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Simultanous Modification of Dimensional Stability and Mechanical Processing of Injection Molded Polypropylene Using Gypsum Waste and Chemical Blowing Agent

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ABSTRACT

The dimensional accuracy of injection molded parts plays an increasingly significant role in the plastics processing industry, as is the utilization of recycled raw materials. To obtain the desired dimensions and properties of injection moldings, various material modification methods are used simultaneously. The conducted research aimed to assess the impact of hybrid modification of non-nucleated heterogeneously isotactic polypropylene using recovered phosphogypsum and a chemical blowing agent on the shrinkage value and mechanical properties of injection molded parts. Additionally, changes in dimensions and properties of composites with solid and porous structures that occur within 1000 hours of their removal from the injection mold were determined. The research showed that the filler used acts as a nucleating agent causing an increase in the shrinkage of the parts, up to 10 wt%. Similar changes were observed in the case of tensile strength. The increase in the value of this parameter at the lowest phosphogypsum contents used was most likely the result of changes in the crystalline structure of polypropylene. Changes in the mechanical properties of the molded parts that occurred during conditioning are correlated with shrinkage changes that occur from the moment the molded parts are removed from the injection mold. Young's modulus and tensile strength increased linearly for both solid and porous moldings. However, the rate of stiffness increases as a function of shrinkage changes with the filler content. Nevertheless, the opposite tendency was observed in the case of changes in impact strength, the values of which decreased as a function of shrinkage to the greatest extent in the case of unfilled polypropylene.

Keywords: post-molding shrinkage, polypropylene, cellular injection molding, gypsum waste, recycling.

INTRODUCTION

Polypropylene (PP) is the most commonly used polymer material in the industry. The production of this material accounts for approximately 19% of all polymeric materials produced [1]. The wider variety of species available on the market than most other plastics evidences its popularity [2]. This is because of the wide possibilities of its modification, allowing it to adapt its properties to recipients' needs. Therefore, polypropylene attracts significant attention across different economic sectors. Various types of organic and inorganic fillers are commonly used to modify polypropylene. Companies often fill commercial grades of PP with chalk [3], talc [4], or glass fibers [5, 6]. However, in scientific research, researchers are increasingly using waste raw materials from various industries such as agriculture [7, 8], wood industry [9, 10, 11], automotive industry [12, 13, 14], and even metallurgy [15] as fillers. Introducing recovered fillers into the polymer matrix allows for the utilization of this type of raw materials. Using recycled fillers is also justified in responding to global challenges related to, among others, climate change. Recycled raw materials significantly reduce the carbon footprint of products, and replacing even part of the basic polymer with an inorganic filler significantly reduces the PCF (Product Carbon Footprint) index. The modification may reduce the cost of the manufactured material and a change in its mechanical properties [16]. Additionally, recovered raw materials can change the less obvious properties of polypropylene. Previous work has shown that recovered silica from the metallurgical industry acts as a heterogeneous nucleating agent, increasing the crystallization temperature of PP, and as an additive for laser marking, enabling the application of graphic symbols to entrusted materials using laser light [17].

The desired effect of filling polymeric materials is also the reduction of shrinkage, i.e. the percentage difference between the size of the injection mold cavity and the size of the molded part 16–24 hours after the processing cycle (primary shrinkage). Because of its semi-crystalline structure, PP shows a relatively high shrinkage value (1.3–2.5%). The injection process parameters can control the geometry of the molded parts, but only to a certain extent. To achieve lower shrinkage of molded parts, it is possible to increase the clamping pressure and/or extend the duration of the clamping phase [18], as well as reduce the temperature [19] and the injection speed [20]. Kościuszko et al. showed that increasing the injection mold temperature from 20 °C to 80 °C results in an increase in the shrinkage value of PP moldings by just over 0.1 percentage point (6%) [21]. An additional increase in dimensional stability characterizes filled polypropylene materials. According to Shelesh-Nezhad's research [4], a polypropylene composite with 20 wt% talc filler has a 0.1 percentage point lower longitudinal shrinkage, measured after 24 hours, compared to the unfilled matrix. In this case, the shrinkage reduction amounted to 6%. The change in geometry was also accompanied by a reduction in stress at the yield point by almost 9% and a 10% increase in bending strength. The results of research by Ryu et al. [22] show that the use of 20 wt% glass fibers as a filler results in a reduction in shrinkage measured 48 h after the injection cycle by 1.4 percentage points, i.e. by over 80%. Tan [23] showed that using plant fibers can achieve a similar reduction in shrinkage. A significant reduction in shrinkage when using fibrous fillers results from the shape of their particles and their arrangement along the flow path in the core layer of the molded part.

Shrinkage phenomena are not limited to linear shrinkage. A method commonly used to reduce shrinkage phenomena is also the technology of physical [24, 25, 26] or chemical [27, 28, 29] blowing injection. In this case, the role of the pressure phase, responsible for compensating the volume reduction of the polymer material during cooling and phase transformation, is taken over by the gas pressure inside the expanding pores [30]. An earlier publication demonstrated that the blowing injection process achieved the highest efficiency in reducing the mass of moldings and collapses when it did not implement the pressure phase. However, the use of a chemical blowing agent did not reduce the longitudinal shrinkage of polypropylene moldings, and even the shrinkage value was higher compared to solid moldings. Researchers have also attempted to hybridly modify polypropylene by simultaneously filling and blowing it. Llewyn [32] and Palutkiewicz [33] used chemical blowing agents together with talc. However, the main goal of their research was to assess the structure and mechanical properties of the obtained materials. The research did not address reducing longitudinal shrinkage.

The dimensions of polypropylene injection moldings after removal from the injection mold and cooling to ambient temperature are not stable [21]. Slow shrinkage of molded parts may still occur many hours after production, which results from ongoing secondary crystallization. Changes in the geometry of the molded parts during conditioning are also accompanied by changes in mechanical properties [31], which are caused by a change in the degree of crystallinity of the polymer material. Chemical changes occurring in the material or physical aging may also cause changes in the mechanical properties of polypropylene moldings during storage or operation [34].

The aim of the research was to assess the impact of simultaneous modification of polypropylene injection moldings using a chemical blowing agent and recovered gypsum from the fertilizer industry on the occurring shrinkage phenomena and mechanical properties. In addition, changes in the dimensional accuracy of the molded parts and the accompanying changes in mechanical properties occurring during conditioning outside the injection mold were examined.

MATERIALS AND METHODS

Materials

The matrix of the manufactured composites was a commercial grade of polypropylene with the trade name Moplen HP 500N (Basell Orlen Polyolefins, Płock, Poland). The value of the mass melt flow rate, according to the manufacturer's declaration, was equal to 12 g/10 min. Additionally, it is worth noting that this material does not include any heterogeneous nucleating agents. The average value of Young's modulus (E) and the stress at yield measured 24 h after demolding were 1020 MPa and 26.11 MPa, respectively. These values were clearly lower than those declared by the manufacturer in the datasheet (1400 MPa).

Additionally, the tests involved the use of calcium sulfate (Aliand S.A., Kleszczów, Poland). The inorganic filler was a raw material recovered from waste generated during the production of phosphorus fertilizers. The filler contained calcium sulfate, with a content ranging from 92 to 98%. In the modifier, there were percentages of zinc oxide (1–2 wt%), calcium oxide (1–3 wt%), and phosphorus oxide (0–3 wt%). The filler had the form of grains whose size ranged from 10 to 200 µm. The range of 10 to 20 µm was the most prevalent fraction in the raw material, as depicted in Figure 1a. The determination of particle size was based on optical analysis conducted using a Keyence VHX-7000 microscope (Osaka, Japan). Figure 1b shows a photograph of filler particles.

A commercial endothermic chemical blowing agent (CBA) as a concentrate under the trade name Hydrocerol ITP 825 by Clariant (Muttenz, Switzerland) was used as a modifier in the research. The active substance content in the modifier was 40% by mass. A comparison of the thermal characteristics of the polypropylene used in the tests and the chemical blowing agent was presented in a previous publication [31].

Samples preparation

The homogenization of PP and phosphogypsum was performed by an extrusion line for granulation, which included a twin-screw extruder ZSE 18 maxx produced by Leistritz (Nürnberg, Germany). The screw diameter (D) was 18.5 mm, and the ratio of the screw length to its diameter (L/D) was 48. The temperature of the plasticizing system was from 160 °C (feeding zone) to 200 °C (metering zone). The head temperature was 200 °C and the rotational speed of the screws was 1000 rpm. Before the extrusion process, the phosphogypsum powder was dried for 4 h at 100 °C using a FED 115 Binder dryer (Tuttlingen, Germany). There were five compositions prepared, each with different assumed content of inorganic filler in the range of 0–40 wt%.

