The influence of calcium carbonate and its modifications on the extrusion process and selected properties of polypropylene cast films

Arkadiusz Kloziński[1)*)] (ORCID ID: 0000-0002-2025-699X), **Małgorzata Szczepańska**[1)],
Paulina Jakubowska[1)] (0000-0002-8638-1216), **Bronisław Samujło**[2)] (0000-0002-2200-8471),
Mateusz Barczewski[3)] (0000-0003-1451-6430), **Grzegorz Lota**[4)] (0000-0002-4329-9423)

DOI: https://doi.org/10.14314/polimery.2022.10.6

Summary: The effect of unmodified and stearic acid-modified calcium carbonate (5, 10, 20 and 30 wt%) on selected properties (tensile strength, puncture resistance, haze and gloss) and processability of polypropylene films (MVR, extensional viscosity) was investigated. The composites were obtained in the twin-screw extrusion process with cold granulation, and the films in the single-screw extrusion process, using a flat die head (so-called cast films) and a chill roll type cooling and pull-back device. It has been shown that stearic acid is an effective modifier of polypropylene processing properties both under shear and tensile flow conditions (lower extensional viscosity of films containing modified calcium carbonate).

Keywords: polypropylene, calcium carbonate, polymer composites, extrusion, films, tensile strength, extensional viscosity, haze, gloss.

Wpływ węglanu wapnia i jego modyfikacji na proces wytłaczania oraz wybrane właściwości użytkowe wylewanych folii polipropylenowych

Streszczenie: Zbadano wpływ dodatku 5, 10, 20 oraz 30 % mas. niemodyfikowanego i modyfikowanego kwasem stearynowym węglanu wapnia na wybrane właściwości użytkowe (wytrzymałość na rozciąganie, odporność na przebicie, zamglenie, połysk) i przetwórcze folii polipropylenowych (MVR, lepkość wzdłużna). Kompozyty otrzymano w procesie dwuślimakowego wytłaczania z granulacją na zimno, a folie w procesie jednoślimakowego wytłaczania, przy użyciu głowicy płaskiej (tzw. *cast films*) oraz urządzenia chłodząco - odciągającego typu *chill roll*. Wykazano, że kwas stearynowy jest efektywnym modyfikatorem właściwości przetwórczych folii polipropylenowych zarówno w warunkach przepływu ścinającego, jak i rozciągającego (mniejsza lepkość wzdłużna folii zawierających modyfikowany węglan wapnia).

Słowa kluczowe: polipropylen, węglan wapnia, kompozyty polimerowe, wytłaczanie, folie, wytrzymałość na rozciąganie, lepkość wzdłużna, zamglenie, połysk.

The plastics processing uses a wide range of materials and methods, which enable the manufacture of products indispensable in a contemporary human everyday life. The constant progress creates the necessity for conducting research aimed at improving the properties of polymeric materials and developing techniques for their processing. In addition to increasing the efficiency of technological processes, research and development work also extends the range of polymers' applications – achieved primarily by developing new polymers or modifying the

---

[1)] Institute of Chemical Technology and Engineering, Faculty of Chemical Technology, Poznan University of Technology, Berdychowo 4, 60-965 Poznan, Poland.

[2)] Department of Technology and Polymer Processing, Faculty of Mechanical Engineering, Lublin University of Technology, Nadbystrzycka 36, 20-618 Lublin, Poland.

[3)] Institute of Materials Technology, Faculty of Mechanical Engineering and Management, Poznan University of Technology, Piotrowo 3, 61-138 Poznan, Poland.

[4)] Institute of Chemistry and Technical Electrochemistry, Faculty of Chemical Technology, Poznan University of Technology, Berdychowo 4, 60-965 Poznan, Poland.

[*)] Author for correspondence: arkadiusz.klozinski@put.poznan.pl

existing [1]. Despite the development and increased production of engineering polymers, increased demand for the manufacture of polyolefins, including polypropylene (PP), is still observed. The increased demand for materials produced at a relatively low cost, and at the same time characterized by many desirable features that can be easily modified and recycled, causes an increase in the demand for polypropylene synthesis [1–4]. The ease of polypropylene modifying and its service properties has made it one of the most often used polymers in the packaging industry – especially for film packaging [4]. Polypropylene is characterized by good processability in the extrusion process [5], thanks to which the obtained films show high weldability [4, 6]. Moreover, PP films are characterized by good mechanical [5, 7] and barrier properties (e.g., water vapour) [4,7], which predestine them to be successfully used in the food industry. By applying the appropriate conditions of processing [8,9] or modification by using additives [10–12], polypropylene films can exhibit varying transparency/haze and gloss. Calcium carbonate ($CaCO_3$), due to unique properties and natural origin, is a filler widely used in the plastic processing [13-16]. Thanks to its good covering power, calcium carbonate is also used in the manufacture of film products, especially in white colour [17], and products of special properties, such as paper-like films [18] or vapour-permeable films [19]. As a powder filler, calcium carbonate tends to form agglomerative [20]; therefore, to improve its homogenization degree in the polymer matrix and enhance interactions at the polymer–filler interface, its surface is modified using, among others, stearic acid [15, 16, 21, 22]. The addition of a filler or its modified form, aside from the expected improvement in specific properties, is very often associated with a spontaneous impairment of other characteristics; for example, while improving the mechanical properties of a composite, its processability is worsened [23]. In most instances, the modification of polymer by adding a filler has the effect of changing its processing/rheological properties [14–16, 24], which directly affects the extrusion process, e.g., by changing its efficiency [14, 25, 26]. The knowledge of the composites behaviour under extrusion conditions enables modification of the technological process by the appropriate setup parameters selection, which will result in obtaining products of strictly planned used properties [15, 27, 28]. For this reason, it becomes essential to test polymer composite materials at every stage of their functioning in the production and post-production cycles.

So far, to the best of the authors' knowledge no research in the literature would comprehensively address the issue of the calcium carbonate addition and modification effect on the course of the extrusion process and the polypropylene films properties. Therefore, the presented study has attempted to analyze the processability of PP containing, respectively, 5, 10, 20, and 30 wt% of unmodified and modified $CaCO_3$ and the course of their extrusion process in the aspect of flow resistance and efficiency. Key film properties such as tensile strength, puncture resistance, haze and gloss were also analyzed. Obtained films were also tested under extensional flow conditions to assess their extensional viscosity, which plays a significant role in forming film products.

EXPERIMENTAL PART

Materials and films preparation

Moplen HP456J isotactic polypropylene (iPP) produced by Basell Orlen Polyolefins Poland, with a density of 0.893 g/m^3 (23°C) and a melt flow rate (MFR; 2.16 kg; 230°C) of 3.3 g/10 min, was used as polymeric matrix.

Commercial calcium carbonate supplied by Calcit d.o.o. (Slovenia) was used as a filler. The same filler in two variants, i.e., unmodified (CalPlex Extra) and modified with stearic acid (CalPlex ExtraT), was used in the tests. Table 1 shows the main physicochemical properties of the fillers used. The analysis of the crystallographic structure of the filler used in the tests revealed that it was calcite [16]. As shown by $CaCO_3$ surface examination, the modification of the calcium carbonate with stearic acid reduced the filler-specific surface area by 1.396 m^2/g.

The iPP modification was carried out in the extrusion process with cold granulation. A twin-screw extruder, model EH16.2D, by Zamak Mercator (Poland), with a screw diameter of 16 mm and L/D ratio of 40 was used. The composites containing 5, 10, 20, and 30 wt% of unmodified or modified calcium carbonate were obtained. In the further part of the article, composites containing unmodified $CaCO_3$ (CalPex Extra) will be designated as UC5, UC10, UC20, and UC30; while composites containing modified $CaCO_3$ (CalPex ExtraT) as MC5, MC10, MC20, and MC30.

