Rheological properties of polypropylene composites with calcium carbonate under high shear rates

Arkadiusz Kloziński[1), *)] (ORCID ID: 0000-0002-2025-699X), **Krzysztof Lewandowski**[2)] (0000-0003-0664-9815),
Jacek Mirowski[2)] (0000-0002-4115-1556), **Mateusz Barczewski**[3)] (0000-0003-1451-6430),
Paulina Jakubowska[1)] (0000-0002-8638-1216)

Abstract: The rheological properties of isotactic polypropylene (iPP) and its composites with unmodified and stearic acid-modified calcium carbonate (5, 10, 20, 30 wt%) were investigated. The processability factor K of the composites was determined based on changes in the mass flow rate (MFR). The assessment of rheological properties was carried out at high shear rates, in the injection process, using a special in-line measuring head. Measurements were performed at a temperature of 230°C, in the range of apparent shear rate from 19,100 to 101,900 s^{-1}, based on the Ostwald-de Waele power-law model. Comparative analysis of the processing and rheological characteristics, as determined with two techniques (off-line measurements and in-line measurements), has shown a diverse behaviour of polymer composites in flows (flow resistances, the behaviour of the flow and viscosity curves, the power law index), resulting from a varying fill degree, applied filler type and measuring shear rate range.

Keywords: polymer composites, injection moulding, rheological properties, in-line rheology.

Właściwości reologiczne kompozytów polipropylenu z węglanem wapnia w warunkach dużych szybkości ścinania

Streszczenie: Zbadano właściwości reologiczne izotaktycznego polipropylenu (iPP) oraz jego kompozytów z niemodyfikowanym i modyfikowanym kwasem stearynowym węglanem wapnia (5, 10, 20, 30% mas.). Współczynnik przetwarzalności K kompozytów określano na podstawie zmian masowego wskaźnika szybkości płynięcia (MFR). Ocenę właściwości reologicznych przeprowadzono w warunkach dużych szybkości ścinania, w procesie wtryskiwania, przy zastosowaniu specjalnej głowicy pomiarowej typu *in-line*. Pomiary wykonano w temperaturze 230°C, w zakresie pozornej szybkości ścinania od 19 100 do 101 900 s^{-1}, w oparciu o model potęgowy Ostwalda-de Waele'a. Analiza porównawcza charakterystyk przetwórczych i reologicznych, wyznaczonych dwoma technikami pomiarowymi (off-line i in-line), wykazała zróżnicowany sposób zachowania się kompozytów polimerowych w przepływach (opory przepływu, przebiegi krzywych płynięcia i lepkości, wykładnik płynięcia), wynikający z różnego stopnia napełnienia, rodzaju zastosowanego napełniacza oraz zakresu pomiarowego szybkości ścinania.

Słowa kluczowe: kompozyty polimerowe, wtryskiwanie, właściwości reologiczne, reologia *in-line*.

The observed unceasing increase in demand for polymeric materials constitutes one of the key factors determining the growth of investigations to develop new and modify the existing polymers. Changing the properties of polymers can be done through their chemical [1], physical [2] or combined modification [3]. Because of the high efficiency and economy of the process, a form of modification that is most often used currently is the physical modification, which involves plasticized-state homogenization of a polymer with another polymer (polymer mixtures [4]), a polymer with modifying additives (e.g., a slip agent [5]), or a polymer with fillers (polymer composites [2, 6]). The changes in specific, planned functional properties of polymeric materials, which occur due to physical modification, are often accompanied by a spontaneous change in their rheological properties [7–10].

[1)] Institute of Chemical Technology and Engineering, Faculty of Chemical Technology, Poznan University of Technology, Berdychowo 4, 60-965 Poznan, Poland.
[2)] Faculty of Chemical Technology and Engineering, Bydgoszcz University of Science and Technology, Seminaryjna 3, 85-326 Bydgoszcz, Poland.
[3)] Institute of Materials Technology, Faculty of Mechanical Engineering and Management, Poznan University of Technology, Piotrowo 3, 61-138 Poznan, Poland.
*) Author for correspondence:
Arkadiusz.Klozinski@put.poznan.pl

To achieve the correct run of a processing routine (such as extrusion, injection moulding, etc.), it is necessary to obtain the appropriate rheological properties of the polymeric materials and maintain their constancy throughout the process [11–13]. The selection of setup parameters, such as temperature or injection temperature, can be made, among other ways, by evaluating the rheological parameters of the polymeric raw material, including the Melt Mass-Flow Rate (MFR) or the behavior of the viscosity curves. The above-mentioned rheological quantities are most determined using highly specialized stationary devices (such as plastometers or rheometers) in laboratory conditions [14–15]. In an analytical approach, tests conducted on a small amount of material taken from either the raw material or the finished product, shifted in time relative to the technological process, are named off-line measurements [16]. Off-line measurements enable an extensive rheological characteristic of polymeric materials to be made; however, they do not allow the control of the technological process as it runs and the assessment of the behavior of the polymers in flows occurring in real processing conditions [16, 17]. The analysis of the actual behavior of a polymer in processing constitutes a basis for the control of the process and its stability and the quality of the finished product [18,19]. An investigation technique that enables the control of the production process and the rheological analysis of the whole polymeric material being processed (100% of flow) are in-line measurements [9, 16, 17]. The processes are conducted in the extrusion or injection moulding, and the function of a rheometer is taken over by a special-design head [10, 20] or injection mould [21, 22]. In the injection moulding process, in-line type rheological measuring techniques are carried out in three ways. The first of them constitutes the same technical solution as in measurements conducted during extrusion, wherein the testing device is a rheological head (a flat measuring channel head or an exchangeable dies head) mounted on the injection moulding machine die. In that case, the technological machine is equipped with molds, and its plasticizing system performs the function of a flow-forcing tool [23–26]. The next two types of measurements are accomplished using injection moulding machines equipped with rheological measuring instruments mounted in the location of the injection mould. Depending on the design solution, the mould can have no injection cavity and act as a rheological measuring head, i.e., it can have the capability to record variations in pressures and melt volume-flow rate during injection [27]. The next type of in-line rheological measurements to characterize the run of the injection moulding process are measurements taken directly in the injection mould. Pressure and temperature sensors placed directly in the cavity of a mould allow the control of the injection process within a tool which is the injection mould, and, above all, they provide a source of information on phenomena occurring as the mould cavity is filled [21, 22]. In-line measurements conducted in polymer processing enable

the determination of the effect of apparatus-related factors, e.g., the design of plasticizing system, the design of the working tool (extrusion head, injection mould), and process setup parameters on the rheological parameters of the polymers [9, 18, 19, 21, 28]. They can also provide a tool for evaluating the effect of adding fillers on the processability of polymer composites [9, 10, 20]. The varying design of the plasticizing systems of processing devices and, therefore, the varying conditions of shear flows, may significantly affect the filler–polymer interactions and the filler structure [20, 25, 26]. That, in practice, can lead to a variation in the rheological characteristics of polymer composites, as determined using different measuring techniques within in-line measurements [9]. It may also be risky to extrapolate off-line measurement results to conditions prevailing in in-line measurements. For this reason, rheological indices determined in off-line measurements are 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 [9, 29].

