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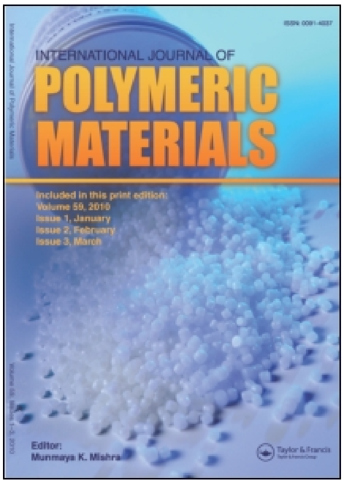

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INFLUENCE OF EXTRUSION COATING CONDITIONS ON STRUCTURE AND TENSILE PROPERTIES OF POLYETHYLENES

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INFLUENCE OF EXTRUSION COATING CONDITIONS ON STRUCTURE AND TENSILE PROPERTIES OF POLYETHYLENES

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It is well known that the properties of a final polymer product are determined not only by the polymer characteristics but also, via process-related structural changes, by the processing technique and by processing conditions such as cooling rate and machine speed. In this study, the influence of the extrusion coating process on the structure and properties of LDPE-, LLDPE-, and m-LLDPE-grades was evaluated. Process variables such as the melt temperature, the draw ratio, the length of the air gap between the die exit, and the laminating nip and the machine speed were studied. The primary interest was in the influence of the process parameters on the degree of orientation and its corresponding impact on the tensile and barrier properties (water vapor transmission rate) of the polymer films. The degree of orientation of the films, assessed by shrinkage measurements, was found to be directly related to the elongational strain rate imposed on the films during the drawing stage of the coating process. Furthermore, the strain at break of the films in the machine direction correlated well with the shrinkage of the films, that is, the strain at break was strongly related to the imposed elongational strain rate. The relation is naturally also dependent on the polymer grade used and on how its rheological properties are affected by the process temperature. The melt temperature had a distinct influence on the water vapor transmission rate through the polymer films. This is discussed in terms of the orientation of the specimens.

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INTRODUCTION

It is well known that the properties of a final polymer product are determined not only by the polymer characteristics but also, via process-related structural changes, by the process technology and by process conditions such as cooling rate and machine speed. The processing can affect structural characteristics, such as the molecular orientation, degree of crystallinity and crystalline morphology, and can induce thermal and mechanical degradation and cross-linking, and this may in turn 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 cooling conditions can affect the crystallinity. The relationship between the process parameters and the resulting structure and mechanical properties has been studied in the case of film blowing (cf, e.g., Hitchcock [1]), but extrusion coating appears to have attracted less interest. Low density polyethylene (LDPE) and Ziegler-Natta-catalysed linear low density polyethylene (LLDPE) have been studied more than metallocene-catalysed linear low density polyethylenes (m-LLDPE).

Metallocene-catalysed linear low density polyethylenes are increasingly used in packaging applications because, in certain respects, they have better characteristics than LDPE and Ziegler-Natta-catalysed LLDPE. The mechanical and physical properties of these polymer films, such as tear and puncture resistance, toughness, impact strength, clarity, anti-blocking properties, and sealing performance are generally improved [2–5]. Compared to Ziegler-Natta catalyzed LLDPE, m-LLDPEs have narrower molecular weight distributions and more well-defined short-chain branch (SCB) distributions (cf Chum et al. [6]). The level and distribution of SCB can control the crystallinity and the crystalline morphology [7–8] and thus the physical properties of the material, because the SCB in principle disrupts the chain regularity.

Legros et al. [9,10] demonstrated how the process conditions during film blowing influenced the tensile properties and the structure of m-LLDPE and compared the behavior to that of LDPE and LLDPE. In this study, attention was in the first place directed toward the development of the orientation. Ghaneh-Fard [11] concluded from his work on film blowing of LDPE, LLDPE and m-LLDPE that, although the process conditions clearly had a significant influence on the film properties, it was difficult to establish any simple relations between these

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properties and the dynamics of the process. Culter [12] discussed the influence of polymer characteristics (i.e., molecular structure) and process-induced structural changes on the barrier characteristics of polymer films, focusing on the water vapor transmission rate (WVTR) of blown HDPE-films (high density polyethylene). Culter [12] and Krohn et al. [13] pointed to a linear relation between the WVTR and the degree of orientation of biaxially oriented blown films, measured as the ratio of the tear strength in the transverse direction to that in the machine direction. In general, higher vapor transmission rates were obtained as the degree of crystallite orientation increased. It can also be mentioned that Jordens et al. [14] studied the effect of the cooling rate (from the molten state) on the tensile properties of m-LLDPEs of different molecular weights. The different thermal treatments led to changes in the density/crystallinity of the specimens, and direct relations between several tensile properties and the degree of crystallinity were noted.

The process conditions can have quite a complicated influence on the structure and crystalline morphology of the polymers. Not only can the thermal history affect, for example, the crystallinity, but the flow field can affect the orientation of the polymer molecules and thus influence the crystallization rate and degree of crystallinity. There is thus a complex interplay between the orienting flow field, the temperature (or thermal history) and the final morphology (cf also Gedde [15]). Furthermore, in practice blends of different polyethylene grades can be used to tailor the product in some desired respect (cf also Rana et al. [16]). Hill and Barham [17] studied binary blends of different m-LLDPEs with different branch contents and different branch types and found a double morphology (i.e., two crystal types, domains of thicker lamellae in a matrix of thinner lamellae) in quenched blends where the components differed in branch content. This further adds to the complexity of the situation.