The test samples were made by injection molding using an Engel e-victory 110 (Schwertberg, Austria) machine with a mold closing force of 1100 kN, screw diameter (D) of 35 mm. The four-cavity injection mold equipped in the machine allowed the production of universal test samples (dog-bone shape) with a geometry complaint with the ISO 3167:2014 standard (type A).

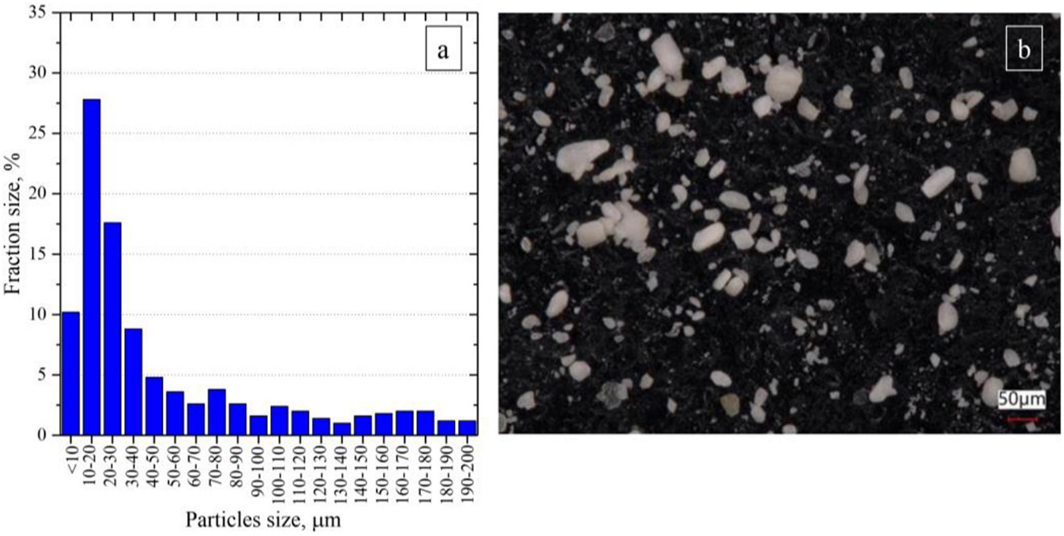

Figure 1. Size distribution of phosphogypsum particles (a), inorganic filler particles (b)

The injection mold was thermostated using the HB 160 device from HB-Therm. In a previous publication [31], the model of the molded part was presented.

The research program assumed the production of two series of polypropylene moldings with different phosphogypsum content. The first series had a solid structure, while the second series became porous because of the addition of 3 weight percent chemical blowing agent into the material. Solid moldings were produced with a pressing time of 21 s. The cycle for producing moldings with a porous structure was devoid of the pressing phase, which was to allow the pores to grow freely in the material's structure. The actual cooling time, i.e. the sum of the pressing time and the setting cooling time, was equal to 45 s in both cases (Table 1).

The injection temperature and mold temperature were 230 °C and 20 °C, respectively. Table 2 includes the summarized constant parameters of the sample injection process. Immediately before the injection process, the granulates were dried for 4 h at a temperature of 100 °C. The obtained samples were conditioned for 1000 h at 23 °C and RH = 50%. Figure 2 shows a diagram illustrating the sample preparation process.

Measurements of sample density

Density (ρ) investigation of composite samples with different filler content was carried out using the immersion method. An AD 50 (Axis, Gdańsk, Poland) laboratory scale was used in these measurements. The device's set allowed it to determine the mass of the samples in the air and, after immersion in a liquid, which was methyl alcohol with a density (ρ_L) of 0.792 g/cm^3. Measurements were made at 23 ± 2 °C after 1 hour and 1000 hours of conditioning. The density of individual samples was calculated using the following formula (1):

$$\rho = \frac{m \cdot \rho_L}{m - m_L} \tag{1}$$

where: the symbols m and m_L denote the mass of the sample determined in the air and in the immersion liquid, respectively.

Based on the determined density of composites with solid and porous structures, the share of the gas phase in the volume of porous materials was estimated. The calculations involved the use of the formula (2).

$$p = \frac{\rho - \rho_a}{\rho} \tag{2}$$

where: the symbol ρ denotes porosity, and ρ_a indicates apparent density, i.e. the density of composites with a porous structure.

Measurements of melting behavior

Measurements of thermal properties of PP composites filled with gypsum were carried out

Table 2. Constant parameters of the injection process

Processing parameters	Value
Feed zone temperature, °C	190
Transition zone temperature, °C	210
Metering zone temperature,°C	230
Nozzle temperature, °C	230
Mold temperature, °C	20
Counter-pressure, MPa	1.5
Injection speed, cm^3/s	75
Holding pressure, MPa	22

Table 1. Samples signature and selected process parameters

Series	Signature	Content of inorganic filler, wt%	Content of CBA, wt%	Holding time, s	Cooling time, s
1 – Solid	G	0	0	21	24
	G5	5	0	21	24
	G10	10	0	21	24
	G20	20	0	21	24
	G40	40	0	21	24
2 – Porous	GP	0	3	0	45
	GP5	5	3	0	45
	GP10	10	3	0	45
	GP20	20	3	0	45
	GP40	40	3	0	45

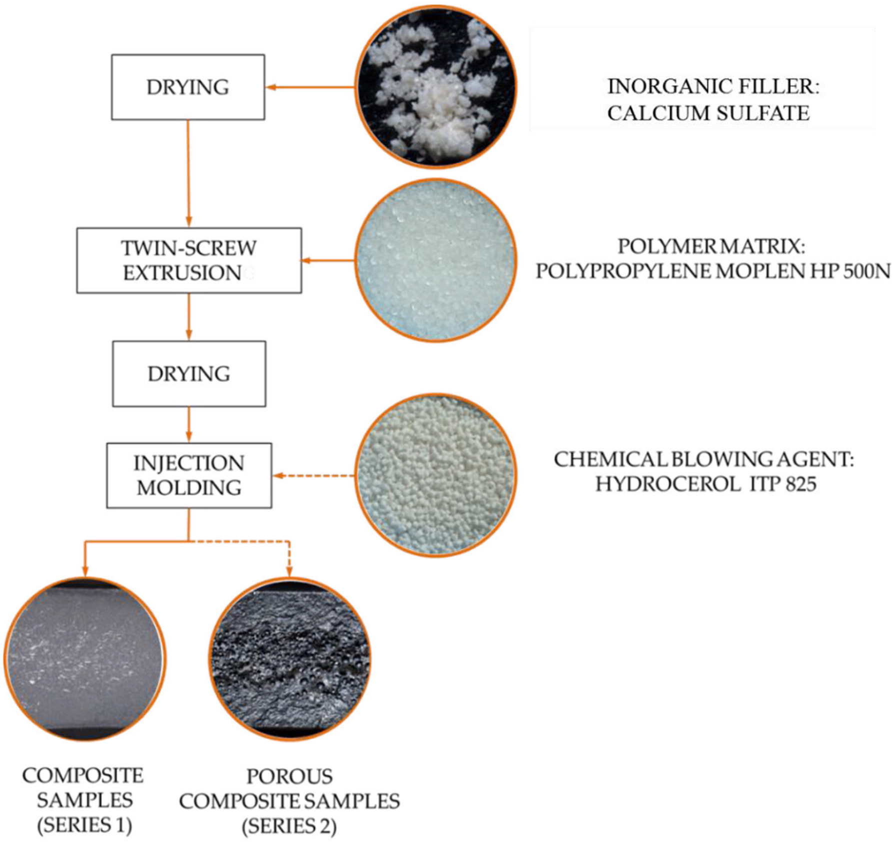

Figure 2. Samples preparation process

using the differential scanning calorimetry (DSC) method using the DSC 214 Polyma apparatus by Netzsch (Selb, Germany). The 8–10 mg samples were heated to 220 °C under nitrogen. After two minutes of exposure the samples were cooled to 25°C. The heating and cooling rate was 10 °C/min. The results of DSC tests were used to determine the degree of crystallinity (X_c) using the following formula:

$$X_C = \frac{\Delta H}{\Delta H_C \cdot \varphi} \cdot 100\% \quad (3)$$

where: ΔH_C is the melting enthalpy of the 100% crystalline PP, and φ is the weight fraction of PP matrix. On the basis of literature data [35], it was assumed that the melting enthalpy of PP with 100% crystallinity is 209 J/g.