One of the widely applied thermoplastic polymer fillers used for fabricating continuous-shaped products, injection-molded parts, and foil products is calcium carbonate ($CaCO_3$). The commonness of this natural powder filler is due to its availability, low price, and positive influence on selected functional properties of products; specifically, it enhances the compressive strength, increases the longitudinal modulus of elasticity, reduces the shrinkage, improves the thermal stability, and contributes to extrusion efficiency [30–32]. Using $CaCO_3$ as a polymer filler may also have some adverse effects, such as impaired rheological properties [32], increased water absorption, and faster wear of processing machines [31]. The properties of composites with an addition of calcium carbonate depend on the content of the filler, its particle size, homogenization conditions, and surface modifiers used [33, 34]. As a powder filler, calcium carbonate tends to form agglomerative [35]; therefore, to improve its dispersion in the polymer matrix and enhance interactions at the polymer–filler interface, its surface is modified using, among others, stearic acid [32, 36, 37]. Stearic acid performs the function of a coupling agent, whose aim is to couple and improve adhesion at the (polymer–filler) interface, as well as to uniformly disperse the filler within the polymer matrix [38]. The use of stearic acid as a calcium carbonate modifier improves selected functional properties of polymer composite products, such as foils [39], but above all, it influences the rheological properties of the polymer matrix and polymer processability [37, 40].

As was demonstrated in a previous study [37], the addition of modified and unmodified calcium carbonate within the filler concentration ranges from 5 to 30 wt% showed a varying effect on the rheological properties of polypropylene, depending on the applied $CaCO_3$ grade and the quantity of the filler used. The rheological characteristic tests were carried out using an extruder rhe-

ometer with an in-line measuring head in low shear rate magnitudes, i.e., in the range from 150 to 700 s⁻¹. As has been shown by investigations carried out for polymer composites, the effect of filler addition on the polymer viscosity decreases with the increase in shear rate [25, 26, 41].

So far, no studies in the literature on the subject would describe the rheological properties of polypropylene composites with $CaCO_3$, as determined under high shear rate conditions. Therefore, this paper will present an investigation to evaluate the effect of modified and unmodified calcium carbonate on the rheological properties of polypropylene, as determined in the injection moulding process using a special-design on-line rheological head in the conditions of high shear rates of up to 102,000 s⁻¹.

EXPERIMENTAL PART

Materials

Specifically, Moplen HP456J isotactic polypropylene (iPP) (produced by Basell Orlen Polyolefins Poland) with a density of 893 kg/m³ (23°C) and a melt flow rate of ($MFR_{2.16; 230°C}$) 3.35 g/10min was used during studies as a polymeric matrix.

Commercial calcium carbonate supplied by Calcit d.o.o. (Slovenia) was used as a polypropylene filler. The same filler in two variants, i.e., unmodified $CaCO_3$ (CalPlex Extra) and modified $CaCO_3$ with stearic acid (CalPlex ExtraT), was used in the tests. Table 1 shows the main physicochemical properties of the fillers used.

T a b l e 1. **Physicochemical properties of calcium carbonate fillers**

Properties	CalPlex Extra	CalPlex ExtraT
Crystallographic form	calcit	calcit
Surface modification	–	stearic acid
Density, g/cm³	2.70	2.70
Particle size distribution (d_{50}), μm	0.75–0.9	0.75–0.9

T a b l e 2. **The composition of investigated materials**

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

Specific surface area (A_{BET}), m²/g	9.210	7.814

The modification of the PP was made in a cold granulation extrusion process. A twin-screw extruder, model EH16.2D, by Zamak Mercator (Poland), with a screw diameter of $d = 16$ mm and an l/d ratio of 40, was used. As a result of homogenization, iPP composites with unmodified and modified calcium carbonate were produced, containing 5, 10, 20, and 30 wt% filler. The concentrations of the composites and sample symbols are summarized in Table 2.

Methods and apparatus

Mass melt flow rate (MFR)

MFR was measured using a Dynisco plastometer model LMI 4004 (Franklin, MA, USA), according to the ISO 1133 standard at a temperature of 230 ± 0.5°C under a load of 2.16 kg. Changes in the processability of polypropylene because of the addition of $CaCO_3$ are represented with the coefficient K, which is the percentage change of MFR, understood as the ratio:

$$K = \frac{MFR_{PC}}{MFR_{PP}} \cdot 100\% \qquad (1)$$

where: MFR_{PC} – melt mass-flow rate of polymer composites [g/10 min], MFR_{PP} – melt mass-flow rate of polypropylene [g/10 min].

Shear viscosity

The examination of the rheological properties of the composites for high shear rates' was carried out under injection moulding using in-line measuring stand. The function of a rheometer was performed by an Engel injection moulding machine, model Victory 120 (Schwartzberg,
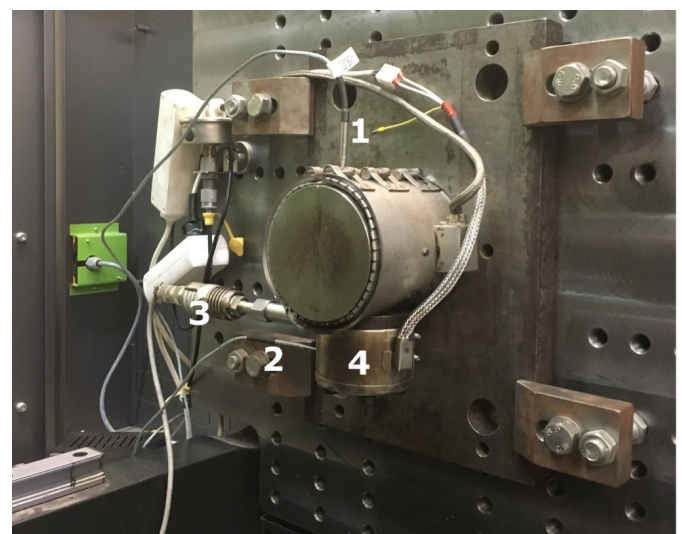

Fig. 1. Rheological head: 1, 2 – thermocouples, 3 – pressure transducer, 4 – segment with measuring capillary

Austria), with a screw diameter of 40 mm and maximum shot volume of 250 cm³, equipped with the Author's rheological head (Fig. 1). The rheological tool is mounted in place of the conventional injection mould. Detailed construction and the operating principle of the measuring head are described in earlier publications [25, 26].

