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Effect of Selected Injection Conditions on the Mechanical Properties and Structure of HDPE

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Abstract
This paper is devoted to research of high-density polyethylene (HDPE), which belongs to one of three main biomaterial groups, i.e. polymeric materials. Hence, due to its unique properties, it still plays an important role in biomedical applications – especially in the production of medical equipment, implants and parts of prostheses. This publication deals with the effect of selected conditions of processing which involved injection moulding on the mechanical properties and structure of HDPE mouldings. Samples for tests were produced on a Krauss − Maffei injection moulder on the basis of a research plan prepared using the STATISTICA program. According to this schedule, the following variable parameters of the injection process were selected: injection temperature T_w in °C, mould temperature T_f in °C and injection velocity v_w in mm/s. In addition, a part of the moldings was subjected to a few processings. Then the samples obtained were subjected to different tests: tensile, impact and hardness tests, Differential Scanning Calorimetry (DSC) and the melt flow rate (MFR) test in order to determine the influence of selected injection conditions and the multiplicity of processing on the mechanical, rheological and structural properties of HDPE.

Key words: *HDPE, high-density polyethylene, injection moulding, mechanical properties, polymer structure.*

Introduction

One of the materials widely applied in biomedical engineering and medicine (including orthopaedic and maxillofacial surgery) is polyethylene (PE), in particular the two varieties of ultra-high molecular weight polyethylene (UHMWPE) and high density polyethylene (HDPE). Application of these materials, mainly in the production of endoprostheses, their parts, external prostheses and implants, results from the fact that, as a biomaterial, polyethylene has unique properties [1, 2]. Firstly it is characterised by high biotolerance and biocompatibility, i.e. it behaves appropriately in contact with tissues and the human body. In addition, this material (and po, sible wear products) is non-toxic because it has no effect on the immune system − it does not cause acute or chronic allergic reactions, nor inflammations, and has no cancerogenic or mutagenic properties. Also it does not lead to haemolysis. Additionally this material is characterised by appropriate, high corrosion resistance in the body environment. Secondly, polyethylene, as a biomaterial, has very good strength properties (including high tensile, bending and fatigue strength, and appropriate wear resistance and hardness), which in the case of HDPE are affected by a high degree of crystallinity and density. HDPE also has good tribological properties, i.a. proper abrasion resistance and a low coefficient of friction [3, 4].

Polyethylene (PE), belonging to the thermoplastic resins, is characterised by good processing ability, which is why in practice it can be processed by every method. However, an important factor, influencing the choice of processing, is the variety of the polymer, in particular its density, degree of crystallinity and molecular weight. One of the methods more commonly used in the case of HDPE is injection moulding, whose parameters can affect the strength or structural properties of polyethylene [2, 4]. Therefore a suitable combination of injection parameters can optimise the properties of the polyethylene components. Hence researchers often use different statistic approaches in order to investigate the correlation between moulding conditions and the properties of products obtained [6-9].

Experimental

Research subject

High-density polyethylene (HDPE) was used in this study as a research material. Granulate, bearing the trade name of Purell GB 7250, was supplied by Basell Orlen Polyolefins, Płock, Poland. The main properties of this material are presented in ***Table 1***, while in ***Table 2*** there are typical processing conditions [10-13]

Table 1. *Physical and mechanical properties of HDPE.*

Property	Value	Test method
Density, g/cm^3	0.952	ISO 1183
Melt flow rate (190 °C/2.16 kg), g/10 min	10	ISO 1133
Tensile modulus, MPa	1000	ISO 527
Tensile strain at yield, %	10	ISO 527
Tensile stress at yield, MPa	24	ISO 527
Charpy impact strength, notched (23 °C), kJ/m^2	2.5	ISO 179
Ball indentation hardness (H1538/30), MPa	46	ISO 2039-1

Table 2. *General processing parameters for HDPE.*

Process parameter	Value
Mould temperature, °C	20 ÷ 95
Injection temperature, °C	200 ÷ 250
Injection pressure, MPa	70.0 ÷ 105.0
Injection velocity	As high as possible