Thermogravimetry

The F1 209 Libra device by Netzsch (Selb, Germany) was used to carry out thermogravimetric tests. Samples of ~20 mg were heated under nitrogen from 25 to 500 °C at a rate of 10 °C/min. The tests were carried out for samples conditioned for 1 h and 1000 h. The residual mass and thermal stability were determined based on thermogravimetric curves. The residual mass approximately corresponds to the actual filler content in the composite material. However, in this case, the temperature at which there is a 1% loss in the mass of the tested sample defines thermal stability.

Measurements of linear shrinkage

The linear shrinkage of composite moldings was determined along the flow path of the material in the injection mold. The calculation of the shrinkage value (S) of the samples was performed using the following formula:

$$S = \frac{L_0 - L}{L_0} \cdot 100\% \quad (4)$$

where: the L symbol denotes the length of the sample, and L_0 denotes the length of the injection mold cavity, which was 168 mm. Shrinkage measurements were performed at 23 °C using a Quick Vision Apex CNC device from Mitutoyo (Takatsuku, Kawasaki, Japan). The samples were conditioned for 1 hour, 24 hours, 168 hours and

1000 hours, respectively, after removing them from the injection mold. The test was performed for 10 samples from each composition.

Optical analysis of structure and sink marks

The analysis of the structure and thickness of the moldings was carried out based on photographs of sample fractures using a high-resolution Keyence VHX-7000 digital optical microscope equipped with a VH-Z100R lens, enabling observations with a magnification of 100x to 1000x. Photographs in the depth of field mode were taken at a temperature of 23 °C ± 2 °C after 1 h, 24 h, 168 h and 1000 h of sample conditioning, respectively. The thickness measurement was made along the cross-sectional axis, which was determined by the point of intersection of the diagonals (Figure 3).

Measurements of the tensile properties

Tensile strength tests were performed using a Z030 testing machine from Zwick/Roell (Ulm, Germany), in accordance with the ISO 527-1:2020-01 standard. The mechanical sample holders of the device had a distance of 116 mm, an extensometer had an initial spacing of 50 mm, and a measuring head had a nominal force of 30 kN. To determine the elastic modulus, the samples were stretched at a speed of 1 mm/min and 50 mm/min to determine the stresses and strains at the yield point. The tests were carried out at a temperature of 23 °C for 10 samples from each test series, which were performed after a conditioning time of 1 h, 24 h, 168 h and 1000 h, respectively.

Measurements of impact strength

The impact strength of test samples using the Charpy method was determined in accordance with the ISO 179-1 standard using the HIT 50P testing device from Zwick/Roell (Ulm, Germany). A 15 J pendulum was used for the tests. The samples had a rectangular shape with dimensions of 80 × 10 × 4 mm. The impact occurred on the short edge of the sample. Because of the hetero phase structure of the molded parts, the tests were performed without a notch. The tests were carried out at a temperature of 23 °C for 10 samples from each test series after conditioning times of 1 h, 24 h, 168 h and 1000 h, respectively.

RESULTS AND DISCUSSION

Density and porosity

The density of composites with a solid structure changed linearly after 1h of conditioning (Figure 4a). With the increase in filler content, this parameter changed from 0.901 g/cm^3 (G) to 1.189 g/cm^3 (G40). The density of the composite with 5% phosphogypsum content was 0.931 g/cm^3 and was similar to that of the polypropylene composite filled with the same amount of waste silica (0.935 g/cm^3) [17]. Chemical porosity of unfilled PP resulted in an 8% reduction in density. The porosity of the GP material structure was less than 9% (Figure 4b). This value was comparable to the value recorded for PP in previous studies [31]. Composites with a porous structure containing up to 20 wt% filler also had a density that was approximately 8% lower compared to compositions with a solid structure and similar

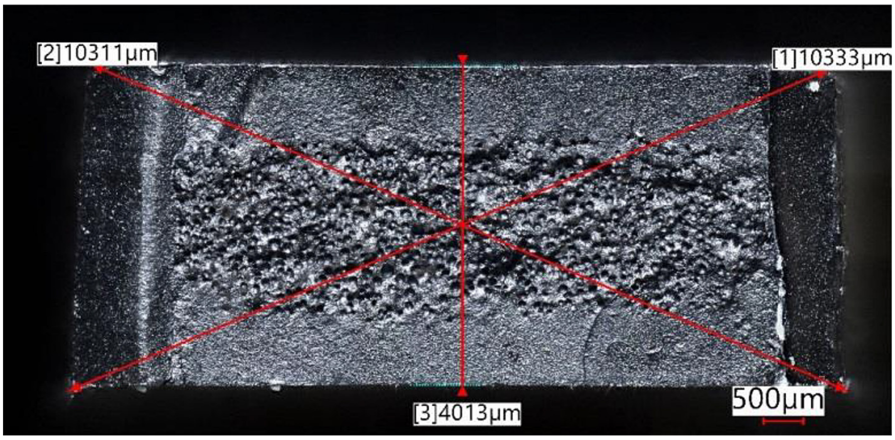

Figure 3. Methodology for measuring the thickness of samples

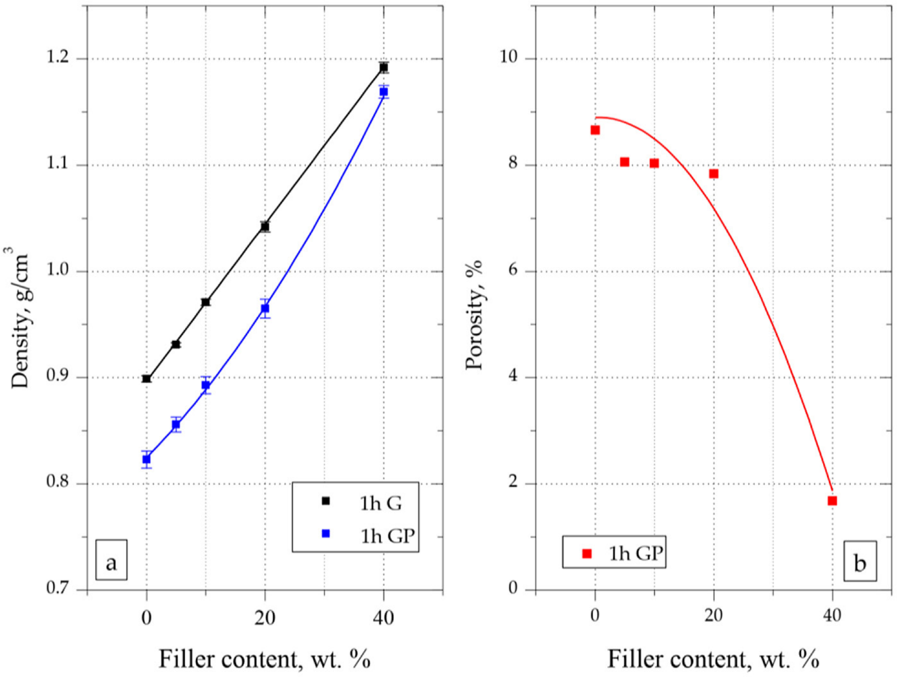

Figure 4. Dependence of composite density (a) and porosity (b) on filler content

composition. The use of phosphogypsum as a filler did not result in a significant reduction in the weight of molded parts with a porous structure. Llewelyn observed this effect in the case of porous polypropylene compacts containing 22 wt% talc [32]. The density of the GP40 composite (1.169 g/cm^3) was only slightly lower compared to G40 (1.189 g/cm^3). This is the effect of a sudden reduction in porosity, which in the case of this material is less than 2%. It should therefore be concluded that, during the processing of composites containing over 20 wt% of phosphogypsum, the gas generated because of the thermal decomposition of the chemical blowing agent does not effectively reduce the density of the material.

Thermal stability

The tests carried out revealed that, despite using a twin-screw extruder for homogenization of composite materials, the actual content of inorganic filler in the tested samples differed from the assumed values by ± 3 percentage points (Table 3). The thermal stability of composites, both with solid and porous structures, significantly depends on the phosphogypsum content in the polypropylene matrix. For example, the thermal stability after 1 hour of conditioning of the G5 composite was 333.5 °C, while with G40 it was 378.2 °C. However, it is important to note that the composites with the lowest filler content showed lower thermal stability compared to the unfilled matrix. Changes that occur in the structure of materials during conditioning also result in an increase in thermal stability. Composite containing 40 wt% filler after 1000 h of conditioning was characterized by thermal stability of 406.7 °C. Figure 5 shows thermogravimetric curves of solid and porous samples containing 20 wt% filler conditioned for 1h and 1000 h, respectively.

