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The impact of flow induced changes of polymers density on rheological measurements

RAPID COMMUNICATION

Summary — The influence of real density of polymers in molten state on the rheological values is presented. The investigations were performed by means of extrusion rheometer, using a rheological dye with exchangeable channel with various length and diameter ratio (L/D). The materials used in the experiments were low density polyethylene (PE-LD), middle density polyethylene (PE-MD) and the blend of PE-LD with PE-MD in 1:1 ratio, for which p-v-T diagrams were determined. Based on p-v-T measurements the real specific volume and the density of the molten polymer in defined processing conditions (p, T), were found (Fig. 4). Density was used for determination of the real mass flow ratio $\dot{Q}$. A significant influence of the channel L/D ratio on changes of density was stated (Fig. 5, Table 1). The dependence of changes of density values on the type of polymer used was confirmed.
Key words: rheological measurements, p-v-T, density, viscosity, polyethylene.

WPŁYW WYWOŁANYCH PRZEPŁYWEM ZMIAN GĘSTOŚCI POLIMERÓW NA POMIARY REOLOGICZNE
Streszczenie — Pomiary przeprowadzono za pomocą reometru wytłaczarkowego używając dysz cylindrycznych o przekroju kołowym z różnym stosunkiem długości do średnicy (L/D). Badano polietylen małej gęstości (PE-LD), polietylen średniej gęstości (PE-MD) oraz ich mieszaninę w stosunku 1:1 wyznaczając diagramy p-v-T. Na podstawie wykresów p-v-T określano objętość właściwą, a następnie gęstość (ρ) polimeru, w warunkach ciśnienia i temperatury (p, T) odpowiadającym wartościom tych parametrów podczas pomiarów reologicznych (rys. 4). To umożliwiło ocenę rzeczywistej wartości objętościowego natężenia przepływu $\dot{Q}$. W przeprowadzonych badaniach wykazano istotny wpływ charakterystycznych wielkości kanału dyszy pomiarowej (L i D) na zmiany gęstości polimeru (rys. 5, tabela 1). Potwierdzono również zróżnicowanie ρ, w takich samych warunkach przetwórczych, dla różnego typu polietylenu.
Słowa kluczowe: pomiary reologiczne, diagram p-v-T, gęstość, lepkość, polietylen.

The rheological properties of molten thermoplastic polymers determine the flow behavior in processing, and may be measured only in flow conditions. The measurements of basic physical and chemical rheological values may be done by application of rheometers, which make the determination of shear stresses (τ) and shear rates (γ̇) in any position of the flow possible [1—5]. In case of such experiments, the rheological equations describing the specific flow relationship, for the defined apparatus, should be known. The rheological measurements are usually done for simple flow where only one component of the velocity vector differs from zero (so called viscometric flow). Assuming that the molten polymer presents a non compressible liquid with a nature of a continuous medium, the relationship between the shear stress and shear rate may be faithfully determined.

By the capillary rheometry, frequently used for the determinations of the rheological properties of molten polymers, the Poiseuille flow in capillary channels, characterized by length (L) and diameter (D) (or radius R) is applied. If the dimensions of the capillary channel are defined, the relationship between the volume rate flow ($\dot{Q}$) and the total pressure drop (Δp_c), caused by internal friction of the liquid, may be described. In this case the Δp_c present the difference between the entry pressure (p_e) and the atmospheric pressure (p_a). Taking into account different values of $\dot{Q}$ (or Δp_c), the flow curves of investigated polymer may be determined [2—9].

The determination of $\dot{Q}$ value in defined processing conditions presents a technical problem, because the temperature and pressure dependent compressibility of

