POLIMERY

Comparison of off-line, on-line and in-line measuring techniques used for determining the rheological characteristics of polyethylene composites with calcium carbonate

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Abstract: The article has presented comparative tests of the rheological characteristics of low-density polyethylene (LDPE) with an addition of calcium carbonate ($CaCO_3$), containing 7, 14, 21 and 28 wt % of filler, respectively. The measurements were carried out by an off-line measuring technique (using a modified dead-weight plastometer), an on-line measuring technique (with a gear pump capillary rheometer) and an in-line measuring technique (with an extruder rheometer). The rheological parameters of the polymeric materials were determined based on the Ostwald-de-Waele power-law model at a temperature of 170 °C. The effect of calcium carbonate addition on the characteristic of operation of each of the employed instruments, the flow curves, the viscosity curves, and the values of power-law index (n) and consistency factor (K) have been determined.

Keywords: polyethylene, calcium carbonate, off-line rheology, on-line rheology, in-line rheology, gear pump, power-law index, consistency factor, viscosity, viscosity curve.

Porównanie technik pomiarowych typu *off-line*, *on-line* i *in-line* stosowanych w ocenie właściwości reologicznych kompozytów polietylenowych z węglanem wapnia

Streszczenie: Przedstawiono badania porównawcze charakterystyk reologicznych kompozytów polietylenu małej gęstości (LDPE) z dodatkiem 7, 14, 21 i 28 % mas. węglanu wapnia ($CaCO_3$). Zastosowano techniki pomiarowe typu *off-line* (zmodyfikowany plastometr obciążnikowy), *on-line* (reometr kapilarny z pompą zębatą) oraz *in-line* (reometr wytłaczarkowy). Parametry reologiczne materiałów polimerowych wyznaczano w temperaturze 170 °C na podstawie modelu potęgowego Ostwalda-de-Waele. Określano wpływ dodatku węglanu wapnia na charakterystykę pracy każdego z zastosowanych urządzeń, przebieg krzywych płynięcia, przebieg krzywych lepkości oraz wartości wykładnika płynięcia (n) i współczynnika konsystencji (K).

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The continuous increase in demands for polymeric materials is one of the major factors determining the growth of studies to develop new and to modify the existing polymers. Each planned modification to a polymer's functional properties (*e.g.,* mechanical, optical, electrical, *etc.*) is very often accompanied by changes in the rheological properties of the polymer. The knowledge of the rheological properties of polymers and their characteristics in flow conditions is the prerequisite for the proper conducting of processing routines, and thus obtaining products of assumed quality. Moreover, the accurate characteristic of the behavior of a polymer during its flow is used in the design of the elements of equipment and the tools of processing machines (such as plasticizing systems, injection molds, extrusion heads); the development of processing strategies; and conducting research in the domain of processing-structure-polymeric material and finished product properties interactions [1, 2]. The assessment of the rheological properties of polymeric materials is made using instruments called rheometers, which provide the capability to determine the values of shear stress and shear rate at an arbitrary point on the device (hence, the term 'multi-point instruments') [3–5]. Depending on the construction and the principle of operation, and consequently the mode of inducing the flow to be examined, we distinguish the following three basic rheometer types: rotary rheometers, capillary rheometers and extensional rheometers [3]. The greatest similarity to the polymer flow occurring in processing tool channels is obtained in measurements conducted using capillary rheometers [6]. Attempts to extend the testing capabilities of capillary rheometers are geared primarily towards using them as measuring instruments directly in technological processes [6–9]. In an analytical approach, depending on the method of installing them relative to the production line, rheometers can be divided into measuring and control devices operating in an off-line, on-line and in-line modes [7, 10–13] (Fig. 1).