The cast film line (Fig. 1a) was composed of a single-screw extruder, model Fairex (manufactured by Mc Neil Arkon Repiquet) with a screw diameter of 25 mm, and a screw length-to-diameter ratio of 24; a flat die (high – 0,5 mm; wide – 120 mm); and a cooling system. As the cooling system, a *chill-roll*-type pull-back system was used, which consisted of a rotating 0.265 m - diameter cooling cylinder and a pull-back roll. The cooling cylinder temperature was 80°C. The flat die temperature for all polymer materials was 230°C. The pull-back system speed (V_{pbs}) was selected to obtain cast films with a thickness of approx. 120 μm. The composition of the tested films is summarized in Table 2.

Table 1. Basic physicochemical properties of fillers

Properties	CalPlex Extra	CalPlex ExtraT
Crystallographic form	calcit	calcit
Surface modification	–	stearic acid
Density, g/cm^3	2.70	2.70
Particle size distribution (d_{50}), μm	0.75-0.9	0.75-0.9
Specific surface area (A_{BET}), m^2/g	9.210	7.814

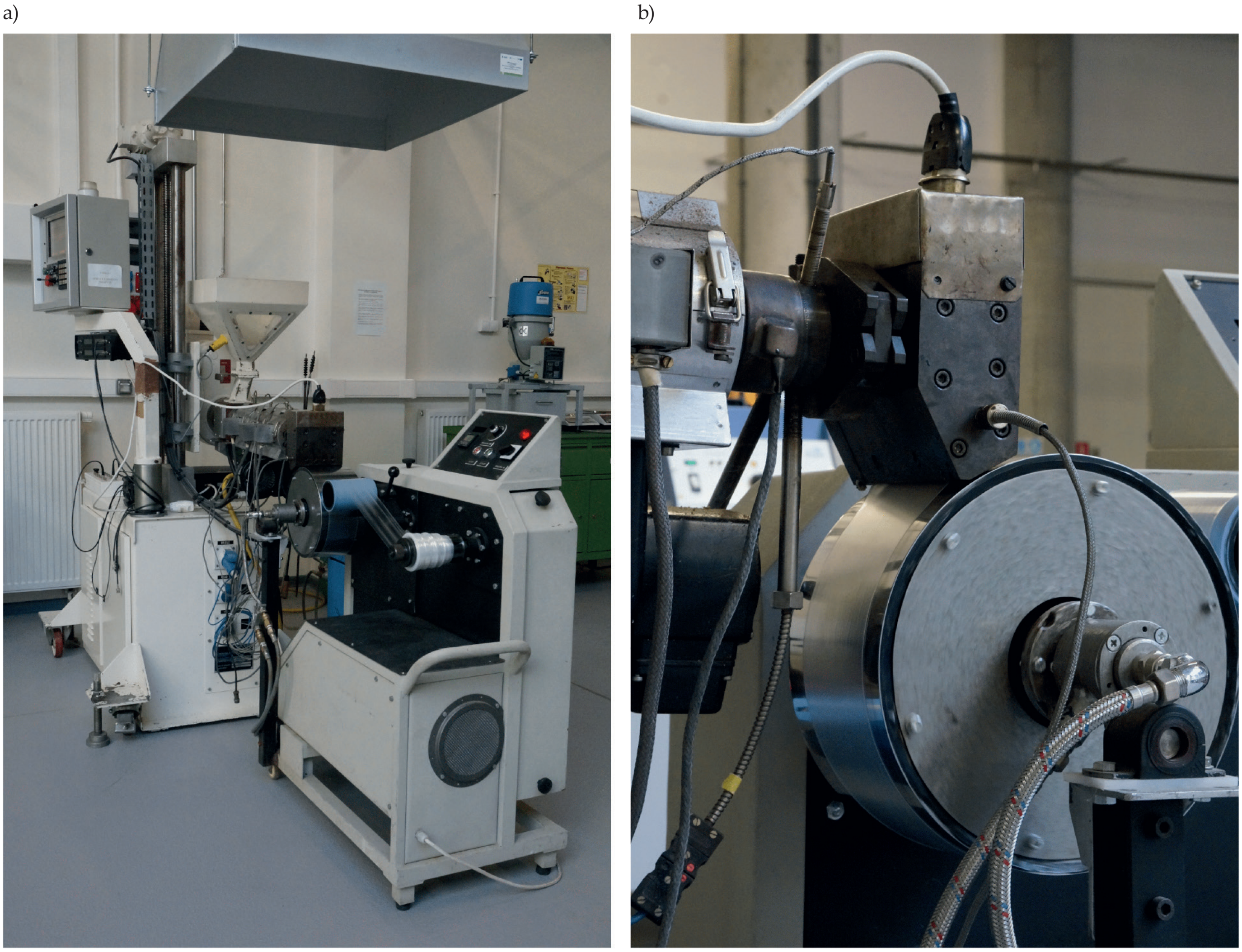

Fig. 1. The cast film line (a), the flat die with a chill-roll system (b)

Methods

The effect of the calcium carbonate addition on the melt volume-flow rate (MVR) index, which constitutes a technical measure of the thermoplastic polymers processability, was determined. The measurements were taken using a Dynisco plastometer, model LMI 4004, according to the ISO 1133 standard. The measurement temperature was 230 ± 0.5°C, and the piston loading was 2.16 kg.

Table 2. The composition of investigated films

Symbol	Content in wt%	
	PP	unmodified $CaCO_3$
PP	100	0
UC5	95	5
UC10	90	10
UC20	80	20
UC30	70	30
	PP	modified $CaCO_3$
MC5	95	5
MC10	90	10
MC20	80	20
MC30	70	30

For the flat die, the characterization of the extrusion process, which included the determination of the relationship between the screw speed (V_s = 25 rpm), the pressure (p), and the volumetric flow rate ($\dot{Q}$) was made. The pressure changes were measured in the last zone of the extruder plasticizing system - before the filter. The value of $\dot{Q}$ was determined based on the mass flow rate ($\dot{M}$ in kg/s). The mass flow rate was determined by cutting off the extrudate every 30 seconds with five samples. The density of the polymers materials under processing conditions was determined from the pVT diagrams that were determined for the PP and all composites used, at a temperature of 230°C and in the pressure range from 0.1 to 150 MPa, using a pVT100 SWO instrument (Germany). From the pVT diagram, the polymer density under flow conditions was read out for pressures obtained in the extrusion process – from the equation $p = f(V_s)$. The full procedure for determining changes in polymer density under real conditions of the extrusion process is described in the previous publication [29]. The volumetric flow rate was determined from the equation below:

$$\dot{Q} = \frac{\dot{M}}{\varrho(p,T)} \ (\mathrm{m^3/s}) \qquad (1)$$

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

Extensional rheological measurements were performed on a SER-2 Universal Testing Platform (Xpansion Instruments LLCd), mounted in the Anton Paar MCR 301 rheometer. The construction, operation principle, and method of determining the extensional viscosity using the SER attachment are described in publications by Sentmanat [30,31] and earlier publications [18]. The extensional viscosity was calculated according to the following formula [30]:

$$\eta_E = \frac{F(t)}{\dot{\varepsilon}_H A(t)} \ (\mathrm{Pa \cdot s}) \qquad (2)$$

where: *F*(*t*) is the instantaneous extensional force at time *t* exerted by the sample as it resists stretch as determined from the measured torque signal (*T*), $\dot{\varepsilon}_H$ is the Hencky strain rate, *A(t)* is instantaneous cross-sectional area.

For a constant drive shaft rotation rate, Ω, the Hencky strain rate (extensional rate) applied to the sample specimen was determined from the following equation:

$$\dot{\varepsilon}_H = \frac{2\Omega R}{L_0} \ (\mathrm{s^{-1}}) \qquad (3)$$

where *R* is the radius of the equal dimension wind-up drums, and L_0 is the fixed, unsupported length of the specimen being stretched, equal to the centerline distance between the active and pasive drums (12.725 mm) [30]. The extensional viscosity measurements (η_E) were taken at a temperature of 165 °C and for a strain rate (Hencky strain rate) of $\dot{\varepsilon}_H = 0.1\ \mathrm{s^{-1}}$.

