Properties of polypropylene composites filled with microsilica waste

Artur Kościuszko[1], [*], Piotr Czyżewski[1], Łukasz Wajer[1], Adrian Ościak[1], Marek Bieliński[1]

Abstract: The paper presents the results of investigations of processability and mechanical properties of polypropylene composites filled with microsilica, which is waste from the metallurgical industry. Composite molded parts containing 10% and 20% of microsilica waste respectively were characterized, among others, by higher Young's modulus value and lower shrinkage value in comparison to the unfilled polypropylene. In addition, a correlation was observed between the changes in the post-molding shrinkage value and the changes in the mechanical properties of the molded pieces that took place during their conditioning within 240 hours after they were taken out of the injection mold.

Keywords: composite, polypropylene, microsilica waste, mechanical properties, post-molding shrinkage.

Właściwości kompozytów polipropylenowych napełnionych odpadową mikrokrzemionką

Streszczenie: Przedstawiono wyniki badań przetwarzalności oraz właściwości mechanicznych kompozytów polipropylenowych napełnionych mikrokrzemionką, stanowiącą odpad z przemysłu hutniczego. Wypraski wtryskowe z kompozytów zawierających, odpowiednio, 10% i 20% odpadowej mikrokrzemionki charakteryzowały się m.in. większą sztywnością oraz mniejszym skurczem przetwórczym niż wypraski z nienapełnionego polipropylenu. Zaobserwowano ponadto korelację zmian skurczu wtórnego i właściwości mechanicznych wyprasek, zachodzących podczas ich kondycjonowania w ciągu 240 h od chwili wyjęcia z formy.

Słowa kluczowe: kompozyt, polipropylen, odpadowa mikrokrzemionka, właściwości mechaniczne, skurcz wtórny.

Molding shrinkage is defined as a percentage difference between the dimension of an injection molding cavity and the real dimension of a molded part (in the temperature of 23 ± 2 °C), as referred to the size of the cavity [1]. A phenomenon of molding shrinkage is caused by a gradual decrease in the volume of the polymer material during cooling of the molding as well as after its removal from the injection mold. Two kinds of shrinkage are distinguished: measured 16 h after the removal of the molded parts from the injection mold, and post-molding shrinkage which is assumed to last up to 1000 h. The change of the molded parts volume during their cooling as well as immediately after their removal from the injection mold results from the material thermal expansion, namely, the correspondence between pressure, volume and the temperature of polymer melt (p-V-T) [2–4].

The processing shrinkage value depends on, *i.a.* geometries of the produced element and the conditions of injection molding process: the temperature of a polymer melt and of the mold, the pressure, the holding time as well as cooling time [5–8]. Lack of a proper shrinkage compensation or anisotropic shrinkage may cause defects in molded parts, such as: sink marks, voids or warpage [9–11]. The value of the processing shrinkage depends on the type of the processed material to a large extent. Semicristalline polymers (*e.g.* polypropylene – PP, polyamide 6 – PA6, polyetheretherketone – PEEK) are characterized by significantly higher values of the shrinkage in comparison to amorphous polymers (polystyrene – PS, polycarbonate – PC, polysulfone – PSU). It results from ordering of the polymer macromolecules structure during the crystallization, and at the same time, during the increase of the polymer density. For example, the density of crystalline polypropylene (~0.94 g/cm³) is higher by about 10 percent when compared to the amorphous PP (~0.85 g/cm³) [12]. Semicrystalline polymer molded parts to a greater extent change dimensions during conditioning and exploitation. Post-molding shrinkage value of

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[1] University of Science and Technology in Bydgoszcz, Department of Material Engineering and Polymers Processing, Al. prof. S. Kaliskiego 7, 85-796 Bydgoszcz, Poland.

[*] Author for correspondence: artkos@utp.edu.pl

amorphous polymers equals about 0.05%, while when it comes to semicrystalline polymers it ranges from 0.1% to 0.3%. Nevertheless, they are not taken in to account defining acceptable dimensional deviations of parts in the documentation.

Processing shrinkage can be reduced through chemical [13, 14] or physical [15, 16] foaming of the polymer material. However, a modification of the molding parts structure may be accompanied by deterioration of mechanical properties such as tensile strength or impact resistance [17, 18]. Another method of improving the dimensional stability of the polymers is to apply various types of fillers. In case of polypropylene, which is one of the most commonly used thermoplastic polymers in the industry, the most popular fillers are chalk and talc. There are also known examples of using other fillers which constitute industry waste, such as phosphogypsum [19], eggshells[20], wood flour [21, 22] or nutshells [23]. By introducing various types of powder fillers into a polypropylene matrix, the stiffness and hardness can be significantly increased. However, at the same time, tensile strength is often decreased.