The **off-line** analysis of the rheological properties is conducted using stationary rheometers. Measurements are realized on a small amount of material taken from the raw material or product and transported to the mea-
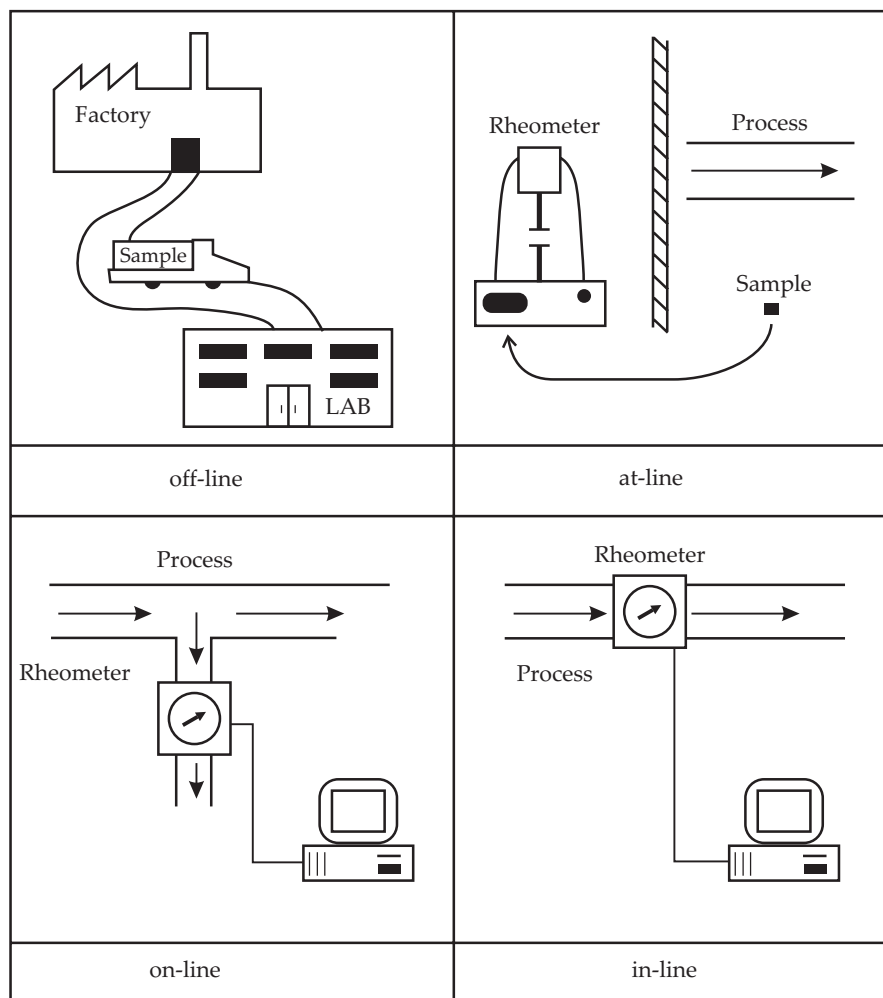

Fig. 1. Schematic configuration of rheometers relative to the technological process: off-line, at-line, on-line and in-line [11, 14]

suring instrument. On account of the need for transporting, and also the type of measurements, there occurs a time shift relative to the processing. A reduction in the time shift is provided by **at-line** measurements, where the measuring instrument is positioned near the technological line [14]. In at-line measurements, less specialized apparatus is normally used; in the assessment of the polymer processing properties, these are mostly plastometers. Off-line and at-line measurements enable an extensive rheological characteristic of polymeric materials to be done; they do not allow, however, the ongoing control of the production process. Such a type of measurement enables the inspection of raw material and product quality and may provide information to make sure that the processing has not been disrupted [7, 14, 15].

Rheological measurements of the **on-line** type provide more engineering information and the capability to control the process. In this case, subjected to analysis is part of the plasticized polymer during the course of processing. They are most often used in the extrusion process [10–12]. Rheometers in on-line measurements can be installed in the plastifying unit of an extrusion machine [3, 16] or in a extrusion head [17]. The installation of the rheometer can be effected by either the bypass [3, 11, 16, 18] or the multipass technique [11, 19]. When installing a rheometer by the bypass technique, an issue can be a large amount of waste forming from the side stream [11]. Nevertheless, in some design solutions, this measurement is distinguished by high flow stability and the possibility of increasing the magnitude of measuring pressure – resulting from the use of a gear pump in the rheometer construction [3]. A rheometer installed by the multipass technique, on the other hand, recycles the tested material that was exposed to different flow/shearing conditions to the main process, which may be of significant importance in the analysis of polymers prone to degradation, as well as to their fraction of the finished product and its quality [11]. Rheological characteristics obtained from on-line measurements are very often compared to those obtained from off-line measurements, which enables the determination of the effect of the technological process and the construction of the plasticizing systems and processing tools on the rheological properties of polymers [11, 18]. The installation of a rheometer in an on-line configuration enables the optimization of the technological process and its partial control to be achieved [3, 7, 11, 18].

The rheological analysis of the whole processed polymeric material is enabled by **in-line** measurements [7, 11]. The rheometer is positioned directly in the processing machine. In an injection process, measurements are conducted in the region of either the injection nozzle [1, 8, 20] or the injection mold [21–23]; in an extrusion process, the testing device is a head of a special design [6, 7, 9, 11, 24]. The mode in which the testing devices are installed enables the determination of the rheological characteristics in the real time of processing, for the 100 % of the

flow. This enables also the control of parameters, such as temperature, pressure, and their optimization, as well as the use of the obtained signals in process control [20, 25]. Advanced design solutions employed in the construction of in-line rheometers enable one to assess the morphology and molecular structure of polymer as it is processed. This is made possible by using microscopic and vision systems [26, 27], near-infrared (NIR) spectroscopy, Raman spectroscopy, as well as ultrasonic systems [28, 29].

By carrying out comparative examinations of the rheological characteristics obtained by the measuring techniques described above, the effect of the processing and the conditions prevailing in the process (on-line and in-line measurements) on the rheological parameters of the polymeric material, as determined using conventional testing instruments (such as off-line rheometers), can be assessed [9, 11, 18, 24, 30]. This effect can be particularly important in the case of composites, either with inorganic fillers (*e.g.* mica) [30] or organic fillers (*e.g.* natural fibers) [8, 9, 24]. The history and conditions of flow in the plasticizing systems (screw systems) of processing machines, as compared to capillary rheometers (piston systems), may significantly influence the filler-polymer interactions and the filler structure (especially wood fibers). This, as a consequence, might lead to a differentiation of the rheological characteristics of the polymeric materials, as obtained in comparable flows. Therefore, the rheological parameters determined in in-line and on-line measurements can be used in relative comparisons, though they usually do not reflect the direct engineering relationships and may deviate from the behavior of polymers under processing conditions [7, 12, 31].

