

Influence of extrusion coating processing conditions on structure and tensile properties of some polyethylene grades

Nils Toft and Mikael Rigdahl

Chalmers University of Technology, Department of Materials Science and Engineering,
SE-412 96 Göteborg, Sweden

ABSTRACT

The effect of the extrusion coating conditions on the structure and tensile properties of some polyethylene grades (films) was evaluated. The degree of orientation and the strain at break of the films exhibited a clear correlation with the elongational strain rate imposed during the drawing phase of the process. The importance of the rheological properties of the melt is discussed.

INTRODUCTION

It is well known that, in addition to the polymer characteristics, the properties of the final product is determined, via process-related structural changes, by the processing technique used and the prevailing processing conditions, e. g. cooling rate and machine speed. The processing can affect structural characteristics, such as the molecular orientation, degree of crystallinity, crystalline morphology and induce thermal and mechanical degradation and cross-linking, which in turn may alter the mechanical performance of the product. For example the shear and extensional flow fields imposed on the polymer melt during the processing step are expected to be reflected in the orientation and the crystallinity can be affected by changes in the cooling conditions. The relationship between the processing parameters and the resulting structure and mechanical properties has been the subject of several

studies in the case of film blowing, cf e.g. Hitchcock¹, but extrusion coating appears to have attracted less interest. With regard to the polymers used, low density polyethylene (LDPE) and Ziegler-Natta catalysed linear low density polyethylene (LLDPE) have been more in focus than metallocene-catalysed linear low density polyethylenes (m-LLDPE).

Legros et al.^{2,3} demonstrated how the processing conditions during film blowing influenced the tensile properties and the structure of m-LLDPE and compared the behaviour to that of LDPE and LLDPE. In this study, the attention was in the first place focussed on the development of the orientation. Ghaneh-Fard⁴ concluded from his work on film blowing of LDPE, LLDPE and m-LLDPE that although it could be ascertained that the processing conditions had a significant influence on the film properties, it was difficult to establish simple relations between these properties and the dynamics of the process.

Here it can also be mentioned that Jordens et al.⁵ studied the effect of the cooling rate (from the molten state) on the tensile properties of m-LLDPEs with different molecular weights. The different thermal treatments produced changes in the density/ crystallinity of the specimens, and direct relations between several tensile properties and the degree of crystallinity were noted

Table 1. Some characteristics of the polymers used.

Type of PE	ρ (g/cm ³)	Cryst. ¹ (%)	T _m ¹ (°C)	MI ² (g/10 min)
A LD	0.918	35	109	7.5
B LLD	0.921	41	111, 124	5.5
C m-LLD	0.910	27	103	15

¹from DSC-measurements, ²(190 °C, 2.16 kg).

Extrusion coating is a commonly used method for producing different types of laminates, e. g. liquid-resistant paperboard. Polymer granules (pellets) are first fed into an extruder and successively melted by shearing and conduction heating. At the end of the extruder, the melt passes through a screen-pack and is then transported by pressure flow through heated piping, down to a heated slit die. After significant expansion in the transverse film direction and compression in the out-of-plane direction in the die, the polymer melt passes through the die exit and is then stretched into a film as it is drawn down into a nip. During the flow through the barrel, the piping and the die, the melt is subjected to shear and extensional deformation, whereas extensional deformation predominates after the die. After the die, the deformation takes place at non-isothermal conditions and these conditions will govern the state of orientation and the morphology of the end product. Attention has also to be paid to any possible mechanical and thermal degradation, which are favoured by high melt temperatures, long residence times and extensive deformations.

AIMS OF THE PRESENT WORK

As mentioned earlier, the extrusion coating process appears to have attracted a somewhat limited interest in the literature. The present work aims at identifying relevant process parameters, which

significantly influence the structure and morphology of different polyethylene grades. Furthermore, it is aimed to clarify the relations between the process parameters and certain end-use properties, primarily mechanical properties, such as elongation and strength at rupture. Finally, the influence of the melt rheology on the process-induced structural changes and resulting film properties will be briefly discussed.

EXPERIMENTAL

Materials

The available characteristics of the different polyethylenes are given in Table 1.