Extrusion coating is a commonly used method for producing laminates such as liquid-resistant paperboard. Polymer granules (pellets) are 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 channels 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 both shear and extensional deformation, whereas extensional deformation predominates after the die. After the die, the deformation takes place under non-isothermal conditions and these conditions govern the state of orientation and the morphology of the end product. Attention has also to be paid to possible mechanical and thermal degradation, which are favored by high melt temperatures, long residence times, and extensive deformations. Expressed in a somewhat simplified manner, the draw ratio experienced by the melt between the die exit and the nip, the machine speed, and the air gap between the die exit and the nip should influence primarily the orientation of the film, whereas the cooling conditions will control the crystalline morphology, although as indicated there can be a rather complex interaction between these factors and features.

In a previous study [18], the rheological behavior and the extrusion coating processability of different grades of metallocene-catalysed polyethylenes (m-LLDPEs) were compared with those of a low-density polyethylene (LDPE) and of a Ziegler-Natta-catalysed LLDPE. In the present work, attention is directed toward how the extrusion coating conditions via structural changes, for example, the orientation and the degree of crystallinity, affect the mechanical properties and some barrier properties of films of LDPE, LLDPE, and m-LLDPE. This does not imply that other properties are more or less unaffected by the processing conditions or that they are less important. For example, in oriented polymer films, a certain degree of shrinkage always takes place after the process step due to relaxation. This shrinkage, which is partly determined by the degree of orientation, is time- and temperature-dependent. Trouilhet and Morris [19] suggested that this shrinkage of the film could be one cause of a loss of adhesion between an extrusion-coated film and a substrate.

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AIMS OF THE PRESENT WORK

The present work aims at identifying those process parameters that significantly influence the structure and morphology of different polyethylene grades. A further aim is to clarify the relations between the process parameters and end-use properties such as tensile modulus, elongation and strength at rupture, and WVTR. The influence of the melt rheology on the process-induced structural changes and resulting film properties is also briefly discussed.

EXPERIMENTAL

Materials

Some characteristics of the different polyethylenes are given in Table 1. Among the metallocene-catalysed polyethylene grades used in the previous study [18], the grade (denoted C here) with the most

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TABLE 1 Some Characteristics of the Polymers Used

Sample	Type	Density (g/cm^3)	Crystallinity* (%) 2nd heating	Melting peaks* (°C) 2nd heating	Melt index g/10 min (190°C, 2.16 kg)	Type of comonomer
A	LDPE	0,918	35	109	7,5	—
B	LLDPE	0,921	41	111, 124	5,5	Octene
C	m-LLDPE	0,910	27	103	15	Hexene

*From DSC-measurements.

favorable processing characteristics with regard to the combination of lateral melt shrinkage and strength characteristics was chosen.

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, given by the ratio of the line speed at the nip (chill roll) to the line speed at the die exit, between 10 and 120. The initial melt velocities (at the die exit) at different screw speeds and melt temperatures were evaluated from previously performed output tests. At screw speeds and melt temperatures where no output tests were available, the initial melt velocities were obtained by extrapolation. 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 onto a paperboard substrate with a smooth surface. The film was then separated from the substrate. In order to avoid too high an adhesion between the polymer film and the board at higher melt temperatures, the polymer was extruded onto a polyester film placed on the board surface. The temperature of the melt at the die exit was monitored by an IR-camera positioned ca 30 mm below the die exit.

Characterization of Degree of Orientation

The degree of orientation can be characterized in various ways. Boldizar et al. [20] 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 with each other. Here, the shrinkage technique was used. This method was chosen primarily because it is quite straightforward to use.

The shrinkage was measured on specimens that had been immersed in hot silicone 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 × 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/10 min, polymer B (LLDPE): 116°C/10 min, and polymer C (m-LLDPE): 97°C/20 min. Because the different polymers had different melting points and exhibited somewhat different shrinkage behavior it is less meaningful to compare the degrees of orientation of the different polymers. The lengths and widths of the specimens were measured before and after immersion in the oil. The average values, S_L and S_T, of the shrinkage from five measurements in the machine and cross directions respectively were calculated as [21]:

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

and

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

where the length of the film sample in the flow direction is denoted l and the corresponding width w; the index o refers to measurement before the heat treatment and the index s to the corresponding measurement after the heat treatment. 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, (elastic modulus, 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 100 mm/min (elastic modulus) or 500 mm/min and a 100 N load cell. The sample dimensions were 6 × 25 mm, and the

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thickness varied between 5 and 81 μm. The average value determined from six measurements was calculated.

Thermal Analysis

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

Moisture Permeability Measurements

The Water Vapor Transmission Rate (WVTR) of the polymer films was measured using a Mocon Permatran-W Twin device according to ASTM F 1249−90 at 24.5°C ± 0.5°C and 50% RH. The exposed measuring area was 50 cm^2. Two measurements were performed on each sample.

