Comparison between a Linear and a Branched Low-Density Polyethylene

G. ATTALLA and F. BERTINOTTI, *Istituto Guido Donegani S.p.A.— Montedison Group, Centro Ricerche Novara, 28100 Novara, Italy*

Synopsis

Two low-density polyethylenes, a linear low-pressure (LLDPE) and a branched high-pressure (LDPE), have been compared. Their shear and extensional behavior and melt fracture phenomena have been investigated, and some mechanical and optical properties of their blown films have been measured. The rheological analysis showed major differences between the samples, both in shear viscosity and in elongational viscosity. The LLDPE exhibited two types of melt fracture, the first of which—a fine scale extrudate roughness—was not shown by the LDPE and appeared at a very low shear rate. The concomitance in LLDPE of a high shear viscosity and a low elongational viscosity and the presence of melt fracture at low shear rate resulted in its more difficult processing into film. The mechanical properties of the LLDPE film approached those of high-density polyethylene while the optical characteristics were in the range of LDPE. Such a coexistence of properties makes LLDPE an interesting material for film production.

INTRODUCTION

In the last few years interest has grown in linear low-density polyethylene (LLDPE) as an alternative to branched low-density polyethylene (LDPE). There are several processes utilized for the preparation of LLDPE and several α-olefines employed as comonomer, and it is still debated which is the best way to compromise between cost and performance.

The major application of LDPE being in film extrusion, we thought that a comparison between LLDPE and LDPE should be carried out as film materials, to evaluate the potential of the former in this field. In this work we have compared an experimental LLDPE sample with a commercial LDPE, in those aspects mainly involved in film production, such as melt rheology and melt fracture, and in film utilization, such as mechanical and optical properties of the films.

MATERIALS

In Table I the molecular and physicochemical characteristics of the samples investigated are shown. PE-1 is an experimental LLDPE obtained by Ziegler–Natta copolymerization of ethylene with butene-1. PE-2 is a commercial film grade LDPE produced by Montedison.

EXPERIMENTAL

Flow curves and melt fracture were determined with a Göttfert constant pressure capillary rheometer at three temperatures (160°C, 180°C, and 200°C)

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TABLE I
Characteristics of the Samples

Sample	C_4^a (mol %)	Crystallinity[b] (%)	Density[c] (g/cm³)	T_m^d (°C)	$[\eta]^e$ (dL/g)	MFR[f] (g/10 min)	M_w^g (g/mol)
PE-1	2.3	40	0.931	122.5	1.34	2.5	105,000
PE-2	—	32	0.919	111.5	0.88	2.1	280,000

[a] From IR spectroscopy on melted samples.
[b] From X-ray diffraction.
[c] ASTM D 1505/63 T, B.
[d] From DSC.
[d] Orthodichlorobenzene, 135°C.
[f] ASTM D 1238/73, B.
[g] From light scattering, α-chloronaphthalene, 135°C.

using a flat-entry capillary die of 1 mm diameter and an L/D ratio of 30. Elongational viscosity and tensile modulus were measured with the approximate method proposed by Cogswell[1] at the temperature of 200°C using a flat-entry capillary die of 1 mm diameter having a zero L/D ratio.

Dynamic-mechanical analysis was done on compression-molded specimens with a homemade free oscillation torsion pendulum. Films were obtained using a film-blowing unit consisting of a 35-mm-diameter single-screw extruder with an annular die having a diameter of 80 mm and a gap of 1 mm. Mechanical tests were carried out on films using an Instron tensile machine. A multiangle automatic photometric Gardner glossmeter was employed to perform the gloss measurements. Haze was determined using a Gardner pivotable sphere hazemeter. Internal haze was evaluated eliminating the scattering of the light due to the surface roughness, using cider oil on both sides of the films.
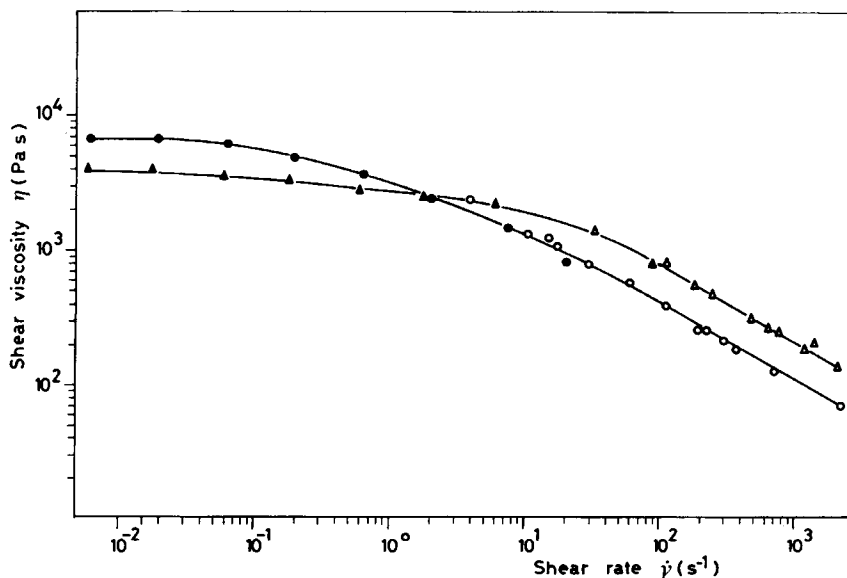