Thermal properties

Introducing phosphogypsum to PP resulted in an increase in its crystallization temperature (T_c), which is clearly visible in the DSC (Differential Scanning Calorimetry) crystallization curves with different filler contents (Figure 6). The T_c value of the G5 samples was 120 °C and was 7 °C higher (113 °C) compared to the unfilled matrix (Table 4). Based on this, it was concluded that phosphogypsum acts as a heterogeneous nucleating agent in relation to homopolypropylene. Increasing the filler content resulted in only a slight increase in the crystallization temperature. The maximum crystallization temperature of PP filled with phosphogypsum was close to the crystallization temperature recorded with modification of this polymer with waste silica (123.3 °C) [17]. Moreover, the crystallization temperature

Table 3. Results of TG measurements

Material	Conditioning time			
	1 h		1000 h	
	Residual mass, wt%	Thermal stability, °C	Residual mass, wt%	Thermal stability, °C
G	0.82	365.6	0.76	371.7
G5	5.83	333.5	4.46	361.0
G10	12.9	348.7	11.4	369.2
G20	23.0	356.7	20.5	388.1
G40	37.9	378.2	37.4	406.7
GP	0.54	343.2	0.41	348.7
GP5	5.74	332.0	5.71	341.0
GP10	12.3	336.1	12.3	349.6
GP20	19.4	338.1	21.3	356.7
GP40	42.5	350.0	41.6	361.4

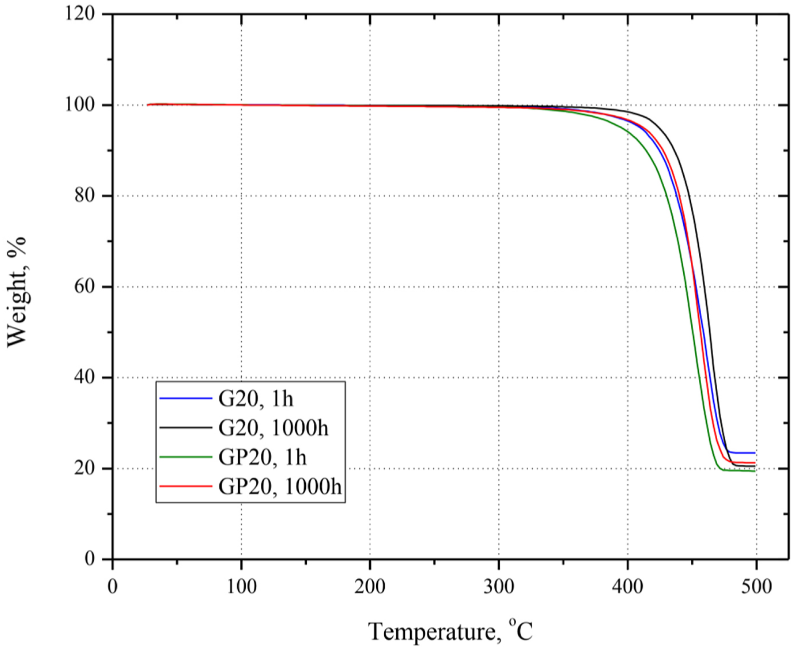

Figure 5. TG curves of PP composites containing 20 wt% of gypsum

values for composites featuring a porous structure showed similarity as well. The presence of phosphogypsum in the polypropylene matrix results in a lower melting enthalpy value, which results from a reduction in the amount of the polymer phase in the composite. At the same time, an increase in the degree of crystallinity was recorded. With unfilled PP, after 1 hour of conditioning, the X_c value was 39.2%, the G40 composite had a value of 43.7%, respectively. An increase in the degree of crystallinity of all compositions, regardless of composition and structure, was also recorded after 1000 h of conditioning. The material's composition and the conditioning time had no significant impact on the change in the melting temperature values of polypropylene, which ranged from 164.8 °C to 166.6 °C.

Linear shrinkage

Contrary to the common belief that introducing fillers into the polypropylene matrix results in a reduction in processing shrinkage, the shrinkage value determined after 1 hour of conditioning for composite samples with a relatively low gypsum content (5–10 wt%) was higher compared to unfilled PP (Figure 7a). Linear shrinkage reached its maximum value at 5 wt% filler content (1.41%).

G5 samples were shorter on average by 0.12 mm compared to those made of unmodified PP. It can be assumed that the increase in shrinkage value at relatively low filler content results from the influence of phosphogypsum particles and the increase in the crystallization temperature of PP. Ullah [36], using the example of PP modified with various pigments, proved that there is a linear correlation between the crystallization onset temperature of this polymer and the shrinkage value. For comparison, Ryu [22] showed that introducing 10 wt% of talc to PP suffices to

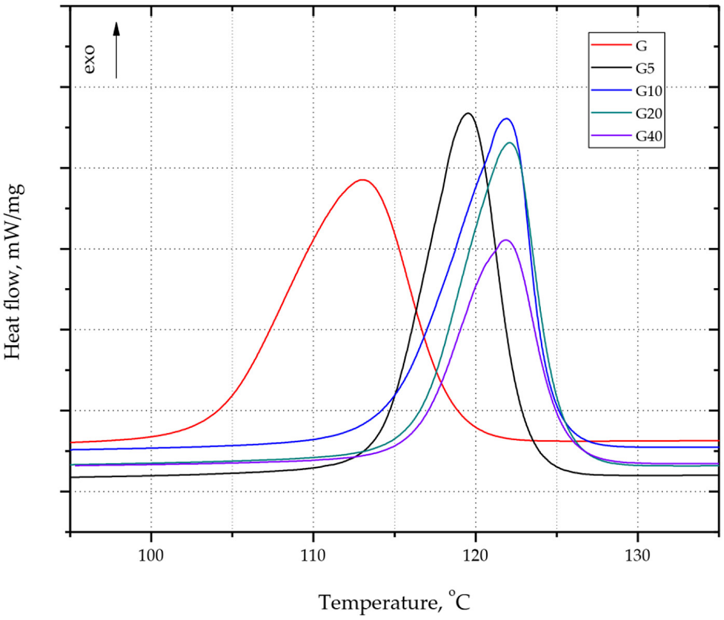

Figure 6. DSC crystallization curves of composites with solid structure after 1 h conditioning

Table 4. Thermal properties of polypropylene composites

Conditioning time	Sample	Melting temperature, °C	Melting enthalpy, J/mg	Crystallization degree, %	Crystallization temperature, °C
1 h	G	166.2	82.02	39.2	113.2
	G5	165.0	83.15	41.9	120.0
	G10	165.4	80.69	42.9	121.9
	G20	165.6	71.44	42.7	122.1
	G40	166.0	54.86	43.7	121.9
1000 h	G	165.5	87.57	41.9	112.8
	G5	166.5	86.02	43.3	119.7
	G10	165.1	81.90	43.5	121.6
	G20	165.0	73.73	44.1	122.4
	G40	166.2	56.30	44.9	122.6
1h	GP	166.6	79.91	38.2	113.0
	GP5	164.9	80.61	40.6	119.5
	GP10	166.3	79.19	42.1	120.1
	GP20	165.5	71.73	42.9	121.3
	GP40	165.7	54.05	43.1	121.9
1000h	GP	165.9	84.23	40.3	113.3
	GP5	164.8	83.19	41.9	119.9
	GP10	166.0	80.88	43.0	120.6
	GP20	165.3	73.90	44.2	121.7
	GP40	165.8	55.80	44.5	122.1