The maximum strength and elongation at break were tested through tensile testing. The tensile tests were performed as per ISO 527 1-3 with a Zwick/Roell Z020TH AllroundLine universal testing machine (ZwickRoell GmbH & Co. KG, Ulm, Germany). The tests used a measuring head with a nominal force of 100 N. The test specimens were prepared in the form of 15 mm wide strips cut from the film in the direction of extrusion – machine direction (MD, 0°). The tensile tests were conducted at 100 mm/min cross-head speed.

Film puncture testing was performed in accordance with the standard ASTM D 4649 using a universal testing machine (Zwick/Roell Z020TH AllroundLine) with a head of a nominal force of 100 N, equiped with a special needle attachment with an indenter diameter of 0.8 mm. Test specimens were prepared as 20 mm – wide strips punctured with a needle of standardized dimensions while recording the elongation force *F = f(*Δ*l)*. The tests were conducted at a cross-bar travel speed of 100 mm/min. The puncture resistance of the film was determined following the standard as mentioned earlier from the formula below:

$$\frac{F}{d} \ (\mathrm{N/m}) \qquad (4)$$

where: *F* – the force needed for film puncture *d* – film thickness.

The haze of the films measurements were also carried out using a Haze Meter HM-150 apparatus from Murakami Color Research Laboratory. The material haze was assessed in accordance with the PN-84/C-89100 standard. The haze value was calculated from the equation shown below:

$$H = \frac{\tau_d}{\tau} \cdot 100\% \ (–) \qquad (5)$$

where: *H* – haze, τ_d – dispersed light transmission coefficient [/], τ – total light transmission coefficient [/].

Film gloss was also measured using a Rhopoint glossmeter, model Novo-Gloss Lite 20/60°. The 60° geometry was used in the examination.

The surface of film samples was analyzed using the VHX-7000 series (Keyence) digital microscope. All photos were prepared using 500× magnification of samples.

RESULTS AND DISCUSSION

Extrusion process characteristics

A filler addition to a polymer matrix often changes its rheological and processing properties [14–16]. As it has been demonstrated in a previous publication [16], the application of calcium carbonate (modified or unmodified) directly influences the value of the polypropylene melt mass-flow rate (MFR). The obtained melt volume-flow rate (MVR) values correlate with the previously discussed relationship between changes in mass-flow rate induced by adding $CaCO_3$. The MVR values determined for PP and composites containing unmodified and modified calcium carbonate, respectively, are shown in Table 3 below. The changes in MVR noted for polymer composites (MC5, MC10, MC20, and MC30) confirmed a double function of stearic acid, which acted not only as a compatibilizer [21] but also as a slip agent [22]. In the whole range of applied concentrations of the modified filler, composites with better processability were obtained, as evidenced by a higher MVR compared to PP. The increase in the modified calcium carbonate content of the polymer matrix results in a drop in the value of the melt volume-flow rate. Composites containing modified $CaCO_3$ were characterized by better processability, as evidenced by a higher MVR. A specific change in MVR values occurred for polypropylene filled with unmodified $CaCO_3$. In reference to previously published results concerning polyethylene composites with unmodified calcium carbonate [15, 31], a decrease in the processability of composites containing chalk with the increase in its content might be expected. The processability of the investigated composites improves at low contents of the filler (UC5 and UC10), which increases the value of the melt volume-flow rate. Similar results were also noted by other researchers, who explained the processability improvement for small calcium carbonate concentrations by the action of the filler similar to that of a "lubricant" causing a slip, which is characteristic of fillers with small particle size [33, 34]. After exceeding a certain limiting value of filler content, a decrease in processability is observed [33], which for the calcium carbonate used occurred starting from its content of 20 wt% (UC20). The smallest MVR value was exhibited by a composite containing 30 wt% (UC30). The noted variations in melt volume-flow rate translated directly into performance of the extrusion process. For all polymeric materials, at an assumed constant screw rotational speed (25 rpm), different values of pressure in the extruder's plasticizing system (upstream the filter), and thus different flow resistance values in the flat die head were obtained. The variations in pressure (p) and melt volume-flow rate ($\dot{Q}$), summarized in Table 3, coincide with the relationships described in the previous publication [16], where curves characterizing the extrusion process are provided, namely: $p = f(V_s)$ and $\dot{Q} = f(V_s)$, during the flow of the composites under discussion through the cylindrical dies within the range of screw rotational speed from 10 to 45 rpm. For extrusion using a flat die head, relationships for p variations resulting from the type of filler and its content are observed, similar to the variations in melt volume-flow rate. The lowest flow resistance occurred when extruding composites containing modified calcium carbonate. In the entire range of filler concentrations used, the value of p was smaller than for unfilled polypropylene (p = 3.67 ± 0.008 MPa). The increase in modified filler content of the polymer caused an increase in pressure from 2.73 MPa for composite MC5 to 4.12 MPa for composite MC30. When extruding composites containing unmodified calcium carbonate, various changes in occurring flow resistances are observed. A filler addition of up to 10 wt% causes a drop in flow resistance ($p\downarrow$). Compared to unfilled PP, an increase in flow resistance ($p\uparrow$) occurs at $CaCO_3$ content amounting to 20 and 30 wt%, respectively. From the extrusion technology point of view, in addition to flow resistance, also the process yield is important [35]. As indicated by the data in Table 3, under the conditions of constant screw rotational speed (V_s = 25 rpm), both the addition and modification of the filler have caused changes in polypropylene volumetric flow rate ($\dot{Q}$). The highest efficiency of the extrusion process was found in the case of PP; while the lowest for a composite containing 5 wt% modified calcium carbonate (MC5). The value of the volumetric flow rate increased ($\dot{Q}\uparrow$) as a function of the modified filler content. For composites containing unmodified calcium carbonate, the most significant value of $\dot{Q}$ was obtained for composite UC30 (30 wt% $CaCO_3$), while the smallest for a composite containing 5 wt% of filler (UC5). When comparing the extrusion process efficiency as dependent on the type of filler used, it was found that a higher volumetric flow rate occurred during processing composites containing modified calcium carbonate in each of the concentrations under consideration. As shown by the variations in flow resistance and volumetric flow rate, the application of calcium carbonate addition and calcium carbonate modification directly affects the extrusion process's performance. In practice, it creates the necessity for changing the setup parameters of the technological extrusion line. The change in volumetric flow rate translates directly into a change in the linear velocity of the polymer stream flowing out from the flat die head (V_{ps}). In the experiment carried out, the values of V_{ps} (see Table 3) were also determined for all test materials from equation [36]:

$$V_{ps} = \frac{\dot{Q}}{S} \tag{6}$$

where: S – flat die head cross-section [m^2].

Obtaining film of the preset thickness (~120 μm) for all test materials at a constant screw rotational speed required changing of the pull-back system speed (V_{pbs}). Polypropylene film was extruded at the highest value of V_{pbs} (0.075 m/s). The lowest pull-back system speed was used when extruding UC5 film. For composites containing modified calcium carbonate, a linear increase in V_{pbs} (from 0.061 to 0.065 m/s) can be noticed with the increase in the quantity of the filler. For composites containing unmodified $CaCO_3$, the linear speed of the pull-back system was increased within two filler concentration ranges, i.e., within the range from 5 to 10 wt% – from 0.048 to 0.060 m/s and within the range from 20 to 30 wt% – from 0.058 to 0.068 m/s. The ratio of pull-back system speed to polymer stream velocity (V_{pbs}/V_{ps}) was contained in the range from 4.45 to 4.58, which might be caused the produced films to have a longitudinal orientation [6,37].

The results show that the addition of calcium carbonate influences the polypropylene processability (in this case, MVR), which directly results in a change in the flow resistance in the extruder and the flat die head, as well as a change in the efficiency of the extrusion process. This effect varies, depending on whether modified or unmodified calcium carbonate is used. As indicated by the values of the other process setup parameters (V_{pbs} and V_{ps}), variations in MVR should be accounted for in the setups of technological lines and the economic balances of the film extrusion process.