This study presents results of the research on the selected properties of polypropylene composites filled with microsilica which constitutes a metallurgic industry waste. The aim of the investigations was to assess the impact of the filler content on rheological and mechanical properties of the polypropylene, as well as on the molding shrinkage of polypropylene molded parts. Moreover, the correlation between the post-molding shrinkage and the properties changes of polypropylene and polypropylene composites moldings has been sought.

EXPERIMENTAL PART

Materials

The material used in the research was commercial polypropylene Moplen HP 548P by Basell Orlen Polyolefins (Poland) designed for plastics processing by injection molding. Melt flow rate (*MFR*) of the material, according to the producer's declaration, was 23 g/10 min (230 °C, 2.16 kg); whereas an elastic modulus (*E*) and tensile strength (R_m) were 1600 MPa and 35 MPa, respectively.

As a filler, microsilica waste obtained from the metallurgical industry under the trade name of SILMIC by Re Alloys (Poland) has been applied. The raw material was a powder with a grain size equalling less than 50 μm. According to the information provided by the supplier, the main component of the waste material was silicon oxide(IV) (SiO_2) in the amount of ~94 wt %. In addition, the powder also contained ~2% of carbon (C), ~1% of magnesium oxide (MgO) and other substances, in particular metal oxides, among others iron oxide(III) (Fe_2O_3), sodium oxide (Na_2O), potassium oxide (K_2O) in amounts not exceeding 1 wt %.

Samples preparation

Homogenization of raw materials was performed on the extrusion line intended for granulation, which included a single screw extruder made by the Institute of Plastics Processing in Torun (Poland). The device was equipped with a head with two bores. The diameter of the extruder screw was 25 mm, and the relation of its length to the diameter (*L/D*) was 30. In the metering zone, the screw was equipped with the elements which intensify mixing. The temperature of individual zones of the plasticizing system were: 150 °C (in a feed zone), 185 °C (in a compression zone), 220 °C (in a metering zone) and 220 °C (in the head). The rotational speed of the screw was 80 rpm. There were three compositions prepared, each with different content of microsilica waste. As assumed, they contained 0 wt % (signature PPQD), 10 wt % (PP QD10) and 20 wt % (PP QD20), respectively. Before the homogenization process, the microsilica waste had been dried for 4 hours at the temperature of 110 °C in the Binder FED 115 dryer (Germany). The introduction of a larger amount of this filler type to the polypropylene matrix using the device described above was not possible.

Test specimens were made by injection molding using the Engel e-victory 110 hybrid injection molding machine (Austria). The machine was characterized by the clamping force of 1100 kN and a maximum injection volume of 154 cm³; the screw diameter was equal to 35 mm. The device was equipped with a four-cavity injection mold [24], which allowed for the production of universal test samples of A-type with dimensions compliant with the ISO 3167 standard. The length of the forming cavities was 168 mm. The temperature in the individual zones of the plasticizing system was 230 °C (the nozzle) and 240 °C, 220 °C, 210 °C, 30 °C (the feed zone), respectively. The temperature of the injection mold was equal to 40 °C, injection speed was 50 cm³/s, and the holding time was 21 s. Immediately before the processing, all materials had been dried for 4 hours at the temperature of 110 °C. The diagram of the specimen preparation process divided into individual stages is shown in Fig. 1.

Methods of testing

Mass melt flow rate

The mass melt flow rate (*MFR*) tests were performed in accordance with ISO 1133 standard using the Aflow plastometer by Zwick/Roell (Germany). The measurements were carried out at the temperature of 230 °C, with a test load of 2.16 kg. The diameter and the length of the capillary in the measuring nozzle were 2.095 mm and 8 mm, respectively. Just before the test, the materials had been dried for 4 hours at the temperature of 110 °C.