Table 3. *Structure of research plan – code and real values of DoE normalised variables.*

Run	Mould temperature T_f		Injection temperature T_w		Injection velocity v_w	
	Code value	Real value, °C	Code value	Real value, °C	Code value	Real value, mm/s
1	-1	20	-1	210	-1	40
2					1	100
3			1	250	-1	40
4					1	100
5	1	90	-1	210	-1	40
6					1	100
7			1	250	-1	40
8					1	100
9	-1	20	0	230	0	70
10	1	90				
11	0	55	-1	210		
12			1	250		
13			0	230	-1	40
14					1	100
15 (C)					0	70
16 (C)						

Table 4. *Variability intervals of HDPE injection conditions.*

Independent variable	Unit	HDPE	
		Lower value	Upper value
Injection temperature T_w	°C	210	250
Mold temperature T_f	°C	20	90
Injection velocity v_w	mm/s	40	100

Sample preparation

The samples used for the tests for determination of the mechanical, rheological and structural properties of HDPE were prepared using injection moulding. Specimens were moulded by a Krauss – Maffei KM 65-160 injection moulder, applying a screw with a diameter of 30 mm and two cavity mould, thanks to which standardised samples of type 1A were obtained according to Standard EN ISO 527-1:2012 [14, 15]. Additionally this machine was equipped with a high-quality C4 control system and Wittmann Tempro Plus 140 thermostat.

Furthermore in order to minimise the errors and disturbances possible to develop during the production of the research samples, the following steps were taken:

- the injection of a series of samples was carried out in the shortest possible time, during one day (then the temperature and ambient humidity were controlled),
- each time when changing the injection conditions, overspray was used for thermal stabilisation of the material in the plasticising system of the injection moulder,
- the samples were cooled to ambient temperature always in the same place, after which they were marked, packed and stored in a room with a temperature of about 23 ± 2 °C and relative humidity of ± 50%.

In addition, a part of the specimens was subjected to milling on a grinder and the three processings repeated in order to determine the effect of the multiplicity of the processing on the properties of high density polyethylene.

Parameters of the process and DoE plan

Samples for tests were made according to the research plan formulated using the STATISTICA program, prepared on the basis of literature in terms of the theory of experiment planning [16-20] and the DoE module of the STATISTICA – program, aiming at statistical data analysis [21, 22]. The plan applied is a central composition plan with a rotatability coefficient α = 1.6818, where each factor (input data i.e. injection parameter) can occur on three levels fixed by the values: -1, 0, +1, which represent the lowest, middle and highest values of their range, respectively. This plan consisted of 16 runs (i.e. layouts, systems of factors), according to which the test samples were made. The structure of the research plan, expressed in code and real values, is presented in ***Table 3***.

In turn, the relationship between a code and real value is described by the following ***Equation 1***:

$$\hat{x} = \frac{2(x_i - x_{avg})}{(x_{upper} - x_{lower})} \quad (1)$$

where, $\hat{x}$ – code value, x_i – real value of next variable, x_{upper}, x_{lower} – upper and lower values of a given real variable, x_{avg} – average value of a given real variable.

In this work, the process of injection moulding was carried out at three variable conditions, which according to the applied research plan, are independent variables. Other parameters were kept at a stable level. The following process parameters: injection temperature T_w in °C, mould temperature T_f in °C and injection velocity v_w in mm/s were selected on the basis of data from literature [7-9, 13] and research [23-25]. In turn, when determining the variable interval of the factors, besides the tests carried out on the injection molder and the properly prepared form, information and recommendations provided by the manufacturer [13] and literature [5, 7] were used. Furthermore it was assumed that each moulding should be prepared correctly, i.e. the cavity should be filled completely and no anomalies should occur. Additionally preliminary tests were conducted at various injection conditions by which the flow of material is constricted (extremely low values of injection velocity, mould and injection temperature), but inversely making it easier due to the low viscosity of the material. In this way, the variability intervals of injection conditions were determined, which are presented in ***Table 4***.