The measurements used a cylindrical capillary of a diameter of 2 mm, a length of 40 mm, and an inlet angle of 120°. The injection moulding machine heating zone temperatures were, respectively: 30, 190, 210, and 230°C. The measurement temperature of the head and the measuring capillary was constant for all test materials under analysis, amounting to 230°C. The plasticizing system took a polymer material dose with a volume of 250 cm³ and plasticized it for 240 s. Next, the injection was done with a defined melt volume-flow rate ($\dot{Q}$) of, respectively: 15, 23, 38, 60, and 80 cm³/s through the rheological head furnished with a measuring capillary. Applying the range mentioned above of test melt volume-flow rate made it possible to carry out rheological characteristics under the conditions of high shear rate in the range from about 19,100 s⁻¹ to about 102,000 s⁻¹. The pressure variation measurement was carried out using a Bagsik sensor, model DA 250-1/2-1000-0, positioned before the inlet to the measuring capillary. The injection process was carried out five times for each polymeric material, and the determined pressure values formed the average of five measurements together with the standard deviation value.

The analysis of the rheological properties of pure polypropylene and polypropylene composites with unmodified and modified calcium carbonate was made based on the Ostwald-de-Waele power law model [15, 32]:

$$\tau_w = k \cdot \dot{\gamma}_a^n \qquad (2)$$

where: k is the consistency or viscosity coefficient index [Pa · sⁿ], n is the power law index [/].

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

$$\tau_w = \frac{\Delta p \cdot R}{2L} \text{ (Pa · s)} \qquad (3)$$

where: Δp is the pressure before entry to the capillary (pressure drop) [Pa], R is the capillary radius [m], and L is the capillary length [m].

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

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

where: $\dot{Q}$ is the volumetric flow rate [m³/s]

The true shear rate was obtained by applying the Rabinovitch correction [14, 15]:

$$\dot{\gamma}_w = \dot{\gamma}_a \cdot \left(\frac{3n + 1}{4n} \right) \text{(s}^{-1}) \qquad (5)$$

where n is the power law index obtained from the slope of the linear plots between ln (τ_w) and ln ($\dot{\gamma}$).

The shear viscosity was therefore calculated as follows:

$$\eta_w = \frac{\tau_w}{\dot{\gamma}_w} \text{ (Pa·s)} \qquad (6)$$

RESULTS AND DISCUSSION

The modification of polymer with a filler has a direct effect on its processing and rheological properties [9, 41]. As has been demonstrated in previous studies, the application of calcium carbonate (in its modified or unmodified form) directly influences the value of the Melt Mass-Flow Rate (MFR) [37] and the value of the Melt Volume-Flow Rate (MVR) of polypropylene [39]. Figure 2 illustrates the variations in the processability coefficient K (Equation 1) as a function of calcium carbonate content. The addition of modified calcium carbonate improves the processability of the composite within the entire range of filler concentrations used concerning the applied polymer matrix. For example, for a composite containing 5 wt% of modified $CaCO_3$ (MC5), processability has improved by 31%. However, an impairment in processability ($K\downarrow$) is observed with the increase in the content of modified calcium carbonate in the composite. But even at a filler concentration as high as 30 wt% (MC30), the processability of the composite is still better than that of pure polypropylene. In this case, an increase in the value of coefficient K by approx. 15 % is observed. The improvement in the processability of composites containing modified calcium carbonate is a consequence of stearic acid that reduces the flow resistance by acting as a slip agent whose task is, among other things, to reduce the internal friction in polymeric material [5, 42]. Comparing the value of the K factor for composites containing two different types of fillers, it was found that for each of the
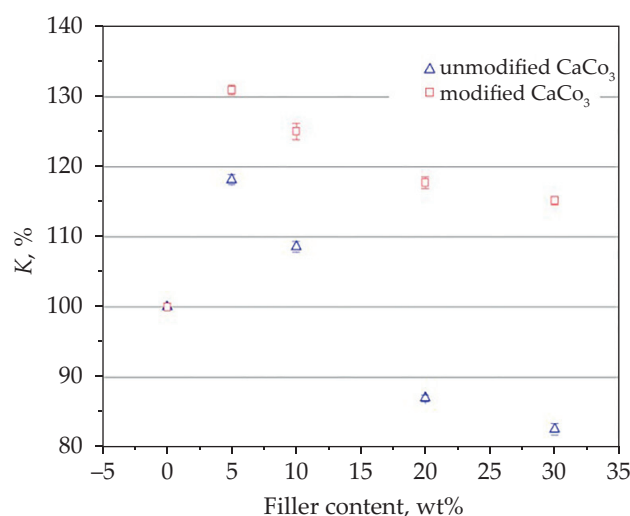

Fig. 2. The changes in processability (K coefficient) of polypropylene as the filler content

concentrations used, systems containing modified $CaCO_3$ had better processability.

Research carried out earlier on the effect of adding calcium carbonate to the polyethylene matrix [10, 32] allowed one to conclude that the addition of unmodified $CaCO_3$ to polypropylene would worsen processability. As follows from the summarized values of coefficient K, adding small quantities of unmodified calcium carbonate (5 and 10 wt%) improves the processability of PP. This phenomenon is characteristic of powder fillers with a small particle size, which acts similarly to plasticizers or lubricators in small quantities. By penetrating into intermolecular gaps, the filler particles reduce polymer–polymer interactions, reducing flow resistance [7]. A worsening of processability takes place for composites containing 20 and 30 wt% $CaCO_3$. For composite UC30, the value of coefficient K decreases by 17.5%. The changes in the processability of composites have found their confirmation in changes in viscosity determined in in-line rheological measurements in the extrusion process [37] and during the analysis of flow resistance in the engineering conditions of extruding composite films [39]. It should be noted that the described rheological characteristics of composites were determined in shear flows, in which the maximum share rate magnitudes amounted to 800 s^{-1}.

