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Postponing sharkskin of metallocene polyethylenes at low temperatures: the effect of molecular parameters

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Abstract

The effect of temperature on extrusion rheometry of single site metallocene-catalyzed polyethylenes and polyethylene copolymers is investigated. Samples of molecular weight, M_w, ranging from 90,000 to 330,000 and short-chain branching degree (SCB) from 0 to 21.2 CH_3/1000C, as well as samples with a small amount of long-chain branching, are analyzed. It is observed that all the samples display a low temperature region, limited by induced crystallization and gross melt fracture, in which smooth extrudates are produced at shear rates similar to those of industrial extrusion. A characteristic temperature of this region, T_s, is defined as the highest temperature at which sharkskin disappears. Clear symptoms of non-slip conditions at the capillary wall, are detected in this low temperature region. We assume that the necessary slip–stick conditions to produce sharkskin, would only be produced at shear rates above those involved in gross melt fracture. The analysis of the effect of the molecular parameters, leads to the conclusion that only SCB has a direct effect on T_s. A linear correlation between T_s and SCB level is established, showing the decrease of the former as the latter is increased. Considering the wide spectrum of the molecular characteristics of our samples, we claim that decreasing temperature is a sound route to postpone sharkskin of any polyethylene.

Keywords: Metallocene polyethylene; Sharkskin instability; Short-chain branching

1. Introduction

The quality of a polymer extrudate depends on the flow defects during polymer melt extrusion, a subject which has received considerable attention in the literature, in particular as to what 'melt fracture' and 'sharkskin' instabilities of polyethylenes are.

The most basic strategy to eliminate or postpone flow instabilities in polymers, is to rise the die temperature. However, the opposite approach, that is a temperature decrease has been suggested by some researchers from time to time since the seventies. A 1972 British Patent (32559172), commented by F.N. Cogswell in a paper in 1977 [1], constitutes one of the first references of decreasing temperature as a way to eliminate instabilities. Applying cooling to the die lip, to lower the temperature to just above the melting point, eliminates sharkskin in polyethylene, polymethyl methacrylate, acetal copolymer and polyvinyl chloride. According to this author, intense stretching flow, combined with the low temperature of the surface, induces some ordering of the molecules, which increases cohesiveness and reduces the tendency to sharkskin. On the other hand, from 1990 to 1996 Keller et al. [2–9] published a series of papers, on what they defined as a 'temperature window of extrudability' of polyethylenes. There is a sharp minimum in applied pressure, so flow resistance is reduced, within a narrow temperature range of 150–152 °C. Under these window conditions, there are no other extrudate irregularities but gross melt fracture is observed. The research carried out by Keller et al. led them to state that this window effect can be traced to the formation of a low viscosity phase, identified with the mobile hexagonal phase: This arises through flow-induced alignment of molecules adsorbed to the capillary. The hypothesis developed by these authors has been used to discuss experimental results, such as those of Pudjijanto and Denn [10] who found the so called 'stable island', where stable flow with smooth extrudates is achieved at 139–146 °C for linear low density polyethylenes (LLDPE). In their turn, Wang and Drda [11] refer to the work of Keller et al. as they propose a flow-induced mesophase, to justify what they consider an anomaly in the variation of the critical stress for the slip–stick transition of polyethylenes in the range 160–200 °C. More recently, Pérez González et al. [12] analyzed capillary flow behavior of a

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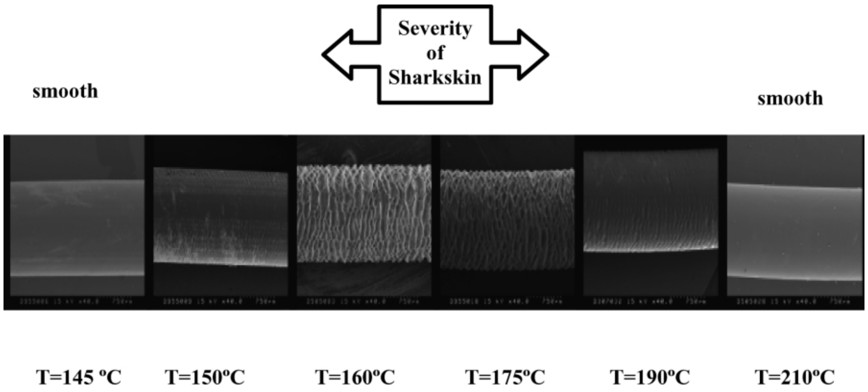