Analytical methods

The research material obtained was subjected to the following tests: tensile, impact and hardness tests, Differential Scanning Calorimetry (DSC), the melt flow rate test and structure studies in order to investigate the influence of selected parameters of the injection process on mechanical, rheological and structural properties of HDPE.

Research of mechanical properties of HDPE

An impact test was carried out at room temperature (23 °C) by Charpy testing with applying a pendulum hammer of rigid construction at an energy of

1 J. This test was done using standardised notched specimens of type 2A. For the purpose of determination of HDPE impact strength, ten measurements were conducted for each case examined, and then an arithmetic average of the results obtained was calculated [26].

In turn, hardness was determined by means of the ball indentation method with a measurement force of 132 N, applying a hardness tester equipped with a steel spherical indenter of 5 mm diameter. For this purpose ten measurements were conducted at room temperature for each case examined, and then an arithmetic average of the results obtained was determined [27].

The mechanical properties of HDPE, such as tensile strength, Young's modulus and elongation at break were investigated during tensile testing using a Hegewald & Peschke Inspekt Desk 20 universal testing machine. For this purpose, standardised specimens 1A were used. The process of elongating was carried out at a speed of 50 mm/min, whereby the breaking test occurred when the value of force (F_m) had decreased by 80% [14, 15].

Research of rheological and structural properties of HDPE

Analysis of the Differential Scanning Calorimetry (DSC) was conducted using inert gas (nitrogen) and a calorimeter – Netzsch DSC 214 Polyma according to Standard EN ISO 113570-1:2016 [28]. Measurements were executed according to the following program:

- heating from 20 to 200 °C (with heating speed of 10 °C/min, within 120 s);
- cooling from 200 to 50 °C (with heating speed of 10 °C/min);
- second heating from 50 to 200 °C (with heating speed of 10 °C/min, within 120 s).

Before this tests, the samples were weighed using a SARTORIUS microchemical balance accurate to 0.01 mg, with the function of internal calibration and possibility of closing the measurement space. The samples' weight was ranged from 0.007 to 0.01 g.

On the basis of DSC thermograms attained, the temperatures of phase transitions, the heating effect (enthalpy) and degree of crystallinity were determined by means of Netzsch Proteus Analysis software [29].

In turn, the Melt Mass Flow Index was determined using an extrusion plastometer – DYNISCO LMI 4002. A test was carried out with the following parameters: melt temperature of 190 °C and load of 2.16 kg, according to Standard EN ISO 1133-1:2011 [30-32].

In addition, research of the HDPE structure was carried out on a NIKON ECLIPSE E200 microscope, equipped with a NIKON DIGITAL SIGHT DS-5M digital camera in transmitted light at a magnification of 400×. The preparations for testing were cut from injected samples by means of a Thermo Shandon Finesse ME+ microtome.

Results and discussion

In this work, in the part concerning statistical analysis, the following parameters: tensile strength, impact strength and degree of crystallinity were assumed as dependent variables (tested). First, residual analysis, which plays an important role in examining the adequacy of the fitted model, was made, where a rest was calculated as the difference between the determined values of the degree of HDPE properties tested and the corresponding values calculated from the model equation. For this purpose, in the first stage of the analysis, it was attempted to make the form of the model equation as simple as possible, which did not always bring satisfactory results [21-22]. As an example, ***Figure 1*** shows the dependence of the expected normal value on the rest of the HDPE crystallinity degree model.

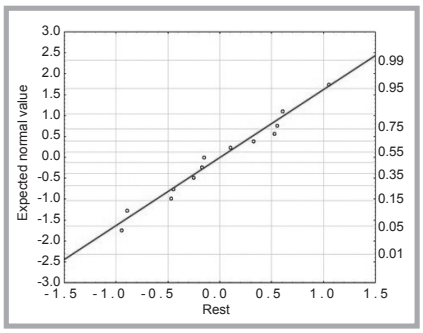


Figure 1. *Expected normal value as a function of the rest of the HDPE crystallinity degree model.*

The vast majority of points lies along a straight line, which proves the correct fit of the model equation to the results of studies of the HDPE crystallinity degree.