Fig. 1. Flow curves of the two samples at 200°C. ($\triangle$,$\blacktriangle$) PE-1; (O,$\bullet$) PE-2; ($\triangle$,O) capillary rheometer; ($\blacktriangle$,$\bullet$) Weissenberg Rheogoniometer.

POLYMER CHARACTERIZATION

Rheology

The flow curves of the two samples at 200°C are reported in Figure 1. The data from capillary rheometer, corrected for pseudoplasticity and entrance effects (cf., e.g., Ref. 2), match fairly well the Weissenberg rheogoniometer data.[3] As it appears from the figure, PE-1, though it has a lower viscosity at low shear rate, according to its lower molecular weight, presents a higher viscosity at shear rate greater than 2 s^{-1}, probably owing to its narrower molecular weight distribution. At lower temperature both samples showed an analogous behavior. At 160°C, however, PE-1 exhibited a critical shear stress (about 3.5 × 10^5 Pa) at which a double-valued shear rate was observed (cf. Fig. 2). This phenomenon, similar to that found by Bagley et al.[4] and Tordella[5] for linear high-density polyethylene, did not appear at higher temperature, though the critical level of stress was reached.

The elongational viscosity and the tensile modulus of both the samples vs. tensile stress at 200°C are reported in Figure 3. The figure shows that the elongational behavior is different from the shear behavior, the elongational viscosity of PE-2 being higher than PE-1 over the entire range of shear stress explored. Relatively little differences are observed in the elastic properties, as indicated by the tensile modulus curves.

Melt Fracture

Considerable differences were presented by the two polymers in the melt fracture phenomena. The first is that melt fracture appeared at lower shear rate for PE-1, independently of temperature (about at 170 s^{-1} compared with 360 s^{-1} for PE-2, at 200°C). A further difference is related to the types of melt
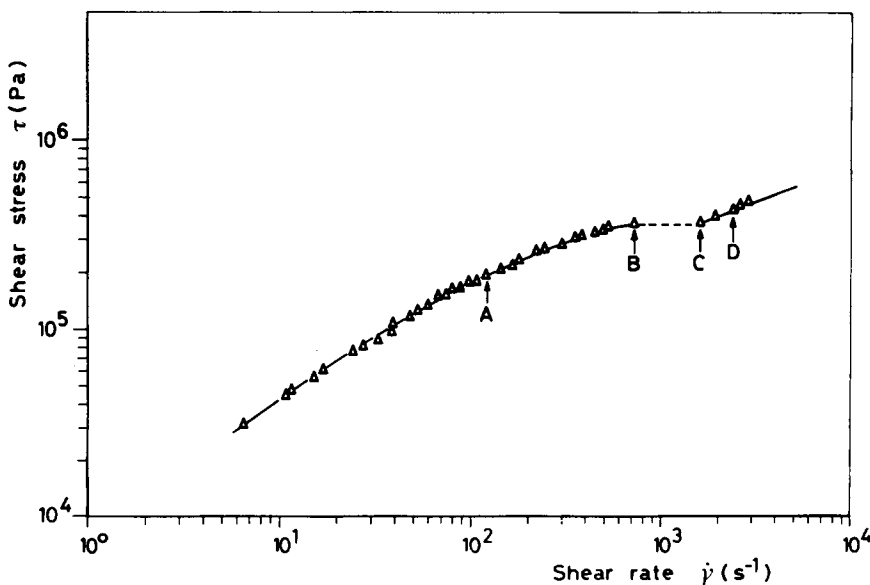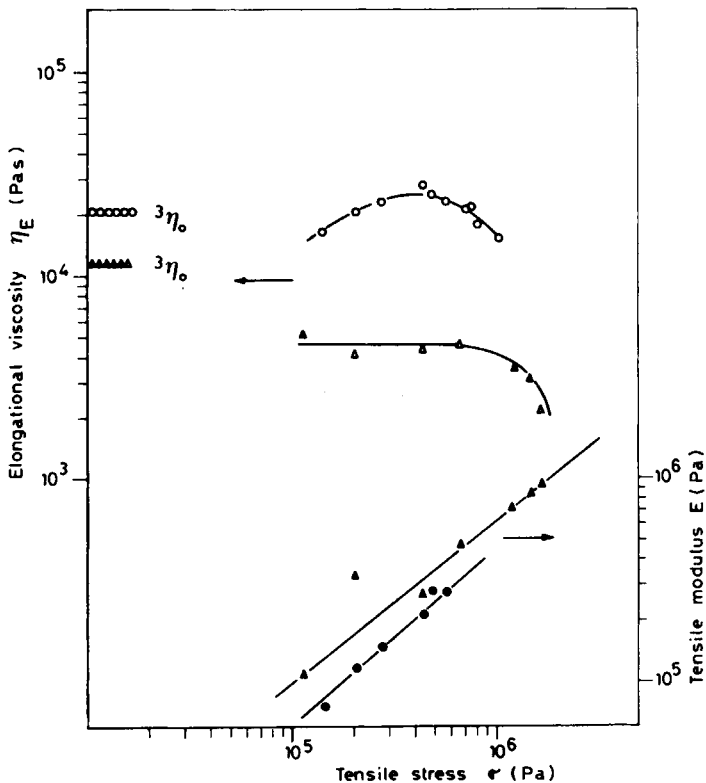