The design of the measuring head and the capability to perform injection at a constant preset melt volume-flow rate made it possible to determine the resistance during flow through the measuring capillary. For each material tested, the value of was determined before entry to the measuring capillary channel in the conditions of the constant preset melt volume-flow rate. Figure 3 shows the diagrams of the relationship for composites containing, respectively, unmodified, and modified calcium carbonate. The obtained variation of pressure drops during the flow of composites containing unmodified $CaCO_3$ partly

coincide with the relationships obtained from the measurements of MFR. The addition of small quantities of the filler does not cause increases in flow resistance. For the composite with the smallest $CaCO_3$ content (UC5), a shift of the curve $\Delta p = f(\dot{Q})$ towards smaller Δp values are observed. For the composite containing 10 wt% of the filler, on the other hand, recorded pressure drops were very similar to those occurring during injection of pure polypropylene. An increase in flow resistance in technological processes entails an increase in energy outlay [43]. The recorded pressure changes revealed a convenient aspect related to the processing of low $CaCO_3$ content composites of series UC. Despite applying the addition of the unmodified filler, composites containing 5 and 10 wt% of calcium carbonates will be able to be processed under polymer matrix processing conditions. A distinct growth in pressure is observed for a propylene fill of 20 and 30 wt% (UC20 and UC30), respectively, which indicates an increase in flow resistance because of increased friction in the shear flow of composite systems [44]. The behaviors of the $\Delta p = f(\dot{Q})$ curves determined during injection of composites UC20 and UC30 are consistent with the variations of the processability coefficient K. No such consistency occurs for composites containing 20 and 30 wt% of the modified filler. As follows from the value of coefficient K, composites MC20 and MC30 should be characterized by smaller magnitudes of flow resistance during injection compared to unfilled polymer; however, no such relationship is observed. A clear shift of the $\Delta p = f(\dot{Q})$ curve towards larger pressure values occurs after the addition of 20 and 30 wt% of the modified filler, as compared to polypropylene. The most significant flow resistances occurred for the composite of the largest fill percentage (MC30). The discrepancies in the assessment of composite processabilities determined with a plastometer, relative to the pressure drop variations in in-line measurements conducted under experi-
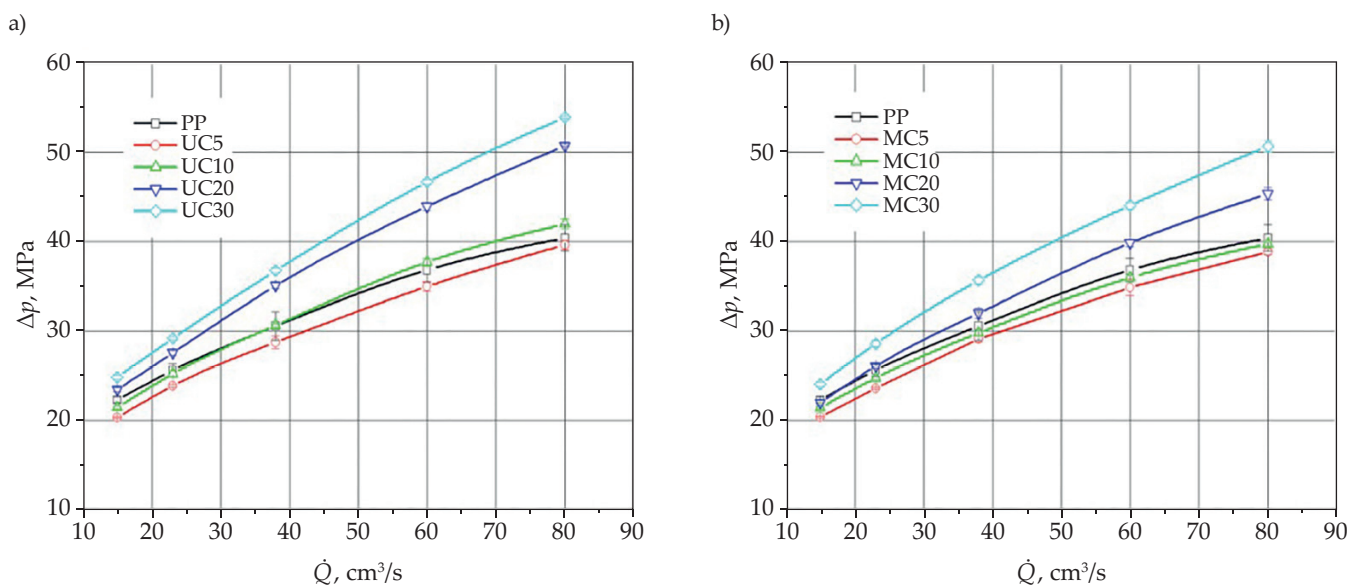

Fig. 3. Pressure drops (Δp) vs. volume flow rate for PP and composites: a) unmodified $CaCO_3$, b) modified $CaCO_3$

ment conditions, might be due to, among other things, variations in flow conditions, i.e., the occurrence of varying test values of the shear rate and shear stress ranges [9]. An analysis of variations in Δp values showed a positive effect of the filler surface modifier (stearic acid) on the flow resistance determined in the adopted experiment conditions. In each of the $CaCO_3$ concentrations considered, smaller Δp values occurred during the flow of a composite containing modified calcium carbonate (MC). For example, in the conditions of a melt volume flow rate of 60 cm^3/s, the magnitude of Δp for composite MC20 was 39.8 ± 0.39 MPa, while for composite UC20 it increased to a level of 43.9 ± 0.44 MPa.

As can be seen from the shape of the curves, the Δp value grows naturally with the increase in $\dot{Q}$. High repeatability of results was obtained from the measurements, and the determined $\Delta p = f(\dot{Q})$ curves are characterized by a substantial monotonicity of variation, which indicates a good homogenization of the composite materials and stability of the flows under analysis [44, 45].

The specificity of the injection moulding machine plasticizing system makes it possible to conduct measurements for fixed preset values of melt volume-flow rates and, thus, for constant preset values of apparent share rate, which were calculated from Equation (4). Using Equation (3), the values of shear stress were also determined from the curves $\Delta p = f(\dot{Q})$. The measurement ranges of apparent share rate ($\dot{\gamma}_a$) and the obtained values of shear stress (τ_w) are collected in Table 3. The variations in the values of τ_w under the adopted shear rate conditions, depending on the type of filler and its content, are identical to the patterns occurring in Δp variations, as discussed above.