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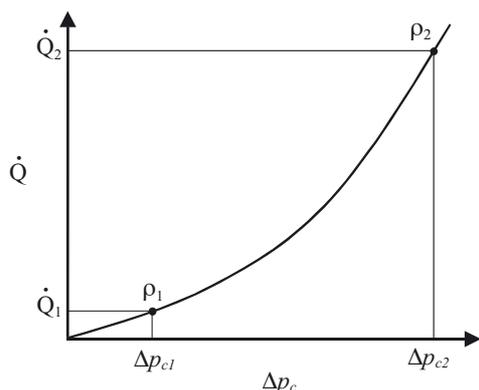
Fig. 1. Typical dependence of volume flow rate ($\dot{Q}$) on total pressure drop (Δp_c); ρ_1, ρ_2 — density

the molten polymer should be taken into account. In Figure 1 a typical run $\dot{Q}$ *versus* Δp_c is presented, where for increasing pressure ($\Delta p_{c1} < \Delta p_{c2}$), a non proportional increase in flow intensity ($\dot{Q}_1 < \dot{Q}_2$) may be noted. For every change of the pressure value, leading to change of the flow of the molten polymer from $\dot{Q}_1$ to $\dot{Q}_2$, another density may be detected, where $\rho_1 < \rho_2$.

For determination of the volume flow rate $\dot{Q}$ in processing conditions (p, T), the real density [$\rho(p, T)$] of the polymer has to be taken into account, according to the formula [10—13]:

$$\dot{Q} = \dot{M} / \rho(p,T) \qquad (1)$$

where: $\dot{M}$ — *mass flow rate*.

The value of $\rho(p, T)$ is commonly used in the description of rheological, thermal and mechanical properties of polymers [4, 14—16], and denotes the inverse value of specific volume [v(p, T)].

The value of the actual ρ of molten polymer may be indirectly determined by application of the thermodynamical equation, relating p, v and T, *i.e.* by means of the p-v-T diagram [2, 4, 14—20].

The knowledge of the p-v-T characteristic of polymeric material is necessary for the description of the processing conditions in the injection mold cavity during filling, packing and cooling phases, and for the optimization of the injection parameters [14, 15, 21—24]. This characteristic may be also treated as a tool in the analysis of the morphology during melting and crystallization stages [25—28].

Beside the case mentioned above, the p-v-T characteristic may also be used for the determination of the intensity of the volumetric flow. According to the literature data, the run of the p-v-T relation is characterized by a significant p and T dependent variation of v. As a consequence the significant changes of ρ value should be taken into account. Thus, by the characterization of the volumetric flow, prior to the determination of the rheological data of the investigated flow, the application of density variation is required for the evaluation of $\dot{\gamma}$.

In this paper the investigation of ρ changes, due to the molten flow by extrusion, measured for the commercial grades of low density polyethylene (PE-LD) and middle density polyethylene (PE-MD), as well as their mixture are presented and discussed. The presented results are a part of investigations of the rheological properties of molten polymers measured in the real processing conditions [29—31].

EXPERIMENTAL

Materials

The following materials were applied in the present study of the molten flow:
— low density polyethylene (PE-LD), trade name Malen E FABS 23-D 022 (Basell Orlen Polyolefins sp. z o.o.), with density of 0.919—0.923 g/cm^3 (23 ^{o}C), and melt flow rate $MFR_{2.16;190} = 1.8$ g/10 min,
— middle density polyethylene (PE-MD), trade name Finathene$^{®}$ HF 513 (Atofina SA), with a density of 0.934 g/cm^3 (23 ^{o}C), and $MFR_{2.16;190} = 0.11$ g/10 min,
— a blend of two types of polyethylene PE-LD (FABS 23-D) with PE-MD (HF 513) in a mass ratio 1/1, with an average density of 0.927 g/cm^3 (23 ^{o}C), and with $MFR_{2.16;190} = 1.01$ g/10 min.

Methods

Rheological measurements

The rheological properties were determined by means of an in-line rheometer [29—31]. The experimental measuring line was composed of a single — screw extruder FAIREX with a screw diameter $d = 30$ mm, screw length and diameter ratio $l/d = 25$, and with an extrusion head with exchangeable dies. The description of the measuring die may be found in our earlier papers [29—31]. The special rheological head with exchangeable cylindrical dies of dimensions: $L = 20$ or 30 mm and $D = 2, 3, 4, 5, 8$ or 10 mm was used in our investigations. The measurements were performed at melting temperature of polymer 170 ^{o}C, and by screw rotational speed (V_s) varying in the range 0.17 and 0.76 s^{-1}.

p-v-T measurements

The determinations of p-v-T curves were carried out by means of a fully automated instrument (PVT 100 SWO Polymertechnik GmbH, Germany). The characterization of p-v-T relations of polyethylene samples was performed during isobaric cooling. The isobars were determined in the temperature range from 30 to 180 ^{o}C. The specific volume was found at following applied measurement pressure values: 20, 40, 80, 120 or 160 MPa, and for cooling rate of 5.0 ^{o}C/min. Specific volume at the atmospheric pressure was evaluated by use of the extrapolation procedure of the corresponding values in the range between 20 and 160 MPa, using the equation of the standard software (PVT-100 SWO, Germany).