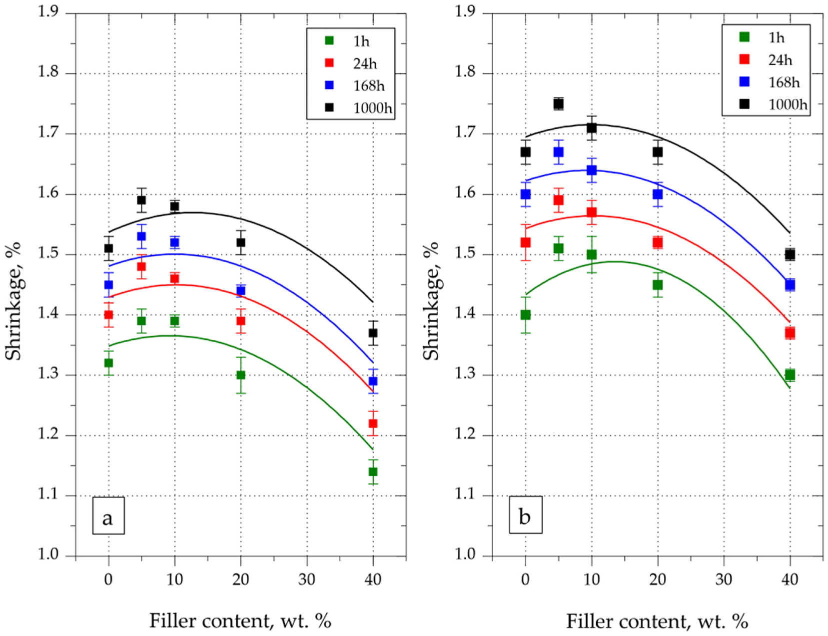

Figure 7. Changes of processing shrinkage values as a function of filler content and conditioning time, solid structure (a), cellular structure (b)

reduce the shrinkage value of the molded parts, and when dosing 5 wt% no changes observed. In turn, the use of calcium nano-carbonate as a filler allows for shrinkage reduction from just 5 wt% dosage [37]. Increasing the gypsum content in the composite resulted in a lower shrinkage value. However, only the G20 composition exhibited a shrinkage slightly lower (1.30%) than unmodified polypropylene. This value is comparable to the shrinkage of polypropylene moldings filled at 20 wt% talc [38], which also has nucleating properties towards PP [39]. Hence, the increase in the shrinkage value of molded parts by 5 wt% and 10 wt% compared to unfilled PP can be attributed to the use of a material grade that lacks a heterogeneous nucleating factor in the tests. During conditioning, there was an average decrease of 0.29 mm in the length of the samples. The results of earlier tests on unfilled polypropylene [21] are in line with the observed trend. Introducing phosphogypsum into the PP matrix did not reduce the shrinkage effects occurring outside the injection mold during conditioning. The length of the G40 samples decreased by 0.34 mm.

The simultaneous use of an inorganic filler and a chemical blowing agent resulted in an increase in shrinkage compared to composite materials with a solid structure. This relationship was observed regardless of the phosphogypsum content in the composition (Figure 7b). The observed trend was consistent with the test results obtained for unfilled PP with a porous structure [31]. For example, the shrinkage of the GP5 composite after 1 hour of conditioning reached a value of 1.51%. This value was 7% higher compared to G5. It is worth noting that among the series of composites with a solid structure, only the GP40 composition exhibited lower processing shrinkage compared to unfilled PP. The extension of the conditioning time of composites with a porous structure also resulted in an increase in the shrinkage value, regardless of the additive content in the composition.

Structure and sink marks

The analysis of the thickness of samples with a solid structure revealed that increasing the filler content in the material leads to a decrease in collapses on the surface of the moldings. The thickness of samples without phosphogypsum after 1h of conditioning was 3853 μm, while G40 had a thickness of 4023 μm (Figure 8a). It is worth noting that even a 5 wt% phosphogypsum content in the material resulted in an increase in the thickness of the moldings by 2.3%, while with a 40 wt% filler content, the increase in thickness reached less than 4.5%. Increasing the conditioning time resulted in a reduction in the thickness of the moldings, with the largest changes recorded for G samples and the smallest for G40. Furthermore,

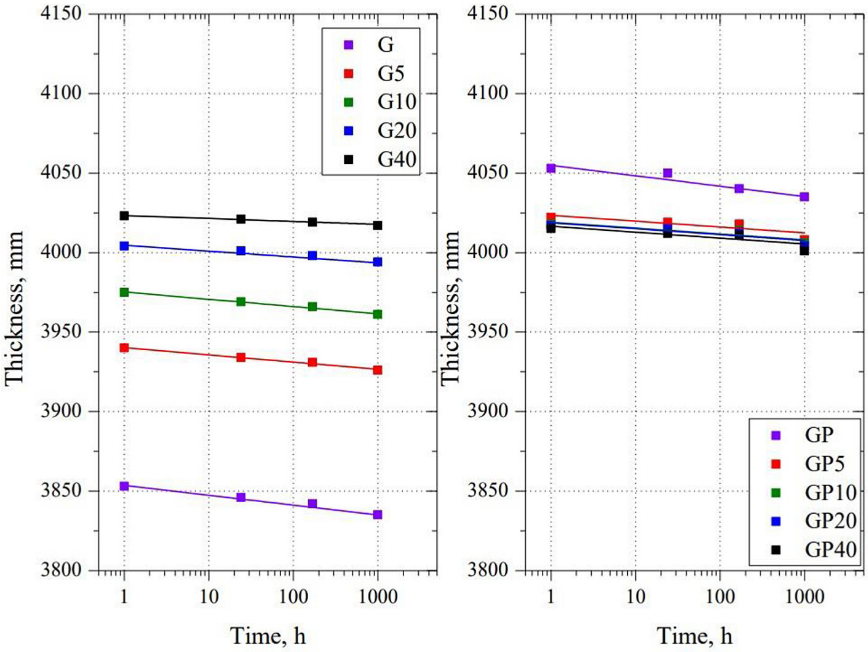

Figure 8. Change in the thickness of solid (a) and porous (b) samples depending on the conditioning time and phosphogypsum content

the greatest thickness reduction for all samples occurred during the initial conditioning period. The photograph in Figure 9 displays the fractures of samples G and G40 after 1000 h of conditioning.

In the case of moldings with a porous structure, the samples without inorganic filler had the highest thickness and the smallest collapses after 1 hour of conditioning (Figure 8b). The thickness of the G samples (4053 µm) was greater than the compacts with a solid structure containing 40 wt% filler (after 1 hour of conditioning). Palutkiewicz [33] obtained the opposite effect in his research. A smaller thickness characterized polypropylene moldings with a porous structure compared to samples with a solid structure, regardless of the inorganic filler content. It can be assumed that this difference results from the use of different processing parameters, in particular the short pressing time. Previous studies have shown that even a short pressing time reduces the possibility of pores forming in the structure of the molded parts [31]. Introducing 5% by weight of phosphogypsum into the material resulted in the opposite effect than with molded pieces with a solid structure. The thickness of the samples was approximately 30 µm smaller. Further increasing the filler content in the polypropylene matrix resulted in only a slight reduction in thickness. As in the case of molded pieces with a solid structure, extending the conditioning time resulted in a reduction in the thickness of the samples, which is the effect of secondary crystallization of polypropylene.

Exemplary fractures in samples with a porous structure are shown in Figure 10. Figures 10a and 10b show photographs of samples GP and GP10 with clearly visible pores located in the core. In the case of GP40 samples (Figure 10c), the number of pores is clearly smaller compared to the

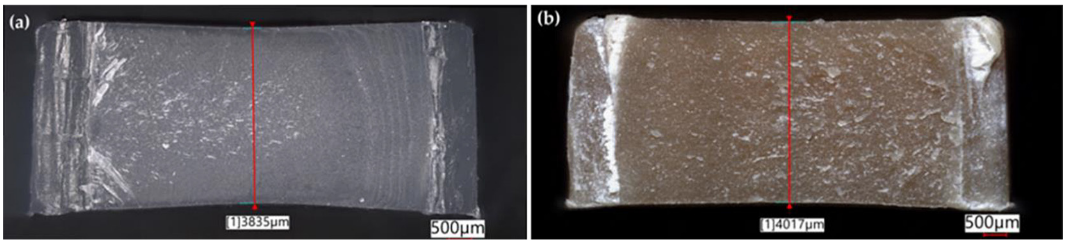

Figure 9. Cross-section of samples with a solid structure: without filler (a), with 40% by mass, phosphogypsum content, after 1000 h of conditioning

composition with a lower filler content. This explains the reasons for the low porosity of this composition. Hence, it is possible to deduce that a significant amount of phosphogypsum particles in the material hinders the formation of gas spaces in the structure of the moldings.