Extensional viscosity

So far, there has been no information in the relevant literature and in industry publications on the effect of the calcium carbonate addition and its modification on the changeability in the rheological parameter, which is the extensional viscosity of PP film. Therefore, the

Table 3. The melt volume-flow rate (*MVR*) of polymers materials and extrusion line process parameters (p, $\dot{Q}$, V_{ps}, V_{pbs}, V_{pbs}/V_{ps})

Materials	$MVR_{(230;\ 2.16)}$ cm³/10 min	p, MPa	$\dot{Q}$, m³/s	V_{ps}, m/s	V_{pbs}, m/s	V_{pbs}/V_{ps}
PP	4.450 ± 0.037	3.67 ± 0.008	$9.90 \times 10^{-7} \pm 1.14 \times 10^{-10}$	0.0165	0.075	4.45
UC5	5.119 ± 0.105	2.80 ± 0.010	$6.43 \times 10^{-7} \pm 1.04 \times 10^{-10}$	0.0107	0.048	4.45
UC10	4.456 ± 0.072	3.08 ± 0.013	$7.86 \times 10^{-7} \pm 6.67 \times 10^{-11}$	0.0131	0.060	4.58
UC20	3.385 ± 0.173	3.76 ± 0.015	$7.61 \times 10^{-7} \pm 9.77 \times 10^{-11}$	0.0127	0.058	4.57
UC30	2.890 ± 0.048	4.12 ± 0.011	$7.96 \times 10^{-7} \pm 5.69 \times 10^{-7}$	0.0133	0.060	4.51
MC5	5.558 ± 0.112	2.73 ± 0.013	$8.16 \times 10^{-7} \pm 1.40 \times 10^{-10}$	0.0136	0.061	4.48
MC10	5.224 ± 0.045	2.84 ± 0.013	$8.24 \times 10^{-7} \pm 1.22 \times 10^{-10}$	0.0137	0.062	4.52
MC20	4.629 ± 0,104	2.91 ± 0.008	$8.57 \times 10^{-7} \pm 8.45 \times 10^{-11}$	0.0143	0.064	4.47
MC30	4.530 ± 0.093	3.14 ± 0.014	$8.62 \times 10^{-7} \pm 8.88 \times 10^{-11}$	0.0144	0.065	4.51

present study has attempted to assess the η_E of composite polypropylene films containing modified and unmodified calcium carbonate. Obtaining the complete characterization of the polymer processability requires a detailed analysis and rheological measurements to be made, including different testing methods, e.g., under shear flow conditions and tensile flow conditions [18]. The testing results provided in the previous paper [16] have shown that filling polypropylene with modified $CaCO_3$ (5, 10, 20, and 30 wt%) decreases the polymer viscosity as a function of corrected shear rate, in proportion to the increase in the filler content of the matrix. In turn, unmodified calcium carbonate causes a viscosity drop for low filler contents, with its growth occurring at the two highest concentrations. The opposite changes are observed for extensional viscosity. Figure 2 represents the relationship of extensional viscosity as a function of stretching duration for polypropylene (PP) film and films filled with unmodified calcium carbonate (UC5 – UC30). The most significant values of extensional viscosity in the shortest stretching duration were obtained for PP film and UC5 film. However, when comparing the relative position of the curves for [$\eta_E = f(t_E)$] the PP and the UC5 series, it can be noticed that the addition of calcium carbonate entails a reduction in the composite film (UC5) extensional viscosity, as compared to the reference film (PP). For example, for a stretching duration of 10 s, the extensional viscosity of a PP film sample was $1.82 \cdot 10^6$ Pa·s. In contrast, for reference UC5 film sample (with a $CaCO_3$ content of 5 wt. %), the extensional viscosity amounted to $7.11 \cdot 10^5$ Pa·s. UC10 and UC20 composite films exhibited similar extensional viscosity values. The lowest extensional viscosity for the stretching duration under consideration (t_E = 10 s), namely $4.09 \cdot 10^5$, was shown by UC30 composite film. The filling of the composite with unmodified calcium carbonate at a level of 30 wt% turned out to be too high for a good-quality film product to be obtained. In stretching UC30 film, its deformation followed the so-called brittle cracking mode. During stretching, a spot failure of the film occurred, involving the formation of discontinuities which were then propagated, resulting in the specimen brittle cracking. The formation of discontinuities results from $CaCO_3$ agglomerates occurring in the film structure, which act as a localized notch [21]. Clusters of unmodified filler adversely affect the extensional viscosity of composite

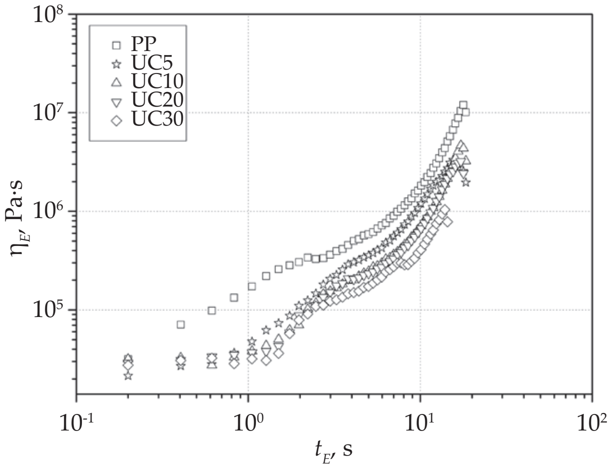

Fig. 2. Extensional viscosity as functions of time (t_E) with extensional rates 0,1 s^{-1}, at 165°C for polypropylene film and composites films with unmodified calcium carbonate (series UC)

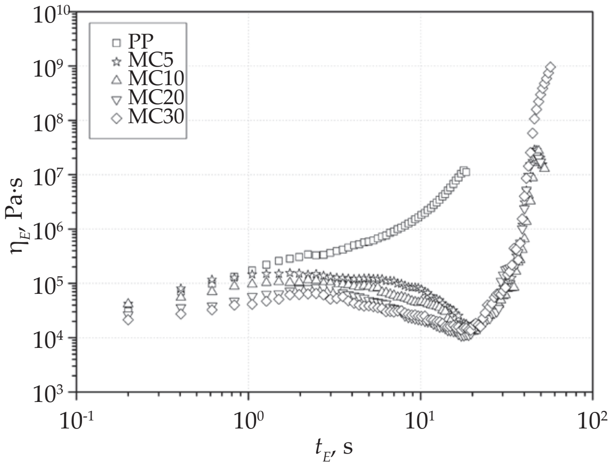

Fig. 3. Extensional viscosity as functions of time (t_E) with extensional rates 0,1 s^{-1}, at 165°C for polypropylene film and composites films with modified calcium carbonate (series MC)