T a b l e 3. Ranges of apparent shear rate, apparent shear stress and the value of the power law index

Sample	Apparent shear rate, s^{-1}	Apparent shear stress, kPa	Power law index n, /
PP		279 - 505	0.360
UC5		254 - 494	0.397
UC10		268 - 524	0.405
UC20		293 - 634	0.466
UC30	19,100 – 101,900	310 - 673	0.468
MC5		255 - 485	0.390
MC10		268 - 496	0.374
MC20		220 - 453	0.434
MC30		300 - 633	0.446

In the adopted measurement range of shear rate, a rectilinear relationship of the flow curves was obtained for all test materials, which allowed the results to be described using the Ostwald-de-Waele power law model [14, 15]. Figure 4 shows the flow curve (on the ln – ln scale) obtained during the flow of a composite containing 10 wt% of unmodified calcium carbonate (UC10), from

which the power law equation constants n and k were determined. The values of the power law index are contained in an interval characteristic of thermoplastic polymers (from 0.19 to 0.80) [14] and are indicative of the pseudoplastic character of the composites examined ($n < 1$) [46]. The addition of calcium carbonate and its modified form changes the n value of polypropylene composites; however, it does not influence the character of the fluid – the composites behave in flow like a shear-diluted liquid throughout the flow. Based on the research results presented in the previous publication [37], the rheological characteristics were determined in the extrusion process for a maximum apparent shear rate of approx. 700 s^{-1} an increase in the pseudoplastic character of PP/$CaCO_3$ composites flow was shown, which meant a drop in n values with increasing $CaCO_3$ content in the polymer matrix. Such dependences were not demonstrated in flows conducted under high shear rates (see Table 3).

An increase in the value of the power low index was found compared to the unfilled polymer material, regardless of the amount and type of filler used. This effect proves a different change in the pseudoplastic properties of the tested materials. Additionally, higher n values were found for composites containing unmodified filler. Higher values of the power law index of composite materials result in a lower shear thinning effect under increasing shear rate. Compared to the analysis performed at lower shear rates [37], most likely, the phenomena related to the increase in viscosity due to the increase of filler content in the composite exceeded the previously observed lubricating effects. Nevertheless, the lubricating effect of stearic acid is still observed, which reduces the n value when comparing composites with the same filler content.

The use of the Rabinovitch correction (5) allowed the measurements to be conducted for non-Newtonian liquids, i.e., a group that includes plasticized polymers and polymer composites [14]. Figure 5 juxtaposes viscosity curves determined for a polypropylene composite con-
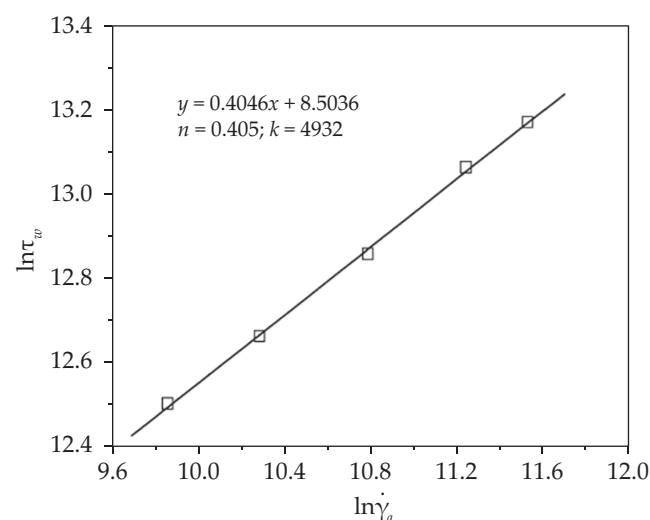
$y = 0.4046x + 8.5036$
$n = 0.405; k = 4932$

Fig. 4. Relationship between $\ln(\tau_w)$ and $\ln(\dot{\gamma}_a)$ for polypropylene composites – UC10 (10 wt% unmodified $CaCO_3$)

taining unmodified (Fig. 5a) and modified (Fig. 5b) calcium carbonate. For all examined polymeric materials, the behaviors of the curve's characteristic of Newtonian pseudoplastic shear-diluted liquids were obtained [15]. Research on composites of thermoplastic polymers with calcium carbonate indicates a varying influence of $CaCO_3$ addition on the polymer viscosity. The variety of interactions may be due to the particle size of calcium carbonate, its quantity [5], as well as the ranges of shear rates occurring in the flow [34, 46]. In the case of the addition of $CaCO_3$ in the amount of 5 wt%, a shift of the $\eta_w = f(\dot{\gamma}_w)$ curves towards smaller viscosity values are observed compared to polypropylene. The shifts of the viscosity curves are very similar in character for both filler types. As mentioned earlier in this paper, a change of this type is a consequence of a specific interaction of small quantities of a small particle-size filler with the polymer matrix. The particles of the filler penetrate the gaps between the polymer chains, where they act as plasticizers, resulting in a reduction of polymer intermolecular interactions, leading to a decrease in polymer viscosity [7, 37].

This effect was observed in the variations of the processability coefficient K discussed earlier and occurred for the addition of 5 and 10 wt% of unmodified and modified $CaCO_3$, respectively. It should be emphasized, however, that the flow of polymeric material in the measuring capillary of a dead-weight plastometer (at a piston load of 2.16 kg) occurs in shear rates not exceeding the value 10 s^{-1} [5, 9]. Under the conditions of acting high shear rates, such a significant decrease in PP viscosity because of filling with calcium carbonate at a level of 5 wt% is no longer observed. For example, the viscosity of polypropylene for shear rate at a level of 70,000 s^{-1} is 5.53 Pa·s, while for composite UC5, 5.23 Pa·s. In the same share rate conditions, the viscosity of a composite containing 5 wt% of modified $CaCO_3$ (MC5) takes on a value of 5.27 Pa·s. From the analysis of the K coeffi-

cient determined in off-line measurements, a decrease in the value of η_w might also be expected for composites containing 10 wt% of the filler. The course of the curves $\eta_w = f(\dot{\gamma}_w)$ suggests that the addition of 10 wt% of either unmodified or modified $CaCO_3$ does not marked reduce the change in the viscosity of composites compared to PP in the 27,000 s^{-1} corrected share rate. Importantly, due to the lower susceptibility to shear thinning (higher n value), the difference in viscosity between PP and composites will change with increasing shear rate. For UC10 composite at $\dot{\gamma}_w$ aprox. 43,000 s^{-1}, the viscosity of the composite begins to be higher than that of PP. Similarly, for composites with a filler modified with stearic acid, this is only observed at approximately 140,000 s^{-1}.