Tensile properties

Introducing phosphogypsum as a filler into the polypropylene matrix resulted in an increase in the value of the Young's modulus (*E*) of the obtained composite materials. A modulus value of 1432 MPa (Figure 11a characterized the G40 composition after 1h of conditioning). This value was higher by over 65% compared to unfilled PP (857 MPa). Similar effects of filling PP with phosphogypsum were also observed by Kowalska [40] when testing the bending module. The stiffness of the material also increased with the conditioning time, with the largest changes in Young's modulus recorded between 1h and 24h. However, after this time, changes in the mechanical properties of the molded parts were also recorded. Between 24 h and 1000 h, the Young's modulus of the G samples increased by 13%, while with the G40 composition an increase of 18% was recorded. The change in the Young's modulus of injection molded parts during conditioning results from progressive slow crystallization, which with PP may occur at a temperature of 23 °C. The increase in stiffness of injection moldings containing

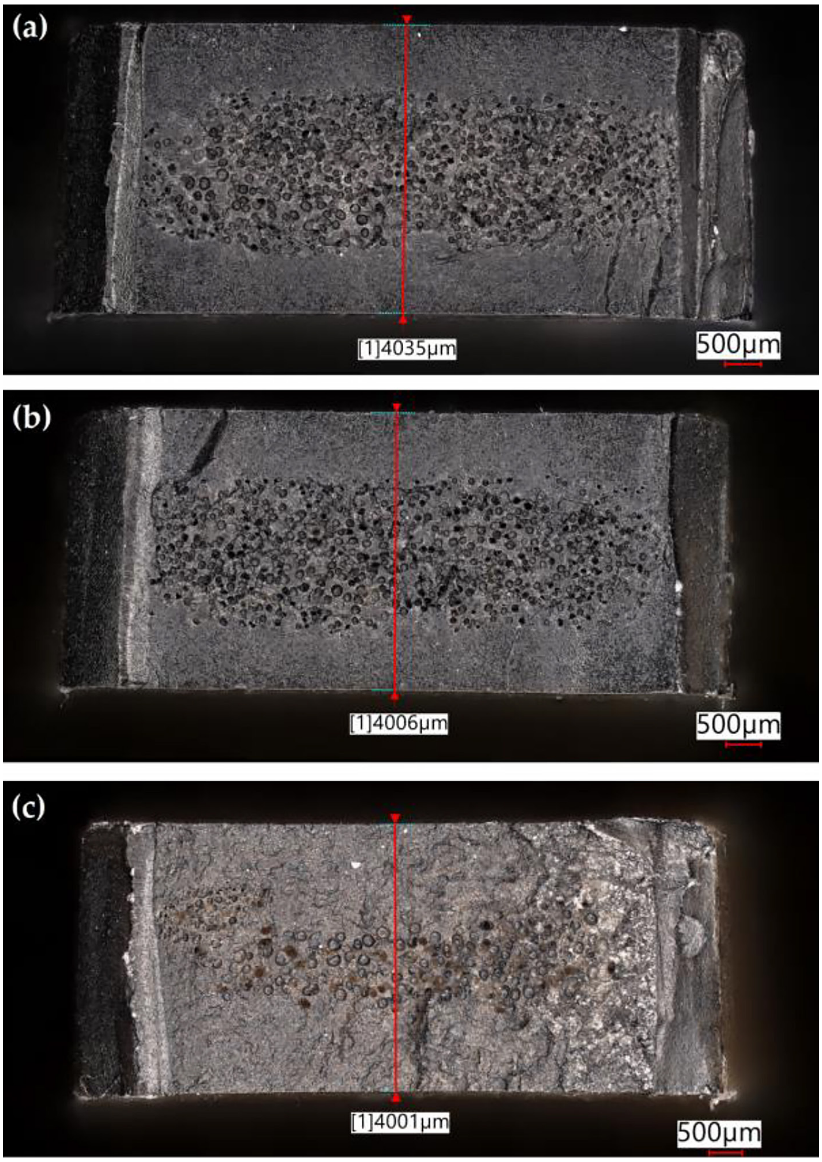

Figure 10. Cross-section of samples with a porous structure after 1000 h of conditioning: GP (a), GP10 (b), GP40(c)

inorganic filler is surprisingly high. Because of the reduction in the amount of polypropylene in the material, especially with moldings with the highest phosphogypsum content, one would expect a reduction in the impact of conditioning time on the change in the mechanical properties of the samples. The relatively high increase in the modulus of PP composites filled with phosphogypsum can be explained by the influence of particles of this type of filler on the crystal structure of polypropylene.

Similar changes in the Young's modulus value as a function of the phosphogypsum content and conditioning time are observed in samples with a porous structure. However, pores in the structure of the moldings, which allowed for a reduction in the density of individual compositions, resulted in a decrease in the Young's modulus. The modulus values for GP and GP40 moldings were 750 MPa and 1214 MPa, respectively (Figure 11b), which is 12% and 15% less than with materials with a similar composition but solid structure. A decrease in the Young's modulus of composites with a porous structure compared to materials with a solid structure was also observed by Llewelyn [32] on the example of polypropylene moldings filled with talc.

Changes in the value of Young's modulus that occur during conditioning show a linear correlation with changes in the shrinkage value of the molded parts during this time. In the case of moldings made of unfilled polypropylene, an increase in the shrinkage value by 0.01 percentage point is associated with an increase in the modulus by 8.36 MPa (Figure 12a). As the phosphogypsum content in the composite material increases, the growth rate of Young's modulus and processing shrinkage increases. With samples GP10 and GP40, it was 11.8 MPa and 17.8 MPa, respectively. This tendency is also clearly visible when analyzing the trend line equations. The value of the slope coefficient in the case of composition G is equal to 0.83, while for G40 it reaches the value of 1.78. Materials with a porous structure showed similar trends (Figure 12b). However, materials of this type exhibit a slower growth rate of elasticity modulus as the change in shrinkage value increases. In the case of the GP and GP40 compositions, the slopes of the trend line equations were 0.37 and 1.15, respectively.

Small amounts of phosphogypsum (G5) in the material resulted in a less than 2% increase in tensile strength (27.1 MPa) compared to G (26.6 MPa). This situation is shown in Figure 13a. This is probably not the result of the strengthening role of phosphogypsum particles, but of their nucleating effect on the polypropylene matrix. However, the above studies did not observe the effect described in Kowalska's research [40]. The PP composites she tested, filled with phosphogypsum in an amount of 10% by mass, were characterized by lower tensile strength compared to the unfilled matrix. A further increase in the inorganic filler content resulted in a decrease in tensile strength (Rm). The G40 composite was characterized by

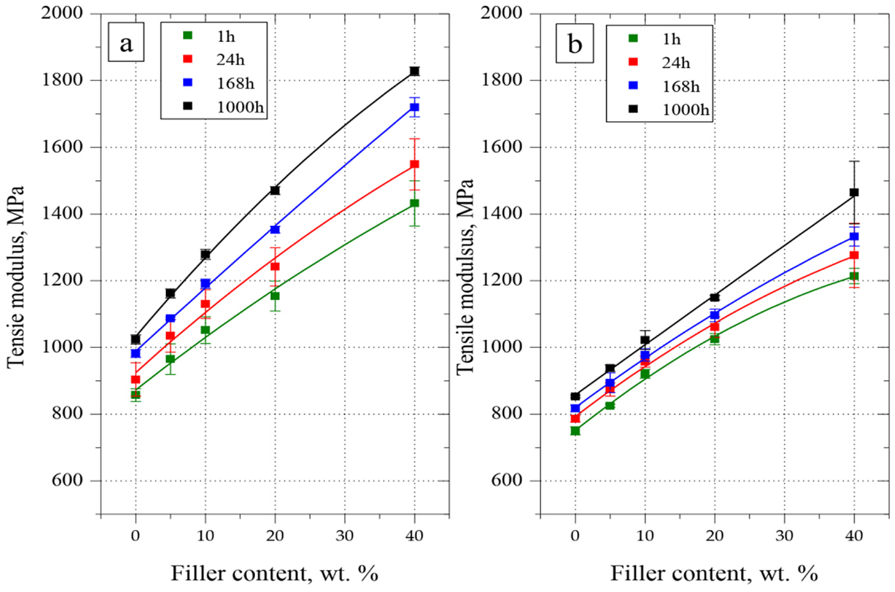

Figure 11. Changes in the value of Young's modulus of composites with a solid (a) and porous structure (b) depending on the filler content and conditioning time

