FLOW-INDUCED CRYSTALLIZATION OF HIGH-DENSITY POLYETHYLENE

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Dedicated to Dr Blahoslav Sedlacek on the occasion of his 70th birthday.

Crystallization induced by flow in the capillary viscometer was studied for four grades of linear poly-
ethylene. From rheological and DSC measurements it follows that crystallization was induced in all
samples under study at temperatures higher than melting temperatures of the same samples crystal-
lized at rest. The maximum temperature of flow-induced crystallization increases with increasing
molar mass of polyethylene. Flow-induced crystallization of injection moulding grades of poly-
ethylene only takes place in a limited interval of shear rates. This effect is explained as a conse-
quence of the shear rate distribution in the capillary.

It is well known that the shear flow affects crystallization of semicrystalline polymers[1–3].
Commonly it is assumed that the shear flow affects mainly the rate of crystallization at
temperatures below the equilibrium melting temperature of the polymer due to its
strong effect on the formation of nucleation centres. Only a weak effect of the shear
flow on the melting temperature, i.e., the maximum temperature at which crystal-
lization is still possible, is expected. This expectation follows from the measurements
of molecular orientation in flow by the flow birefringence method and from the as-
sumption that the shift of the melting temperature is purely entropic[1]. This statement
does not fully agree with the results of the studies on flow-induced crystallization during
injection moulding[2,4–6], where a highly oriented skin layer was found. The skin layer is
also formed in a simple shear flow in the slit capillary under constant undercooling[2].
Flow-induced crystallization, manifested by the existence of highly oriented crystalline
materials[2,7–9], was also detected after rapid quenching of the polymers flowing at high
temperatures.

With the aim to contribute to the elucidation of flow-induced crystallization at
higher shear rates, crystallization induced by flow in a capillary viscometer was inves-
tigated. Conditions of crystallization in the viscometer are much simpler than in the
case of injection moulding. Samples of linear polyethylene varying in molar mass were

used with the aim to elucidate the effect of molecular structure on flow-induced crystallization. The behaviour of several commercial grades of ethylene homopolymers and copolymers containing a small amount of 1-butene was compared.

EXPERIMENTAL

Materials

Four grades of high-density polyethylene Liten (Chemopetrol Litvinov, Czech Republic) were used. Their basic characteristics are summarized in Table I.

Capillary Viscometry

Capillary viscometer Rheograph 2001 (Gottfert, Germany) was used. HDPE samples were measured at temperatures slightly above their equilibrium melting temperatures. At a constant temperature the shear rate was gradually increased during measurements. The same procedure is common for determining a flow curve. Blockage of the capillary by solidified HDPE occurred at temperatures when a certain shear rate was reached. Before the blockage, the flow-induced crystallization is signalled by an increasing difference between pressures measured on the piston and in the pressure hole. In some cases, at very high shear rates, the flow-induced crystallization disappears again (neither blockage of the capillary nor any difference between the stresses acting on the piston and in the pressure hole were detected). Shear rates, at which flow-induced crystallization disappears, were found by the trial and error method.

DSC Measurements

The melting and crystallization behaviour of HDPE Liten MB 82 and Liten BB 29 was studied using a Perkin–Elmer DSC 7 apparatus (calibrated with indium and tin prior to use). The heat flow as a function of temperature was recorded for both the virgin samples and samples crystallized in flow, i.e. the extrudates taken from the capillary viscometer at different temperatures and shear rates. Samples of approximately 10 mg were subjected to DSC analysis in nitrogen at a rate of 20 °C/min in the temperature interval 30 to 200 °C.

TABLE I
Characteristics of high-density polyethylenes

HDPE	Recommended processing technology[a]	Type[b]	$[\eta]^c$, cm^3/g	MFI[d], g/10 min
Liten MB 82	IM	H	94	15.0
Liten MB 62	IM	H	111	6.0
Liten MB 57	IM	C	–	4.0
Liten BB 29	BM	C	200	0.14

[a] IM injection moulding, BM blow moulding; [b] H homopolymer, C copolymer with a low amount of 1-butene; [c] limiting viscosity number in trichlorobenzene at 130 °C; [d] melt flow index at 190 °C.