Fig. 1. Vanishing of severe sharkskin instability observed at $T = 175$ °C for sample mPE6 (Table 1), as temperature is increased or decreased.

metallocene-catalyzed LLDPE with hexene as the comonomer (melting temperature, $T_m = 91$ °C), over a wide range of temperatures. Interestingly enough, they find that unstable spurt flow is avoided and a remarkable improvement on the extrudate appearance is obtained at a much lower temperature, 112–116 °C, than the aforementioned cases. The results obtained with LLDPE, as well as the shift of the minimum in extrusion pressure to a lower temperature ($T = 145$ °C) observed by Waddon and Keller [2] for moderately branched PE, indicate that there is a certain effect of the molecular architecture on the phenomenon.

In recent years, we have been working with a large series of well characterized single-site metallocene-catalyzed polyethylenes and polyethylene copolymers. We have analyzed systematically the effect of temperature on extrusion rheometry results, arriving at the conclusion that all the samples display a low temperature region for smooth extrudability, whatever their molecular parameters are. In this paper representative results are presented, analyzing the effect of molecular weight, short-chain branching degree (SCB) and small amounts of long-chain branching (LCB), on the temperature range of this region.

2. Experimental part

2.1. Materials

The materials under study are metallocene-catalyzed polyethylenes and copolymers of different molecular weights, ranging from $M_w = 92,000$ to $M_w = 335,000$, different degree of SCB, ranging from SCB = 0 CH_3/1000C to SCB = 21.2 CH_3/1000C and polydispersity index of approximately $M_w/M_n = 2$.

Molecular weight distribution curves were determined with a Waters 150 gel permeation chromatograph, coupled with differential refractive index and a 150R model viscosimeter detector.

A Brucker DPX-300 NMR Spectrometer operating at 75 MHz was used to measure the level of short chain branching.

A Perking–Elmer Differential Scanning Calorimeter (DSC-7) was used to determine the melting point of the samples at a heating rate of 5 °C/min.

2.2. Rheological measurements

Capillary extrusion experiments were performed in a Göttfert Rheograph 2002 rheometer using a flat entry capillary tungsten die of 1 mm diameter and a L/D ratio of 30.

The surface of the sharkskin distorted extrudates was analyze by scanning electron microscopy with a Hitachi 2100 microscope.

The viscoelastic functions were determined in a ARES Rheometric Scientific rheometer operating in the oscillatory shear mode, using parallel plates geometry with $d = 25$ mm, in the frequency range from 10^{-2} to 10 Hz.

Table 1
Limit temperature for smooth extrudate, T_s, (see text) of four completely linear polyethylenes (SCB = 0 CH_3/1000C) of different molecular weight M_w, and two polyethylene copolymers of practically the same SCB level and different molecular weight

Material	M_w	M_w/M_n	SCB (CH_3/1000C)	T_s (°C)
mPE6	118,000	2.15	0	150
mPE7	158,000	2.16	0	149
mPE8	214,900	2.41	0	151
mPE9	195,000	2.0	0	145
mPE3	128,100	1.78	8.6	145
mPE10	174,500	3.28	8	145

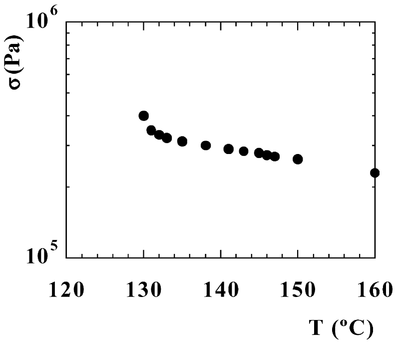


Fig. 2. Variation of the shear stress, taken at a constant shear rate $\dot{\gamma}_{21} = 36.1\ \mathrm{s}^{-1}$, as a function of temperature for sample mPE4 (Table 2). The deviation at low temperatures is associated to shear induced crystallization (see text).

3. Results and discussion

3.1. Description of the temperature limit for smooth extrudates

Our experience with metallocene catalyzed polyethylenes allows to assert that decreasing the temperature appears to be a suitable option to eliminate sharkskin. A representative example is shown in Fig. 1. Starting from the very severe sharkskin at 175 °C, smooth extrudates are obtained increasing the temperature to 210 °C, but also lowering it to 145 °C.