Density and ash content measurements

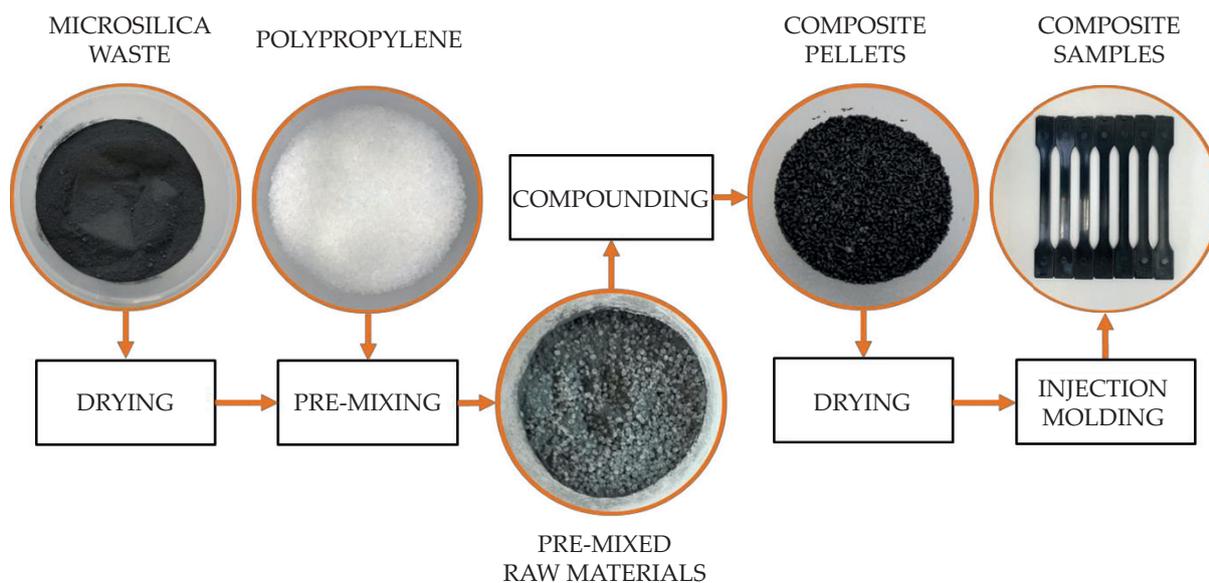The density of composites filled with microsilica waste was determined using the immersion method. The mea-

Fig. 1. Diagram of samples preparation process

surements were performed with the use of an AD 50 scale by Axis (Poland) equipped with a set allowing to determine the density of solids. The research was carried out at the temperature of 23 °C, using methyl alcohol with a density of 0.792 g/cm^3 as an immersion liquid. The dimensions of the specimens were approximately 20 mm × 10 mm × 4 mm. The measurements were taken 24 hours after removing the molded parts from the injection mold. This study aimed was to assess the effect of the filler content on the density of the obtained composite.

Additionally, in order to determine the actual content of microsilica in the composite, the tests of the amount of ash after calcinating of the composite specimens was investigated. Pre-ground composite samples and the unfilled PP with a mass of 5 g placed in ceramic crucibles were burnt in a gas burner. Next, the residue was calcinated at the temperature of 900 °C in the NT 1313 furnace by Neoterm (Poland). On the basis of the remaining ash content, the actual filler content in the prepared composites was determined. For each composition measurements of the two samples were made. Due to the fact that the residue after roasting of the PP unfilled samples was less than 0.5% of the initial mass, it was assumed that the ash content constitutes a mass fraction of the filler in the composite.

Processing shrinkage measurements

The values of the processing shrinkage (S) of individual polypropylene compositions with a variable content of microsilica waste were calculated on the basis of the length measurements of the test specimens (L_T) with the use following formula:

$$S = \frac{L_F - T_T}{L_F} \cdot 100\% \qquad (1)$$

where L_F – length of the mold cavity.

The measurements were carried out using the MarCal 16ER caliper by Mahr (Germany) 24 hours (one day of conditioning) and 240 hours (ten days of conditioning) after the removal of molded parts from the injection mold. Conditioning and testing took place at the temperature of 23 °C. The measurements were performed for the 10 samples in each measurement series.

Tensile measurements

Research on mechanical properties during a static tensile test was carried out using the universal testing machine Z030 by Zwick/Roell (Germany) equipped with a force measuring head of a nominal value of 30 kN. The extension rate during the determination of the elastic modulus was 1 mm/min, then the extension was carried out at a rade of 50 mm/min until the specimens were broken. The tests were carried out at the temperature of 23 °C for 10 specimens from each measurement series 24 h and 240 h after removing the molded parts from the injection mold.