RESULTS AND DISCUSSION

The flow-induced crystallization was found for all samples under study in a certain range of temperatures above the equilibrium melting temperature of HDPE. During flow-induced crystallization, complete blockage of the capillary occurred. In order to remove the solidified polymer from the capillary, it was necessary to raise the temperature of the capillary wall above the melting point of polyethylene. The surface of polyethylene extruded at low shear rates was smooth. At shear rates approaching the conditions of the flow-induced crystallization, the output rate and the extrudate cross-section decreased and the whole process of extrusion was rather unstable. In the case of polyethylene Liten BB 29, the extrudate surface was also influenced by flow oscillations. Time dependences of the pressure measured on the piston and in the pressure hole are compared in Fig. 1. The same dependences for the sample, where flow oscillations also occurred, are plotted in Fig. 2. It can be seen from Figs 1 and 2 that both pressure dependences are similar if crystallization is absent. If the polymer melt starts to crystallize in the capillary, the pressure exerted on the piston begins to increase much faster than the pressure measured in the pressure hole and the rheometer stops measuring automatically once the limiting value of pressure (ca 176 MPa in our case)
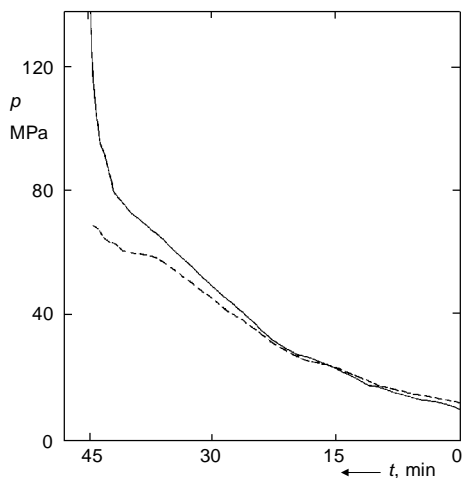

Fig. 1

Time dependence of the pressure measured in the pressure hole (− − −) and on the piston (——) for Liten BB 29 at 144 °C
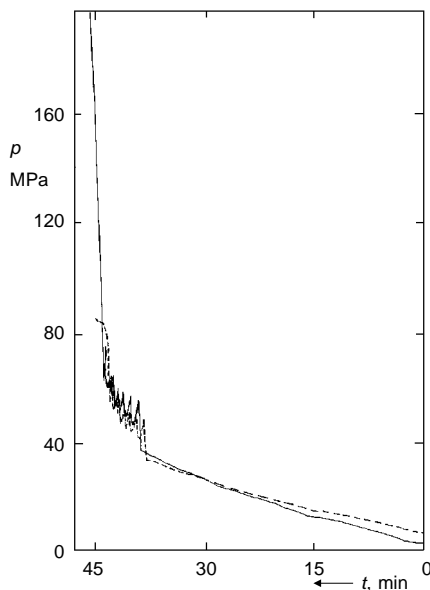
Fig. 2

Time dependence of the pressure measured in the pressure hole (− − −) and on the piston (——) for Liten BB 29 at 146 °C (the measurement where flow oscillations occurred)

is reached (i.e., before complete blockage of the capillary). We suppose that the reason why the pressure measured in the pressure hole does not increase in the same way as that exerted on the piston might be solidification of the polymer melt in the pressure hole, which prevents transmission of the pressure acting in the cylinder of the rheometer into the pressure hole and onto the pressure transducer.

For all injection moulding grades of HDPE (Liten MB 82, Liten MB 62 and Liten MB 57) in a certain temperature range, the upper critical shear rate was found, where flow-induced crystallization disappears again. Samples can be extruded without problems through the capillary at higher shear rates. However, the extrudate has a coarse

TABLE II
Conditions of the flow-induced crystallization of high-density polyethylene

T, °C	$\dot{\gamma}_{min}^{app,a}$, s^{-1}	$\dot{\gamma}_{max}^{app,b}$, s^{-1}	τ_{min}^{c}, kPa	τ_{max}^{d}, kPa
		Liten MB 82		
141	1 800	8 700	270	420
140	900	9 200	180	440
139	800	9 200	180	460
138	600	12 900	170	490
137	460	15 200	150	500
		Liten MB 62		
142	280	7 400	140	480
141	180	8 700	120	490
		Liten MB 57		
141	280	6 000	180	460
140	280	6 900	180	470
		Liten BB 29		
147	2 800	–	670	–
146	2 300	–	620	–
145	460	–	630	–
144	280	–	550	–
143	230	–	545	–

[a] Minimum apparent shear rate; [b] maximum apparent shear rate; [c] minimum shear stress; [d] maximum shear stress.

surface with numerous defects. Apparently, crystallization is induced by flow at shear rates (shear stresses) lying in a limited range only.