Industrial polymer extrusion involves shear rates typically above $100\ \mathrm{s}^{-1}$, which constitutes an important factor in the context of this work, because it is well known that shear rate can induce crystallization at temperatures slightly above melting [13]. Therefore, attempts to eliminate sharkskin by lowering the temperature, but maintaining a moderate or high shear rate, can lead to a crystallization process. Clear evidence of crystallization during extrusion at low temperatures can be seen in Fig. 2. Experiments performed at constant shear rate, show that at a certain temperature the viscosity increases significantly, deviating from the Arrhenius-like viscosity–temperature dependence:

$$\eta_0(T) = A \exp\left(\frac{E_a}{RT}\right) \qquad (1)$$

where E_a is the activation energy of flow.

A detailed sketch of the evolution of shear stress and extrudate characteristics with time, at different temperatures and shear rates, is given in Fig. 3. At the higher temperatures considered, 150 and 160 °C, four different surface features can be observed, as the shear rate is increased: smooth, sharkskin, slip–stick and melt fracture. An unusual phenomenon is noticed at 150 °C, with respect to 160 °C: smooth extrudates are obtained at high shear rates, in the range between slip–stick and melt fracture. This result has been reported in the literature for conventional polyethylenes, and resembles the trait described by Keller et al. [2–9] in their ‘temperature window’ research. However, the very clear reduction of flow resistance (a dramatic pressure decrease, after slip–stick oscillations) reported by these authors, is not observed in our metallocene-catalyzed polyethylenes. We note that at 140 °C sharkskin instability does not appear, so that smooth extrudates can be obtained at shear rates typical of industrial extrusion. This leads us to define a limit temperature for smooth extrudate, T_s, as the highest temperature (of the low temperature range) at which sharkskin disappears. Decreasing temperature to $T = 130$ °C in Fig. 3, confirms the stable flow and the absence of sharkskin over a wide range of shear rates; but favors the crystallization process, associated with the shear stress increase over time, at the highest shear rate.

Gathering all the results relative to the surface characteristics of the samples, as well as the induced crystallization data, temperature–shear rate maps for the surface morphology of the extrudates can be drawn. These maps, two of which are shown in Fig. 4, allow the extrusion conditions to be defined for: (a) stable flow with smooth extrudates, (b) sharkskin, (c) slip–stick, (d) gross melt fracture and (e) induced crystallization. It is important to note that in the slip–stick region, shear rates are not actually constant because the observed pressure oscillation leads the melt to be compressed to different extents [14]. The most interesting result is that a region of stable flow and smooth morphology conditions, limited at high shear rates by melt fracture and at low temperatures by crystallization, is obtained at low temperatures and high shear rates. Maps like those of Fig. 4 have been obtained for all the analyzed samples, confirming that in all the cases, shear rates similar to those of industrial processing can be used to obtain

Table 2
T_s and T_m data of polyethylene copolymers of very similar molecular weight, but different degrees of short chain branching. Data of Ref. [12] are also included

Material	M_w	M_w/M_n	SCB (CH_3/1000C)	T_s (°C)	T_m (°C)
mPE1	128,900	1.06	4.87	153	120.0
mPE2	124,400	1.17	5.73	151	120.3
mPE3	128,100	1.78	8.58	145	117.3
mPE4	123,000	2.3	10.99	141	112.6
mPE5	115,800	2.14	21.23	117	95
EXACT Ref. [12]				116	91