RESULTS AND DISCUSSION

The flow of the molten polymer in extrusion, and the related variation of the molten flow volume may be adjusted by changes of V_s value. This is the reason why the relationship between $\dot{M}$ and Δp_c, due to the friction in the flow, may be established and studied for various V_s applied. For all polymers used in our experiments the corresponding characteristisc of the extrusion processes, *i.e.* the relations among V_s, Δp_c and $\dot{M}$ were determined. Furthermore, by use of dies characterized with different length and diameter ratios, various domains of Δp_c were reached.

In the Figure 2 the runs of Δp_c dependence on V_s for PE-MD, measured using the dies with various D values and constant $L = 30$ mm are presented. An increase in Δp_c value with increasing V_s may be clearly noted. The higher Δp_c values were observed for the dies with lower D, due to the higher flow resistance. On the contrary, almost similar runs of Δp_c *versus* V_s curves were noted for die diameters 8 and 10 mm (Fig. 2, curve 5 and 6).
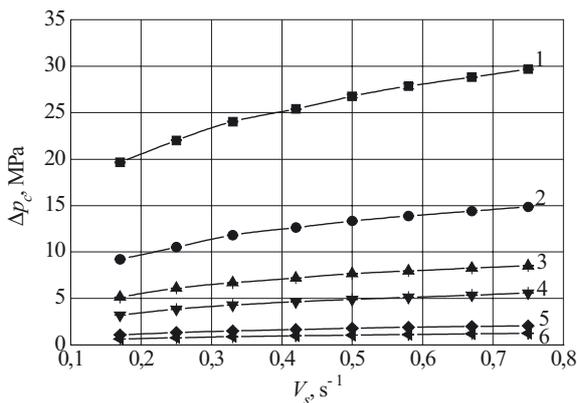
Fig. 2. Plot of total pressure drop (Δp_c), measured at entrance channel area, versus screw rotational speed (V_s) for PE-MD, using dies of $L = 30$ mm and D equal to (in mm): 1 — 2, 2 — 3, 3 — 4, 4 — 5, 5 — 8, 6 — 10

The Δp_c value for the flow of molten polymer through the die is apparently also the channel length dependent. An increase in L from 20 to 30 mm leads to a remarkable rise of Δp_c value from 1.7 MPa to 3 MPa, and this difference is more significant for higher V_s.

Beside the dimensional relation of the dies (L/D), also the type of polymer used may significantly influence the value of Δp_c. Such effect may be seen in our experiments realized for PE-LD, PE-MD and their mixture. As it follows from Figure 3 the highest Δp_c value was observed during the flow of the molten PE-MD, and the lowest for PE-LD. The curve $\Delta p_c = f(V_s)$ determined for the mixture of polyethylenes, is located between the curves for both types of pure polyethylenes. Its run looks very regular, with small deviation, what may be an evidence of high homogeneity of PE-LD and PE-MD blend.
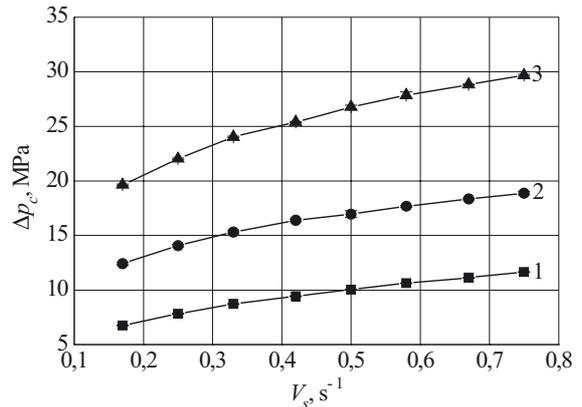
Fig. 3. Plot of total pressure drop (Δp_c), measured at entrance channel area using dies of D = 2 mm and L = 30 mm, versus screw rotational speed (V_s) for: 1 — PE-LD, 2 — PE-LD/PE-MD, 3 — PE-MD