In Table II the values of minimum shear stress, τ_{min}, minimum apparent shear rate, $\dot{\gamma}_{min}^{app}$, maximum shear stress, τ_{max}, and maximum apparent shear rate, $\dot{\gamma}_{max}^{app}$, at which flow-induced crystallization occurred, are given as functions of temperature. At temperatures higher than those given in the Table, the whole flow curves were measured for related samples and no flow-induced crystallization was found. It follows from Table II that the width of the interval of shear stresses (shear rates), where crystallization is induced, increases with decreasing temperature of measurement. At temperatures lower than those given in the Table, the width of the interval should be larger. However, measurement at these temperatures was practically impossible due to very high viscosity of the samples.

For highly viscous Liten BB 29 only the minimum shear stress, τ_{min}, and minimum apparent shear rate, $\dot{\gamma}_{min}^{app}$, were determined. The maximum shear stress and maximum apparent shear rate were not found at any temperature. τ_{min} and $\dot{\gamma}_{min}^{app}$ for individual temperatures are indicated in Table II. Also for this sample, τ_{min} and $\dot{\gamma}_{min}^{app}$ decrease with decreasing temperature.

It follows from the comparison of the results for individual samples that the highest temperature, at which crystallization can be induced by flow in the capillary, increases with increasing molar mass of HDPE (cf. Table II and Table I). At a certain temperature, the width of the interval of shear stresses at which crystallization is induced in-

TABLE III
Thermal characteristics of high-density polyethylene

HDPE	1st run		Cooling		2nd run	
	T_m, °C	ΔH_f, J/g	T_c, °C	ΔH_c, J/g	T_m, °C	ΔH_f, J/g
Virgin polymer						
Liten MB 82	133.0	192.6	111.2	220.6	133.7	221.2
Liten BB 29	130.6	191.6	114.7	197.2	131.9	196.8
Extrudate						
Liten MB 82[a]	132.3	211.9	111.4	217.1	132.0	217.9
Liten MB 82[b]	138.2	214.5	109.2	217.3	137.8[c]	213.6
Liten BB 29[d]	142.5	203.4	109.5	204.8	141.0	203.8

[a] $\dot{\gamma}^{app} = 460$ s^{-1}, $T = 138$ °C; [b] $\dot{\gamma}^{app} = 829$ s^{-1}, $T = 138$ °C; [c] double peak of melting, the other peak has $T_m = 130.8$ °C; [d] $\dot{\gamma}^{app} = 460$ s^{-1}, $T = 145$ °C.

creases with increasing molar mass of the samples. It seems from the comparison of the results for Liten MB 62 and Liten MB 57 that, at comparable molar mass, the homopolymer has somewhat broader range of conditions in which crystallization occurs than the copolymer.

In order to understand the influence of polymer melt flow on crystallization of polyethylene in the capillary, the extrudates were examined by the DSC method. The melting point, T_m, and the heat of fusion, ΔH_f, from the first and second heatings as well as crystallization temperature, T_c, and the heat of crystallization, ΔH_c, extracted from the DSC scans are listed in Table III. The data in Table III highlight the significance of the processing step in determining the degree of orientation and anisotropy since the melting temperature and enthalpy of melting have been significantly changed by shear flow (Fig. 3). When making the comparison with the reference (virgin sample), it is evident that the lower shear rate ($\dot{\gamma} = 460$ s^{-1}) is produced in the case of Liten MB 82 (at 138 °C), an extrudate with practically unchanged T_m but having a higher volume fraction crystallinity (expressed here as a higher value of ΔH_f). The further increase in shear rate up to $\dot{\gamma} = 829$ s^{-1} caused, on the other hand, a pronounced effect on both the melting temperature and volume fraction crystallinity of the extrudate (Table III). Only the crystallization temperature of the latter sample ($\dot{\gamma} = 829$ s^{-1}) is slightly shifted to lower temperatures and a double peak of melting is observed in the second DSC run. Interesting is that the shear stress-induced higher part of the T_m double peak persisted in this sample even when the stress already relaxed (i.e., during heating in the DSC pan where the sample was completely melted in the first run and then cooled down from 200 to 30 °C without any stress). In this connection, when the crystallization takes place at a lower temperature than in the virgin polymer, a more detailed study of the influence of ther-
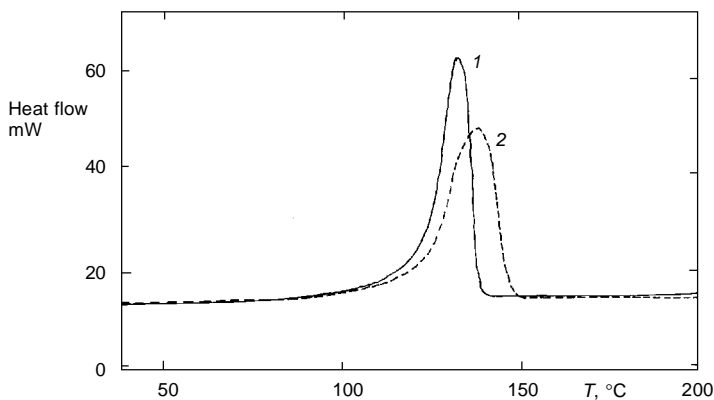