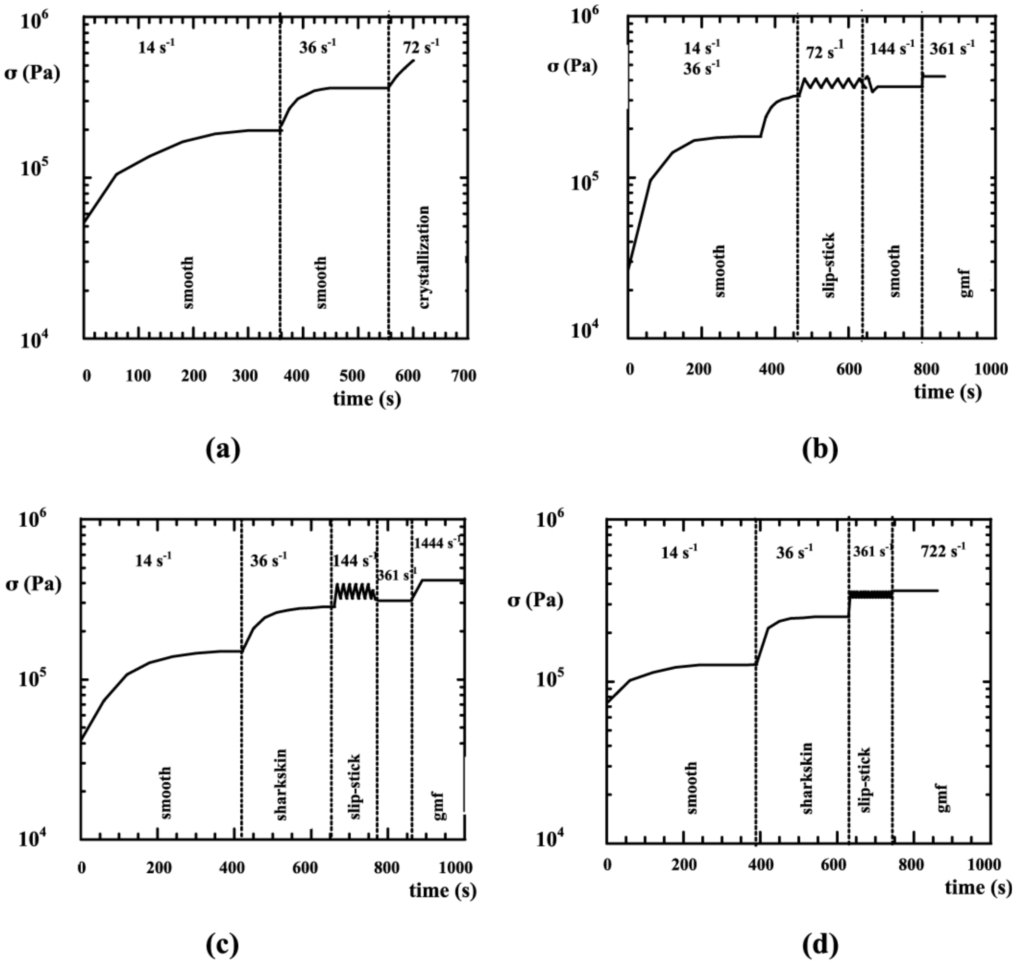
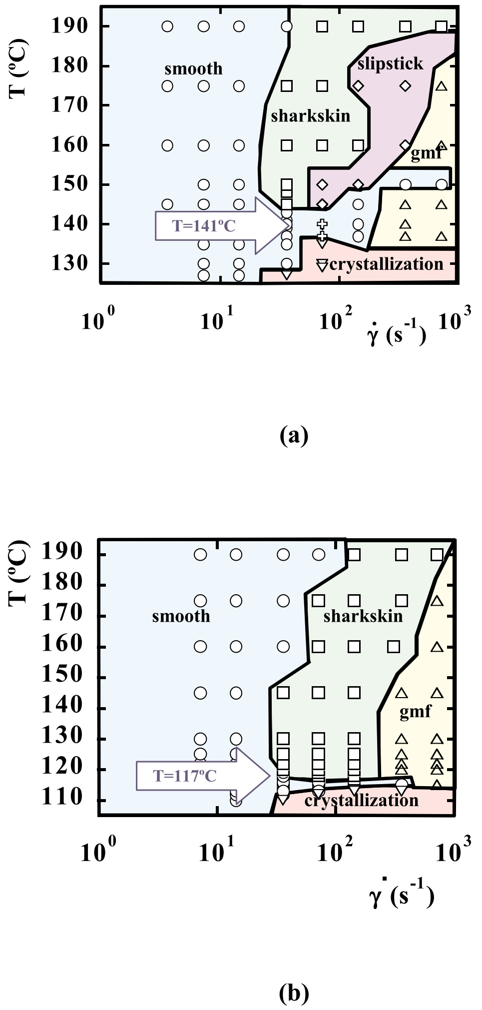


Fig. 3. The evolution of shear stress and extrudate surface characteristics with time, at different temperatures and shear rates for sample mPE3 (Table 2): (a) $T = 130$ °C; (b) $T = 140$ °C; (c) $T = 150$ °C and (d) $T = 160$ °C.