One of the commonly used inorganic powder fillers of thermoplastic polymers is calcium carbonate ($CaCO_3$). Calcium carbonate reduces the cost of the polymeric raw material, while improving some functional properties, such as rigidity, thermal resistance and colorization intensity – especially for products in white color. It is of key importance in the film manufacture industry (enhancing film puncture and tear resistance) and the manufacture of paper-like and water vapor permeable films [32–35]. Earlier publications describe the effect of calcium carbonate addition on the rheological properties of low-density polyethylene (LDPE) in in-line rheological measurements using a cylindrical [7] and a slit dies [36]. The present article discusses comparative examinations of the rheological characteristics of composites with LDPE and calcium carbonate (containing 7, 14, 21 and 28 wt % $CaCO_3$, respectively), as determined in off-line, on-line and in-line measurements.

EXPERIMENTAL PART

Materials

Commercial low-density polyethylene (LDPE) Malen E, FGNX 23-D022 delivered by Basell Orlen Polyolefins (Poland), with a density of d = 0.924 ± 0.002 g/cm³ and

melt flow rate $MFR_{(190\,°C,\,2.16\,kg)}$ = 1.89 ± 0.03 g/10 min, was used as the test material. Used polymer is dedicated for the manufacture of film and containers by the blow extrusion method.

The polymer was filled with commercial calcium carbonate by the trade name of OMYACARB 2-VA, manufactured by Omya Sp. z o.o. (France). The chalk used in the tests was calcite of an average grain size of d_{50} = 3.86 μm and a specific surface area of A_{BET} = 3.5 m²/g [7].

Preparation of polymer composites

Polyethylene composites containing calcium carbonate were produces using a laboratory cold-granulation twin-screw extrusion line – details of the technological line are provided in previous publications [7, 36]. As a result of extrusion, a uniform granulate containing 7, 14, 21 and 28 wt % $CaCO_3$ was obtained, which later on in this text is referred to as K7, K14, K21 and K28, respectively. The composite systems and the polymer (LDPE) making up the matrix of the composites were subjected to assessment for rheological properties using three measuring techniques.

Methodology

The rheological analysis was made by off-line measurements (using a dead-weight plastometer), on-line measurements (using a capillary rheometer with a gear pump) and in-line measurements (using an extruder rheometer).

The rheological analysis of the polyethylene and its composites for all measuring methods was carried out with using the Ostwald-de-Waele power-law model [37]:

$$\tau_w = K \cdot \dot{\gamma}_a^{\,n} \tag{1}$$

where: $\dot{\gamma}_a$ – apparent shear rate, τ_w – shear stress, K – consistency or viscosity coefficient index, n – power-law index.

The shear stress on the measuring die wall was determined from the following equation:

$$\tau_w = \frac{\Delta p \cdot R}{2L} \ \ (Pa) \tag{2}$$

where: Δp – total pressure drop across the capillary die, R – die radius, L – die length.

The apparent shear rate at the wall was evaluated using the equation:

$$\dot{\gamma}_a = \frac{4 \cdot \dot{Q}}{\pi \cdot R^3} \ \ (s^{-1}) \tag{3}$$

where: $\dot{Q}$ – volumetric flow rate.

The true shear rate was obtained by applying the Rabinowitsch correction [5, 38]:

$$\dot{\gamma}_w = \frac{4 \cdot \dot{Q}}{\pi \cdot R^3} \cdot \left(\frac{3n+1}{4n} \right) \ \ (s^{-1}) \tag{4}$$

where: n – power-law index obtained from the slope of the linear plots between $\ln(\tau_w)$ and $\ln(\dot{\gamma}_a)$.

The true shear viscosity was therefore calculated as follows:

$$\eta_w = \frac{\tau_w}{\dot{\gamma}_w} \ \ (Pa \cdot s) \tag{5}$$

In on-line measurements, the volumetric flow rate was determined from the rotational speed of the gear pump – *i.e.*, its characteristic [39]. In off-line and in-line measurements, the value of volumetric flow rate ($\dot{Q}$) was determined based on the mass flow rate ($\dot{M}$), allowing for the changes in polymer and composite densities under given processing conditions [ϱ(*p*, *T*)], as determined from the pVT diagrams (pVT 100 SWO instrument, Germany), from the equation:

$$\dot{Q} = \frac{\dot{M}}{\varrho(p,T)} \ \ (m^3/s) \tag{6}$$

where: $\dot{M}$ – mass flow rate, ϱ – polymeric material density in given processing conditions (pressure *p*, temperature *T*).

Off-line measurements

The off-line rheological measurements were performed using a dead-weight plastometer, model LMI D4004, produced by Dynisco. Variable piston loading was employed in the measurements to bring the plastometer operation closer to the operation of the capillary rheometer.