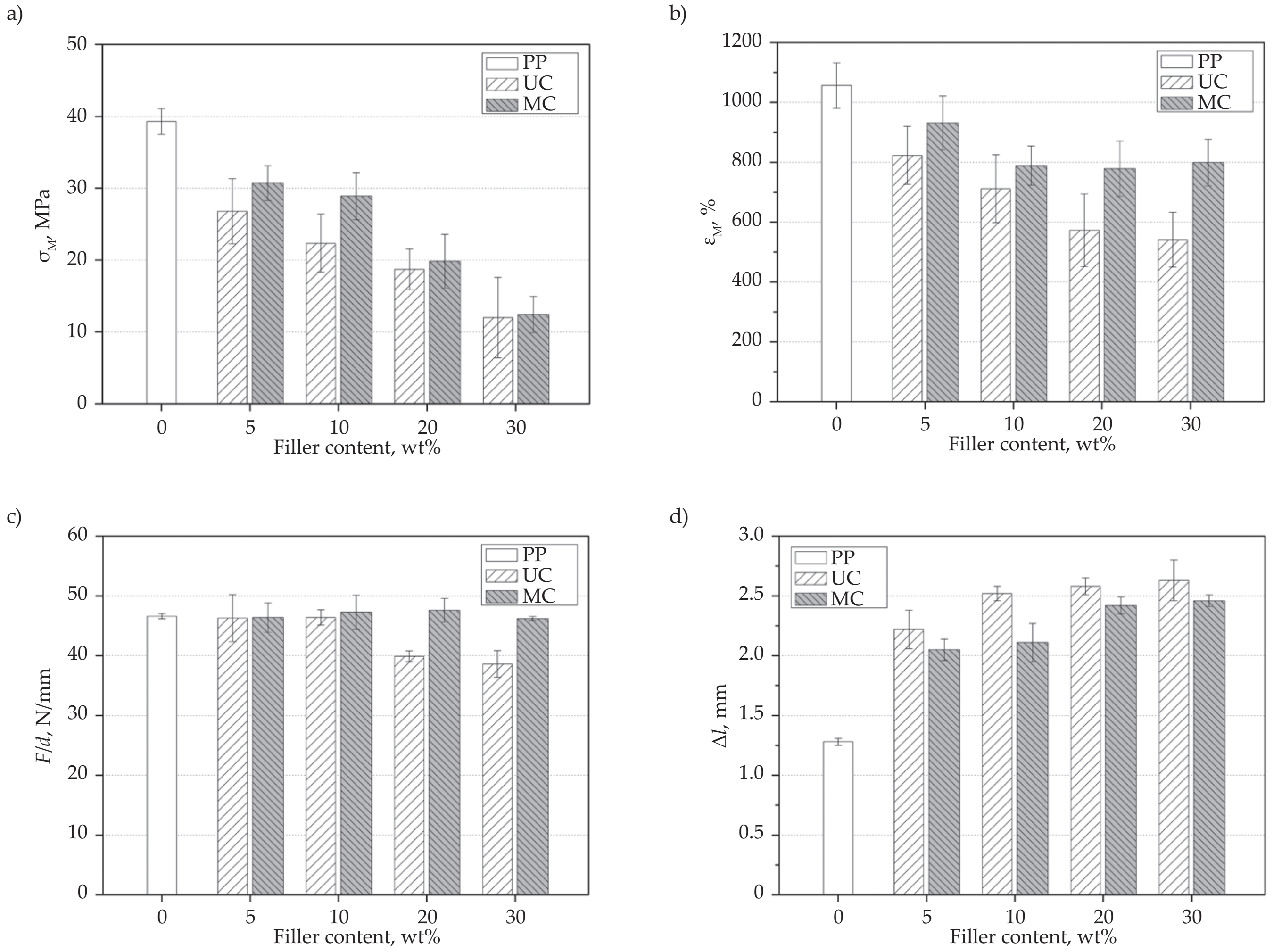

Fig. 4. Tensile properties of polypropylene (PP) and composites films as a function of filler content (series UC and MC): a) maximum strength, b) elongation at break, c) puncture resistance (*F*/*d*), d) elongation at puncture (Δl)

film and its properties, such as strength and gloss, which will be discussed later in the paper.

Variations in the extensional viscosity of composite films containing modified calcium carbonate are illustrated in Figure 3. By analyzing the behaviour of the curves $\eta_E = f(t_E)$, it can be predicted that each of the materials only exhibits a uniform increase in η_E up to a point, and the values meet within a similar region, with slight shifts being noticeable. The values of η_E for films filled with modified calcium carbonate were much smaller than those filled with unmodified filler. For instance, for a stretching duration of 3 s, the extensional viscosity of a UC10 film specimen was $2.07 \cdot 10^5$ Pa·s. In comparison, for an MC10 sample, the extensional viscosity had a smaller value of $9.9 \cdot 10^4$ Pa·s. The tests show that the filler modification reduces the extensional viscosity value for composite films. This is advantageous from the film extrusion technology point of view, as it improves the processability of the film in the region of its formation by facilitating the deformability/formation of a film sheet in the case of cast films and in the blown extrusion process.

Optical and mechanical properties

Obtained films were also examined for selected performance and optical properties, including mechanical properties under static tensile conditions, puncture resistance, haze, and gloss. Static tensile tests were performed for samples taken in the machine direction (MD) to determine the mechanical parameters most important for film products, namely the ultimate strength (σ_M) and the elongation at break (ε_B). The tensile strength of polypropylene film and composite films as a function of the unmodified (UM) and modified filler (MC) content, respectively, are summarized in Figure 4a.

The greatest strength during stretching was exhibited by polypropylene film (39.3 MPa). The addition of filler, irrespective of its type, caused a drop in σ_M value. The tensile strength reduction of the composite films filled with modified and unmodified calcium carbonate occurred within the entire range of $CaCO_3$ concentrations. The lack of reinforcement effect may result from the inhomogeneity of the composite film structure. Surface defects in the form of filler agglomerates create weakening spots

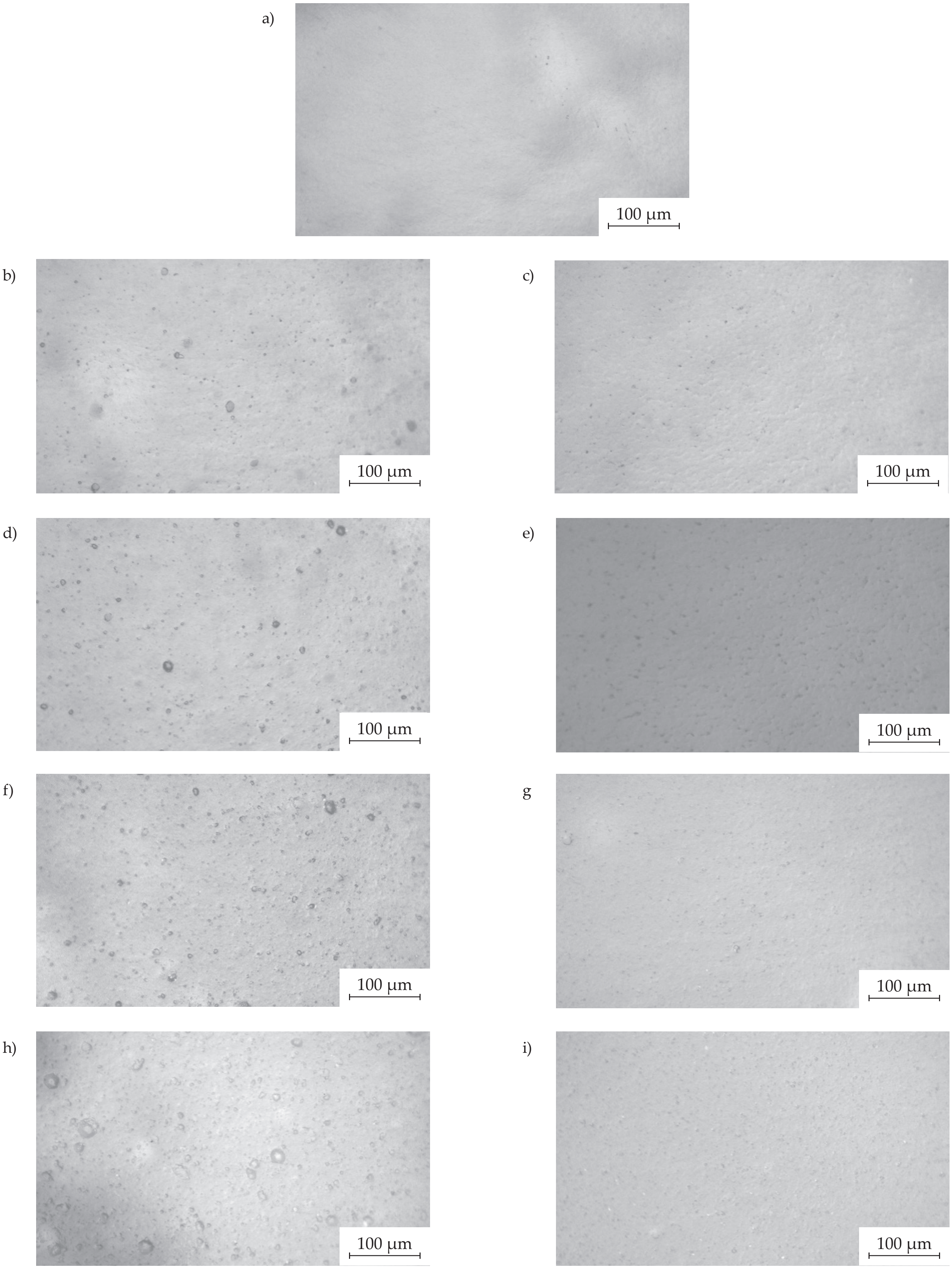

Fig. 5. Microscopic view of polypropylene and composites films (series UC and MC): a) PP, b) UC5, c) MC5, d) UC10, e) MC10, f) UC20, MC20, g) UC30, h) MC30