Fig. 3
Melting behaviour of Liten MB 82 extrudate at 138 °C at shear rates $\dot{\gamma}^{app}$: *1* 460 s^{-1}, *2* 829 s^{-1}

mal history on the number of nuclei would be needed. The temperature difference between the melting temperature and the temperature of crystallization is namely an empirical measure of crystallization rate in semicrystalline polymers.

The rather big difference in thermal characteristics of the same polymer, Liten MB 82, "extruded" from the capillary at two different shear stresses, has an obvious correlation with mechanical properties of both samples. The first ($\dot{\gamma}$ = 460 s^{-1}) was thin and elastic while the second sample ($\dot{\gamma}$ = 829 s^{-1}) was thick and very brittle.

Also the sample of HDPE Liten BB 29, crystallized in the capillary flow at 145 °C, had T_m and ΔH_f values considerably higher than the same sample crystallized in the absence of flow. With this polymer of higher molar mass and viscosity, the upper limit of crystallization interval was not detected. Therefore, the extrudate normally obtained at shear rates higher than those necessary for induction of crystallization was not available.

The temperatures of crystallization obtained from rheological measurements as well as the results obtained from the DSC experiments show that, under conditions of polymer melt flow in a capillary, polymer chains are oriented so that the polymer crystals formed have higher temperature of melting, T_m, than those formed in the quiescent polymer melt. The process of flow-induced crystallization in the capillary rheometer is therefore more complicated than that observed in rotational rheometers where only the rate of nucleation is influenced by flow[1]. Data in Table II show that the temperature at which flow-induced crystallization may occur increases with the maximum shear stress attained in the measurement.

Present theoretical considerations cannot account for the fact that flow-induced crystallization of injection moulding grades of polyethylene Liten takes place in the limited interval of shear rates only. They cannot explain why, at high shear rates, this phenomenon vanishes. In our opinion, this effect is a result of the flow field formed in the round capillary. It is well known that in such capillary the highest shear rate is found at the capillary wall whereas by approaching the axis of the capillary, the shear rate decreases to zero. Hence, at the capillary wall, the polymer chains may be expected to have the highest degree of orientation. Therefore, flow-induced crystallization may also be expected to take place at the capillary wall whereas near the capillary axis the polymer will remain in the molten state. Thus flow-induced crystallization will result in diminishing the effective cross-section of the capillary. As a result, at a constant output rate, the shear rate and shear stress will increase in the flowing polymer melt. Simultaneously, the flowing liquid will exert an increasing shear stress on the crystalline layer covering the capillary wall. If this stress is not high enough to tear the crystallized polymer off the wall, it causes further polymer molecules to crystallize and to form further layers of solidified polymer until the whole capillary is filled with the solid crystallized polymer. On the other hand, if the adhesion of the crystallized polymer to the wall or the cohesion of crystallized polymer molecules is lower than the force

exerted on the crystalline polymer surface by the flowing polymer melt, the crystalline phase is washed out and no blockage of the capillary occurs.

Our results indicate that adhesion to the capillary wall and cohesion of crystallized polyethylene molecules increase with decreasing temperature and increasing molar mass of polyethylene. The effect of molar mass is fully in agreement with the results on adsorption of polymer molecules on filler particles[10]. It may be assumed that, in the case of high-molecular-weight grade of polyethylene (Liten BB 29), the adhesion and cohesion are very high and therefore these polymers cannot be washed out in our measurements with the capillary rheometer.

CONCLUSIONS

High-density polyethylene crystallizes at flow in the capillary viscometer at temperatures which are higher than its equilibrium melting temperature. The highest temperature, at which crystallization occurs, increases with increasing molar mass of polyethylene.

Flow-induced crystallization of injection moulding grades of polyethylene takes place only in the limited interval of shear rates. This effect can be explained as a consequence of the shear rate distribution in the capillary cross-section.

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