A significant increase in viscosity is observed only at a calcium carbonate fill of up to 20 and 30 wt%. There are noticeable shifts of the viscosity curves towards larger values of η_w. It should also be noted that the position of the viscosity curves for composites containing modified calcium carbonate (MC20 and MC30) is not identical with the changes in the processability coefficient K (see Fig. 2). The K value, even at a modified $CaCO_3$ fill of 20 and 30 wt%, was greater than that of the polymer matrix ($K = 100\%$). As shown by the relative position of the viscosity curves in Figure 5b, the addition of the modified filler in the amount of 20 and 30 wt%, respectively, increases the resistance of flow in the head's measuring capillary, increasing the value of . Additionally, considering the previously described n relationships, an increase in the relative viscosity difference between the composites and PP is visible. The viscosity of UC30 was 17% higher at 30,000 s^{-1} and as much as 36% higher at 130,000 s^{-1} than PP. Similarly, for MC 30 composites, this difference was 13% and 28%, respectively.

It can be said that the viscosity modification functions attributed to calcium carbonate and stearic acid [47] in high shear rate conditions are to some extent limited.
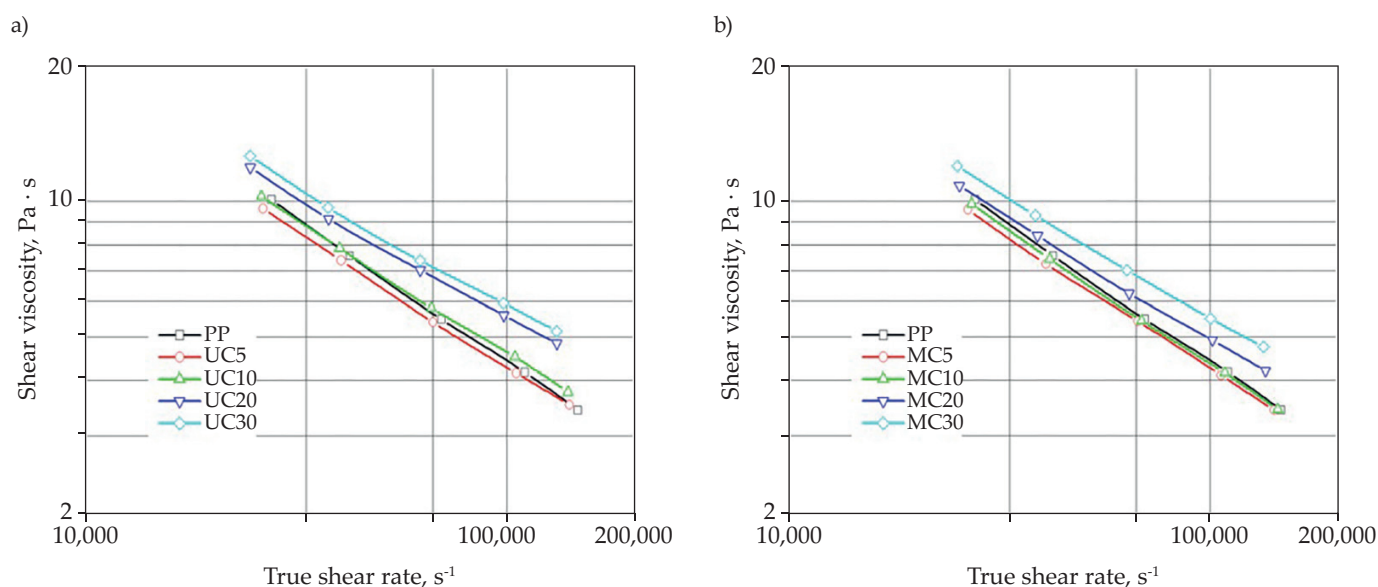
a)

b)

Fig. 5. Shear viscosity vs. true shear rate for PP and composites: a) unmodified $CaCO_3$, b) modified $CaCO_3$

Thereby, the behavior of composite materials in injection process conditions deviates from the characteristics made by off-line measurements (with a dead-weight plastometer). The increase in viscous flow resistance due to the introduction of calcium carbonate to the polymer matrix in the concentrations mentioned above can be explained by the occurrence of the forces of adhesion of polymer macromolecules to the surface of the solid body ($CaCO_3$), resulting in an increase of viscous energy dissipation in the fluid [48]. The change in the nature of the filler's influence on the rheological properties of PP/$CaCO_3$ composites at high shear rates may also result from the migration of fillers transverse to the channel axis during the flow of filled fluids. As a result of the heterogeneous system of shear forces in the channel cross-section, the fillers migrate to the channel axis. As a result of this phenomenon, a smaller amount of filler is observed in the thin layer wall channel region than would result from the composition of the composite. This layer facilitates flow, exhibiting effects like process lubricants or wall slip effects [40, 48–51]. Due to the large share of filler in composites containing 20% and 30% of filler, the migration of filler particles may be significantly limited; hence, the rheological characteristics may differ from those for composites with lower $CaCO_3$ contents. Similar conclusions were drawn in the works [25, 26], but additional effects were also attributed to the rotation of the longer filler particles. However, as it has been shown, both in the analysis of the flow index and in the viscosity curves, in the case of symmetrical fillers such as $CaCO_3$, the impact of the filler on the rheological and pseudoplastic properties at high shear rates is different.

When analyzing the viscosity variations from the point of view of the application of the filler surface modifier, one can notice some degree of influence of stearic acid on the viscosity of MC series composites, compared to composites of series UC; this applies to systems with identical filler content. For each applied filler concentration, smaller viscosity values occurred in the flows of composites containing modified calcium carbonate. Figure 6 shows viscosity variation curves determined for composites containing unmodified and modified $CaCO_3$ in the amount of 20 wt%. Modification of the filler surface entails a reduction of flow resistance and, thus, a lowering of composite viscosity. For the shear rate 110,000 s^{-1}, the difference in the value of η_w between composites UC and MC is 0.59 Pa·s. The value of the absolute difference in viscosity is not great, but it represents a 10% reduction in viscosity compared to composites based on unmodified filler. Under technological conditions, with fast injection cycles of thin-walled products, such a difference in viscosity may have some technological significance.