Fig. 2. Flow curve of PE-1 at 160°C.

Fig. 3. Elongational viscosity and tensile modulus of the two samples vs. tensile stress at 200°C: (△,▲) PE-1; (○,●) PE-2.

fracture exhibited, while PE-2 showed, in the entire range of temperature tested, the common melt fracture typical of branched polyethylene,[5] consisting of an extrudate distortion increasing with shear rate (cf. Fig. 4), PE-1 exhibited two types of melt fracture. At high temperatures (180–200°C) and low shear rate the extrudate presented a fine surface roughness, similar to that described by Tordella[5] for high-density polyethylene (cf. Fig. 5, photographs at 540 and 1980 s^{-1}). The roughness increased with shear rate up to a maximum, and then decreased, disappearing completely, as shown by the extrudate's photograph at 4440 s^{-1} in Figure 5. At a higher shear rate a distorted extrudate appeared (cf. Fig. 5, bottom photograph), and the distortion continuously increased with shear rate. At low temperature (160°C) the fine surface roughness appeared at point A in Figure 2, continuoulsy increasing up to point B (cf. Fig. 6, top photograph). Corresponding to the jump in shear rate (point C), the extrudate became smooth, as shown in the photograph at 1600 s^{-1} in Figure 6. The extrudate remained smooth up to point D, at which a gross distortion appeared (cf. Fig. 6, bottom photographs). This behavior is similar to that reported by Tordella[5] for high-density polyethylene.

Dynamic-Mechanical Properties

The dynamic-mechanical spectra of the two polymers are reported in Figure 7. The peak in logarithmic decrement curve at −20°C in polyethylene is related to the motion of short-side chains (1–4 carbon atoms) and its intensity is pro-
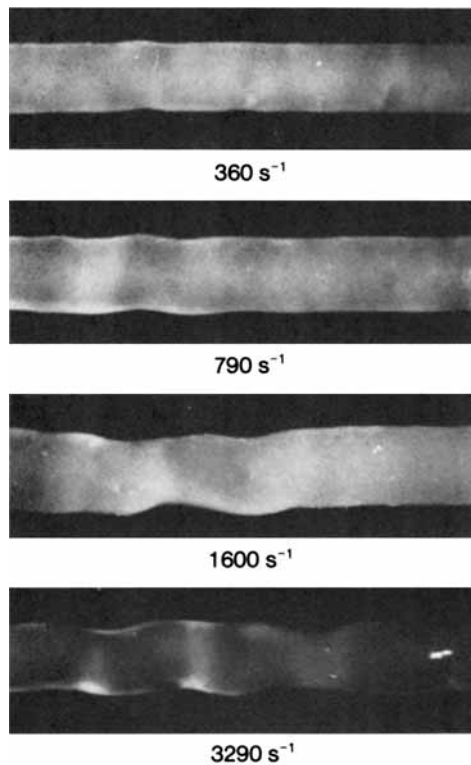
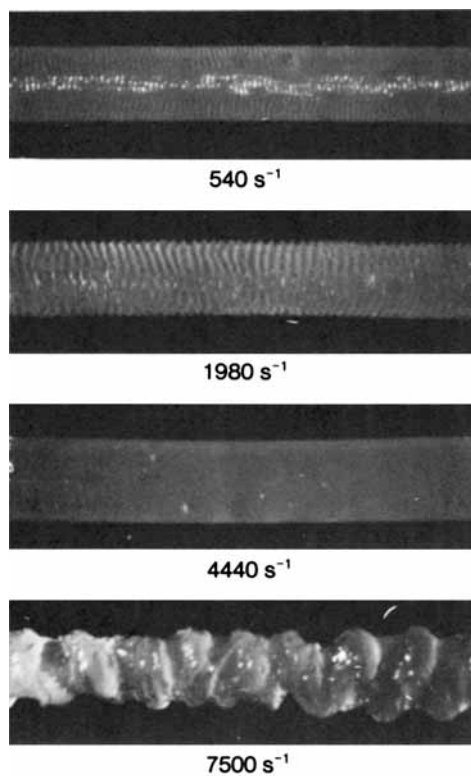Fig. 4. Melt fracture of PE-2 at various shear rates at 200°C.