The measurement of Δp_c during the flow of molten polymer, used for the evaluation of τ, is also necessary for the determination of ρ and its changes during the processing. The ρ value of the polymer, in defined processing conditions may be found by use of the *p*-v-*T* diagrams. Based on the *p*-v-*T* diagram, the relationship
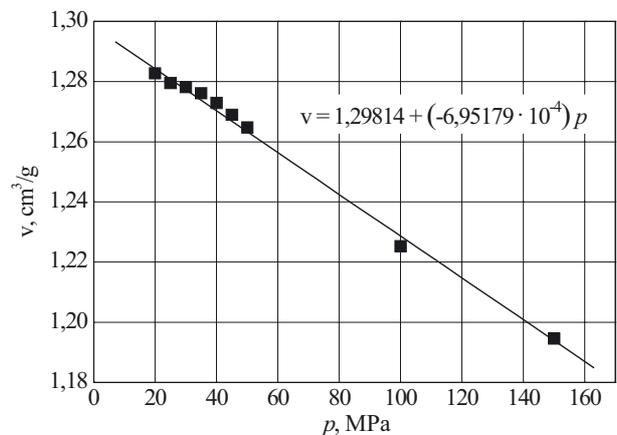
Fig. 4. Plot of specific volume (v) versus pressure (p) for PE-MD at temp. 170 ^{o}C and appropriate equation of linear regresion

between v and p can be evaluated at selected constant temperature. Such exemplary relationship for PE-MD at 170 ^{o}C is shown in Figure 4. This dependence may be presented in a linear form:

$$v = a + b \cdot p \qquad (2)$$

This equation applied for $p = p_e$ found in rheological measurements makes possible the simple transformation

$$v = a + bp_e - bp_a + bp_a = a + bp_a + b(p_e - p_a) \qquad (3)$$
$$v = a' + b\Delta p_c \qquad (4)$$

Thus, the specific volume of the molten polymer, in defined processing conditions, may be evaluated.

By application of the procedure described above the densities of molten polymers and their mixture during the molten flow through the dies with various L/D ratio, were determined in rheological measurements (Table 1).

T a b l e 1. The density ranges and corresponding pressures variations in rheological measurements

Die length mm	PE-LD		PE-LD/PE-MD		PE-MD	
	Δp_c MPa	ρ kg/m³	Δp_c MPa	ρ kg/m³	Δp_c MPa	ρ kg/m³
20	0.1—8.7	758.5—762.1	0.1—14.3	766.9—773.0	0.4—20.8	770.5—779.0
30	0.3—11.6	758.5—763.3	0.3—18.8	767.0—774.9	0.6—29.7	770.6—782.8

The highest Δp_c values were found for the flow of the polymers through the dies of $L = 30$ mm (Table 1); consequently, in these cases the most significant changes of polymer density were noted as well. For PE-MD, extruded in the pressures varying in the range between 0.6 and 29.7 MPa, the changes of density of about 12 kg/m³ were noted. Due to the highest Δp_c values, the most important changes of density were found for the flow of the molten polymers through the dies with the lowest diameter.