The calculation procedure whereby the operation of the plastometer can be brought in line with the principle of operation of the capillary rheometer is described in detail in the publications [5, 40, 41]. The magnitude of shear stress was determined from Eq. (2) which, for measurements taken with a plastometer, assumes the following form [5, 40, 41]:

$$\tau_w = \frac{\Delta p R}{2L} = \frac{M \cdot g / \pi R_c^2}{2L} \cdot R \ \ (Pa) \tag{7}$$

where: M – piston load, g – gravitational acceleration, R_c – plastometer cylinder radius (4.775 mm).

The true shear rate was determined from Eq. (4) and the viscosity from Eq. (5), at a measurement temperature of 170 °C. The plastometer die dimensions, in accordance with standard ISO 1133, were as follows: R = 1.0475 mm and L = 8 mm. Seven piston loads were used in the measurements, namely: 1.01, 2.17, 3.78, 5.03, 5.92, 7.09 and 8.70 kg.

On-line measurements

The on-line rheological measurements were carried out using a gear pump capillary rheometer, model CMR4, produced by Dynisco, installed in a single-screw extrusion machine. The on-line capillary rheometer was positioned between the extrusion machine's plasticizing unit (by the bypass installation technique) and the extrusion head (Fig. 2).
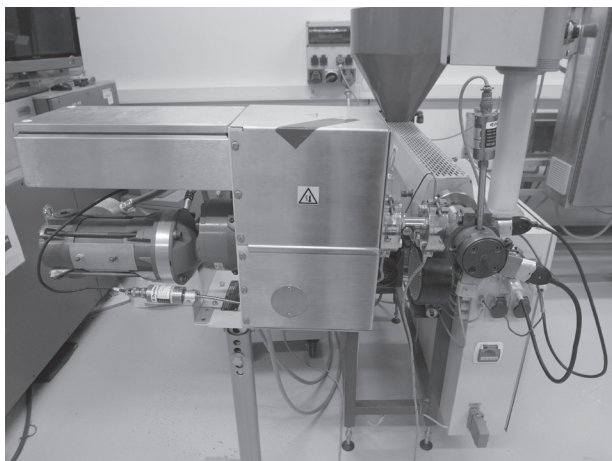
Fig. 2. On-line rheometer with Dynisco gear pump (CMR4 model), mounted in a single-screw extruder

The on-line tests were carried out on a Metalchem single-screw extrusion machine, model W25-30D, of a screw diameter of $d = 25$ mm, with the ratio $l/d = 34$. The temperature setup during measurements at extrusion process was 170 °C. The measurements were taken for a constant extrusion machine screw rotational speed (V_s = const) of 30 rpm, with a variable gear pump rotational speed (V_{gp}) of 10, 20, 30, 40, 50, 60 and 70 rpm, respectively, during flow through a cylindrical die of a radius of $R = 3.275$ mm and a length of $L = 25$ mm.

In-line measurements

In-line rheological measurements were carried out using an extruder rheometer. The function of a rheometer was performed by a Mc ARKON REPIQUET single-screw extrusion machine, model Fairex, with a screw diameter of $d = 25$ mm and an l/d ratio of 24, and a rheological measuring head with interchangeable cylindrical dies. The test stand and the construction of the measuring head are described in detail in previous publications [6, 7, 38]. A cylindrical die with radius $R = 2.5$ mm and length $L = 50$ mm was used in the tests. The rheological extrusion experiments were performed at a temperature of 170 °C (melt polymer temperature) and screw speed (V_s) in the range from 10 to 45 rpm (with the step 5 rpm).

RESULTS AND DISCUSSION

As has been shown in previous publications [7, 36], the addition of calcium carbonate used in the investigation has a direct effect on the processability of low-density polyethylene. This causes, among others, a reduction in the value of a technical processability index, which is the mass flow rate index (*MFR*). It also influences the polymer viscosity, which, as a consequence, contributes to a shift of the curves of the flow and viscosity of produced composites, relative to the pure LDPE [7, 36]. As a result of the addition of $CaCO_3$, an increase in the resistance to flow through the measuring die is noted, which results in variations in the pressure drop recorded in conducted measurements (on-line and in-line). In off-line tests, the measurement is conducted for constant values of Δp resulting from the load applied to the plastometer piston. The test values of Δp and their corresponding values of shear stress (τ_w) resulting from the employed plastometer piston loading, are summarized in Table 1.

Applying the variable plastometer piston loading (from 1.01 to 8.70 kg) produced a flow, in which the total pressure drop was contained in the range from 130.77 to 1131.84 kPa. In those conditions, the shear stress at the plastometer die wall assumed a value from 8.17 to 70.74 kPa.