smooth, good quality, extrudates at low temperatures. This clearly opens a route to facilitate the extrusion of metallocene-catalyzed polyethylenes that are known to present flow instabilities at very low shear rates. The results outlined in our surface morphology maps, show evident similarities with low temperature anomalies found in conventional polyethylenes, such as the aforementioned temperature window of extrudability of Keller et al. [2–9] and the stable island (where the extrudates become smooth) discovered by Pudjijanto and Denn. Contrary to our results of Fig. 4, the alleged stable island lies exclusively inside the slip–stick region, neither limiting with crystallization nor with melt fracture. On the other hand, 'window' experiments would correspond to an ascending vertical line (increasing temperature at an apparent constant shear rate) which, starting from the smooth region, crosses it and reaches slip–stick and sharkskin regions. In the analysis carried out by Keller et al., the applied pressure falls substantially at a certain temperature. A pressure drop is also noticed in the stable island of Pudjijanto and Denn. However, in the set of experiments performed with our metallocene-catalyzed polyethylenes, we have not found such a noticeable pressure decrease when smooth extrudates are obtained in the low temperature region.

The upper border of the smooth zone of low temperatures which extends to high shear rates (Fig. 4) is marked by T_s, the highest temperature at which sharkskin disappears. This analysis can also be considered from the point of view of the effect of temperature on the critical shear stress value, σ_s, for the inception of sharkskin, which in our case implies the compilation of the shear stress values following the smooth/sharkskin border of surface maps (Fig. 4). A plot of σ_s versus temperature is given for one of the samples in Fig. 5, which also includes σ_s/T versus T plots to analyze the linearity of the dependence. The variation is linear ($\sigma_s/T = \text{constant}$) only in the range 160–190 °C. A minimum is denoted at 145 °C, giving rise to an asymptotic increase in both σ_s and σ_s/T as the temperature is decreased from 145 to 118 °C. The asymptote of σ_s drawn in the figure, marks the highest temperature (of the low temperature region) at which sharkskin is not detected, designed as T_s, also defined in Fig. 4. It is seen that at a temperature of 117 °C, which corresponds to T_s defined in both Figs. 4(b) and 5, the progressive increase of shear stress does not lead



(a)

(b)

Fig. 4. Temperature–shear rate maps for the surface morphology of the extrudates, obtained gathering all the results relatives to the surface characteristics of the samples, as well as induced crystallization data. (a) and (b) correspond, respectively to sample mPE5 (Table 2) and sample mPE4 (Table 2) The borders are drawn on the basis of the experimental results marked by circles. The arrow labels the characteristic temperature, T_s, defined in the text. The crosses (instead of circles) of two of the experimental data in (a), indicate that smooth samples are obtained not withstanding pressure oscillation is observed. A comment on the reliability of data in the slip–stick region is made in the text.

to sharkskin, even though gross melt fracture is detected at high shear rates. Therefore, in Fig. 5 we define a stable flow zone, delimited by T_s and the crystallization temperature, in which sharkskin is forbidden. This leads us to estimate that within this temperature range, the tensile stress at the entrance of the die necessary to gross melt fracture [15], is developed at a lower shear rate than the critical shear rate for sharkskin. All the metallocene-catalyzed PEs studied showed the same general behavior, although the limiting temperatures vary according to the characteristics of each sample. In particular, the effect of the molecular parameters on T_s is analyzed below.

Wang and Drda [11] analyze the variation of the critical stress value of the slip–stick, σ_C, with temperature.

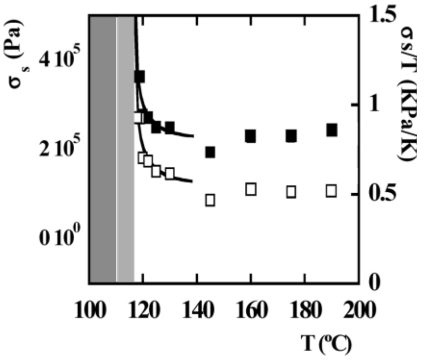


Fig. 5. σ_s (full symbols) and σ_s/T (empty symbols) versus temperature plots for the sample of Fig. 4(b). The flow induced crystallization temperature is determined using plots like those of Figs. 2 and 3. The data at low temperatures are fitted to an asymptotic function. In region I (in bright), sharkskin is forbidden and in region II (in dark) flow is blocked because crystallization.

