

# The influence of heterogonous nucleation on the processing shrinkage and mechanical properties of polypropylene injection moldings

Filip Patalas<sup>1</sup>, Natalia Kiełpińska<sup>2\*</sup>, Artur Kościuszko<sup>3</sup>

<sup>1</sup> Bydgoszcz University of Science and Technology, Al. prof. S. Kaliskiego 7, 85-796 Bydgoszcz, Poland

<sup>2</sup> Department of Manufacturing Techniques, Faculty of Mechanical Engineering Bydgoszcz University of Science and Technology, Al. prof. S. Kaliskiego 7, 85-796 Bydgoszcz, Poland

<sup>3</sup> Department of Manufacturing Techniques, Faculty of Mechanical Engineering Bydgoszcz University of Science and Technology, Al. prof. S. Kaliskiego 7, 85-796 Bydgoszcz, Poland

\* Corresponding autor: natalia.kielpinska@pbs.edu.pl

**Summary:** The aim of the research was to assess the influence of heterogonous nucleation and conditioning time on the processing shrinkage and mechanical parameters of polypropylene moldings. The tests used commercial polypropylene Moplen HP 500N with NJ STAR NU-100 nucleant in an amount of 0.25%. Processing shrinkage and mechanical properties were tested after 1 h, 24 h, 48 h, 72 h, 164 h, and 504 h after production, respectively. The presence of the nucleant in PP contributed to the increase in primary shrinkage. Molded parts made of nucleated PP changed their dimensions less during conditioning. The use of a nucleating agent therefore results in an increase in the dimensional stability of PP moldings. The addition of the nucleant resulted in a decrease in the Young's Modulus and Yield Stress. In the Elongation at break case parameter, the presence of the nucleant PP resulted in an increase in this parameter compared to the unmodified material. Despite the deterioration of the mechanical properties of nucleated polypropylene, the use of nucleation contributed to the stabilization of the material and a more accurate prediction of the value of processing shrinkage and mechanical properties over time.

**Key words:** polypropylene, heterogeneous nucleation, post-molding shrinkage, mechanical properties

## 1. Introduction

An important feature of polymer materials that determines their utility value is the degree of crystallinity. All crystallizing polymers form a metastable system containing, in various proportions, depending on the type of polymer, auxiliary substances and crystallization conditions, a crystalline and amorphous phase [1, 2]. A large share of the crystalline phase improves the mechanical and physicochemical properties of the material [3, 4]. Primary and secondary crystallization are two distinct types. Primary crystallization, which results in the formation of large supermolecular structures such as spherulites and fibrils, distinguishes from secondary crystallization. This process results in the formation of crystal structures in the free spaces between the primary crystallites [6, 7]. The crystallization process is significantly affected by the initial stage of nucleation, which can be divided into homogeneous and heterogeneous [7, 8]. Homogeneous (spontaneous) nucleation occurs rarely, in the absence of crystallization nuclei in the polymer melt or polymer solution. Heterogeneous nucleation, i.e. induced by an external factor such as impurities, electric current or mixing process, is the first stage of crystallization [8-10]. The nucleation process, apart from producing crystallites, also leads to the homogenization of the structure and physicochemical properties of the polymer. This limits the impact of processing parameters on the properties of the material, which is called nucleation-controlled crystallization [4, 8, 11]. One of the parameters influenced by nucleation is processing shrinkage [12, 13]. It characterizes all plastics processed by injection molding. We can distinguish between primary shrinkage, which is observed during

the cooling of the molded part in the cavity and in the first hours after it leaves the cavity, and secondary shrinkage, which is observed after this time. The sum of both these phenomena is called total shrinkage [13-15]. The amount of processing shrinkage depends on many factors, such as the type of material being processed [16], its crystallinity [12], mass flow rate [17, 18], additives substances present in the material [14, 15, 17, 19, 20], mold construction [21], or processing parameters [17, 18, 22]. Inappropriate mold structure or poorly selected processing parameters may lead to shrinkage defects, such as collapses, voids, shrinkage stresses, or warping [23]. Mold designers can estimate the shrinkage of unmodified materials with high accuracy, but commonly added nucleants can significantly affect the magnitude of this phenomenon. The aim of the study was to assess the influence of heterogenous nucleation and conditioning time on the processing shrinkage and mechanical parameters of polypropylene moldings.