The assessment of the pressure drop in on-line and in-line rheometers is made directly using a pressure sensor positioned in the region of measuring die channel entry. This type of a technical solution is commonly used in classic capillary rheometers with cylindrical dies [3–5, 42]. In an on-line rheometer, the flow is induced by change in gear pump rotational speed – the total pressure drop and volumetric flow rate are determined by the value of V_{gp} [42]. Figure 3 illustrates the relationship of variations in the total pressure drop as a function of gear pump rotational speed for LDPE and composites with calcium carbonate (K7–K28). The on-line rheometer was characterized by very high flow stability. The symbols in the diagram denote Δp for specific values of V_{gp}, while the function graphs plotted based on the polynomial regression equation are shown with a solid line. The curves of $\Delta p = f(V_{gp})$ are distinguished by a strong monotonicity, as confirmed by the high values of regression coefficients, R^2. For example, for composite K28, the value of the polynomial regression coefficient was 0.999. The flow stability of the employed on-line rheometer results from the specificity of operation of the gear pump. The advantages of gear pumps are often exploited in technological extrusion lines in which, due to product quality demands, high process stability or high extrusion pressure value are necessary. In that case, gear pumps are installed between the plasticizing unit and the head of the extrusion machine [43].

Figure 4 illustrates the relationship of variations in the total pressure drop as a function of extruder rheometer

T a b l e 1. The piston loads (*M*) and corresponding total pressure drop (Δ*p*) and shear stress (τ*w*) variations in rheological measurements (off-line measurements)

M, kg	1.01	2.17	3.78	5.03	5.92	7.09	8.70
Δp, kPa	130.77	282.49	492.35	653.99	770.26	921.99	1131.84
τ_w, kPa	8.17	17.66	30.77	40.87	48.14	57.62	70.74

Fig. 3. Total pressure drop (Δp) *versus* gear pump speed (V_{gp}) for LDPE and composites (on-line rheometer)
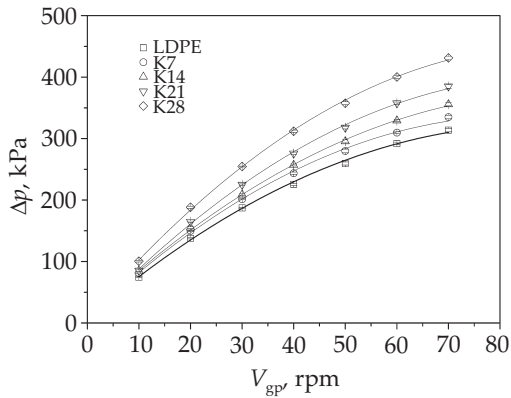

Fig. 4. Total pressure drop (Δp) *versus* screw speed (V_s) for LDPE and composites (in-line rheometer)

screw speed for LDPE and composites with calcium carbonate (K7–K28). The relationships of $\Delta p = f(V_s)$, as determined in in-line measurements, were not characterized by so great monotonicity of their graphs, compared to those determined from on-line measurements. In the case at hand (the in-line measurements), the polynomial regression coefficients assumed smaller values. For example, for a composite containing 14 wt % calcium carbonate, the value of R^2 was 0.993. The lower stability of flow in the in-line rheometer may be the result of the specificity of operation of the screw plasticizing system. And above all, it can be due to technological flow instabilities occurring in the extrusion process [44, 45].

The effect of the calcium carbonate addition on the flow of polyethylene was visible also in variations in $\dot{Q}$, determined in off-line measurements. The addition of $CaCO_3$ reduced the magnitude of composite volumetric flow rate, at the identical piston loading (M = const → Δp = const), with the increase in the filler content of the polymer matrix (Fig. 5). For example, with a piston load of 7.09 kg (Δp = 921.99 kPa), the value of LDPE volumetric flow rate was $1.73 \cdot 10^{-8}$ m³/s. For the identical measurement conditions, for polyethylene containing 21 wt % calcium carbonate (K21), the $\dot{Q}$ value decreased to a level of $1.22 \cdot 10^{-8}$ m³/s. Its should be emphasized that the shear rates obtained in the plastometer (with the applied piston
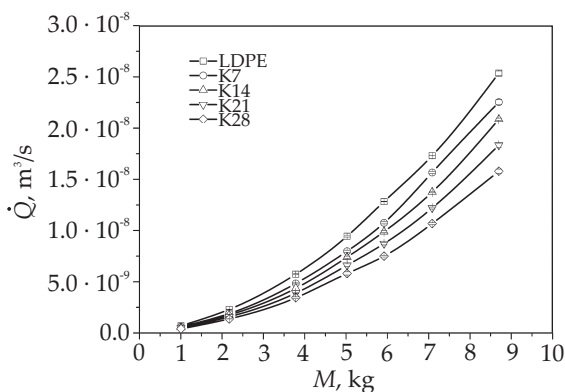
load) are very low and might not be fully reflected, compared to the conditions prevailing in real manufacturing processes. Increasing differentiation in volumetric flow rate as a function of $CaCO_3$ content occurred with the increase in piston loading ($M\uparrow$) or the increase in Δp value.

The diagram of variations in volumetric flow rate as a function of extruder rheometer screw speed (Fig. 6), as compared to Fig. 5, shows a difference in the mode of operation of plasticizing unit used in measuring instruments. The screw plasticizing unit of the in-line rheometer provides a linear increase in $\dot{Q}$ with the increase in V_s. From the position of the $\dot{Q} = f(V_s)$ curves relative to one another, a relationship opposite to that for off-line measurements can be seen. The magnitude of polymer volumetric flow rate increases with increasing filler addition. In the case at hand (in-line measurements), no clear, proportional changes in $\dot{Q}$ are observed with the increase in the $CaCO_3$ content of the composite. Similar relationships, for the test materials under analysis, were obtained during measurements conducted using an in-line extruder rheometer using a rheological head with a flat measuring channel [36].