in the film, which, under tension conditions, act as localized notches [38, 39] and contribute to a reduction of the film strength. The strength decrease is due to a reduction in interaction/adhesion at the filler–polymer interface in the regions of occurring agglomerates [21, 40, 41]. A confirmation of this type of imperfection is provided by film surface images taken using an optical microscope, as shown in Figure 5. As it can be seen, structure disturbances in the form of inclusions occur on the composite film surface, which differs in size and shape, with an oval shape being predominant. It can also be noticed that the inclusions in films filled with unmodified calcium carbonate are more numerous and more prominent. Unmodified $CaCO_3$ tends to form agglomerates [22], even when effective homogenization techniques are used, as was the case during the composites under discussion in twin-screw extrusion production. Stearic acid as a calcium carbonate modifier allowed film of a better structure (see Fig. 5) to be extruded, which showed higher strength than films containing the unmodified filler. For example, the strength of composite film with a modifier filler content of 10 wt% (MC10) amounted to 28.9 MPa. In contrast, a tensile strength film filled with unmodified calcium carbonate (UC10) decreased to 22.3 MPa.

The filler addition caused changes also in the elongation of film specimens (Fig. 5b). Like for the strength, the magnitude of elongation for composite film specimens was smaller than for polypropylene film (ε_B = 1056.54%). For composite films containing unmodified calcium carbonate, a relatively proportional decrease of elongation at break is observed with the increase in filler content. There are no steady variations in the case of films containing modified chalk. For films from series MC, a modified filler addition of 5 wt% reduced the film elongation to 931.61%. An additional increase in $CaCO_3$ content up to 10 wt% entails a further reduction of ε_B. Allowing for the magnitudes of measurement error, it can be stated that films containing 10, 20, and 30 wt% of unmodified calcium carbonate were characterized by a similar elongation of about 785 %. The drop in the magnitude of elongation at break with the increase in the degree of fill in composite films is a consequence of the agglomeration of filler particles in the polymer matrix, as also demonstrated in other studies [21, 38, 39].

Depending on their application, film products should be characterized by appropriate resistance to forces acting in the plane of their symmetry (axis) and forces acting in the direction perpendicular to their surface [42]. Film surface failures resulting from the action of perpendicular forces causing their puncture are among the most frequent defects of packaging films, protective films, or films used in agriculture and horticulture. Therefore, from the point of view of the film products operation, it becomes essential to determine their puncture resistance. With the resistance of a material, the force at which that material fails can be determined [41]. For the puncture resistance of the film, the film thickness is of great importance [42], with the puncture resistance being defined as the ratio of force needed for damaging the film surface to film thickness (4). A parameter that is also determined in film puncture testing is the elongation at puncture (Δl). In some way, this quantity defines the film's susceptibility to localized deformation due to the action of a spot force perpendicular to the film surface and is related directly to film rigidity [42, 43]. The evaluation of mechanical parameters under static tensile conditions and the assessment of puncture resistance provide a basis for determining the functionality of film products and are decisive to their purpose. Therefore, for all films being the subject of this publication, the puncture resistance (Fig. 4c) and the elongation at the puncture (Fig. 4d) have been determined. As shown by the puncture resistance values illustrated in the figure above, adding applied fillers does not significantly influence the variations of the *F*/*d* magnitude compared to unfilled PP. A fairly significant decrease is only observed for composite films containing 20 and 30 wt% of unmodified calcium carbonate. The lowest puncture resistance is shown by UC30 film (38.6 MPa). In this case, a filler addition of 30 wt% has significantly reduced puncture resistance by approx. 17% compared to polypropylene film. The impairment in the puncture resistance of composite films UC20 and UC30 may be due to the lack of appropriate interaction between the filler and the polymer matrix (clusters of agglomerates), as a result of which the reinforcement does not carry the load during the puncture test, and this results in a drop in *F*/*d* value [43–45]. A positive effect of adding calcium carbonate (depending on its type) on another parameter determined in the puncture test, which is the elongation at puncture, can be observed. The value of film elongation at puncture increases with increasing calcium carbonate content. Films containing unmodified $CaCO_3$ are characterized by greater Δl values. Differences in elongation at puncture between films containing modified and unmodified calcium carbonate may be the consequences of differences in their rigidity. As it has been demonstrated in previous publications [37, 45], there is an inversely proportional relationship between Young's modulus (as an indirect measure of rigidity) and the elongation at the puncture of film. In the entire considered range filler concentrations (from 5 to 30 wt%), films containing modified calcium carbonate exhibited greater values of Young's modulus. As a consequence, films of series MC undergo a smaller deformation during puncture ($\Delta l\downarrow$).

One of the essential polymer films features, which enhances their applicability in various fields, is the capability to regulate their opaqueness–transparency [46]. This plays a significant role, e.g., in food film packaging or films used in agriculture or horticulture (by changing the transparency of film, the level of insolation of crops can be regulated). From the physics perspective, the transparency of film is the quantity of light that passes through its structure. A more often determined quantity that characterizes the transparency of film products is their haze, as defined by Equation (5) [46, 47]. An increase in the haze of film translates into a decrease in its transparency, and it may be due to numerous causes, such as film surface roughness, surface defects, the presence of impurities in the film structure, the use of various types of additives (dyes, pigments, fillers, etc.) [48]. On the other hand, an increase in film haze can be caused by forced orientation [8, 9] or the addition of clarifying agents [11]. Considering the great importance of haze as the functional property of film products, the present study has also made an endeavour to assess the influence of the quantity and type of the applied filler on the value of *H* of produced composite films. The haze values for all test films are summarized graphically in Figure 6. Adding a small quantity of calcium carbonate causes a considerable increase in the haze of polypropylene film. At a $CaCO_3$ content of 5 wt%, the haze increases to approx. 49%, compared to PP film. Increasing the filler content results in a proportional increase in film haze. When comparing the values of *H*, depending on the type of filler used, a minimal increase in haze can be noticed for films filled with unmodified calcium carbonate compared to films containing modified chalk. However, the differences in film transparency for the same filler contents are very small. It can be said that calcium carbonate exhibits a prominent effect in modifying the transparency of film and confirms its covering properties noted earlier on thick-walled products and in paints [15, 17]. A calcium carbonate addition of 20 wt% makes already the film non-transparent – with a haze of 97.3 for film UC20 and 96.8 for film MC20. The addition of calcium carbonate reduces the regions responsible for the transmission of light, which, as a consequence, leads to a reduction of film transparency as the filler content increases [49, 50].