In turn, the results of the Pareto analysis regarding the influence of selected injection conditions on the degree of crystallinity for HDPE are shown in ***Figure 2***, where was plotted on a vertical solid line, showing the statistical significance corresponding to value p = 0.05. According to this chart, the elements of the equation whose statistical significance is less than 0.05 are outside this line, which indicates that the probability of observing random differences describing the variable examined is not more than 5% and that, at the same time, all differences observed are reliable with a probability of not less than 95%. It can be seen in this figure that the mould temperature and injection temperature are the main factors determining the structure, tensile strength and impact strength, while the injection velocity much less affected it. Additionally the signs at

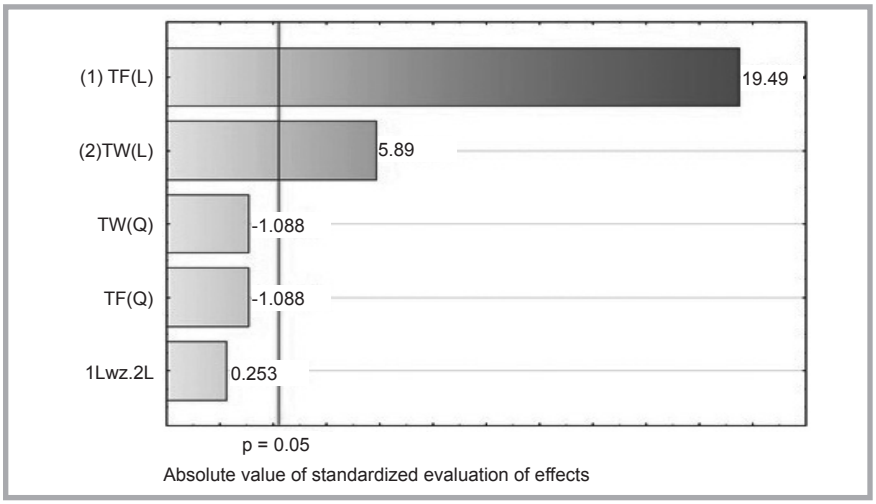


Figure 2. *Pareto analysis of standardised effects of crystallinity degree model for HDPE.*

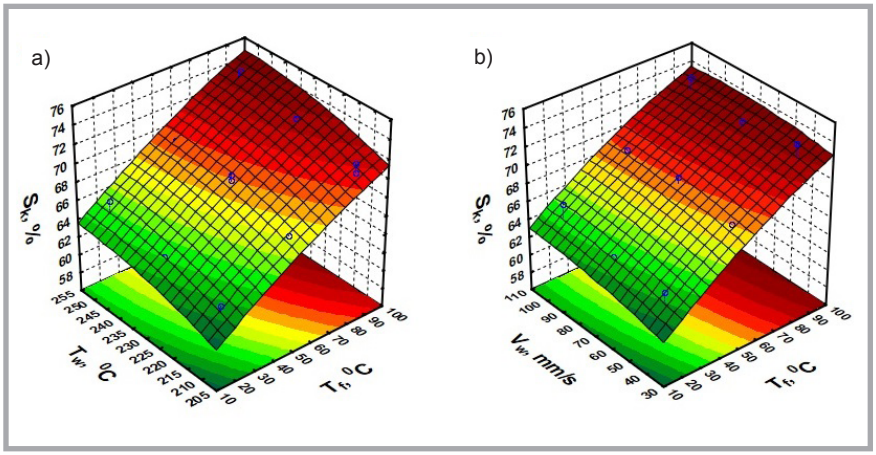


Figure 3. *Value of the crystallinity degree as a function of: a) injection temperature and mould temperature and b) injection velocity and mould temperature.*