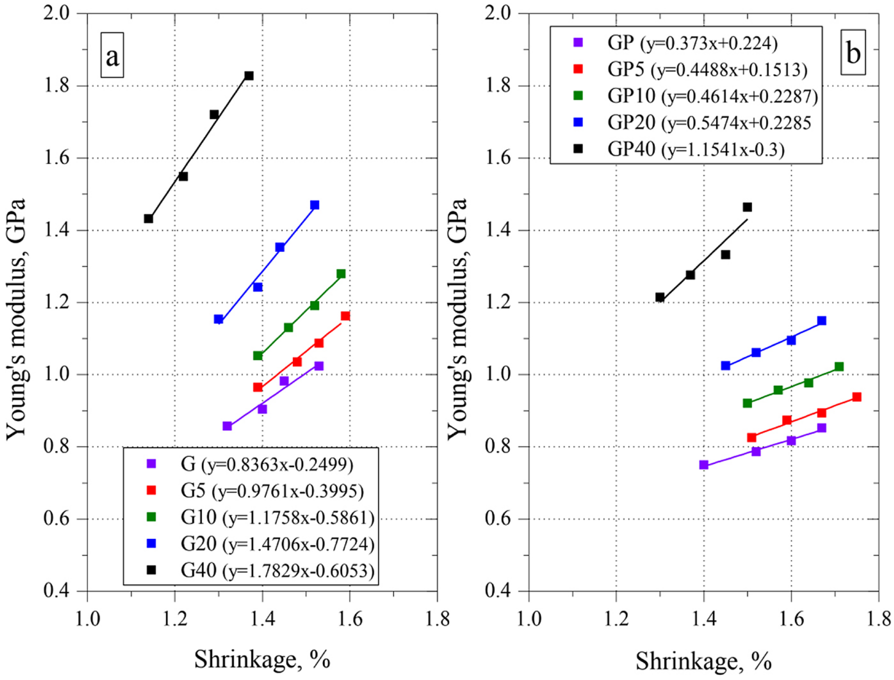

Figure 12. Correlation of the value of Young’s modulus of composites with a solid (a) and porous structure (b) with changes in shrinkage values occurring during conditioning

a Rm of 22.4 MPa. The increase in the degree of crystallinity during 1000 h of conditioning resulted in an increase in the tensile strength of all compositions. In the case of G10 samples, it was 8%, with the highest rate of Rm increase taking place in the initial conditioning period.

However, composites with a porous structure (Figure 13b) did not show an increase in tensile strength with the lowest phosphogypsum content. The presence of pores in the materials resulted in a decrease in this parameter compared to samples with a solid structure. The strength of this series of materials decreased from 21.6 MPa (GP) to 16.9 MPa for the composite containing 40 wt% filler (GP40). The effect of conditioning was an increase in the strength of all

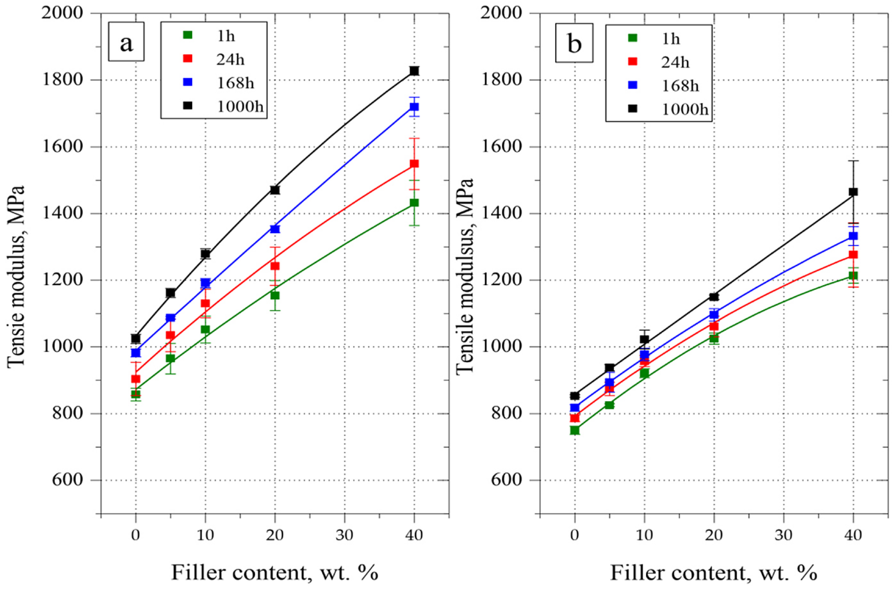

Figure 13. Changes in the tensile strength of composites with a solid (a) and porous structure (b) depending on the filler content and conditioning time

compositions. A similar tendency was also observed by Palutkiewcz in his research [33].

Figure 14 shows the graphs of the dependence of the tensile strength of polypropylene composites with a solid structure (Figure 14a) and porous structure (Figure 14b) on the changes in the shrinkage value that takes place during conditioning of the molded parts for 1000h. Similarly to the elastic modulus, Rm increases linearly with increasing shrinkage value. However, the rate of change in tensile strength as a function of shrinkage does not depend significantly on the filler content in the material, as with the elastic modulus. This is confirmed by the slope coefficients of the trend line equations for solid and porous materials, the value of which is approximately 10 regardless of the filler content. It is also worth noting that filling polypropylene affects the length of samples removed from the injection mold, but does not have a significant impact on the shrinkage that occurs during conditioning. The shrinkage of all molded pieces with a solid structure, regardless of the phosphogypsum content, increased by approximately 0.2 percentage points during conditioning. A similar situation occurs for molded parts with a porous structure. The increase in the shrinkage value between 1 h and 1000 h of conditioning is 0.21 percentage points, except for GP where a change of 0.27 percentage points was recorded.

Charpy impact strength

The presence of phosphogypsum particles in the structure of solid PP results in a significant reduction in impact strength. Samples made of unfilled polypropylene did not crack during the unnotched Charpy impact test, but deformed plastically, regardless of the conditioning time (Figure 15a). The impact strength (*acU*) of the composite containing 5 wt% filler after 1 h of conditioning was 77 kJ/m^2, while a value of this parameter of only 19 J/m^2 characterized the G40 samples. Changes occurring in the structure of materials during conditioning also resulted in an impact strength. In the case of G5 samples, 1000h after removing the moldings from the injection mold cavity, the impact strength decreased by 30% (57 J/m^2), with the largest changes recorded in the initial conditioning period. The impact strength of composites with higher filling changed to a lesser extent during conditioning. For G40, the change in impact strength between 1 h and 1000 h was 8%.

Porosity of polypropylene composites filled with phosphogypsum resulted in a reduction in the impact strength of all compositions, regardless of their composition. Polypropylene samples with a porous structure did not withstand the test, resulting in a recorded impact strength of 66 kJ/m^2 (Figure 15b). In the case of GP5 and GP40 composites, the

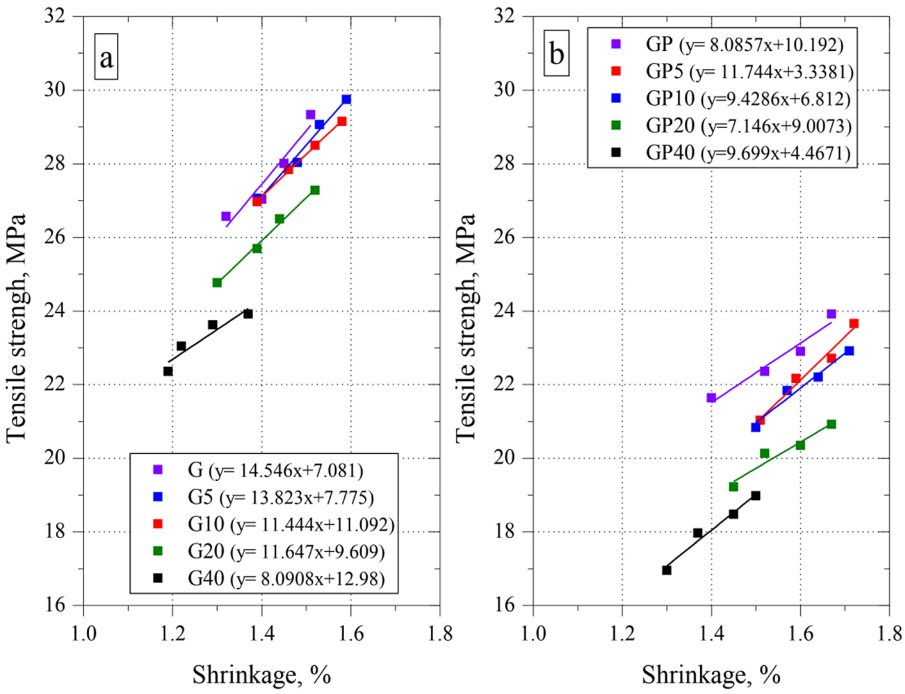

Figure 14. Correlation of tensile strength for composites with a solid (a) and porous structure (b) with changes in shrinkage values occurring during conditioning