Capillary Viscometer Measurements (Determination of the Elongational Viscosity)

A conventional capillary viscometer (Rheoscope 1000, Ceast 6742/000) was employed to estimate the elongational viscosity of the melts as a function of deformation rate using the simple approach, based on pressure loss measurements, envisaged by Cogswell [22,23]. For these measurements at 190, 220, and 250°C, a capillary of approximately zero length and a diameter of 1 mm was used. The measurements are described in detail by Toft and Rigdahl [18].

RESULTS AND COMMENTS

Extrusion Coating Conditions and Results

Table 2 summarizes the process conditions used during the extrusion coating and also some of the results obtained. Typically, during a given experiment, one of the parameters (melt temperature, extrusion rotational velocity, air gap, and draw ratio) was changed, whereas the others were kept constant.

The velocity of the melt at the die exit (initial film speed) is denoted v_o and the velocity at the nip (line speed) v_1. The draw ratio (DR) is calculated as v_1/v_o and the elongational strain rate experienced by the film during the drawing is obtained, cf Baird and Collias [24], as

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TABLE 2 Extrusion Coating Conditions and Some Results

Run no.	Melt temp (°C)	Screw speed (rpm)	Draw ratio (v_1/v_o)	Air gap (mm)	Elongational strain rate (1/s)	Initial film speed, v_o (m/min)	Line speed at the nip, v_1 (m/min)	Motor load (A)
Material A (LDPE)								
A-01	190	30	20	115	11,3	1,3	26	29
A-02				155	8,4	1,3	26	29
A-03				205	6,3	1,3	26	29
A-04			~40	155	17,6	1,3	46	29
A-05		60	20	155	16,8	2,6	52	38
A-06	300	30	10	155	3,5	1,4	14	16
A-07			20	155	9,1	1,4	28	16
A-08			40	155	22,6	1,4	57	16
A-09			~120	155	84,6	1,4	165	16
A-10		60	20	155	18,0	2,8	56	22
A-11		120	20	155	36,1	5,6	112	31
Material B (LLDPE)								
B-01	190	30	20	115	11,7	1,34	27	45
B-02				155	8,7	1,34	27	45
B-03				205	6,6	1,34	27	45
B-04			40	155	21,4	1,34	54	45
B-05		60	20	155	17,4	2,68	54	65
B-06	300	30	10	155	3,2	1,33	13	22
B-07			20	155	8,7	1,33	27	22
B-08			40	155	21,0	1,33	53	22
B-09			120	155	82,4	1,33	160	22
B-10		60	20	155	17,4	2,66	54	34
B-11		120	20	155	34,8	5,32	108	50
Material C (m-LLDPE)								
C-01	190	30	20	115	12,2	1,38	28	30
C-02				155	9,0	1,38	28	30
C-03				205	6,8	1,38	28	30
C-04			40	155	21,8	1,38	55	30
C-05		60	20	155	17,7	2,75	55	—
C-06	300	30	10	155	3,7	1,50	15	15
C-07			20	155	9,7	1,50	30	15
C-08			40	155	23,8	1,50	60	15
C-09			120	155	92,7	1,50	180	15
C-10		60	20	155	19,4	3,00	60	22
C-11		120	20	155	38,7	6,00	120	35

$$\dot{\varepsilon} = (v_1/h)\ln(v_1/v_o) \tag{3}$$

where h is the air gap between the die exit and the chill roll (nip).

Some comments with regard to Table 1 are required. In two of the runs (A-04 and A-09), the melt film ruptured before the targeted line

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speed was reached. Nevertheless, the draw ratio was reached within 10%. Due to the different flow characteristics of the different polymers, the velocity at the nip, v_1, had to be changed slightly in order to keep the draw ratio constant.

Thermal Analysis (DSC)

Table 3 shows the crystallinities and the melting points of the different polymer films. The values refer to the first heating in the DSC-instrument. The values obtained from the second heating did not differ significantly from those of the polymer granules (cf Table 1). The LLDPE-films exhibited the highest melting points and the highest degrees of crystallinity, and the lowest values were noted for the metallocene-catalyzed material. A comparison between Table 3 and Table 1 shows that the degree of crystallinity was lower for the extruded polymer specimens. This is probably due primarily to the rather rapid cooling of the film after it leaves the slit die. However, the variations in process conditions used here (melt temperature, draw ratio, machine speed) had no significant effect on either the melting point or the degree of crystallinity of the extruded films.