## **2. Materials and Methods**

### **2.1. Material**

The researchers used Moplen HP 500N polypropylene, manufactured by Lyondell Basell (Płock, Poland), in their research work. The properties of Moplen HP 500N polypropylene declared by the manufacturer are: density 0.90 g/cm<sup>3</sup>, Young's modulus (E) 1400 MPa, maximum stress (*R<sub>m</sub>*) 35 MPa, and mass melt flow rate (MFR<sub>230°C</sub>, 2.16 kg) 12 g/10 min. A compound with the trade name NJ STAR NU-100 (N,N'-dicyclohexyl-2,6-dicarboxamide), manufactured by New Japan Chemical Co., was used as a heterogeneous nucleating agent. Ltd. This compound belongs to the group of β-nucleants and is intended primarily for use with polypropylene. Its use improves the mechanical and physicochemical properties of polypropylene, such as thermal resistance, stiffness, and impact strength.

### **2.2. Samples Preparation**

Both pure and nucleated polypropylene granulates were prepared on an extrusion line consisting of a single-screw extruder manufactured by the Toruń Institute of Plastics Processing Metalchem (Toruń, Poland). The diameter of the screw (D) was 25 mm, the ratio of length to diameter (L/D) was equal to 30. Additionally, the screw in the dosing zone was equipped with elements that intensified mixing, and the temperatures in the zones of the plasticizing system were equal to 140, 180, 200, 200°C (head), respectively, measured from the feed zone to the head. The samples used for the tests were made in the injection process using an e-victory 110 injection molding machine manufactured by Engel (Schwertberg, Austria). This injection molding machine is characterized by a mold closing force of 1100 kN, maximum injection volume of 154 cm<sup>3</sup>, screw diameter of 35 mm. The injection molding machine was equipped with a mold allowing the production of type A test samples in accordance with the PN-EN ISO 3167 standard. The injection parameters are presented in Table 1.

**Table 1.** Parameters of the injection process

Parameter	Value
Temperature of the plasticizing system zones I, °C	190
Temperature of the plasticizing system zones II, °C	200
Temperature of the plasticizing system zones III, °C	210
Temperature of nozzle, °C	210
Mold temperature °C	30
Injection rate, cm <sup>3</sup> /s	100
Holding pressure, MPa	25
Holding time, s	25
Real cooling time, s	50

The process resulted in obtaining samples of 100% polypropylene, marked as PP and samples of polypropylene with 0.25% nucleant were obtained and marked as PP-N.

### 2.3. Methodology

The weight of the samples was determined using an AD50 scale from Axis with an accuracy of 0.001 g. Processing shrinkage was determined based on the measurement of the length of the samples made using a MarCal 16ER caliper from Mahr with an accuracy of 0.01 mm. These measurements were carried out on 10 moldings from both types of materials, made in an injection mold with a socket length of 165 mm, which were measured and stored at 20°C. Processing shrinkage was calculated as the quotient of the difference between the measured initial dimensions of the measuring universal test sample (LP) and the dimensions obtained as a result of further measurements over time (LN) to the initial dimensions (LP) and was expressed as a percentage, according to formula 1.

$$S_L = \frac{L_P - L_N}{L_P} \cdot 100\% \quad (1)$$

The tests of the mechanical properties of the samples during the static tensile test were carried out using the Z030 universal testing machine from Zwick/Roell (Ulm, Germany), equipped with a force measuring head with a nominal value of 30 kN. The tests of each measurement series were carried out on 10 samples at the temperature of 23°C ± 2°C. When determining the modulus of elasticity, the samples were tested at a speed of 1 mm/min and 50 mm/min while determining the stress and strain at the yield point.

Tests of the properties of polypropylene samples were carried out after 1 h, 24 h, 48 h, 72 h, 168 h (1 week), and 504 h (3 weeks) after removing the moldings from the injection mold.