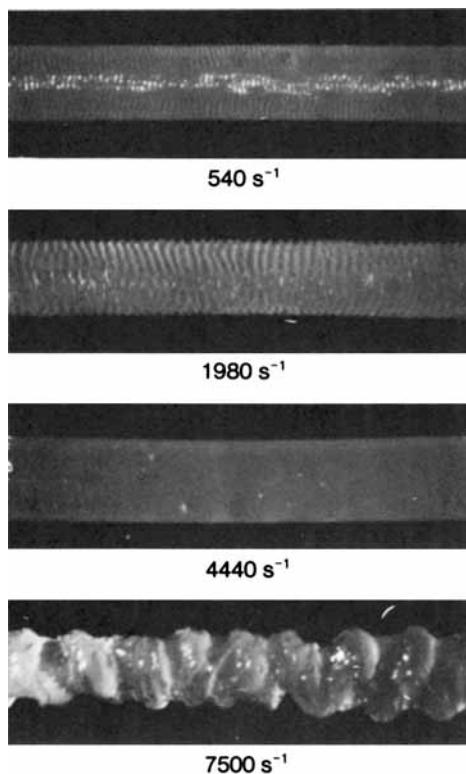Fig. 5. Melt fracture of PE-1 at various shear rates at 200°C.

Fig. 6. Melt fracture of PE-1 at various shear rates at 160°C.

portional to their number (cf. Ref. 6). The lower intensity of the peak of PE-1 indicates a lower content of short-chain branching. IR spectroscopy showed that this consisted only of ethyl groups. As a consequence of the lower short-chain branching content and of the absence of long-chain branching, PE-1 reaches a higher cyrstallinity (cf. Table I) that is responsible for the higher shear modulus at temperature over −50°C.

FILM PROPERTIES

Mechanical Properties

Some mechanical properties of the films were measured, both in longitudinal and transverse directions. The results are reported in Table II. From the data two aspects come out: the film obtained from PE-1 shows higher values of the mechanical properties, and these are more balanced along the two normal directions. The first fact is due both to the higher crystallinity and to the linearity of PE-1; the second is related to its lower elongational viscosity, which reduces chain orientation during film extrusion.

Optical Properties

Table III shows some optical properties of the films. PE-1 exhibits higher gloss and lower haze values. It is well known (cf., e.g., Ref. 7) that haze in poly-
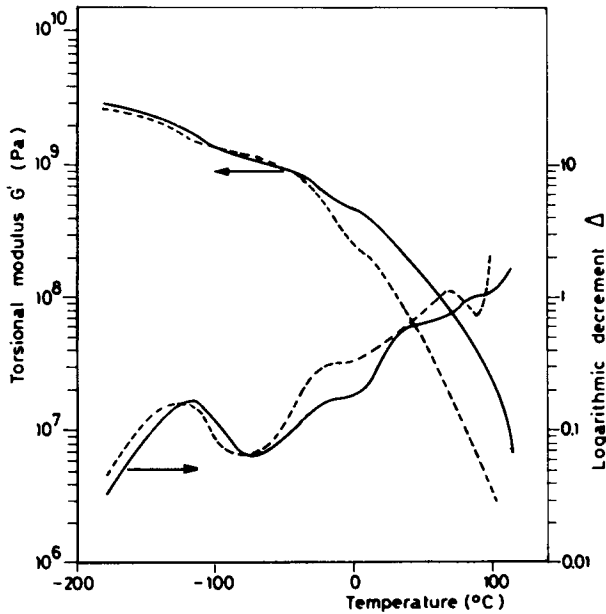
Fig. 7. Dynamic-mechanical spectra of the two polymers: (——) PE-1; (- - -) PE -2.

