4350	0.72
G	113	0.61	3650	1.21
H	109	0.61	3800	0.77
I	115	0.74	4450	0.67
J	131	0.90	4300	1.06
K	113	0.62	4850	0.49
L	113	1.11	4650	0.90
M	120	0.65	5350	0.40
N	113	1.42	4200	0.77
O	112	0.72	4850	0.29

There are considerably differences in both level of G' and η_0 and also consistency among the different LDPE grades. These differences will have high impact on the extrusion coating performance of the different LDPEs.

CONCLUSION

LDPE from high-pressure autoclave reactors for extrusion coating with a MFR from 7 to 9 g/10 min and with a density of 917-920 kg/m^3 has for a long time been considered as a uniform commodity. However, as the evolution goes towards faster coating lines, it has been possible to detect differences in processing performance between various LDPE grades.

The parameters MFR and density gives very limited information on the processing performance of the product. Very often a resource demanding test run of the LDPE material in a pilot or production coating line is necessary in order to determine the processability.

Extrusion coating performance can be conveniently, and considerably less resource demanding, determined and predicted by the rheological method described in this paper.

The advantages with this method are as follow:

- Very good correlation with processing behaviour.
- Reduced costs in the evaluation process.
- Improved quality of the LDPE, which reduces the LDPE edge trim and risk for manufacturing defects.

REFERENCES

1. Shroff, R and Mavridis, H., “New Measurs of Polydispersity from Rheological Data on Polymer Melts”, Journal of Applied Polymer Science, vol. 57, 1605-1626 (1995).
2. Roberts, G.P., Barnes, H.A., Mackie, C., "Using the Microsoft Excel solver tool to perform non-linear curve fitting, using a range of non-Newtonian flow curves as examples", Applied Rheology 11, 2, 271-276 (2001).
3. SIMCA-P10, Umetrics AB, Umeå, Sweden.