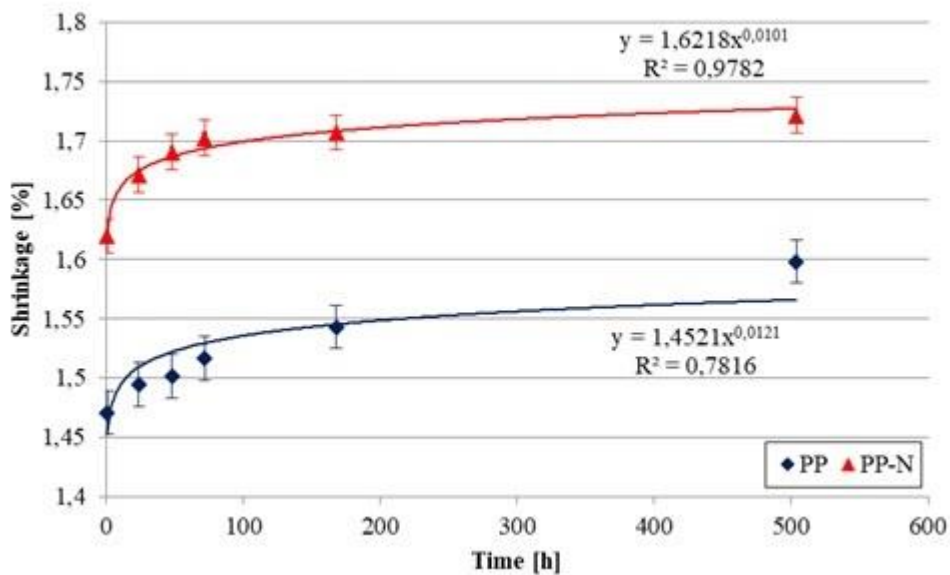
### 3. Results

#### 3.1. Mass, length and shrinkage

Table 2 shows the results of the mass and length of the tested samples over time. Fig. 1 shows the change in shrinkage of the tested materials over time conditioning.

**Table 2.** Summary of masses and lengths of tested samples over time

Material	Mass [g]	Length by time [mm]					
		1h	24h	48h	72h	168h	504h
PP	8.485	165.53	165.49	165.48	165.45	165.41	165.32
PP-N	8.451	165.28	165.19	165.16	165.14	165.13	165.11