Methods

Extrusion coating

The coating equipment used in the pilot-scale experiments was a 2.5" single screw extruder, with a length/diameter ratio of 33 for the screw, and a coat-hanger die. The thickness of the die-slit opening was 0.6 mm and its width was 400 mm. Certain process parameters were varied in steps during the experiments: the rotational velocity of the screw was changed between 30 and 120 rpm, the processing temperature between 190 and 300 °C, and the draw-ratio (DR), given by the ratio between the line speed at the nip (chill roll) and the line speed at the die exit, between 10 and 120. In some experiments, the air gap between the die exit and the chill roll (the nip) was also varied in steps between 115 and 205 mm.

The polymer films were extrusion coated on a paperboard-substrate with a smooth surface. The film was then separated from the substrate and in order to avoid a too high adhesion between the polymer film and the substrate at higher melt temperatures, polyester films were placed on the substrate.

Characterisation of degree of orientation

The degree of orientation can be characterised in different ways. Boldizar et. al.⁶ compared results from far-infrared

birefringence (FIR), wide-angle X-ray scattering (WAXS) and shrinkage measurements on high density polyethylene, and found that the methods correlated well to each other. Here the shrinkage technique was used for assessing the degree of orientation. The reason for this is mainly that the experiments are quite straightforward to perform.

The shrinkage was measured on specimens that had been immersed in hot silicon oil (Baysilone M5, Jacobi AB F.A.W.), The temperature of the oil was controlled with a precision thermostatic bath (Grant W14). The initial size of the specimens was 15 x 100 mm, with the longer side coinciding with the machine direction. The following oil temperatures and immersion times were used: Polymer A (LDPE): 105°C/ 10min, polymer B (LLDPE): 116°C/ 10min and polymer C (m-LLDPE): 97°C/ 20 min. Since the different polymers had different melting points and somewhat different shrinkage behaviour it is somewhat less meaningful to compare the degree of orientation between the different polymers. The average value of the shrinkage from five measurements in the machine and cross directions was calculated as (Menges and Wübken⁷).

$$S_L = 1 - \left\{ 1 + \frac{l_o}{l_s} - \sqrt{1 - S_T} \right\}^{-1} \quad (1)$$

and

$$S_T = 1 - \left\{ 1 + \frac{w_o}{w_s} - \sqrt{1 - S_L} \right\}^{-1} \quad (2)$$

where S_L and S_T are the shrinkage degrees in the flow (machine) direction and the transverse direction, respectively. The length of the film sample in the flow direction is denoted l and the corresponding width w ; the index s refers to the measure after the heat treatment and the index o to the corresponding measure before the

immersion in the hot fluid. In the following, only the shrinkage S_L in the flow direction of the melt is considered.

Tensile properties

The tensile properties at room temperature, 23 °C, (strength and strain at break in the machine direction and in the cross direction) were determined with an Instron 4502 tensile tester using a crosshead speed of 500 mm/min and a 100 N load cell. The sample dimensions were 6 x 25 mm, and the thickness varied between 5 and 81µm. The average value determined from six measurements was used in the following.

Thermal analysis

The melting points and the degrees of crystallinity of the materials before (granules) and after (films) processing were evaluated using differential scanning calorimetry (DSC), MDSC from TA Instruments. Indium was used for the calibration of the measurements. The specimens were first heated from 35 to 150 °C (first heating) with a heating rate of 10 °C/min, then cooled down to 35 °C with a cooling rate of 10 °C/min and then reheated again to 150 °C (second heating) at a heating rate of 10 °C/min. The crystallinity of the specimens was evaluated using a heat of fusion of 293 J/g for crystalline polyethylene.

Capillary viscometer measurements

(determination of the elongational viscosity)

A conventional capillary viscometer (Rheoscope 1000, Ceast 6742/000) was employed for estimating the elongational viscosity of the melts as a function of the deformation rate using the simple approach, based on pressure loss measurements, envisaged by Cogswell^{8,9}. For these measurements, which were performed at 190, 220 and 250 °C, a capillary of approximately zero length and a diameter of 1 mm was used. The results are described in detail by Toft and Rigdahl¹⁰.