CONCLUSIONS

The investigation results presented in this paper describe the effect of the addition of modified and
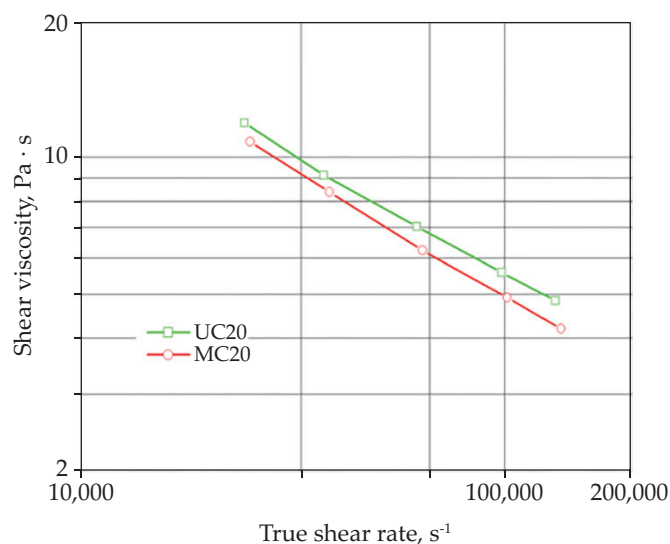

Fig. 6. Shear viscosity vs. true shear rate for polypropylene composites (UC20, MC20)

unmodified calcium carbonate on the rheological properties of polypropylene composites, as determined in the conditions of high shear rates in the injection moulding process. Comparison of processing and rheological characteristics determined by two techniques (off-line and in-line measurements) has shown a diverse behavior of polymer composites in flows, resulting from a varying fill degree, type of applied filler, and measuring range of shear rate. The variations in the processability coefficient *K* (being the percentage ratio of composite MFR to polymer matrix MFR) have only partially confirmed changes in composite viscosity determined in injection process conditions. Therefore, it becomes reasonable to claim that measurements conducted using off-line testing apparatus (in this case, the dead-weight plastometer) do not reflect the direct technological relationships and may deviate from the behavior of polymers in processing conditions [9, 29]. Comparing the obtained results with the previously described tests [37], it can also be said that different rheological characteristics are obtained in in-line measurements carried out in various technological processes. The dominant factor influencing the rheological parameters (*e.g.*, η, *n*) is the shear rate - its ranges. The investigation has also demonstrated that the comprehensive rheological characteristics require different types of research techniques to be used, and approaching a material's behavior in processing conditions creates the need for conducting measurements at the appropriate shear rate magnitudes.

REFERENCES

[1] Abbasian M., Shahparian M., Bonab S.E.S.: *Iranian Polymer Journal* **2013**, 22, 209.

https://doi.org/10.1007/s13726-012-0120-4

[2] Bulanda K., Oleksy M., Oliwa R. *et al.*: *Polymers* **2021**, *13*, 2455.
https://doi.org/10.3390/polym13152455

[3] Wang X., Tzoganakis C., Rempel G.L.: *Journal of Applied Polymer Science* **1996**, *61*, 1395.
https://doi.org/10.1002/(SICI)1097-4628(19960822)61:8<1395: AID-APP21>3.0.CO;2-

[4] Aid S., Eddhahak A., Ortega Z. *et al.*: *Journal of Applied Polymer Science* **2017**, *134*, 44975.
https://doi.org/10.1002/app.44975

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

[6] Stepczyńska M., Pawłowska A., Moraczewski K. et al.: *Materials* **2021**, *14*, 4241.
https://doi.org/10.3390/ma14154241

[7] 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

[8] Barzegari R.M., Alemdar A., Zhang Y., Rodrigue D.: *Polymer Composites* **2012**, *33*, 353.
https://doi.org/10.1002/pc.22154

[9] Kloziński A., Barczewski M.: *Polimery* **2019**, *64(2)*, 83.
https://doi.org/10.14314/polimery.2019.2.1

[10] Kloziński A., Jakubowska P.: *Polymer Engineering and Science* **2019**, *59(s2)*, E16.
https://doi.org/10.1002/pen.24941

[11] Broadhead T.O., Patterson W.I., Dealy J.M.: *Polymer Engineering and Science* **1996**, *36*, 2840.
https://doi.org/10.1002/pen.10685

[12] Abu-Zahra N.H.: *International Polymer Processing* **2003**, *18*, 362.
https://doi.org/10.3139/217.1759

[13] Chakravorty S., Allen C.R.G., Brown C.S.: *Polymer Testing* **1997**, *16*, 445.
https://doi.org/10.1016/S0142-9418(97)00007-X

[14] Schramm G.: "A Practical Approach to Rheology and Rheometry". Gebrueder HAAKE GmbH, Karlsruhe 1994.

[15] Mezger T.G.: "The Rheology Handbook 2nd Edition", Vincentz Network GmbH and Co. KG 2006.

[16] Callis J.B., Illman D.L., Kowalski B.R.: *Analytical Chemistry* **1987**, *59*, 624A.
https://doi.org/10.1021/ac00136a001

[17] Kelly A.L., Woodhead M., Coates P.D.: *SPE ANTEC Techn. Papers* **1997**, *43*, 1119

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

[19] Barczewski M.: *Polimery* **2015**, *61*, 248.
https://doi.org/10.14314/polimery.2016.248

[20] Mazzanti V., Mollica F.: *Polymer Testing* **2015**, *47*, 30.
http://dx.doi.org/10.1016/j.polymertesting.2015.08.003

[21] Sykutera D., Czyżewski P., Kościuszko A. *et al.*: *Journal of Polymer Engineering* **2018**, *38*, 63.
http://dx.doi.org/10.1515/polyeng-2016-0321

[22] Sykutera D., Wajer Ł., Kościuszko A. *et al.*: *Macromolecular Symposia* **2018**, *378*, 1700056.

http://dx.doi.org/10.1002/masy.201700056

[23] Kelly A.L., Gough T., Whiteside R., Coates P.D.: *Journal of Applied Polymer Science* **2009**, *114*, 864.
https://doi.org /10.1002/app.30552

[24] Fernandez A., Muniesa M., Javierre C.: *Polymer Testing* **2014**, *33*, 107.
https://doi.org/10.1016/j.polymertesting.2013.11.008

[25] Lewandowski K., Piszczek K., Zajchowski S., Mirowski, J.: *Polymer Testing* **2016**, *51*, 58.
https://doi.org/10.1016/j.polymertesting.2016.02.004

[26] Lewandowski K., Piszczek K., Skórczewska K. *et al.*: *Composites Part A: Applied Science and Manufacturing* **2022**, *154*, 106804.
https://doi.org/10.1016/j.compositesa.2022.106804

[27] Friesenbichler W., Duretek I., Rajganesh J., Kumar S.R.: *Polimery* **2011**, *56(1)*, 58.
https://doi.org/10.14314/polimery.2011.58

[28] Kloziński A.: *Polymer Testing* **2019**, *73*, 186.
https://doi.org/10.1016/j.polymertesting.2018.11.020

[29] Dealy J.M., Saucier P. C.: "Rheology in Plastics Quality Control", Hanser Publishers, Munch 2000.