The density of the mixture of PE-LD with PE-MD, as a function of Δp_c, determined at temp. 170 °C during the flow through the dies of 30 mm in length and different diameters, is presented in Figure 5. The various pressure values applied in the experiments allow to draw the run of the density in a relatively wide range, *i.e.* from 767.0 to 774.9 kg/m³, where for each of the die used another domain of the polymer density was found. Similar relations, but for another domains of pressure and density,
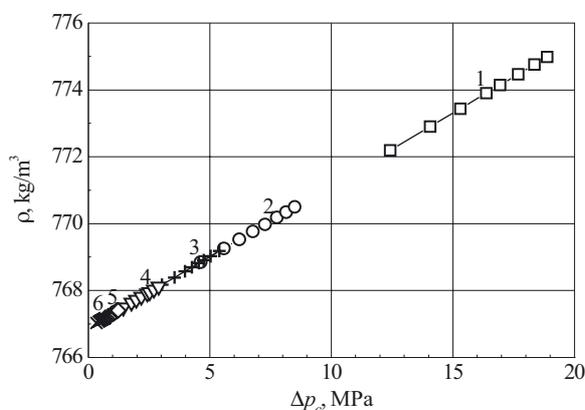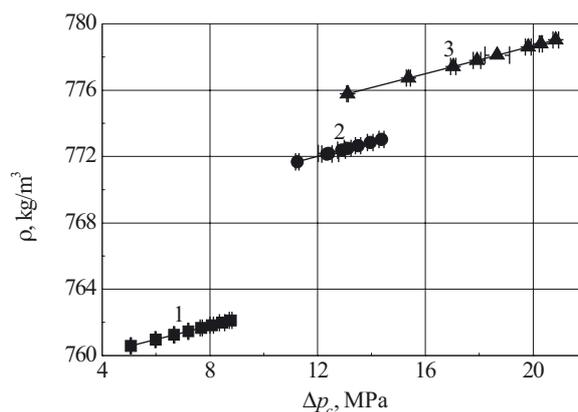
Fig. 6. *Plot of density* (ρ), *at 170 °C, versus total pressure drop* (Δp_c) *determined during flow through the die of D = 2 mm and L = 20 mm for: 1 — PE-LD, 2 — PE-LD/PE-MD, 3 — PE-MD*

were found for PE-LD and PE-MD, hence the experiments were realized for dies of $L = 20$ and 30 mm.

Concerning the positions of the particular curves in Fig. 5 it may be concluded, that for the flow of molten polymers through the dies with different dimensions, various values of density were found due to the diverse pressure drop Δp_c noted for those conditions of molten flow.

As it follows from the results presented in Figure 3 and Table 1, the type of analyzed polymer directly influences the range of measured pressure drop and the density changes. The curves presenting the density at temp. 170 °C as a function of total pressure drop, during the flow through the dies with $L = 20$ mm and $D = 2$ mm are presented in Figure 6. The highest flow resistance, *i.e.* the highest Δp_c, was noted for the flow of PE-MD. Consequently for this polymer the widest range of ρ changes of 3.239 kg/m³, for Δp_c changes of 7.7 MPa, was noted. The ρ changes for the flow of PE-LD were in the range of 1.532 kg/m³, with the change of Δp_c 3.7 MPa. Comparing the results obtained for PE-LD and PE-MD, it may be noted that in the flow of PE-LD ρ value changes are about 50 % lower than in the case of PE-MD. For the mixture of PE-LD with PE-MD the change of ρ value was 1.348 kg/m³, by Δp_c change of 3.128 MPa.

CONCLUSION

The determination of the density changes in defined processing conditions (p and T) allows to evaluate the real value of $\dot{Q}$. By taking into account the flow induced compressibility of the polymer, based on the $\dot{M}$ value and the changes of the polymer density, the corrected value of $\dot{Q}$ may be determined. On this way the real run of the relationship $\dot{Q} = f(\Delta p_c)$, crucial for the evaluation of basic rheological parameters like shear stress (τ), shear rate ($\dot{\gamma}$), coefficient of the power low (n), and the apparent viscosity (η), may be revealed. Therefore, the deter-

Fig. 5. *Plot of density* (ρ), *at 170 °C, versus total pressure drop* (Δp_c) *for PE-LD/PE-MD blend determined during flow through the dies of L = 30 mm and D equal to (in mm): 1 — 2, 2 — 3, 3 — 4, 4 — 5, 5 — 8, 6 — 10*

mination of the p-v-T relationship, prior to the rheological investigations, seems to be necessary for the accurate evaluation of the $\dot{Q}$ value. Furthermore, the rheological measurements by capillary rheometry, beside taking into account the changes of density, requires also corrections related to the slippage on the wall, as well as the pressure drop in the die entry [30, 31].

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