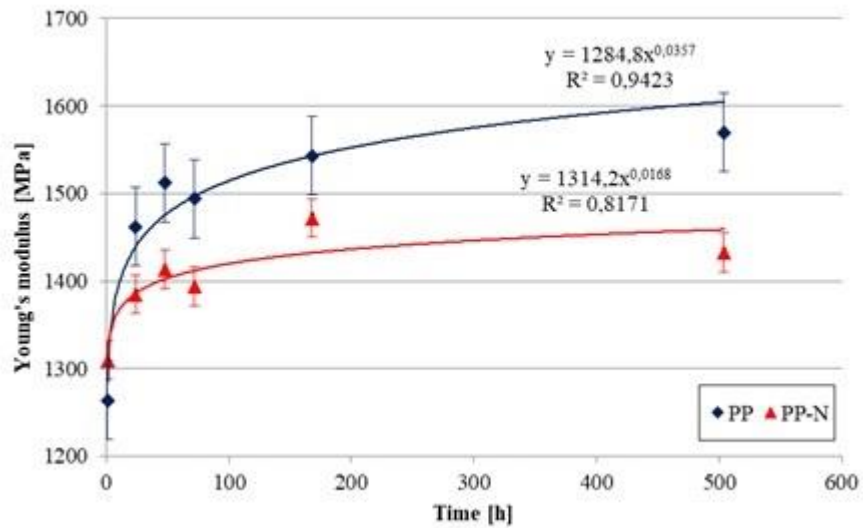


**Fig. 1.** Shrinkage versus time

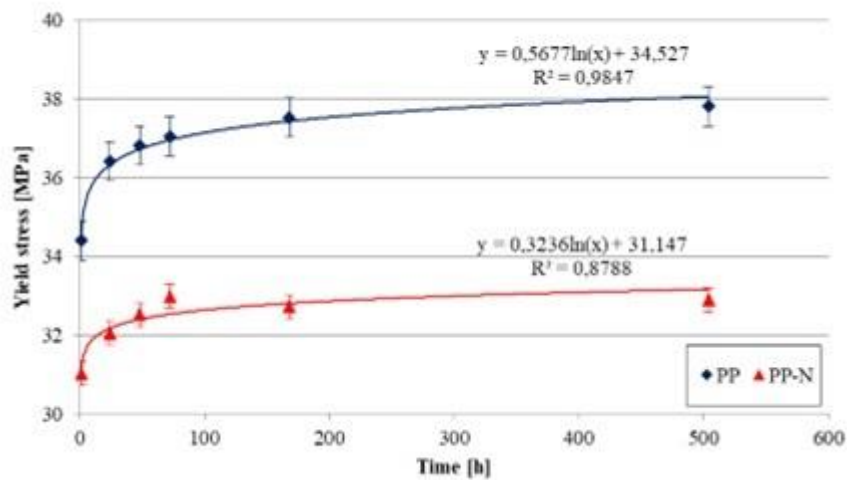
Based on the analysis of the results obtained, it should be concluded that the presence of the nucleant influences the quantitative increase in processing shrinkage. However, it is visible that, in addition to increased shrinkage, the characteristics of shrinkage changes over time. In the case of PP, apart from the primary shrinkage of 1.49% observed in the 24th hour of the study, the secondary shrinkage in the third week of the study was 1.59%, which means an increase of 0.1 percentage points. For comparison, PP-N after 24 hours had an average shrinkage of 1.67%, and after 3 weeks of testing it was 1.72%, which means an increase of 0.05 percentage points. This means that the phenomenon of secondary shrinkage has been reduced by 50% quantitatively. The PP-N samples were also characterized by smaller differences between individual samples. These discrepancies prove that the use of a nucleant can make it easier to predict the shrinkage and also affect the dimensional stability of molded parts over time. On the other hand, the fact that not only the characteristics of shrinkage changes over time but also its quantitative dimension shows that it is necessary to distinguish between unmodified and filled materials in the mold design process.

### 3.2. Static tensile test

Figs. 2, 3, and 4 show the results of the static tensile tests.



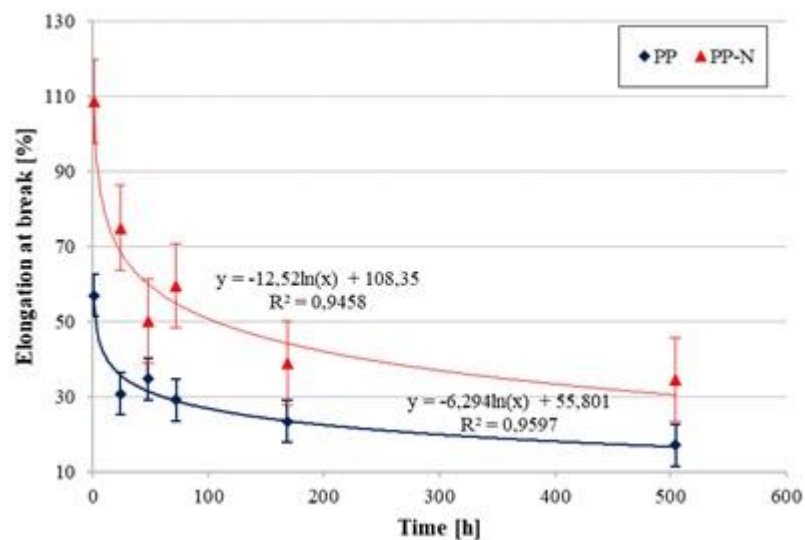
**Fig. 2.** Young's modulus versus conditioning time