The specificity of operation of the on-line rheometer did not allow the determination of the effect of calcium carbonate addition on the volumetric flow rate. Measurements were conducted for constant values of gear pump rota-

Fig. 5. Volume flow rate ($\dot{Q}$) *versus* piston loads (M) for LDPE and composites (off-line rheometer)

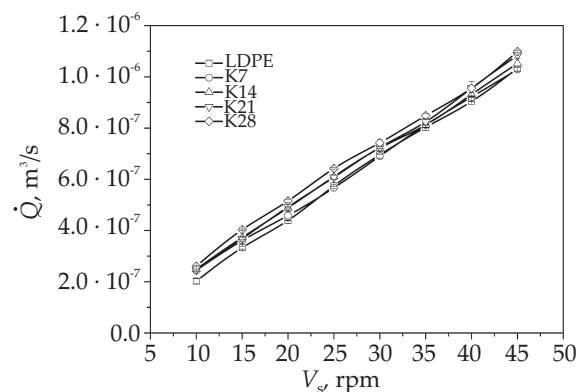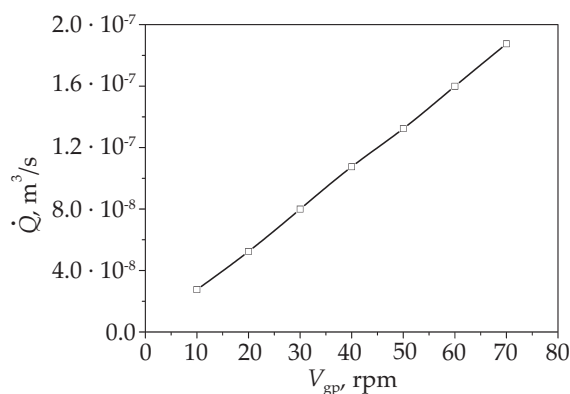**Fig. 6. Volume flow rate ($\dot{Q}$) *versus* screw speed (V_s) for LDPE and composites (in-line rheometer)**

Fig. 7. **Volume flow rate** ($\dot{Q}$) ***versus*** **gear pump speed** (V_{gp}) **for LDPE and composites (on-line rheometer)**

Fig. 8. **Ranges of apparent shear rate** ($\dot{\gamma}_a$) **for in-line, on-line and off-line measurements**

tional speed (see the on-line measurement methodology), which, as a consequence, enabled the determination of the rheological properties of polymers for constant values of $\dot{Q}$ in the range from $2.76 \cdot 10^{-8}$ m³/s to $1.88 \cdot 10^{-7}$ m³/s. The diagram of variations in volumetric flow rate as a function of gear pump rotational speed, which was used in on-line rheometer tests, is shown in Fig. 7.

The determined characteristic of the employed devices, representing the relationships of variations in the total pressure drop and volumetric flow rate in the adopted rheometer operation ranges (M, V_{gp}, V_s), helped to determine the magnitudes of shear stress and shear rate during flow in measuring die channels. Figure 8 collates graphically the $\dot{\gamma}_a$ ranges obtained during flow through the rheometer die in off-line, on-line and in-line measurements. For the off-line and in-line rheometers, the measuring ranges of $\dot{\gamma}_a$ showed also a differentiation, resulting from the filler content of the composite. Therefore, for these two measuring methods (off-line and in-line), the limiting values of apparent shear rate are shown. As indicated by the graph in the figure below, different ranges of apparent shear rate have been obtained for each of the measuring techniques. Loading of the plastometer piston (off-line measurements) enabled the rheological parameters to be determined under the conditions of shear rate from 0.51 to 32.3 s⁻¹. The smallest $\dot{\gamma}_a$ value was obtained for the flow of composite K28, while the greatest value of $\dot{\gamma}_a$ occurred during the flow of unmodified polyethylene. The on-line measurements were conducted in an identical apparent shear rate range, *i.e.*, from 1.0 to
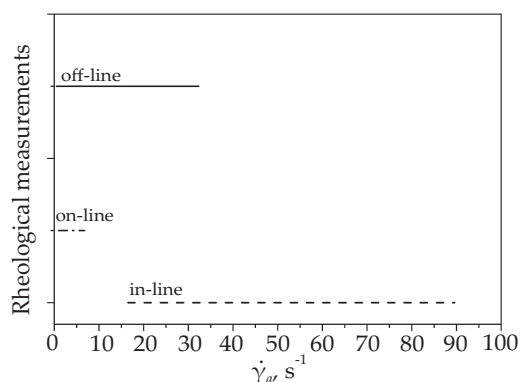
6.8 s⁻¹, for all polymeric materials. The largest measuring shear rate range was obtained for measurements conducted by the in-line technique. In that case, the $\dot{\gamma}_a$ value was contained in the range from 16.5 to 89.6 s⁻¹.