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TABLE 3 Melting Points and Degrees of Crystallinity of the Extruded Polymers (First Heating in the DSC-Equipment)

		Processing parameters					
Material		Melt temp. (°C)	DR	$\dot{\varepsilon}$ (1/s)	Screw speed (rpm)	Crystallinity (%)	T_m (°C)
LDPE	A-02	190	20	8,4	30	28	108
	A-07	300	20	9,1	30	27	109
	A-09	300	120	84,6	30	28	108
LLDPE	B-02	190	20	8,7	30	32	121
	B-07	300	20	8,7	30	34	120
	B-09	300	120	82,4	30	31	123
	B-11	300	20	34,8	120	32	123
m-LLDPE	C-02	190	20	9,0	30	21	105
	C-07	300	20	9,7	30	19	105
	C-09	300	120	92,7	30	21	101
	C-11	300	20	38,7	120	22	105

Shrinkage/Orientation of the Polyethylene Films

Shrinkage is here taken to be a measure of the degree of orientation of the extruded film. In many cases, a good correlation has been found between the shrinkage in the flow direction and the elongational strain rate experienced by the melt between the die exit and the nip. Figure 1 shows one example of this where the air gap and draw ratio 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. LDPE exhibited the highest shrinkage and m-LLDPE the lowest. Although it is difficult to compare the shrinkage behavior of different polyethylene grades, it is significant that a higher elongational viscosity corresponds to a higher degree of shrinkage (or orientation). This is shown in Figure 2, where the shrinkage is plotted against the elongational viscosity for the three materials at the same melt temperature and at comparable elongational strain rates. The elongational viscosity was here evaluated from results of the capillary extrusion experiments reported in detail by Toft and Rigdahl [18]. Figure 2 refers to a melt temperature of 190°C and one specific strain rate, but the same type of relation is noted at other conditions.

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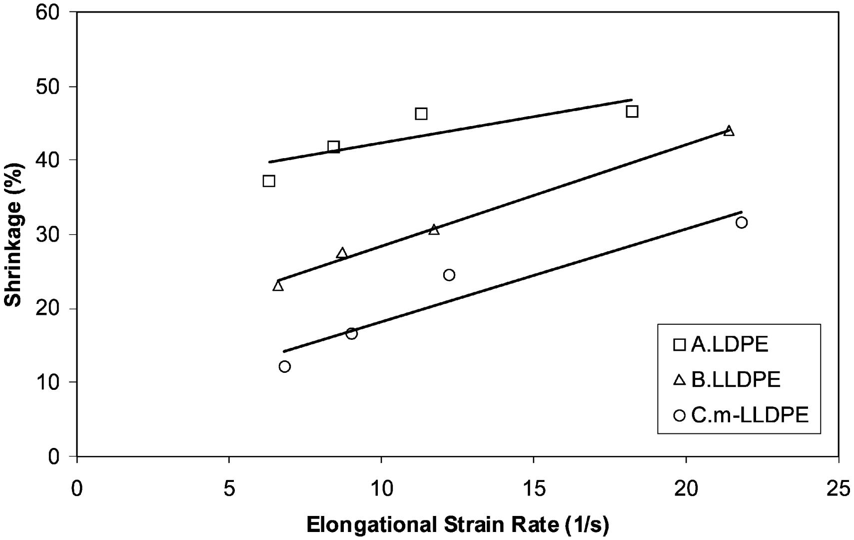

FIGURE 1 Shrinkage in the flow direction vs. elongational strain rate for materials A–C at a melt temperature of 190°C and an extruder rotational velocity of 30 rpm.

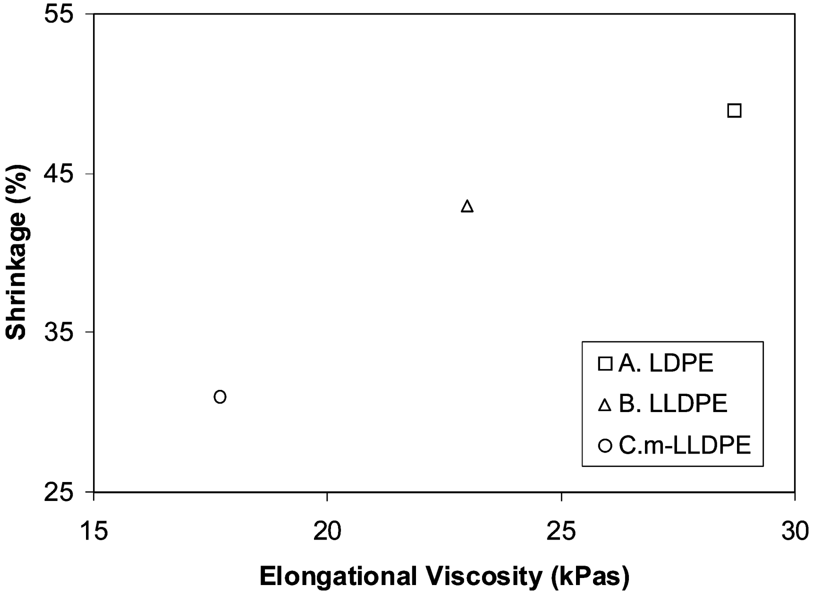

FIGURE 2 Shrinkage in the flow direction vs. elongational viscosity for the polymers A–C at the melt temperature 190°C and an extruder rotational velocity of 30 rpm corresponding to an elongational strain rate of 20 s^{-1}.

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As the melt temperature was increased to 300°C, the shrinkage decreased, but the relation between shrinkage and elongational strain rate was still more or less linear (Figure 3). Figure 3 shows data for LLDPE, but the same behavior was noted with the other two grades. A higher melt temperature (and thus a lower elongational viscosity) permits a greater degree of molecular relaxation during the cooling stage, and this 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 the draw ratio constant, reduces the elongational strain rate, cf Eq. 3, and this is reflected in a lower shrinkage of the films as illustrated in Figure 4 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 it can also be expected that the longer cooling time experienced during the drawing with longer air gaps can influence the results.