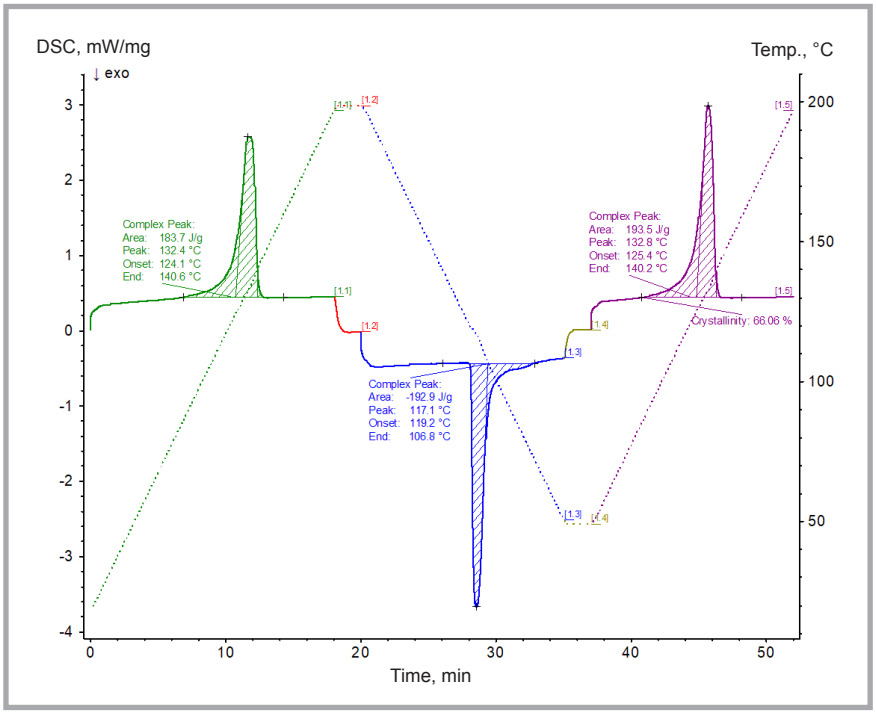


Figure 4. *Example DSC thermogram for moulding injected with the following parameters: T_f = 55 °C, T_w = 230 °C and v_w = 70 mm/s.*

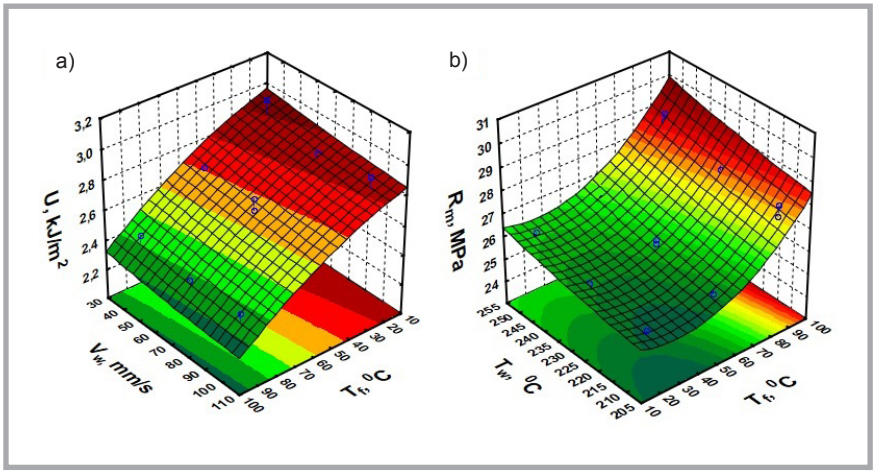


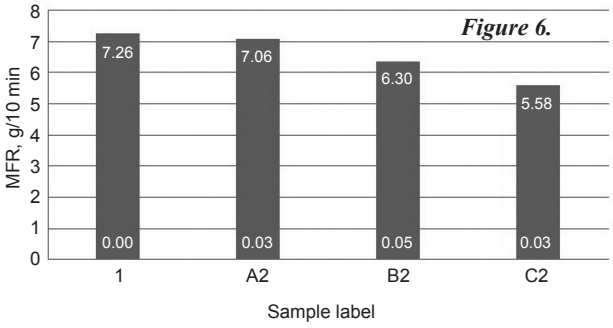
Figure 5. *Value of a) impact strength as a function of injection velocity and mould temperature and b) tensile strength as a function of injection temperature and mould temperature.*