For unmodified polyethylene and all composite materials, flow curves were plotted, based on which (using the power-law model) the viscosity variations resulting from the calcium carbonate addition were determined. The rheological parameters (n and K) determined based on the Ostwald-de-Waele power-law model are summarized in Table 2. For each of the measuring techniques, different power-law index and consistency factor values were obtained. Regardless of the technique used, the value of the consistency factor, constituting a measure of fluid viscosity [3, 5, 7, 42], grew with increasing calcium carbonate content of LDPE. The largest values of K occurred during the flow of a given polymeric material in the die of the in-line rheometer, while the smallest, during flow in the on-line rheometer die. These changes should be reflected in the behavior of the viscosity curves, which will be presented later on in this article.

The impact of the measuring technique on the rheological parameters became also visible in variations in power-law index magnitude. Regardless of the type of conducted measurement, n for LDPE would assume a value characteristic of pseudo-plastic fluids ($n < 1$) [46]. In each case, the n value was also contained in a value range characteristic of thermoplastic polymers, *i.e.*, from 0.19 to 0.80 [3, 5, 7, 42]. The power-law index magnitude is influenced by the material properties of polymer (such

T a b l e 2. **Power-law constants for composites of low density polyethylene with calcium carbonate determined in off-line, on-line and in-line measurements**

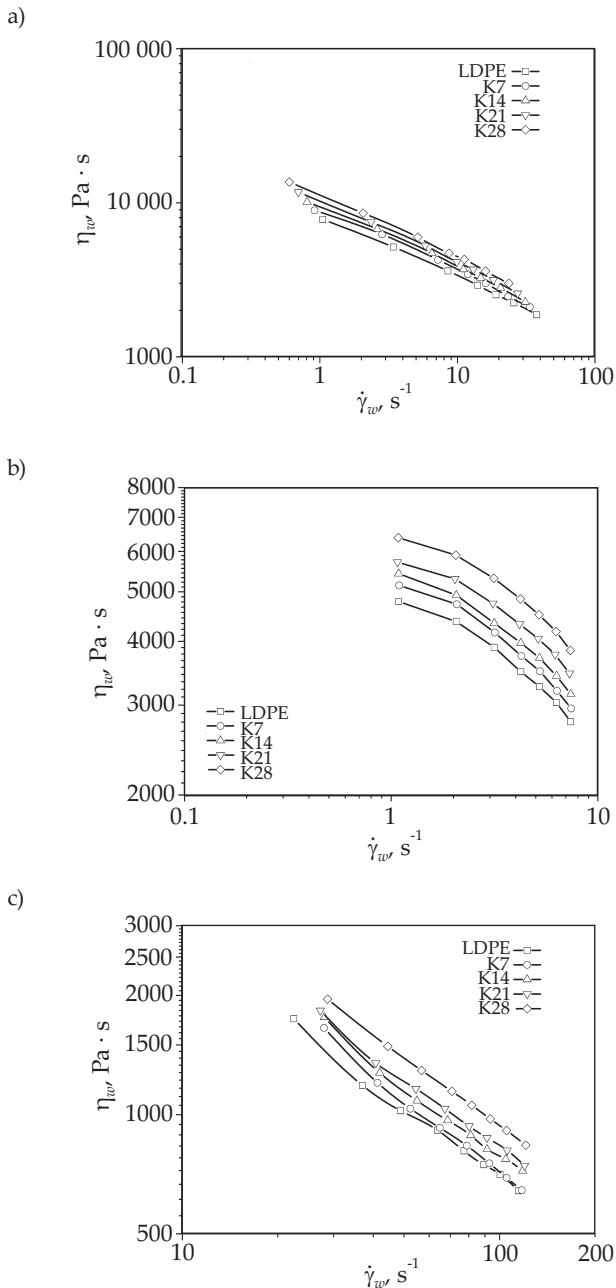| Polymer materials	off-line		on-line		in-line	
	n	K, Pa · sⁿ	n	K, Pa · sⁿ	n	K, Pa · sⁿ
LDPE	0.602	9007	0.744	5250	0.409	11 873
K7	0.595	10 003	0.730	5757	0.384	13 959
K14	0.592	10 663	0.742	5960	0.398	14 203
K21	0.590	11 499	0.779	6078	0.412	14 986
K28	0.589	12 488	0.753	7107	0.416	15 601

a)

b)

c)

Fig. 9. Shear viscosity (η_w) *versus* true shear rate ($\dot\gamma_w$) for: a) off-line, b) on-line, c) in-line measurements

as molecular mass, the filling ratio), as well as flow conditions (shear rate, shear stress, temperature) [3, 7, 42, 47]. As shown by literature information, the magnitude of the power-law index of thermoplastic polymer composites decreases with increasing filler content of the matrix, thus enhancing their pseudo-plastic character [48, 49]. The data summarized in Table 2 confirms this type of relationship only for the flow in the off-line rheometer's die. For the two remaining measuring techniques, no decreasing trend is observed in power-law index magnitude with the increase in the filler content of LDPE.

By determining the flow index value, a correction to the apparent shear rate was made by allowing for the Rabinowitsch correction, and thus the true viscosity curves were determined [5, 38]. Figure 9 shows the

graphs of true viscosity variations as a function of true shear rate for LDPE and its composites (K7–K28), as determined using the off-line (Fig. 9a), on-line (Fig. 9b) and in-line (Fig. 9c) measuring techniques.