If the line velocity at the nip is increased while keeping the initial velocity (or the extrusion rotational velocity) constant, as was done in

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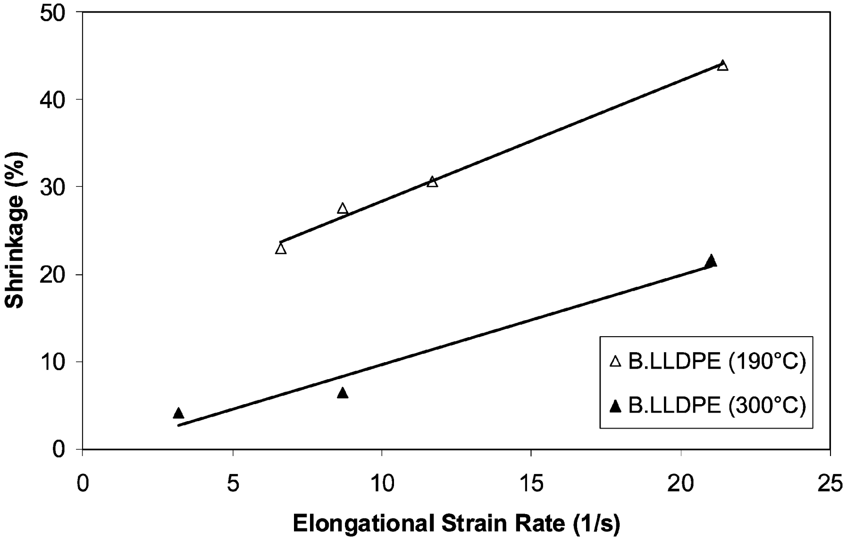

FIGURE 3 Shrinkage in the flow direction vs. elongational strain rate for material B (LLDPE) at the melt temperatures 190°C and 300°C and an extruder rotational velocity of 30 rpm.

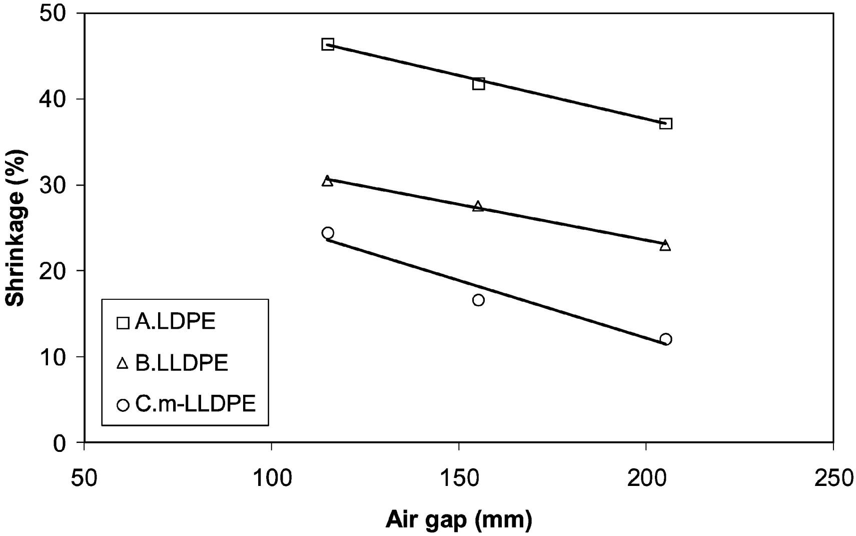

FIGURE 4 Shrinkage in the flow direction vs. the length of the air gap for materials A–C at a melt temperature of 190°C with an initial film velocity (at the die) of 1,3–1,4 m/min and a draw ratio of 20.

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some cases, the film thickness decreases. This can effect the degree of orientation "frozen" into the samples, because the cooling rate of the film also depends on the film thickness. This is regarded as an additional factor that can influence the degree of orientation and shrinkage behavior. This was highlighted by a series of experiments in which 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 had to be changed in a corresponding manner, thus changing the elongational strain rate, but the film thickness could be kept constant at 35 μm within 10 percent. Figure 5 shows that, even at constant film thickness, the elongational strain rate has a strong effect on the degree of shrinkage, that is, higher strain rates correspond to a higher degree of shrinkage.

Tensile Properties of the Extruded Films

Before reporting on the mechanical properties, it may be worthwhile to consider that Ward and Hadley [25] have pointed out that for oriented films of polymers like polyethylene, the mechanical anisotropy, as revealed by, for instance, the tensile modulus, can be significantly less than that expected from orientation measurements. The reason may be