Considering that slip–stick is an interfacial phenomenon, they use the expression derived by Brochard and de Gennes [16]:

$$\sigma_C = nKT/D \tag{2}$$

where n is the density of adsorbed chains and D the entanglement distance, to assume that σ_C should scale linearly with temperature. This is experimentally confirmed over decreasing temperatures in the range 260–200 °C with their HDPEs, and at lower temperature ranges (typically from 190 to 160 °C) in our polyethylene samples, as can be seen in Fig. 5. However, at lower temperatures, decreasing from 200 to 160 °C, Wang and Drda [11] report an anomalous behavior, consisting of the non-linearity of the correlation between σ_C and T (σ_C/T is lowered as T is decreased). This is also observed, in the range 190–140 °C, with a metallocene-catalyzed LLDPE investigated by Pérez et al. [12], and in the range 160–145 °C (see Fig. 5), for the inception of sharkskin σ_s, with our metallocene-catalyzed PE samples. Considering that at low temperatures the density of adsorbed chains, n, is only expected to increase as temperature decreases, Wang and Drda argue that the decrease of σ_C/T with temperature, should be explained by assuming an increase in the distance between entanglements, D. They suggest that the formation of a flow-induced ordered phase, near the PE/wall interface, may be the origin of this anomaly, since chains would disentangle easier due to local orientation. Therefore, the research of Keller et al. on the formation of a phase through flow-induced alignment of presumably adsorbed molecules, which gives rise to the temperature window of extrudability, supports the observed decrease of σ_C/T as temperature is lowered. But the rapid increase of both, σ_s and σ_s/T, as temperature is decreased from 145 to 118 °C (Fig. 5), cannot be explained solely by the formation of a mesophase. Actually, considering Eq. (2) the increase of σ_C/T implies the reduction of D and/or an increase in the density of adsorbed chains, n. The process may imply incipient crystallization close to the wall. Our

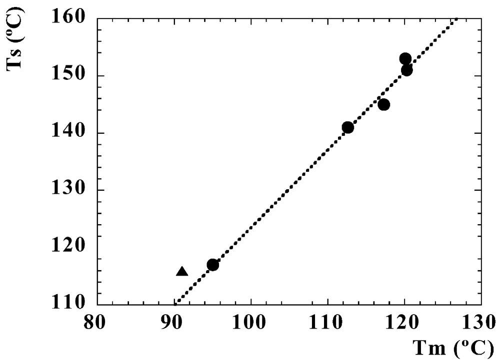


Fig. 6. Correlation between the highest temperature at which sharkskin disappears, T_s, and melting temperature, T_m. Symbol ▲ represents the result of a commercial metallocene catalyzed LLDPE, taken from reference [12]. The molecular parameters of the samples are given in Table 2.

guess is that stretching at the exit (which combined with adhesion conditions at the wall gives rise to sharkskin) may promote local crystallization at these low temperatures. In any case, the evolution of the shear stress for inception of sharkskin, σ_s, with temperature, indicates that adhesion is enhanced at low temperatures. In the range of smooth stable extrudates, between T_s and crystallization temperature, the extrudate swell of the samples increases with shear rate and lies typically within the range from 1.2 and 1.4: this is a symptom of non-slip conditions at the capillary wall. Therefore, according to the results of Figs. 4 and 5, the necessary slip–stick conditions to produce sharkskin, would only be produced at shear rates above those involved in gross melt fracture. To the best of our knowledge, such behavior has never been reported in the literature. Only the result reported by Ramamurthy for highly branched LDPE [17] resembles in some sense to our finding: this author observes that the shear rate for the onset of gross melt fracture is extremely close to that of sharkskin.

3.2. Effect of molecular architecture on T_s

The following molecular parameters of all the samples studied in this work, are considered: weight average molecular weight, M_w, which ranges from 92,000 to 335,000; polydispersity index, M_w/M_n (where M_n is the number average molecular weight), always close to 2; and short chain branching level, SCB, which ranges from 0 to 21.2 CH_3/1000C. The presence of small amounts (typically less than one branch per molecule) of long chain branches is also considered.

Our results show that there is no effect of the molecular weight on T_s, over the range of M_w investigated. As can be seen in Table 1, for the same or similar SCB level, the same value of T_s is observed for different molecular weights. It is also noticed that T_s decreases when short branches are incorporated in the chain. A substantial effect of SCB [2,5,6], and a practically insignificant effect of molecular weight [5,6], on the temperature location of pressure minimum of the 'extrusion window', have been reported for high molecular weight (2.5×10^5–10^6) and polydisperse conventional polyethylenes. Within the framework of the explanation offered for the temperature window, Waddon and Keller interpret the effect of SCB in terms of the $-CH_3$ groups lowering the temperature for a mobile hexagonal mesophase.