**Fig. 3.** Yield stress versus time

The plots of Young's modulus and stresses at the yield point indicate that the modification of PP with the nucleating agent used leads to a decrease in the stiffness and strength of the material. Based on the data presented in Fig. 3, it was found that the nucleation of polypropylene resulted in a reduction of stresses at the yield point regardless of the length of the conditioning time. For PP after 24 h, the value of this parameter was 36.42 MPa, and for PP-N this value is lower by 12% (32.06 MPa). The modulus of elasticity and the stress at the yield point both increase with the extension of the conditioning time. For PP, the level of stress at the yield point increased by 3.82% during conditioning from 24 h to 500 h. During the same conditioning time for PP-N, this value increased by 2.62%. In the case of PP, the Young's modulus (24 h) reached 1462 MPa, and after 500 h 1570 MPa,

which gives an increase in this parameter during conditioning (24 h and 500 h) of 7.39%. For the nucleated material, the change in Young's modulus during conditioning (between 24 h and 500 h) was much smaller and quantity to 3.47%. In their research work, Raab and his team [25] also obtained a decrease in the value of Young's modulus and yield strength for polypropylene with the addition of nucleant compared to unmodified polypropylene. However, one can observe that, similar to the shrinkage phenomenon, nucleation leads to greater stability of the material's properties over time. There is a noticeable reduction in the measurement error for PP-N compared to PP. As a result, the properties of PP-N moldings can be predicted more accurately and have greater repeatability.



**Fig. 4.** Maximum deformation versus time

The last analyzed parameter was a strain at break. Fig. 4 shows that PP-N is characterized by a higher  $\epsilon_b$  value compared to unmodified PP. This is most likely due to a reduction in the size of the crystallites. In the case of both materials, however, it is visible that the value of this parameter decreases over time, which is the effect of physical aging [24]. Elongation at break for samples measured after 24 hours is 74.9% for PP-N and 30.81% for PP. After 500 h, a decrease in this parameter was recorded for PP-N of 53.7%, which gives an elongation at break value of 34.6%. However, for unmodified PP, a decrease of 43% was recorded, which gives the value of this parameter to 17.56%.

All three graphs based on the results of the static tensile test show that both pure and modified polypropylene stabilize over time, which leads to its strengthening.

## 4. Conclusions

As a result of the research, it was concluded that the presence of the nucleant in polypropylene increases the value of processing shrinkage. Additionally, we observed changes in contraction characteristics over time. For samples containing nucleant, a reduction in secondary shrinkage was achieved. Based on small scatters in the values of the analyzed parameters, it was found that molded parts made of nucleated PP are characterized by more repeatable properties, which is most

likely due to a more uniform crystal structure. The share of the nucleant in polypropylene resulted in a lower Young's Modulus and Yield stress compared to the unmodified material. Additionally, both tested materials showed an increase in Young's Modulus and Yield stress. As a result of PP modification, opposite results were recorded for the Elongation at break parameter. The material containing the nucleant obtained a higher value of this parameter than PP. Moreover, a decrease in the value of this parameter was observed for both materials over time. Modification of polypropylene with a nucleant contributed to the stabilization of the material and, consequently, smaller differences in measurements at subsequent time intervals. The obtained test results confirm the validity of the use of the polypropylene nucleation process.