Another essential surface property of film products being decisive to their application is the gloss. The surface gloss makes it possible to determine the product's functional properties and potential use as a decorative element. The gloss phenomenon occurs due to the dispersion or reflection of an incident light beam either immediately above the material surface or on it. Another way of defining the gloss is by using the intensity of light reflected at the angle at which the light beam was falling on the surface [52]. The gloss of the film product surface may be determined by many factors, including the index of refraction, light absorption, and the surface roughness and the material surface morphology [52, 53]. As for the transparency, the gloss of composite film is also determined by the contents of modifiers (such as fillers or nano-fillers) and, above all, by their dispersion within the polymer matrix [54]. The determined values of the gloss of extruded test films are represented graphically in Figure 7. According to the applicable scale [51], polypropylene film can be characterized as exhibiting semi-gloss in terms of its gloss of 31.5 ± 0.3 GU. The calcium carbonate addition in the amount of 5 and 10 wt%, respectively, reduces the gloss of polypropylene film and declassifies it to a semi-glossy material. Further, increasing the filler content reduces the gloss of composite film to that of matt materials. So significant gloss changes indicate that calcium carbonate can be a very effective gloss modifier. A filler addition within the concentration range under consideration not only changes the value of gloss numerically but also the classification of the film product in terms of its character from a glossy product (GU = 52 – 80) to a matt product (GU < 15). According to research on the surface properties of film products, a factor responsible for reducing the gloss of film with the increase in its filler content is the quality of the film surface [52, 54]. An increasing number of occurring imperfections in the form of filler agglomerates (see Fig. 5) contributes to an increase in the surface roughness of composite film, thereby reducing its gloss [54]. The difference in surface topography can also be used to explain the greater values of gloss for composite films containing modified calcium carbonate compared to films with the addition of modified chalk. Better dispersion of the modified filler (stearic

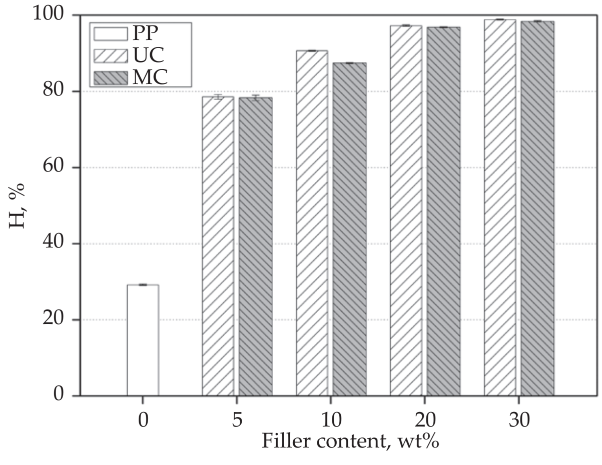

Fig. 6. Haze in polypropylene (PP) and composites films (series UC and MC) as a function of filler content

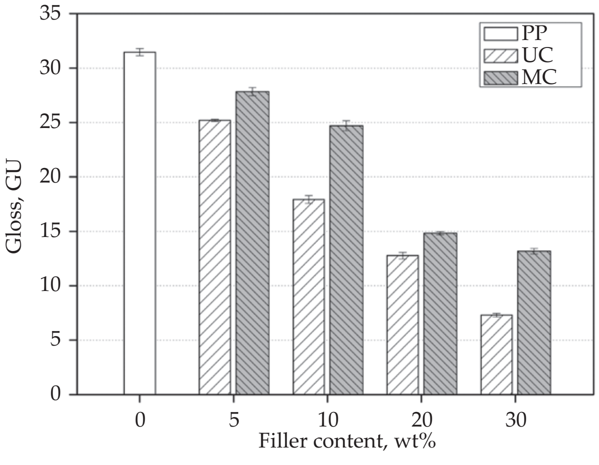

Fig. 7. Gloss in polypropylene (PP) and composites films (series UC and MC) as a function of filler content

acid) within the polymer matrix translates directly into a smaller number of film surface imperfections, which results in a better gloss [54].

CONCLUSIONS

The influence of the modified and unmodified calcium carbonate addition on the polypropylene extrusion process and the selected functional properties of cast composite films was investigated. In the considered range of filler concentrations (from 5 to 30 wt%), a different effect of the filler on MVR and polymer processability is observed, depending on the type of $CaCO_3$. Unexpected variations in MVR were obtained for composites containing unmodified calcium carbonate (series UC). For low concentrations of the unmodified filler (5–10 wt%), an increase in MVR was observed, which can be explained by a specific interaction at the filler–polymer interface. Further, increasing of the filler content reduces MVR. The effect of $CaCO_3$ addition on the polymer matrix melt volume-flow rate resulted in a variation of the processing characteristic of the extrusion process. The observed changes in the composites MVR, as a consequence of changes in flow resistance, had a direct impact on the speed of linear extrusion (V_{ps}). Obtaining film of a fixed preset thickness from composite materials with varying calcium carbonate content and differing filler type (either modified or unmodified $CaCO_3$) requires the adjustment of extrusion process setup parameters (screw rotational speed or pull-back system speed). A direct effect of the calcium carbonate addition and its modification on the extensional viscosity of composite films under examination was also demonstrated. The magnitude of η_E decreased with the increase in the filler content of the composite. The tests also showed that stearic acid was an effective modifier of processing properties in shear flow conditions and under extensional flow conditions – smaller η_E values were exhibited by films containing modified calcium carbonate. No reinforcing effect of calcium carbonate addition on the mechanical properties of composite films, as determined under static tensile conditions, was observed. For both filler types, a decrease in strength and elongation during stretching occurred with the increase in $CaCO_3$ content. Whereas films containing modified filler were characterized by greater σ_M and ε_B values. Also, the calcium carbonate addition did not cause any significant changes in film puncture resistance – a slight reduction of puncture resistance was noted for the film with the unmodified $CaCO_3$ highest filler content, i.e., 20 and 30 wt%. The only parameter that improved was the elongation at puncture – it increased with an increasing filler content of the composite film. Greater Δl values are exhibited by films containing unmodified calcium carbonate (UC), which could be associated with their lower rigidity than films containing modified filler (MC). As a filler, calcium carbonate also showed an effect on one of the most important functional properties of film products, the haze. It turned out to be a very effective factor in reducing the transparency of polypropylene film, causing an increase in its haze with the increase in the filler content of the composite. The modification of the filler had no significant influence on variations in H value – a minimal haze occurred for films filled with unmodified chalk. $CaCO_3$ modification contributed to variations in another film functional property under consideration, that is, the gloss. Films extruded from composites containing modified calcium carbonate were characterized by higher gloss. Irrespective of the type of $CaCO_3$, the gloss of PP film surface decreased as the fill increased. A distinct effect of the calcium carbonate addition on the value of GU was observed, which caused a numeral change in gloss and changed the film classification from the glossy product (PP film) to matt product (films containing 30 wt% filler). In the majority of instances, the observed impairment in some of the considered functional properties of composite films resulted from imperfections of film structure and surface, as confirmed by microscopic observations. The tendency of calcium carbonate to form agglomerates has a particularly unfavourable effect on thin-walled composite products, which are films. This effect could be mitigated by modifying the filler surface with stearic acid. As has been demonstrated in the study, the effect of adding filler and its modification is noticeable not only in the properties of composite films but also at every stage of processing. Therefore, the planning of composite system processing in the film extrusion process (to obtain film of desired quality) requires the implementation of appropriate corrections to process setup parameters resulting from changes caused by filler addition.

ACKNOWLEDGMENTS

The results presented in this paper were funded with grants for education allocated by the Ministry of Science and Higher Education in Poland executed under the subject of No 0912/SBAD/2203.

REFERENCES

[1] Żuchowska D.: „Polimery konstrukcyjne", WNT, Warszawa 2000.

[2] Szlezyngier W., Brzozowski Z. K.: „Tworzywa sztuczne, Tom I", Wydawnictwo Oświatowe FOSZE, Rzeszów 2012.

[3] Saechtling H.: „Tworzywa sztuczne. Poradnik", WNT, Warszawa 2000.

[4] Antosik A.K., Kowalska U., Stobińska M., Dzięcioł P., Pieczykolan M., Kozłowska, K., Bartkowiak A.: *Polymers* **2021**, *13*, 3478. https://doi.org/10.3390/polym13203478

[5] Maddah H.A.: *American Journal of Polymer Science* **2016**, *6*, 1. https://doi.org/10.5923/j.ajps.20160601.01

[6] Kloziński A., Jakubowska P.: *Przetwórstwo Tworzyw* **2013**, *3* (*153*)/*19*, 195.

[7] Karian H.G.: “Handbook of Polypropylene and Polypropylene Composites”, Taylor and Francis e-Library, 2009.