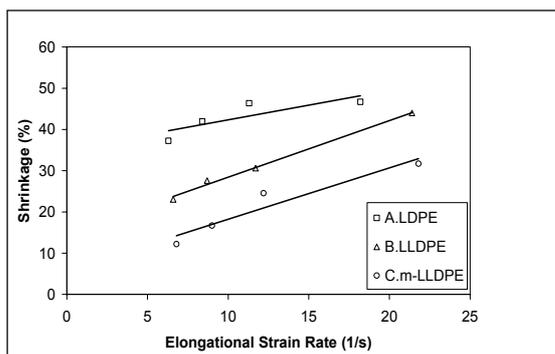


Figure 1. Shrinkage in the flow direction vs. elongational strain rate for materials A-C at a melt temperature of 190°C and at an extruder rotational velocity of 30 rpm.

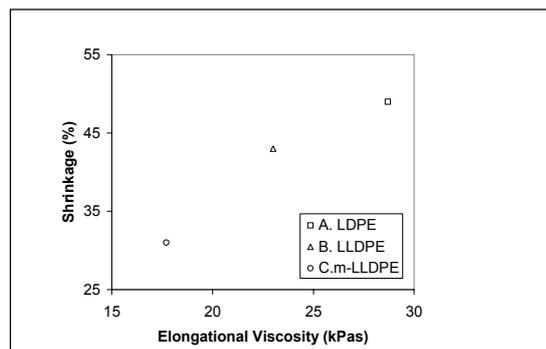


Figure 2. Shrinkage in the flow direction of the films vs. elongational viscosity for the polymers A-C at the melt temperature 190 °C at an extruder rotational velocity of 30 rpm corresponding to an elongational strain rate of 20 s⁻¹.

RESULTS AND COMMENTS

Thermal analysis (DSC)

The LLDPE-specimens exhibited the highest melting points and the highest degree of crystallinity, whereas the lowest values were noted for the metallocene-catalysed material. The degree of crystallinity was lower for the extruded polymer specimens than for granule samples. These effects should primarily be attributed to the rather rapid cooling of the film after leaving the slit die. However, the processing conditions varied here (melt temperature, draw ratio, machine speed) did not have any significant effect on the melting point or on the degree of crystallinity for the extruded films.

Shrinkage/orientation of the polyethylene films

Shrinkage is here taken to be measure of the orientation of the extruded polyethylene films. In many cases, a good correlation between the shrinkage in the flow direction and the elongational strain rate experienced by the melt between the die exit and the nip was noted. Fig. 1 constitutes one example of this where the air gap and draw ratios were varied (thus changing the elongational strain rate) while keeping the melt temperature at 190 °C and the extrusion rotational velocity

at 30 rpm (corresponding to a velocity at the die exit of 1.3 – 1.4 m/min). For each polymer grade, the relation was almost but not perfectly linear, which is not very surprising. Here LDPE exhibited the highest shrinkage and m-LLDPE the lowest.

Although it has been pointed out that it is difficult to compare the shrinkage behaviour of the polyethylene grades, it is anyway of significant importance to point to that a higher elongational viscosity corresponds to a higher degree of shrinkage (or orientation). This is shown in Fig. 2 where the shrinkage is plotted against the elongational viscosity for the three materials at same melt temperature and at comparable elongational strain rate. The elongational viscosity was here evaluated from the capillary extrusion experiments and these results were reported in detail by Toft and Rigdahl¹⁰. Fig. 2 refers to a melt temperature of 190 °C and a specific strain rate, but the same type of relation is noted at other conditions.

As the melt temperature was increased to 300°C, the shrinkage decreased, but the relation between the shrinkage and the elongational strain rate was still linear. A higher melt temperature (and thereby a lower elongational viscosity) allows for greater extent of molecular relaxation during

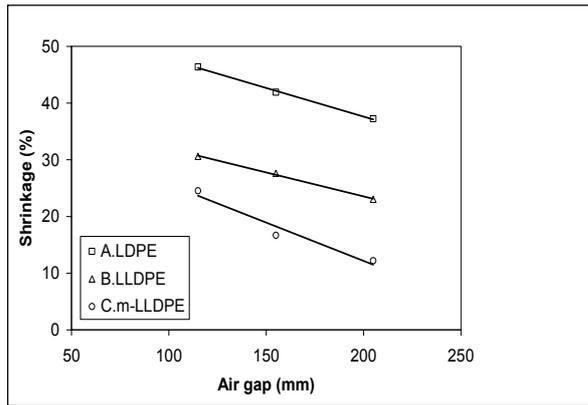


Figure 3. Shrinkage in the flow direction vs. the length of the air gap for materials A-C at a melt temperature of 190°C with an initial film velocity (at the die) of 1.3 – 1.4 m/min and at a draw ratio of 20.

the cooling state, which in turn decreases the degree of orientation and consequently the shrinkage.