ethylene films is related to two aspects. Crystallinity is reponsible for internal scattering of the light: the higher it is, the higher internal haze is. Most of the reduction in transparency, however, has to be ascribed to light scattering by surface irregularities of the films. Therefore, external haze is related to the smoothness and regularity of the surfaces. The lower value of total haze pre-

TABLE II
Mechanical Characteristics of the Films

	PE-1	PE-2
Thickness (μm)	25	20
Tensile strength (ASTM D 882)		
σ_Y (MPa)		
L	11	6
T	9	4.5
σ_B (MPa)		
L	28	16
T	18	6
ϵ_Y (%)		
L	15	20
T	12	8
ϵ_B (%)		
L	630	90
T	890	350
E (MPa)		
L	180	100
T	210	140
Tear strength (ASTM D 1938)		
σ_Y (MPa)		
L	10.5	6
T	10.5	5

TABLE III
Optical Characteristics of the Films

	PE-1	PE-2
Thickness (μm)	25	20
Gloss (‰) (ASTM D 2457/70)		
45°	59	55
60°	98	76
Haze (%) (ASTM D 1003/61)		
Total	12	13.5
Internal	2.5	0.5
External	9.5	13
Absorption coefficient (cm^{-1})	15	30

sented by PE-1 is mainly due to its lower external haze, the internal being higher, in accordance to its higher crystallinity. Both higher gloss and lower haze of PE-1 are related to the state of its surface, smoother and more regular than PE-2, as it appears from the optical micrographs in Figure 8.
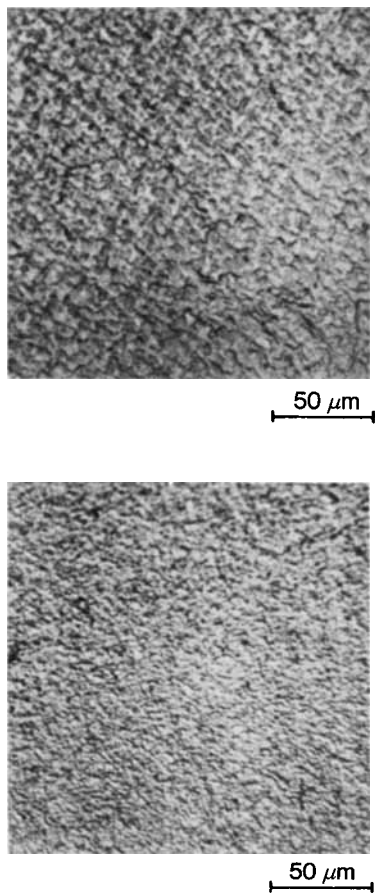

50 μm

50 μm

Fig. 8. Surface micrographs of the two films: PE-1 bottom.

DISCUSSION AND CONCLUSIONS

The general picture coming out from the study of the rheological behavior of the two polymers indicates that processing of PE-1 requires an approach different from that of PE-2.   The higher shear viscosity, the lower elongational viscosity, and the onset of melt fracture at a lower shear rate cause major difficulties in film extrusion of PE-1 in comparison with PE-2.   Such difficulties can be successfully overcome using a wider die gap,[8] which delays the onset of melt fracture, and choosing an extrusion temperature compromised between the opposite requirements of a high output and a sufficient bubble stability.   The use of a wider die gap is allowed by the possibility of stretching PE-1 at high ratios in the melt state, without producing unbalanced film.   The outstanding mechanical properties of the PE-1 film, together with its good optical characteristics, suggest that it is worthwhile to make an effort to overcome the difficulties encountered in processing this polymer.

The particularly interesting properties of the PE-1 film are to be ascribed to the linearity and crystallinity of the polymer.   The molecular structure of PE-1 is essentially linear, owing to the Ziegler–Natta catalysis, and presents ethyl branches due to copolymerization with butene-1.   The crystallinity of PE-1, though much lower than a linear high-density polyethylene, is higher than PE-2. This, together with the linearity of the molecular chains, positively affects the mechanical properties of the film without depressing its optical characteristics. The good optical properties represent a surprising result deriving from the beneficial effects of linearity and crystallinity on the surface regularity of the film.   This produces an increase of gloss and counterbalances the negative influence of crystallinity on internal haze.

In conclusion, as far as shown by the samples investigated in the present work, it is evident that the experimental LLDPE sample shows mechanical properties approaching those of high-density polyethylene, maintaining optical characteristics at the level of a commercial film-grade LDPE.   Such a coexistence of properties is not otherwise achievable.

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