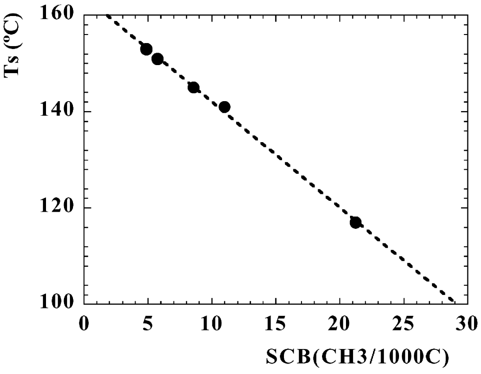


Fig. 7. Variation of T_s as SCB level is increased. The molecular parameters of the samples are given in Table 2.

The effect of short chain branching on T_s is depicted in Table 2, where samples of very similar molecular weight and polydispersity, but different levels of SCB, are considered. Since it is known that chain defects, in the form of alkyl branches, lower the melting temperature [18], in Table 2 we have also included melting values, T_m, as determined by DSC. The correlation between the melting temperature and the highest temperature (of the low temperature range) at which sharkskin disappears, T_s, is shown in Fig. 6. Also shown in this figure is the equivalent of T_s (defined in this case as the lowest temperature for total elimination of surface defects) of a commercial metallocene catalyzed LLDPE, taken from Pérez et al. The very significant decrease of T_s as the SCB level is increased, can be observed in Fig. 7, which also shows the similar effect of short branches on T_m. Unfortunately, the result of the LLDPE used by Pérez et al., shown in Table 2 and Fig. 6 can not be plotted in this figure, because its degree of branching is not known. The correlation between T_s and SCB level is given by the equation:

$$T_s = 164 - 2.2\ \mathrm{SCB}(\mathrm{CH_3/1000C}) \tag{3}$$

This equation provides a clear guide to find the temperature at which smooth extrudates can be obtained, on the basis of the level of short branches, that is to say the presence of hexane comonomer units.

Our experimental results cover all the singular temperatures reported in the literature for smooth extrudability: temperature window of extrudability; stable island of Pudjijanto and Denn and the 'easy flow' of Pérez et al. The window effect has been extensively investigated by Keller et al. from 1990 to 1996, but with a reduced number of linear, polydisperse, polyethylene samples of M_w ranging from 130,000 to 1,000,000 and one PE with a methyl branch density of 4.9 CH_3/1000 carbons. The specific temperatures,

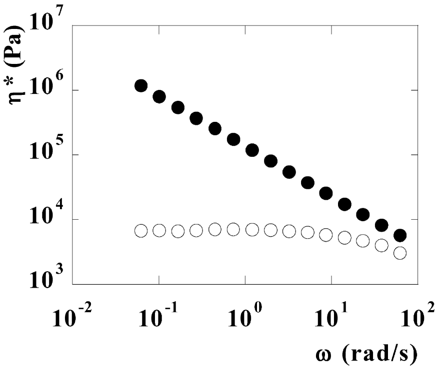


Fig. 8. Complex viscosity as a function of frequency for two samples defined respectively, in Tables 2 and 3 (mPE11: full symbols and mPE3: empty symbols). The two samples have very similar molecular weight, polydispersity and SCB level, but sample mPE11 possesses a very low amount of LCB.

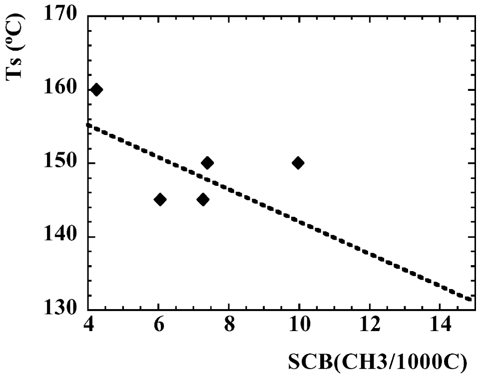


Fig. 9. T_s versus SCB level for samples which are very slightly long-chain branched. The line correspond to Eq. (3), obtained for samples completely free of LCB (see Fig. 7). The samples can be identified by their SCB level given also in Table 3.

defined for these polymers at the minimum in the pressure–temperature trace, are $T = 150$ to 152 °C for linear PE s and $T = 145$ °C for the short branched polymer. These data fit well with our T_s values, as can be seen in Tables 1 and 2. On the other hand, the stable island, where the extrudates become smooth, in the slip–stick region of a LLDPE of $M_w = 114,000$, lies between $T = 139$ and 146 °C. These critical temperatures are lower than those reported by Keller et al., which is consistent with the high SCB level of the LLDPEs. The result shown by Pudjijanto and Denn is compatible with the effect of the SCB on T_s, shown in Fig. 7. This sensitivity of the transition temperature to changes in the level of SCB, also explains the smooth extrudability found by Pérez González et al. for a metallocene LLDPE at a very low temperature, $T = 116$ °C. This result has been discussed earlier, together with the results of Fig. 6.