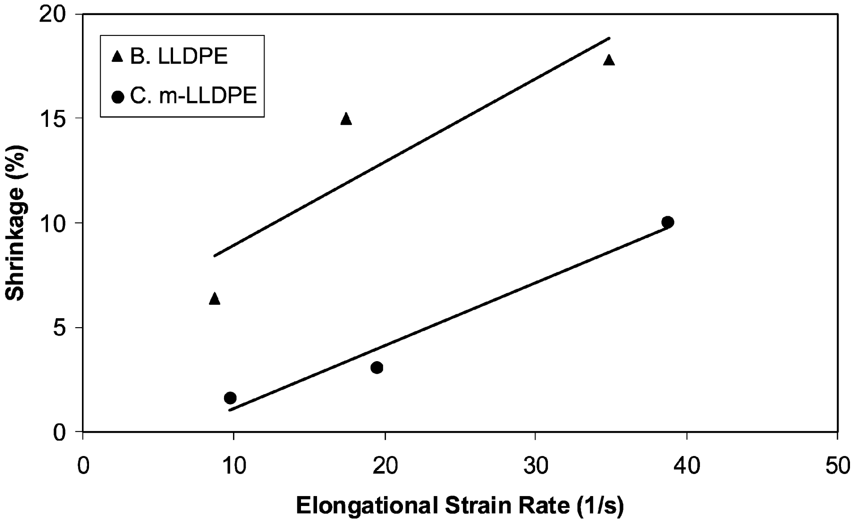

FIGURE 5 Shrinkage in the flow direction vs. elongational strain rate for materials B and C, (melt temperature 300°C, draw ratio 20 and extruder rotational velocity of 30, 60, and 120 rpm) The final film thickness was kept constant at 35 μm.

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that within the amorphous fraction there may be only a limited number of sufficiently long chain segments that are actually oriented and then effectively contribute to the mechanical performance.

Figure 6 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 (with a constant extrusion rotational velocity of 30 rpm). A decrease in the 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 is the ultimate deformation, which is not very surprising. This, in itself, underlines the importance of the process conditions for the mechanical properties of the final film. In the case of 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 cannot however be considered to have a general validity.

The observed behavior indicates that an increase in the elongational strain rate during the drawing phase of the process is, in a rather straightforward manner, reflected in a lower ultimate strain. This is also evident in the fact that an increase in 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.

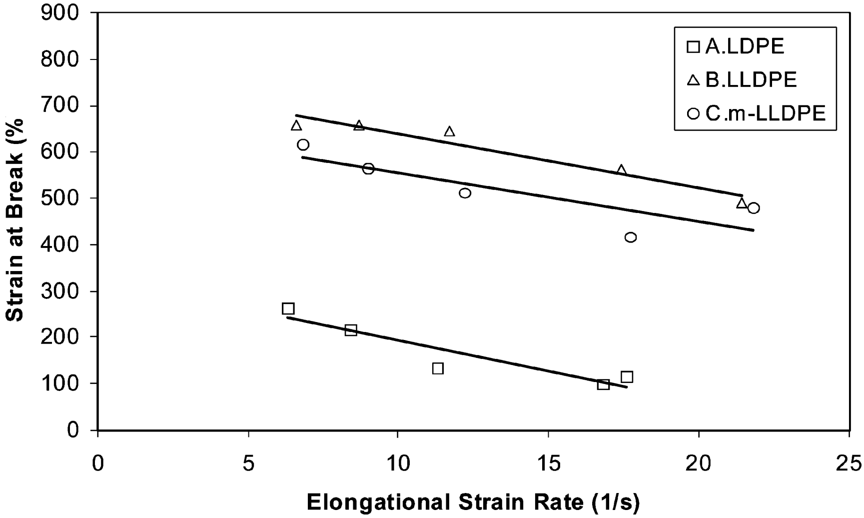

FIGURE 6 Strain at break in the flow direction vs. the elongational strain rate for materials A–C at a melt temperature of 190°C.

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A good relation was found between the strain at break in MD and the corresponding shrinkage (representing the degree of orientation), irrespective of the processing temperature, see Figure 7. Because there is a strong correlation between the shrinkage and the elongational strain rate, this certainly indicates that the elongational strain rate during the drawing step is a parameter that primarily determines the deformability of the final film. Effects of the cooling rate, especially for thinner films, can be important, but this was not evident in this study.

There was no clear relation between the elongation at break in the cross (or transverse) direction (CD) and the elongational strain rate in this case. The ductility in CD was however in general lower than that in MD. In general, a higher strain at break corresponded to a higher ultimate mechanical strength.

In all cases, the tensile modulus was highest for the LLDPE-grade and lowest for the metallocene-catalyzed polymer, in accordance with the degree of crystallinity, (Table 3), but there may be other structural reasons for this difference, because the grades differ substantially with regard to their molecular structures. The magnitudes of the elastic moduli observed in this study were about half those reported by Ghaneh-Fard [11] and Legros et al. [9,10], but the film-blowing grades