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

[31] Stasiek A., Raszkowska-Kaczor A., Formela K.: *Przemysł Chemiczny* **2014**, *93*, 888.
https://doi.org/10.12916/przemchem.2014.888

[32] Kloziński A.: *Polimery* **2016**, *61(11-12)*, 788.
https://doi.org /10.14314/polimery.2016.788

[33] Nwabunma D., Kyu T.: "Polyolefin Composites", Wiley – Interscience, Canada 2008.

[34] Upadhyay R. D., Kale D.D.: *Journal of Polymer Research* **2001**, *8*, 175.
https://doi.org/10.1007/s10965-006-0148-2

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

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

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

[38] Żenkiewicz M., Richert J., Rytlewski P. *et al.*: *Polimery* **2010**, *55*, 119.
https://doi.org/10.14314/polimery.2010.119

[39] Kloziński A., Szczepańska M., Jakubowska P. *et al.*: *Polimery* **2022**, *67*, 509.
https://doi.org/10.14314/polimery.2022.10.1

[40] Barczewski M., Lewandowski K., Schmidt M., Szostak M.: *Polymer Engineering and Science* **2017**, *57*, 998.
https://doi.org/10.1002/pen.24477

[41] Steller R.T.: *Journal of Applied Polymer Science* **2005**, *97*, 1401.
https://doi.org/10.1002/app.21156

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

[43] Teixeira S. C. S., Moreira M. M. *et al.*: *Journal of Applied Polymer Science* **2006**, *101*, 2559.

https://doi.org/10.1002/app.23920

[44] Sikora J.W., Samujło B.: *Polymer Engineering and Science* **2014**, *54*, 2037.
https://doi.org/10.1002/pen.23756

[45] Samujło B., Sikora J.W.: *Journal of Polymer Engineering* **2013**, *33*, 77.
https://doi.org/10.1515/polyeng-2012-0100

[46] Nakason C., Kaesaman A., Samoh Z. *et al*.: *Polymer Testing* **2002**, *21*, 449.
https://doi.org/10.1016/S0142-9418(01)00109-X

[47] Jakubowska P., Sterzyński T., Samujło B.: *Polimery* **2010**, *55*, 379.

https://doi.org/10.14314/polimery.2010.379

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

[49] Stabik J.: *Polimery* **2004**, *49*, 712.
https://doi.org/10.14314/polimery.2004.712

[50] Barczewski M., Lewandowski K., Rybarczyk D., Kloziński A.: *Polymer Testing* **2020**, *91*, 106768.
https://doi.org/10.1016/j.polymertesting.2020.106768

[51] Shenoy AV, editor.: "Rheology of Filled Polymer Systems", Springer Netherlands, Dordrecht 1999.

Received 12 VI 2023

Katedra Inżynierii i Technologii Polimerów
Politechniki Wrocławskiej
zaprasza do udziału w

XXVI Konferencji Naukowej
MODYFIKACJA POLIMERÓW
11–14 września 2023 r., Karpacz

„Modyfikacja Polimerów" będąca najstarszą cykliczną konferencją polimerową w kraju, stanowi doskonałą okazję do spotkania przedstawicieli uczelni wyższych, instytutów naukowych, firm produkcyjnych, jak i osób zaangażowanych w opracowywanie zastosowań najnowszych materiałów polimerowych.

Celem konferencji jest prezentacja i wymiana doświadczeń wynikających z prowadzonych prac naukowych w obszarze szeroko pojętej fizycznej i chemicznej modyfikacji polimerów.

Przewodniczący Konferencji i Komitetu Organizacyjnego
prof. dr hab. inż. Andrzej Trochimczuk

Sekretarz Konferencji
dr inż. Sylwia Ronka

Konferencja będzie poświęcona multidyscyplinarnym zagadnieniom związanym z polimerami, począwszy od podstawowej syntezy i metodologii do nanoskali i materiałów inspirowanych polimerami naturalnymi.

Tematyka konferencji:
* Modyfikacja chemiczna i fizyczna oraz reaktywne przetwarzanie polimerów
* Synteza, struktura i morfologia polimerów
* Kompozyty i Nanokompozyty polimerowe
* Biomateriały i ich zastosowanie biomedyczne
* Materiały kompozytowe reagujące na bodźce
* Tworzywa polimerowe z surowców odnawialnych i wtórnych
* Biodegradowalne polimery i strategia recyklingu
* Nowe zastosowania oraz metody badań i właściwości polimerów

Opłaty konferencyjna:
1750 zł (pełna opłata); 1500 zł (opłata za doktoranta/studenta)
1300 zł (opłata za osobę towarzyszącą)
Opłata konferencyjna obejmuje: uczestnictwo w konferencji, pełne wyżywienie – od kolacji 11 września do obiadu 14 września (śniadania wyłącznie dla gości zakwaterowanych w hotelu Green Mountain), uroczystą kolację, przerwy kawowe, publikację artykułu w pracy zbiorowej: „Modyfikacja Polimerów Stan i Perspektywy w roku 2023", materiały konferencyjne.
Opłata za hotel: opłata konferencyjna nie zawiera noclegów. Każdy z uczestników dokonuje rezerwacji indywidualnie. Cena noclegu dla uczestników konferencji (na hasło MODPOL23) wynosi odpowiednio: 360 zł (opłata za 1 noc w pokoju 1-osobowym), 400 zł (opłata za 1 noc za pokój 2-osobowy – 200 zł/os.).

Miejsce konferencji: Hotel Green Mountain, Karpacz

modpol.pwr.edu.pl