In comparison with Ziegler–Natta catalysts, single-site metallocenes produce a better control of molecular architecture, leading to narrower molecular weight and short chain branch distribution. However, the production of small amounts of LCB (0.1 to 1 long branch per molecule) during the metallocene-catalyzed polymerization process is difficult to control, because it depends on several factors such as the polymer and monomer concentrations, temperature, comonomer, hydrogen concentration, etc. [19]. The effects that small amounts of LCB produce on the rheological properties are particularly remarkable at low frequencies and shear rates [20], but classical methods such as size exclusion chromatography (SEC) and NMR are not useful to evaluate this low level of LCB [21,22]. Therefore, in the case of metallocene-catalyzed PEs, one is often obliged to refer to samples 'suspected of possessing small amounts of LCB'. This is shown in Fig. 8, where two samples of very similar M_w, polydispersity index and SCB, give, however, completely different dynamic viscoelastic results. The extremely high viscosities at low frequencies, observed for one of the samples, denotes that repetition is delayed [23]. This is considered a symptom of the presence of a very small amount of LCB. In Table 3 three samples of unknown LCB level are presented, together with two samples of low LCB, as determined by SEC. A copolymer of ethylene and propylene produced by Brookhart's type single-site catalysts, with a dynamic viscoelastic response reflecting extremely long relaxation times [24], is also included in Table 3. In spite of the complex architecture attributable to these samples, smooth extrudates can be obtained by decreasing the temperature to the T_s values indicated in Table 3. This is particularly relevant in the case of Brookhart's type copolymer, which has been shown to exhibit sharkskin and the hydrodynamic phenomenon known as 'flow-split' [24], at high temperatures and very low shear rates. Since these samples posses a well defined degree of SCB, in Fig. 9 the T_s results as compared with those obtained with

Table 3
T_s data of slightly long chain branched samples. Different molecular weights and SCB are considered. Sample BPE is a copolymer of ethylene and propylene produced by Brookhart's type single-site catalysts

Material	M_w	M_w/M_n	SCB (CH$_3$/1000C)	LCB (CH$_3$/1000C)	T_s (°C)
mPE11	129,900	2.62	9.98	[a]	145–150
mPE12	211,866	3.14	4.26	[a]	160
BPE	335,000	2.3	7.4	–	150
mPE13	108,000	2.16	7.27	0.137	145
MPE14	92,600	2.24	6.06	0.132	145

[a] Samples suspected of containing small amounts of LCB.

Eq. (2) are shown. Although clear deviations are noticeable, it is seen that the influence of SCB on T_s is also followed by these rather peculiar samples. Small amounts of LCB, which clearly alter the rheological response of polyethylenes (see Fig. 8), have practically no effect on the limiting temperature, T_s, to obtain stable flow at low temperatures. Needless to say, we do not try to make a generalization on the effect of LCB, since samples with high levels of LCB are not considered. However, the results obtained with samples of such different characteristics can be considered as prove of the 'universality' of lowering temperature as a route to produce smooth extrudates in polyethylenes.

4. Conclusions

A large series of single-site metallocene-catalyzed polyethylenes of different molecular architectures, has been investigated. It is observed that all the samples show a low temperature region, limited by induced crystallization and gross melt fracture, where smooth extrudates (free of surface defects), are produced at shear rates similar to those of industrial extrusion. A characteristic temperature of this region, T_s, is defined as the highest temperature at which sharkskin disappears. The results indicate that good polymer/wall adhesion (non-slip conditions) is associated with this low temperature stable region. Therefore, sharkskin and slip–stick instabilities are avoided, because the shear stress necessary for slip is very high, above that involved in melt fracture. The analysis of the effect of molecular weight, SCB level and the presence of small amounts of LCB, leads to the conclusion that only SCB has a significant effect on T_s. A linear correlation between T_s and SCB level is established, showing the decrease of the former as the latter is increased. Considering the wide spectrum of the molecular characteristics of the samples studied, we claim that decreasing temperature is a sound route to postpone processing instabilities of any polyethylene.

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