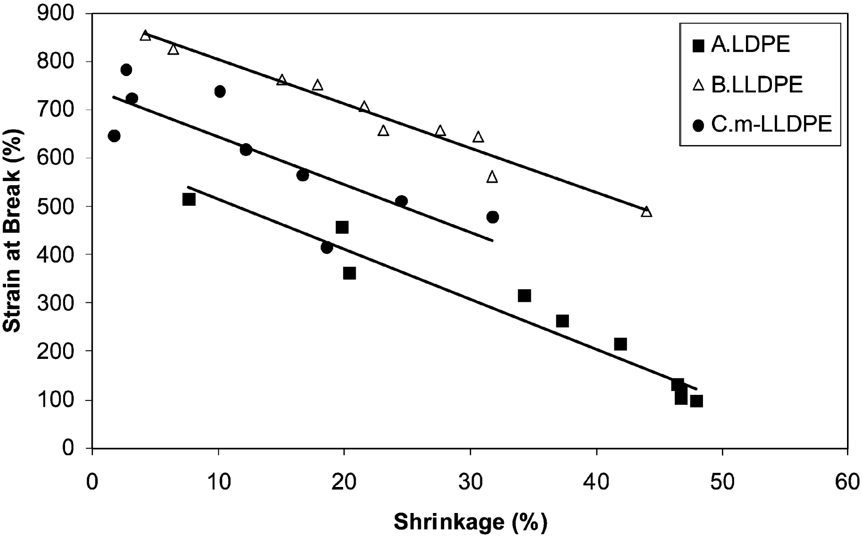

FIGURE 7 Strain at break in the flow direction vs. shrinkage in the flow direction for materials A–C at melt temperatures of 190°C and 300°C, and at different processing conditions.

used by them had a significantly lower melt index (higher molecular weight). The general impression was that the tensile stiffness was not strongly influenced by the process conditions, although some trends were apparent. Figure 8 shows the tensile modulus in MD for LDPE and m-LLDPE as a function of the length of the air gap. Here, the melt temperature was kept constant at 190°C, the extrusion rotational speed was 30 rpm and the draw ratio was 20, which means that the elongational strain rate increased as the air gap was reduced and this corresponded to a higher shrinkage and also to a slight increase in the elastic modulus.

The elongational strain rate is not however the only factor that is important for the stiffness of the films. This is illustrated in Figure 9, which shows the tensile modulus in MD vs. the initial velocity at the die exit at a draw ratio of 20. The air gap was here 155 mm and the melt temperature 190 or 300°C. There is a slight trend toward lower stiffness values with increasing initial film velocity. The increase in elongational strain rate as the initial film velocity increased apparently had no great effect in this case. An increase in the melt temperature from 190 to 300°C raised the elastic modulus quite

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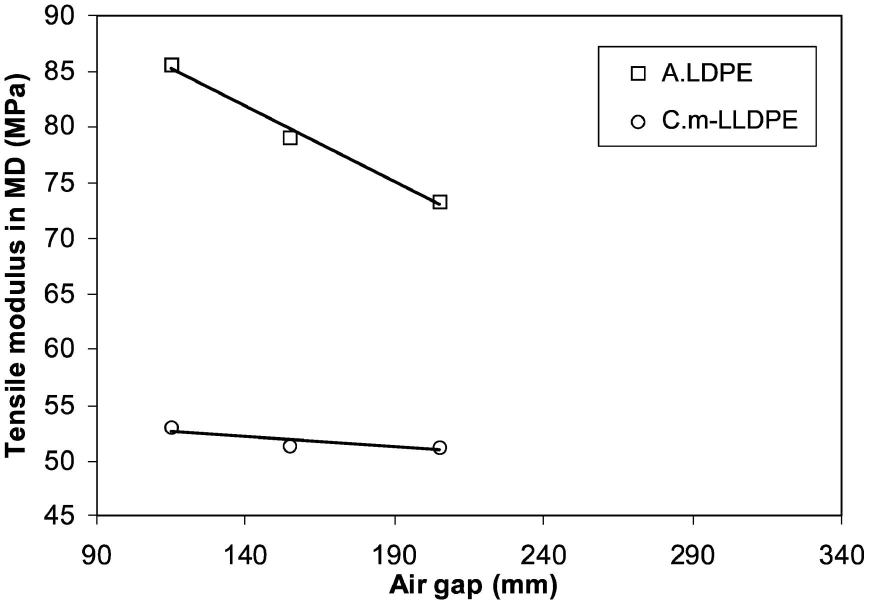

FIGURE 8 The tensile modulus in MD vs. the length of the air gap for LDPE and m-LLDPE at a melt temperature of 190°C, a draw ratio of 20, and an extruder rotational velocity of 30 rpm.

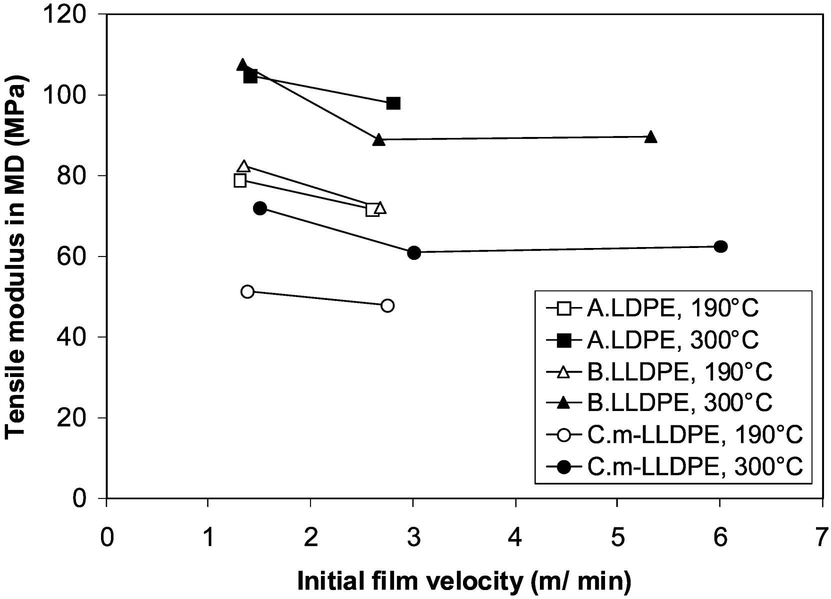

FIGURE 9 The tensile modulus in MD as a function of the initial film velocity at the die exit with a draw ratio of 20 and an air gap of 155 mm.

appreciably, however. The reason for this behavior has not yet been entirely clarified.