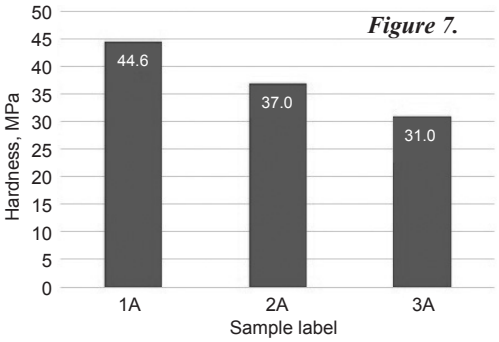
the absolute value explain the direction of dependence. A minus sign ("–") means that increasing the value of the ariable causes a decrease in the variable analysed, while a plus sign ("+") at T_w and T_f indicates that an increase in these parameters also leads to an increase in the degree of crystallinity. In turn, the L and Q symbols visible on the Pareto chart, connected with the injection parameters, indicate the linear and quadratic components of the model equation, respectively, while 1L wz. 2L refers to the interactions of components 1(T_f) and 2 (T_w).

Figure 3 presents the dependence of the change in the degree of crystallinity (Sk) as a function of the mould temperature, injection temperature and injection velocity for the HDPE material. This chart (***Figure 3.a***) shows that maximum values of the degree of ordering the structure are obtained by HDPE samples moulded at temperatures: T_w = 250 °C and T_f = 90 °C. The moldings obtained at a higher mould temperature are characterised by a higher value of the crystallinity degree, which is related to the thermodynamic state of the material during the cooling phase, which, in turn, causes an increase in the cooling time. In this way, increased mobility occurs, which makes the polymer structure easier to organise. In turn, the higher injection velocity results in shortening the filling time of the forming cavity and in reducing heat losses in the material flow path (***Figure 3.b***). Furthermore an increase in the degree of crystallinity caused an increase in tensile and impact strength.

For example, ***Figure 4*** shows one of the DSC thermograms obtained during the DSC tests and then analysed by means of Netzsch Proteus Analysis software, thanks to which the degree of crystallinity was determined. ***Figure 4*** refers to HDPE moulding composed of the following parameters: T_f = 55 °C, T_w = 230 °C and v_w = 70 mm/s.

Figure 5.a shows the dependence of the change in impact strength values for HDPE as a function of mould temperature and injection velocity. According to this chart, the samples exhibit the highest impact strength at a mould temperature of 20 °C and injection velocity of 40 mm/s, which means that at the low temperature of the mould, the proportion of the crystalline phase is smaller and the samples





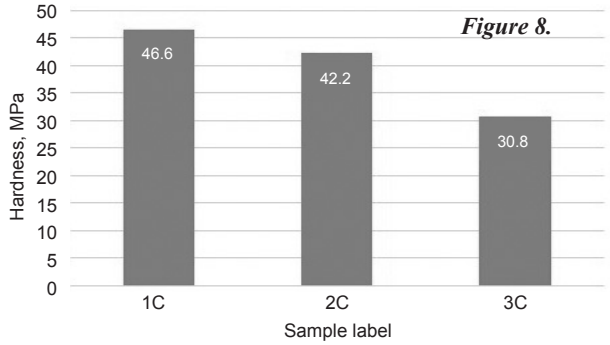


Figure 6. *Average value of MFR and its standard deviation for samples before granulation (1) and after two granulations at different injection conditions (A2 – at the lowest T_w and T_f, B2 – at the middle T_w and T_f, and C2 – at the highest T_w and T_f).*

Figure 7. *Average value of HDPE hardness for samples injected at the lowest T_w and T_f before granulation (1A), and after one (2A) and two granulations and injection processes (3A).*

Figure 8. *Average value of HDPE hardness for samples injected at the highest T_w and T_f before granulation (1C), and after one (2C) and two granulations and injection processes (3C).*

are more flexible. In turn, ***Figure 5.b*** presents the dependence of the change in tensile strength values for HDPE as a function of mould temperature and injection temperature. The highest values of this property are obtained at maximum mould and injection temperatures.