Increasing the air gap between the die exit and the nip, while keeping the melt temperature, the melt velocity at the die and draw ratio constant, reduces the elongational strain rate. This is reflected in a lower shrinkage of the films as illustrated by Fig. 3 for the three polyethylene grades at a melt temperature of 190 °C and DR-value of 20. The decrease in shrinkage is quite significant in this case and here it can also be expected that the longer cooling time experienced during the drawing with longer air gaps also can have an influence on the results.

When the line velocity at the nip is increased while keeping the initial velocity constant (or the extrusion rotational velocity), as done in some of the cases described above, the film thickness will decrease. This can have effect on the degree of orientation “frozen” into the samples since the cooling rate of the film depends also on the film thickness. This may be regarded as an additional factor, which can influence the degree of orientation and shrinkage behaviour. In order to highlight this, a series of experiments were

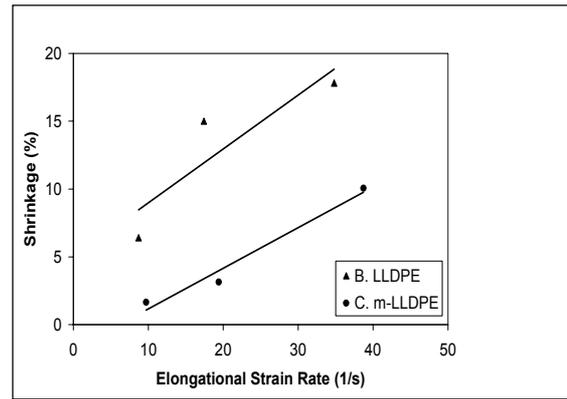


Figure 4. Shrinkage in the flow direction vs. elongational strain rate for materials B and C, (melt temperature 300° C, draw ratio 20 and extruder rotational velocity of 30, 60 and 120 rpm) The final film thickness was kept constant at 35 µm).

performed, where the extrusion rotational velocity was increased in steps (30, 60 and 120 rpm) while keeping the draw ratio constant at 20. The film velocity at the nip will have to be changed in corresponding manner, thus changing the elongational strain rate, but the film thickness could within ten per cent be kept constant at 35 µm. Fig. 4 shows that even at constant film thickness, the elongational strain rate has a strong effect on the degree of shrinkage, i.e. higher strain rates corresponds to a higher degree of shrinkage.

Tensile properties of the extruded films

Fig. 5 shows the strain at break for the three polymer films in the flow or machine direction (MD) as a function of the elongational strain rate at a melt temperature of 190°C (keeping the extrusion rotational velocity at 30 rpm). A decreased elongation at break corresponds to a higher degree of orientation expressed in terms of a higher measured shrinkage. The more oriented the film initially is, the lower the ultimate deformation will be, which is not very surprising. This, in itself, underlines the importance of the processing conditions with regard to the mechanical properties of

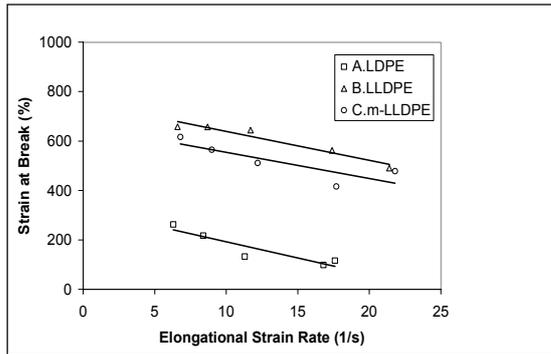


Figure 5. Strain at break in the flow direction vs. the elongational strain rate for materials A-C at a melt temperature of 190°C.

the final film. With the grades used here, the deformability of the LLDPE was higher than that of the other grades. The lowest elongation at rupture at a given elongational strain rate was obtained with the LDPE-grade. This result can however not be considered to have a general validity.