For all the measuring methods employed in the investigation, the viscosity curve behaviors were obtained, which were characteristic of Newtonian pseudo-plastic liquids – *i.e.*, exhibiting shear thinning [3, 5, 38]. An identical effect of the calcium carbonate addition on the polyethylene viscosity is also observed, regardless of the measuring technique used. The increase in composite filler concentration causes the viscosity curves to shift towards greater values of η_w. The most distinct effect of the calcium carbonate addition on the polymer viscosity is observed for measurements taken with the on-line technique. These shifts are also the most proportional. The monotonicity of variations in $\dot Q$ and Δp, occurring in both off-line and on-line measurements, has translated into the behaviors of the viscosity curves. The $\eta_w = f(\dot\gamma_w)$ curves for these two measuring techniques are distinguished by high uniformity of variation, compared to in-line measurements. The juxtaposition of the viscosity curves in Fig. 9 shows differences in shear rate ranges obtained for individual measuring techniques and their effect on viscosity. The highest viscosity was exhibited by polymers in off-line measurements, that is in the conditions of the lowest shear rate magnitudes. By contrast, the lowest viscosity was shown by polymeric materials under in-line measurement conditions, that is with a true shear rate of approx. 115 s⁻¹. For two measuring techniques, the assessment of viscosity was successfully made in overlapping shear rate ranges. This is true for off-line and on-line measurements in the $\dot\gamma_w$ range from approx. 1 s⁻¹ to approx. 8 s⁻¹. Under identical shear rate conditions, higher viscosity values are shown by polymeric material in off-line measurement conditions, compared to on-line measurements. For example, for a shear rate of 2.1 s⁻¹, the viscosity of composite K28 in off-line measurements was 8571 Pa · s, while in on-line measurements 5900 Pa · s. This difference may be due to the impact of the construction of the plasticizing unit of rheometers used and different flow conditions prevailing in them. So great discrepancies in viscosity confirm the view that off-line measurements do not reflect the behavior of polymers under actual engineering conditions and may therefore considerably deviate from them [7, 12]. Therefore it seems justifiable to conduct testing using rheological measuring techniques that are able to characterize polymeric material as it is processed (*i.e.*, on-line and in-line measurements).

CONCLUSIONS

– The tests discussed in this article, which were carried out to compare the rheological characteristics of polyethylene and calcium carbonate-filled polyethylene composites, as determined using three different testing techniques, have shown a direct effect of the employed measuring techniques on the obtained testing results. As has been

demonstrated, each of the measuring techniques (off-line, on-line, and in-line) has some limitations that may have an effect on obtained characteristics. The lack of the capability to directly measure the pressure drop in the upgraded dead-weight plastometer (off-line measurements) does not allow the effect of filler addition on variations in Δp to be determined during flow through the plastometer die. Using an on-line gear pump rheometer allows testing to be conducted for constant volumetric flow rate magnitudes, which does not enable the determination of the effect of calcium carbonate addition on the process efficiency. The addition of calcium carbonate causes an increase in polymer viscosity as a function of filler quantity. This effect is observed in the behaviors of viscosity curves determined by either of the employed measuring techniques. This does not translate explicitly into variations in volumetric flow rate. In off-line measurements, volumetric flow rate decreases with increasing $CaCO_3$ concentration. In in-line measurements, the opposite relationship occurs – $\dot{Q}$ increases with increasing calcium carbonate content of composite. The performed tests have also demonstrated that the flow exponent does not represent a constant material quantity, but instead depends on flow conditions and may change as a result of filler addition.

– The comparison of the viscosity value of examined composites for off-line and on-line measurements, under identical shear rate conditions, has shown differences in η_w as determined using each of the measuring techniques. Its should be emphasized, that such comparisons require a high degree of convergence of experimental parameters to be maintained. In the techniques being compared, different measuring dies were employed, which might have contributed to increasing the differences in the values of viscosities examined.

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W kolejnym zeszycie ukażą się m.in. następujące artykuły:

R. Wyrębiak, E. Olędzka, M. Sobczak – Dendrymery domino jako innowacyjne nośniki substancji leczniczych

M. Adamczak, G. Kamińska, J. Bohdziewicz – Preparowanie, struktura i właściwości membran nanokompozytowych wytwarzanych metodą inwersji faz

M. Osińska-Broniarz, A. Martyła, M. Kopczyk – Polimerowe materiały separacyjne w magazynach energii do e-mobilności

F. Ścigalski, A. Obrębowska – Merkaptoalkoksy-tioksantony jako nowe fotoinicjatory polimeryzacji rodnikowej (*j. ang.*)

P. Biniecka, M. Pieńkowska, A. Opalska – Innowacyjna metoda otrzymywania polioli poliestrowych przeznaczonych do produkcji spodów obuwniczych

M. Wróblewska, J. Słyż, K. Winnicka – Właściwości reologiczne i mechaniczne hydrożeli, zawierających siarkę jako modelową substancję leczniczą, sporządzonych z wykorzystaniem różnych polimerów (*j. ang.*)