Hardness measurements

The tests of hardness of the prepared materials were performed using the Shore D method. The measurements were made using digital hardness tester by Zwick/Roell (Germany). The tests each measurement series were carried out on 10 samples at the temperature of 23 °C after 24 and 240 hours from the removal of molded parts from the injection mold.

RESULTS AND DISCUSSION

Processing properties

On the basis of the results of the mass melt flow rate (Fig. 2), it was found out that this parameter decreases

linearly together with the increase in the content of microsilica waste in the composite. The *MFR* of the unfilled PP reached the value of 27 g/10 min, whereas for the PP QD20 composition it was 18.9 g/10 min. Despite a significant decrease in the mass melt flow rate in comparison with the PP QD, the processing properties of the composite with the highest degree of filling allowed for its effective processing by injection molding method.

Density and ash content

Introduction of a mineral filler, such as microsilica waste, into a polypropylene matrix, resulted in an increase in the material density (Fig. 2). The PP QD10 composite was characterized by of a density of 0.95 g/cm^3, whereas in case of PP QD20 the recorded value was 1.02 g/cm^3. Non-linear course of density changes as a function of the filler content in the composite results from the differences between the assumed and the actual mass content of microsilica in the material. In the PP QD10 composition the ash content after its calcination was equal to 7 wt % (the assumption was 10 wt %) while for PP QD20 the obtained value was 17 wt % (versus the assumed 20 wt %). Most probably, it is a results of uneven feeding by the screw of the extruder pre-mixed components and retenting of the mineral raw material in the plasticizing system.
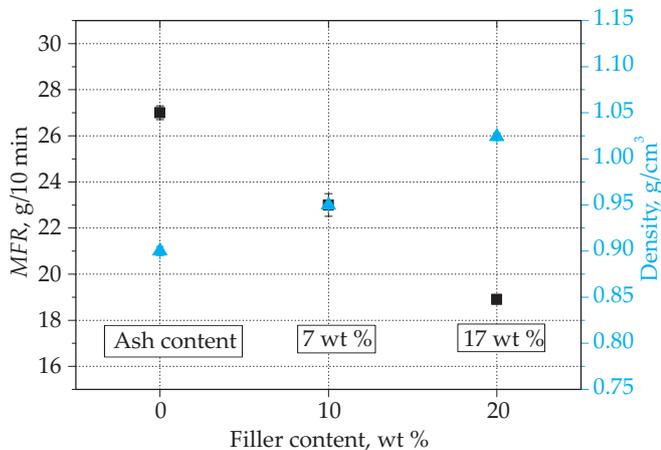

Fig. 2. Mass flow rate, density and ash content of polypropylene/ microsilica composites *vs*. filler content

Processing shrinkage

Along with the increase of the filler content in the polypropylene matrix, a beneficial effect of reducing the molding shrinkage value was observed (Fig. 3). Variations of this parameter have a non-linear course. After 24 hours from removing the molded part from the injection mold, the shrinkage of the unfilled polypropylene was 1.48%. In case of compositions of PP QD10 and PP QD20, the determined values were equal to 1.44% and 1.36%, respectively. The decrease in the shrinkage value along with
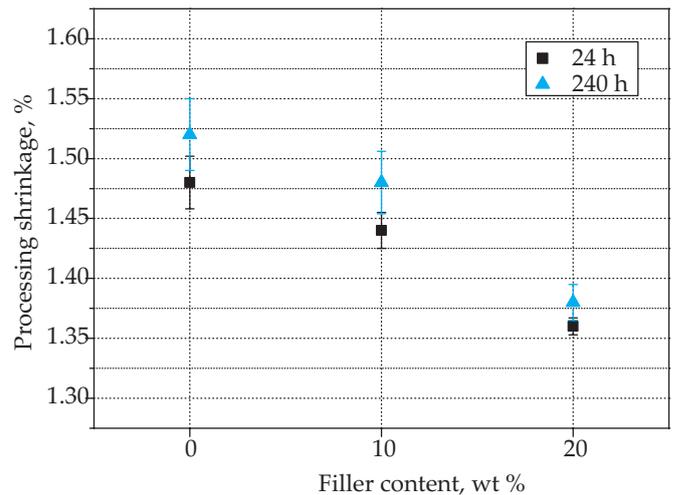

Fig. 3. Molding shrinkage of polypropylene/microsilica composites *vs*. filler content

the increase of the microsilica content results from the reduced mass content (in the composition) of the polymer characterized by a much higher value of the thermal expansion coefficient in comparison with the mineral filler.