The noted behaviour indicates that an increase in the elongational strain rate during the drawing phase of the process would in a rather straightforward manner be reflected in a lower ultimate strain. This is also noted here, for example an increase of the air gap between the die exit and the nip (keeping the other conditions constant) gives a lower elongational strain rate and thus a higher strain at rupture.

There was a very good relation between the strain at break in MD and the corresponding shrinkage (representing the degree of orientation), irrespective of the processing temperature, see Fig. 6. Thus, since there is a strong correlation between the shrinkage and the elongational strain rate, this certainly points to that the elongational strain rate during the drawing step is a parameter that to a large extent governs the deformability of the film. Effects of the cooling rate especially for thinner films to the film thickness can be of importance, but this was not evident in this case. No evident relation between the elongation at break in the cross (or

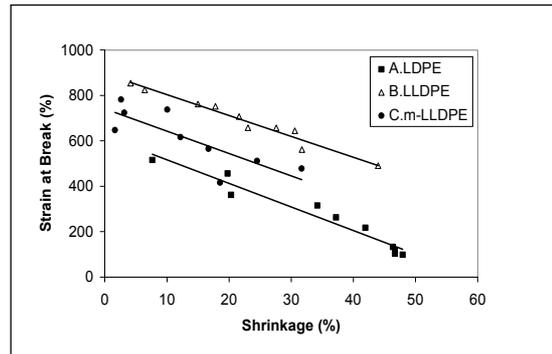


Figure 6. Strain at break in the flow direction vs. shrinkage in the flow direction for materials A-C at melt temperatures of 190°C and 300°C, and at different processing conditions

transverse) direction (CD) and the elongational strain rate could be ascertained in this case. The ductility in CD was however in general lower than that in MD for a given specimen. With regard to the stress at break, the general trend was that a higher strain at break corresponded to a higher mechanical strength.

FINAL REMARKS

Process-related factors that may influence the degree of orientation of solidified extrusion coated polymer films are the elongational strain rate, the melt temperature (via the melt rheology) and the cooling rate (time of solidification). The results arrived at here point to that the degree of orientation, measured as shrinkage, is to a large extent governed by the elongational strain rate. This implies that, if the influence of the film thickness is accounted for, that the processing parameters, which determine the elongational strain rate (such as the machine speed, the air gap and the draw ratio), will affect the degree of orientation rather significantly. The elongational strain rate imposed during the drawing step then will constitute an important tool for the manufacturer when aiming at controlling the structure and properties of the final product. The cooling rate will also affect the shrinkage behaviour (degree of orientation),

but its influence appears to be less than that of the elongational strain rate. Changing the melt temperature affects as expected the degree of orientation, and the controlling parameter is likely to be associated with the elongational viscosity of the melt. A lower elongational viscosity (higher temperatures) is likely to be less effective in producing a highly oriented structure as indicated by the results shown in Fig. 2. This certainly implies that the rheological properties of the melt, as reflected for instance in the elongational viscosity have a direct effect on the solid state behaviour of the final film. In fact, if further work is performed it may be possible to establish direct correlation between the elongational viscosity, via orientation measurements and evaluation of the morphology, and the film properties. This is however beyond the scope of the present study.

A clear result from this study is that the strain at break in MD is strongly related to the degree of orientation as given by the shrinkage, Fig. 6. Thus at given melt temperature, the ultimate strain is governed by the elongational strain rate and the processing conditions that control this variable during the drawing operation. Considering the relation between the strain at break and the strength of the films for the polymers used here, the elongational strain rate appears to be a valuable concept for the manufacturer when aiming at controlling the ultimate mechanical properties of the film.

Once again it should be made clear that the used elongational strain rate (and the elongational viscosity) can provide useful information on how the orientation of the specimens will be affected by changes in the processing conditions during the extrusion coating. It will however not provide a quantitative tool for predicting how the physical properties of different polyethylene grades will be changed. For a given polymer grade, such relations may however possibly be established.

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