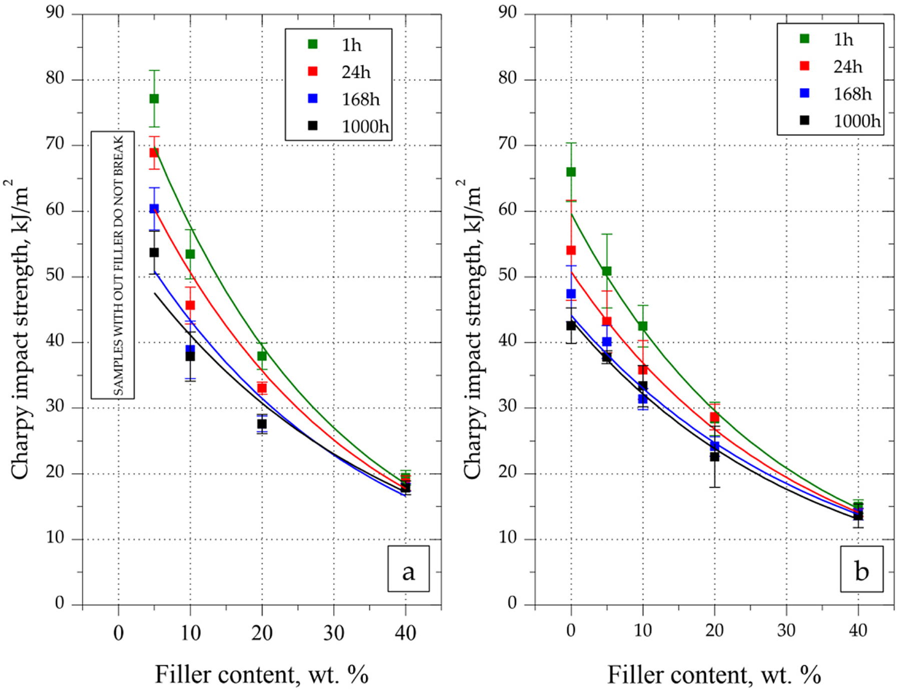

Figure 15. Changes in the impact strength values of composites with a solid (a) and porous structure (b) depending on the filler content and conditioning time

recorded Charpy impact strength values were lower by 34% (51 kJ/m^2) and 23% (23 kJ/m^2), respectively, compared to samples with a porous structure. As a result of conditioning, the impact strength further deteriorated for all compositions. The dependence of Charpy impact strength on changes in shrinkage values occurring during conditioning is also linear. Unlike the modulus of elasticity and tensile strength, impact strength decreases with increasing shrinkage values (Figure 16a and Figure 16b). The dynamics of the increase in brittleness of composite materials depending on the shrinkage value varies

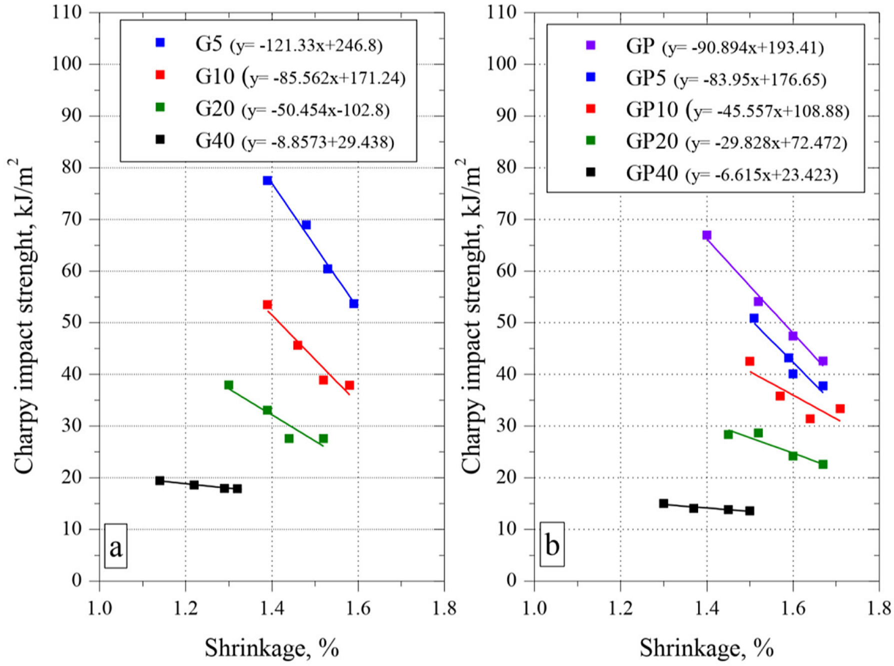

Figure 16. Correlation of the Charpy impact strength for composites with a solid (a) and porous structure (b) with changes in shrinkage values occurring during conditioning

Table 5. Collective summary of research results

Parameter	Result
Density	An increase in the concentration of the inorganic filler resulted in an increase in the density parameter both for samples with and without the blowing agent. The density of samples without a blowing agent was higher for each test series than for those containing a blowing agent.
Thermal stability	The thermal stability of the composites increases with both increasing conditioning time and filler content. This tendency was observed for composites containing and without a blowing agent. The addition of a blowing agent reduces thermal stability.
Thermal properties	The content of phosphogypsum in the polypropylene matrix does not affect the melting temperature of samples, both for those with and without the presence of a blowing agent. Introducing an inorganic filler to PP resulted in an increase in the crystallization temperature for all test series. Waste phosphogypsum acts as a heterogeneous nucleating agent in relation to homopolypropylene.
Linear shrinkage	Test samples containing a blowing agent were characterized by greater processing shrinkage than those without a blowing agent. Increasing the phosphogypsum content in the composite for both series of tests resulted in a lower shrinkage value. However, the shrinkage value of only the G20 composition was slightly lower than unmodified polypropylene. Further increases in filler resulted in a greater decrease in processing shrinkage.
Structure and sink marks	In the case of samples without blowing agent, an increase in the concentration of the inorganic filler reduces the formation of collapses. Even smaller collapses were obtained for samples containing a blowing agent. Additionally, an increase in the concentration of phosphogypsum limits the growth of pores in the internal structure of the composites.
Tensile strength	The increase in conditioning time and filler content both results in an increase in tensile strength for both test series. Samples without the blowing agent were characterized by a higher value of the described parameter compared to those with the blowing agent.
Charpy impact strength	Increasing the conditioning time and the concentration of inorganic filler leads to a decrease in impact strength in both samples containing blowing agents and those without them. Moreover, composites lacking a blowing agent demonstrated a higher impact strength parameter in comparison to those with a blowing agent.

depending on the filler content. Materials with the lowest modifier content recorded the greatest changes. Composites with a porous structure have a slightly lower rate of change in impact strength as a function of shrinkage compared to solid materials, which is confirmed by the values of the slope coefficients of the trend line equations.

CONCLUSIONS

The analysis of the test results revealed that, when phosphogypsum is introduced into the polypropylene matrix with a filling degree exceeding 10 wt%, it results in a reduction in the linear shrinkage value. Regardless of the type of structure, the obtained composites exhibit a higher value of processing shrinkage compared to unfilled polypropylene when using a lower dosage of filler. This is the result of heterogeneous nucleation of inorganic filler particles. It is important to note that materials with a porous structure, regardless of the composition, showed a higher shrinkage value compared to materials with a solid structure. Filling polypropylene with phosphogypsum did not increase the dimensional stability of the moldings as a function of the time that had passed since demolding. The shrinkage value of composite moldings increases during conditioning, regardless of the phosphogypsum content in the material. During conditioning, growth, thermal stability, modulus of elasticity and tensile strength, as well as a decrease in impact strength also occur, and their changes are linear as a function of shrinkage. The dynamics of changes in the elastic modulus as a function of shrinkage increases with the phosphogypsum content in the polypropylene matrix. Composite materials with the lowest inorganic filler content showed the highest rate of change in impact strength. Changes in the properties of composite materials during conditioning are the result of changes occurring in the crystal structure of the materials. A summary of the parameters analyzed in the article is presented in Table 5.

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