The length of the samples made from the unfilled polypropylene 240 hours after its removal from the injection mold was decreased by approximately 0.06 mm on average. It resulted in the increase of the shrinkage value by 0.04% (1.52%) in comparison with the molded parts tested 24 hours after the end injection molding cycle. In case of PP QD20 composition, a slight decrease in the post-molding shrinkage value was observed. After 240 h from the removal of the molded parts from the injection, its value equalled 1.38%. The length of the PP QD20 samples decreased by 0.03 mm average within 9 days of conditioning. Such length change is most probably a result of polypropylene secondary crystallization. It was possible due to the fact that conditioning was carried out at the temperature 23 °C, higher than PP glass transition temperature. The increase of dimensional stability of the composites containing microsilica waste results from reduced content of crystallising polymer in the material.

Mechanical properties

Increasing the content of microsilica in the PP matrix resulted also in a gradual increase in Young's modulus (*E*) of the composite moldings (Fig. 4). After 24 hours from the deforming, the composition of PP QD10 was characterized by *E* value of to 1516 MPa, whereas in case of PP QD20 the recorded value was 1731 MPa. This was an increase in comparison with the unfilled PP (1425 MPa) by 6% and 21%, respectively.

Moreover, it was observed that the value of Young's modulus of tested composites determined after 240 h from the removal of the molded parts from the injection mold, was higher than the value of *E* obtained 24 h after the end of processing. In case of the unfilled polypropylene, an increase in *E* value by 115 MPa (by 8%) was
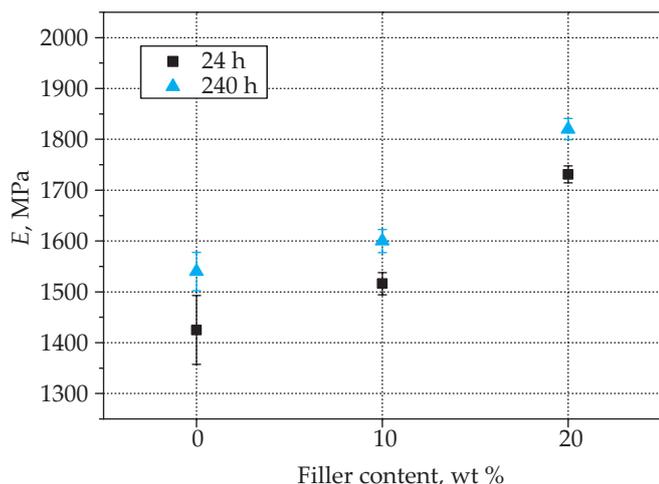
Fig. 4. Tensile modulus of microsilica/polypropylene composites *vs*. filler content

Fig. 5. Tensile strength of microsilica/polypropylene composites *vs*. filler content

recorded after 9 days. Young's modulus value of the PP QD20 composition increased by 89 MPa (5%) at the same time. The E value of the composite containing 10 wt % of microsilica waste determined 24 h after the molded parts production is comparable to the results obtained by Jakubowska [25]. Nevertheless, PP QD10 composite was characterized by greater stiffness after 240 h of conditioning.

The unfavourable effect related to the use of microsilica waste as a filler is lower tensile strength value (R_m) of all tested composites, when compared to the polypropylene matrix (33.8 MPa). Determined 24 h after the removal of the molded parts from the injection mold, R_m values of PP QD10 and PP QD20 compositions were equal to 30.6 MPa and 28.6 MPa, respectively. Thus, the introduction of 20 wt % of the microsilica waste to the polypropylene matrix resulted in a reduction of the R_m by 15%. Tensile strength value of the PP QD10 composite was 10 MPa lower than the value determined by Niemczyk [26] for a composite with the same filler content. However, it is worth to note that in this case R_m of polypropylene used as the matrix equalled over 40 MPa. The results of tensile strength measurements are shown in Fig. 5.

Similarly to the modulus of elasticity, after 9 days of conditioning an increase in the tensile strength of PP QD composition was observed. The recorded average value of R_m was equal to 34.6 MPa, constituting an increase by 2% when compared to the value determined 24 hours after the removal of the molded parts from injection mold. After 240 hours of conditioning, the value of the tensile strengths of the PP QD10 and PP QD20 compositions were already very similar to the values determined 24 hours after the preparation of the specimens.