When the other process parameters were kept constant, an increase in the draw ratio (higher elongational strain rate) resulted in a somewhat higher tensile modulus. This was evident at a melt temperature of 190°C, but was less clear at 300°C. In this case, an increase in elongational strain rate during the processing also corresponded to a higher degree of orientation and was accompanied by a higher tensile stiffness of the films.

Water Vapor Barrier Properties

The water vapor transmission rate was evaluated for only a few of the films and only limited conclusions can be drawn from the results obtained. The tested films were produced at a constant draw ratio of 20 and the elongational strain rate during the processing was approximately constant, of the order of 10 s^{-1}. The process temperature was either 190 or 300°C. The results are shown in Table 4, where the barrier properties are also given in terms of a permeability coefficient obtained as the WVTR-value multiplied by the thickness of the film.

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TABLE 4 Water Vapor Transmission Rates (WVTR) and Permeability Coefficients for Some of the Produced Films

		Process conditions				
Material		Melt temp. ($^\circ$C)	DR	$\dot{\varepsilon}$ (s^{-1})	WVTR (g/m^2 24 h)	Permeability coefficient (g/m^2 24 h) μm
LDPE	A-02	190	20	8,4	6,2	223
	A-07	300	20	9,1	4,5	158
LLDPE	B-02	190	20	8,7	6,3	189
	B-07	300	20	8,7	3,8	125
m-LLDPE	C-02	190	20	9,0	6,4	211
	C-07	300	20	9,7	5,5	192

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It is well known that a higher crystallinity promotes the barrier properties of a material [12,13] and this is the probable reason for the lower permeability values for the LLDPE-grade than for the other materials. The metallocene-catalyzed polymer appears to be somewhat inferior to the other two materials, which is probably also due to its lower crystallinity.

Crystallinity is not however the only factor of importance. For all three polyethylene grades, it was noted that a better barrier against water vapor was obtained at the higher melt temperature, 300°C, although the crystallinity was only marginally affected. A possible explanation is that micropores are created to a greater extent at the lower process temperature. This is not unlikely because the deformability of the melt is lower at lower temperatures (cf Toft and Rigdahl [18]). Investigations using optical transmission techniques failed, however, to reveal any difference in pore population between the samples. Another explanation, provided by Krohn et al. [13], is that an alignment of the crystallites with increasing orientation reduces the tortuousity of the pathway for the water molecules and thus increases the permeability. The shrinkage measurements indicate a higher degree of orientation for the films produced at 190°C, which would account for their higher permeability in this case.

CONCLUSION

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

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rate (time of solidification). The results obtained in this study indicate 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 taken into account, the process parameters that determine the elongational strain rate (such as the machine speed, the air gap, and the draw ratio) will significantly affect the degree of orientation. The elongational strain rate imposed during the drawing step may thus be a valuable tool enabling the manufacturer to control the structure and properties of the final product. The cooling rate can also affect the shrinkage behavior (degree of orientation), but its influence appears to be less than that of the elongational strain rate. As expected, the melt temperature affects the degree of orientation (cf Figure 3), and the controlling parameter is probably associated with the elongational viscosity of the melt. A lower elongational viscosity (higher temperature) is probably less effective in producing a highly oriented structure, as indicated by the results shown in Figure 2. This implies that the rheological properties of the melt, as reflected for instance in the elongational viscosity, have a direct effect on the solid state behavior of the final film. In fact, further work may make it possible to establish a direct correlation between the elongational viscosity, via orientation measurements and 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, Figure 7. At a given melt temperature, the ultimate strain is governed by the elongational strain rate and by the process conditions that control this variable during the drawing operation. The relation between the strain at break and the strength of the polymer films used here confirms that the elongational strain rate is a valuable concept for the manufacturer. The elastic modulus appeared to be less affected by the degree of orientation (and the related process parameters). This may appear to be somewhat surprising, but it is to some extent in line with the statement by Ward and Hadley [25] that the stiffness is not affected to the extent expected from measurements of the orientation. Further studies relating to the effect of the process conditions on the water vapor permeability are required, but it is evident that the crystallinity and the morphology are important parameters. That higher degrees of orientation, obtained by varying the process parameters, led to a less favourable behavior certainly warrants further studies.

It must be made clear that the elongational strain rate (and the elongational viscosity) can provide useful information as to how the orientation of the specimens will be affected by the process conditions during extrusion coating. It will not however provide a quantitative tool for predicting how the physical properties of different polyethylene grades will be changed. For a given polymer grade, it may however be possible to establish such relations.

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