## References

- [1] Nakamura, K., Shimizu, S., Umamoto, S., Thierry, A., Lotz, B., Okui, N.: Temperature dependence of crystal growth rate for  $\alpha$  and  $\beta$  forms of isotactic polypropylene. *Polymer Journal* 40, 915-922 (2008)
- [2] Greco, R., Ragosta, G.: Isotactic polypropylenes of different molecular characteristics: influence of crystallization conditions and annealing on the fracture behavior. *Journal of Materials Science* 23, 4171-4180 (1988)
- [3] Farotti, E., Mancini, E., Belleze, T., Sasso, M.: Investigations of the effects of mold temperature, test temperature and strain rate on mechanical behavior of polypropylene. *Journal of Dynamic Behavior of Materials*, 5, 344-360 (2019)
- [4] Ziabicki, A.: *Nauki techniczne u progu XXI wieku: Struktura polimerów i modelowanie procesów technologicznych*. IPPT PAN, Warszawa 155-172 (2002)
- [5] Thomann, R., Wang, C., Kressler, J., Jungling, S., Mulhaupt, R.: Morphology of syndiotactic polypropylene. *Polymer* 36, 3795-3801 (1995)
- [6] Gahleitner, M., Wolfschwenger, J., Bachner, C., Bernreitner, K., Neibl, W.: Crystallinity and mechanical properties of PP-homopolymers as influenced by molecular structure and nucleation. *Journal of Applied Polymer Science* 61, 649-657 (1996):
- [7] McGenity, P.M., Hooper, J.J., Paynter, C.D., Riley, A.M., Nutbeem, C., Elton, N.J., Adams, J.M.: Nucleation and crystallization of polypropylene by mineral fillers: relationship to impact strength. *Polymer* 33, 5215-5224, (1992)
- [8] Macauley, N.J., Harkin-Jones, E.M.A., Murphy, W.R. The influence of nucleating agents on the extrusion and thermoforming of polypropylene. *Polymer Engineering and Science* 38, 516-523 (1998)
- [9] Setz, S., Stricker, F., Kressler, J., Duschek, T., Mulhaupt, R.: Morphology and mechanical properties of blends of isotactic and syndiotactic polypropylene with SEBS block copolymers. *Journal of Applied Polymer Science* 59, 1117-1128, (1996)
- [10] Przygocki, W., Włochowicz, A.: *Uporządkowanie makrocząstek w polimerach i włóknach*. PWN, Warszawa (2018)
- [11] Housmans, J.W., Gahleitner, M., Peters, G.W.M., Meijer, H.E.H.: Structure-property relations in molded, nucleated isotactic polypropylene. *Polymer* 50, 2304-2319 (2009)
- [12] Titomanlio, G., Jansen, K.M.B.: In-mold shrinkage and stress prediction in injection molding. *Polymer Engineering and Science* 36, 2041-2049 (1996)
- [13] Baur, E., Osswald, T., Rudolph, N.: *Plastic handbook the resource for plastics engineers*. Hanser Publishers Monachium (2019)
- [14] Kościuszko, A., Rojewski, M., Nowinka, B., Patalas, F.: Post-Molding Shrinkage, Structure and Properties of Cellular Injection-Molded Polypropylene. *Materials* 15, 7079, (2022)
- [15] Kościuszko, A., Czyżewski, P., Rojewski, M.: Modification of Laser Marking Ability and Properties of Polypropylene Using Silica Waste as a Filler. *Materials* 14(22), 6961 (2021)
- [16] Jachowicz, T., Красінський, В.: Skurcz wtryskowy wyprasek napełnionych. *Transfer Inovacji*, 22, 10-15 (2012)
- [17] Azaman, M.D., Sapuan, S.M., Sulaiman, S., Zainudin, R.S., Kalina, A.: Shrinkages and warpage in the processability of wood-filled polypropylene composite thin-walled parts formed by injection molding. *Materials and design* 52, 1018-1026 (2013)
- [18] Wilczyński, K.: *Wybrane Zagadnienia Przetwórstwa Tworzyw Sztucznych*. OWPW, Warszawa, (2011)
- [19] Kościuszko, A., Czyżewski, P., Wajer, Ł., Ościak, A., Bieliński, M.: Properties of polypropylene composites filled with microsilica waste. *Polimery*, 65, 99-104 (2020)

- [20] Jachowicz, T., Godlewska, A.: Skurcz przetwórczy wyprasek wtryskowych napełnionych włóknem szklanym. *Postępy Nauki i Techniki* 7, 195-204 (2011)
- [21] Altan, M.: Reducing shrinkage in injection moldings via the Taguchi, ANOVA and neural network methods. *Materials and design* 31, 599-604 (2010)
- [22] Guang-hong, H.U., Zhen-shan, C.U.I.: Effect of packing parameters and gate size on shrinkage of aspheric lens parts. *Journal of Shanghai Jiaotong University (science)*, 15, 84-87 (2010)
- [23] Plastic design guide, Autronic Plastics, INC. <https://www.apisolution.com/plastic-design-guide.php> (access: 26.03.2022)
- [24] Kościuszko, A., Marciniak, D., Sykutera, D.: Post-Processing Time Dependence of Shrinkage and Mechanical Properties of Injection-Molded Polypropylene. *Materials* 14(1), 22 (2021)
- [25] Raab, M., Ščudla, J., Kolařík J.: The effect of specific nucleation on tensile mechanical behaviour of isotactic polypropylene. *European Polymer Journal* 40(7), 1317-1323 (2004)



© 2023 by the authors. Submitted for possible open access publication under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).