The hardness of the tested materials determined after 24 hours from the removal of molded parts from the injection mold increases gradually from 67.8°ShD for the unfilled polypropylene to 72.8°ShD in the case of PP QD20 composition (see Fig. 6). After next 9 days of conditioning, the hardness of the PP QD10 and PP QD20 did not dif-
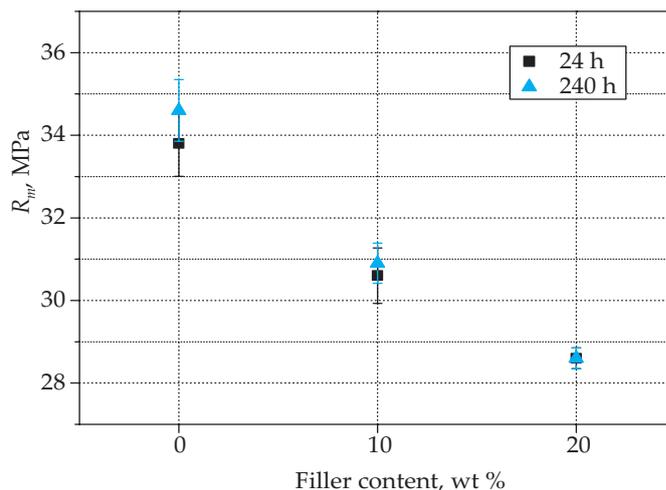
fer from the values recorded before. However, the hardness of the unfilled polypropylene increased by 1°ShD (68.9°ShD). Despite the fact that the registered changes in PP QD hardness after 9 days of conditioning are subtle, it should be emphasized that they confirm the tendencies observed during the investigation of the shrinkage and the tensile strength. In addition to the changes in the length of the molded parts, the modifications occurring in the polypropylene structure during the course of the post molding shrinkage caused also the changes in their mechanical properties as well. The presence of microsilica in the composition affects the greater dimensional stability and mechanical properties of the molded parts. Although the registered changes in tensile strength and hardness were relatively small, in case of Young's modulus the increase in the value was unexpectedly quite distinct (8%). The presence of microsilica in the composition improves the dimensional stability and mechanical properties of the molded parts. The results of the research indicate that what has to be also taken into consideration when designing PP products is possible changes in their mechanical properties during their usage.

CONCLUSIONS

On the basis of the results of the research it has been concluded that the introduction of the microsilica waste into the polypropylene matrix causes a predictable increase in density, stiffness and hardness of the material, in contrast to the unfilled matrix.

For instance, 20 wt % content of the filler in the polypropylene matrix resulted in the increase of Young's modulus value by 21%. Drops in the value of melt flow rate, tensile strength and molding shrinkage have also been observed. The value of R_m of the composite with the highest obtained filling was lower by 15% in comparison to PP. It was also confirmed that along with the time passing from the removal polypropylene molded parts from the injection mold, the dimensions of the parts de-
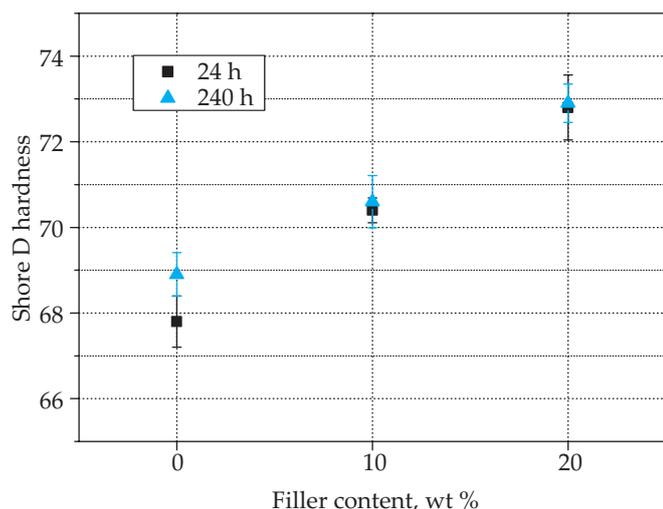
Fig. 6. Shore D hardness of microsilica/polypropylene composites *vs*. filler content

crease. Furthermore, it was found that the changes in the dimensions of the polypropylene parts occurring during the post-molding shrinkage are accompanied by the increase in the values of Young's modulus (8%), tensile strength and hardness, which most probably result from the change in the polymer crystalline structure. The presence of microsilica waste in the composition contributes to reducing the effects of structure changes that occur in the polypropylene during the conditioning in the temperature above the glass transition.

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