[8] Di Sacco F., Gahleitner M., Wang J., Portale G.: *Polymers* **2020**, *12*, 1636. https://doi.org/10.3390/polym12081636

[9] Billham M., Clarke A.H., Garrett G. *et al.*: *Developments in Chemical Engineering and Mineral Processing* **2003**, *11*, 137. https://doi.org/10.1002/apj.5500110214

[10] Essche G., Kromminga T., Schmidt A.: *Journal of Plastic Film and Sheeting* **2000**, 16. https://doi.org/10.1106/AKBB-0EVN-UC1N-PHYF

[11] Bernland K., Goossens J.G.P., Smith G., Tervoort T.A.: *Journal of Polymer Science, Pat B: Polymer Physics* **2016**, *54*, 865. https://doi.org/10.1002/polb.23992

[12] Wallner G.M., Resch K., Teichert Ch. *et al.*: *Monatshefte für Chemie* **2006**, *137*, 887. https://doi.org/10.1007/s00706-006-0480-6

[13] Thenepalli T., Jun A.Y., Han. Ch. *et al.*: *Korean J. Chem. Eng.* 2015, *32*, 1009. https://doi.org/10.1007/s11814-015-0057-3

[14] Kloziński A., Barczewski M.: *Polimery* **2019**, *64*, 83. https://doi.org/10.14314/polimery.2019.2.1

[15] Kloziński A.: *Polimery* **2016**, *61*, 788. https://doi.org/10.14314/polimery.2016.788

[16] Kloziński A.: *Przemysł Chemiczny* **2019**, *98*, 442. https://doi.org/10.15199/62.2019.3.16

[17] Żarczyński A., Dmowska A.: „Napełniacze mieszanek gumowych”, WNT, Warszawa 1970.

[18] Kloziński A., Jakubowska P.: *Polymer Engineering and Science* **2019**, *59*, E155. https://doi.org/10.1002/pen.24894

[19] Wu P.C., Jones G., Shelley Ch., Woelfli B.: *Journal of Engineered Fibers and Fabrics* **2007**, *2*, 49. https://doi.org/10.1177/155892500700200105

[20] Rahmani M., Ghasemi F.A., Payganeh G.: *Mechanics and Industry* **2014**, *15*, 63. https://doi.org/10.1051/meca/2014009

[21] Supaphol P., Harnsiri W., Junkasem J.: *Journal of Applied Polymer Science* **2004**, *92*, 201. https://doi.org/10.1002/app.13432

[22] Jakubowska P., Kloziński A.: *Przemysł Chemiczny* **2013**, *92*, 575.

[23] Kaseem M., Hamad K, Deri F., Ko Y.G.: *Journal of Wood Chemistry and Technology* **2017**, *37*, 251. https://doi.org/10.1080/02773813.2016.1272127

[24] Mazzanti V., Mollica F.: *Journal of Polymers and the Environment* **2017**, *25*, 1044. http://dx.doi.org/10.1007/s10924-016-0876-2

[25] Kloziński A., Jakubowska P.: *Journal of Polymer Engineering* **2019**, *39*, 422. https://doi.org/10.1515/polyeng-2018-0199

[26] Kloziński A., Jakubowska P.: *Polymer Engineering and Science* **2019**, *59*, E16. https://doi.org/10.1002/pen.24941

[27] Barczewski M.: *Polimery* **2015**, *60*, 612. https://doi.org/10.14314/polimery.2015.612

[28] Barczewski M.: *Polimery* **2015**, *61*, 248. https://doi.org/10.14314/polimery.2016.24

[29] Kloziński A., Sterzyński T., Samujło B.: *Polimery* **2009**, *54*, 57.

[30] Sentmanat M.L.: *Rheologica Acta* **2004**, *43*, 657. https://doi.org/10.1007/s00397-004-0405-4

[31] Sentmanat M., Wang B. N., McKinley G.H.: *Journal of Rheology 2005*, *49*, 585. https://doi.org/10.1122/1.1896956

[32] Liang.Z.: *Journal of Applied Polymer Science* **2007**, *104*, 1692. https://doi.org/10.1002/app.25804

[33] Da Silva A.L.N., Rocha M.C.G., Moraes M.A.R. *et al.*: *Polymer Testing* **2002**, *21*, 57. https://doi.org/10.1016/S0142-9418(01)00047-2

[34] Stabik J.: „Wybrane problemy reologii uplastycznionych polimerów napełnionych”, Zeszyty Naukowe – Politechnika Śląska nr 1616, Gliwice 2004.

[35] Cantor K.: „Blown Film Extrusion – 2nd ed.”, Carl Hanser Verlag, Munich 2011.

[36] Rauwendaal Ch.: “Polymer Extrusion”, Hanser Publisher, Monachium 2001.

[37] Kloziński A., Jakubowska P.: „Wpływ warunków wytłaczania na właściwości folii orientowanych”, Zeszytach Naukowe Politechniki Poznańskiej, Budowa Maszyn i Zarządzanie Produkcją 2010, nr 12, str. 151. Wydawnictwo Politechniki Poznańskiej, Poznań 2010.

[38] Shelesh-Nezhad K., Orang H., Motallebi M.: *Journal of Thermoplastic Composite Materials* **2012**, *26*, 544. https://doi.org/10.1177/0892705712454 86

[39] Zuiderduin W.C.J., Westzaan C., Huétink J., Gaymans R.J.: *Polymer* **2003**, *44*, 261. https://doi.org/10.1016/S0032-3861(02)00769-3

[40] Lam T.D., Hoang T.V., Quang D.T., Kim J.S.: *Materials Science and Engineering* **2009**, *501*, 87. https://doi.org/10.1016/j.msea.2008.09.060

[41] Eiras D., Pessan L. A.: *Materials Research* **2009**, *4*, 517. https://doi.org/10.1590/S1516-14392009000400023

[42] Kloziński A., Jakubowska P.: *Inżynieria i Aparatura Chemiczna* **2010**, *49*, 61.

[43] Kloziński A., Jakubowska P.: *Inżynieria i Aparatura Chemiczna* **2012**, *51*, 231.

[44] Pérez E., Alvarez V., Pérez C.J., Bernal C.: *Composites Part B: Engineering* **2013**, *52*, 72. https://doi.org/10.1016/j.compositesb.2013.03.035

[45] Jakubowska P., Kloziński A.: *Przetwórstwo Tworzyw* **2013**, *3* (*153*)/*19*, 182.

[46] Andreassen E., Larsen A., Nord-Varhaug K *et al.*: *Polymer Engineering and Science* **2002**, *42*, 1082. https://doi.org/10.1002/pen.11014

[47] Patel R.M.: *Journal of Plastic Film and Sheeting* **2005**, *21*, 217. https://doi.org/10.1177/8756087905057

[48] Molnár J., Sepsi Ö., Erdei G. *et al.*: *Journal of Polymer Science* **2020**, *58*, 1787.

https://doi.org/10.1002/pol.20200027

[49] Sun X., Li N., Hang J. *et al.*: *Optica Applicata* **2015**, *45*, 393.
https://doi.org/10.5277/oa150311

[50] Ru Y., Zhang X., Wang L. *et al.*: *Polymer Chemistry* **2015**, *6*, 6632.
https://doi.org/10.1039/C5PY01072A

[51] Broniewski T., Kapko J., Płaczek W., Thomalla J.: „Metody badań i ocena właściwości tworzyw sztucznych", WNT, Warszawa 2000.

[52] Wang L., Huang T., Kamal M.R. *et al.*: *Polymer Engineering and Science* **2000**, *40*, 747.
https://doi.org/10.1002/pen.11204

[53] Schael G.W.: *Journal of Applied Polymer Science* **1966**, *10*, 891.
https://doi.org/10.1002/app.1966.070100606

[54] Soulestin J., Rashmi B.J., Bourbigot S. *et al.*: *Macromolecular Materials and Engineering* **2012**, *297*, 444.
https://doi.org/10.1002/mame.201100202

Received 15 IX 2022.