Moreover research related to the impact of the multiplicity of processing on the structural properties of HDPE showed that along with the subsequent granulation processes and injection moulding, the MFR value decreases by about 15% from the previous value, which is presented in ***Figure 6***. It is caused by the thermal and mechanical degradation of polymer chains of macromolecules, which succumb to tearing [33]. It should be noted here that ***Figure 6*** shows average values of the Mass Flow Rate (MFR) calculated on the basis of 10 measurements. Additionally the bottom values visible in ***Figure 6*** indicate the standard deviations of the MFR for the samples tested.

In addition, DSC results indicated that the subsequent granulation and injection moulding processes caused a decrease in the crystallinity degree, which, in turn, worsened the values of tensile strength and hardness and increased the impact strength. As an example, ***Figures 7*** and ***8*** show the changes in hardness after the subsequent processings for the HDPE samples, injected at the lowest and highest values of injection and mould temperatures.

Furthermore the decrease in the crystallinity degree reveals changes in the HDPE structure, because the subsequent granulation and injection processes, i.e. thermal processes, cause decreasing crystallisation, a decrease in spherulites and the appearance of a more branched, irregular structure, which is related to the decrease in values of the crystallinity degree [33, 34]. It is presented in ***Figure 9***.

Conclusions

The investigations carried out are very significant due to the fact that they characterise the impact of real parameters of processing during injection moulding on the structure of HDPE, and consequently its mechanical, rheological and structural properties. Hence a suitable combination of injection parameters can optimise the properties of polyethylene. It is especially important in the production of components applied in biomedical engineering and medicine that are required to be characterised by appropriate high strength and good

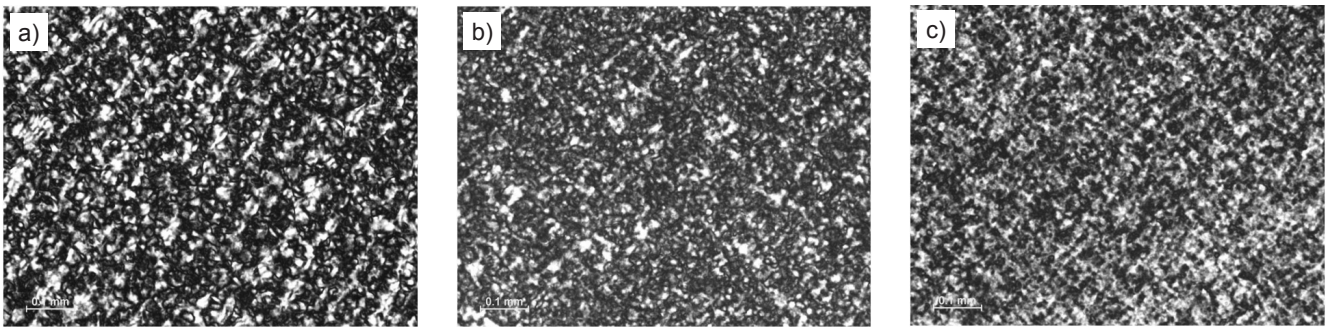


Figure 9. *Structure of HDPE sample injected at middle Tw and Tf: a) before granulation, b) after regranulation, c) after two regranulations.*

tribological properties with good technological properties at the same time.

The following conclusions can be drawn from these research results:

- The injection conditions selected, particularly the mould temperature and to a lesser degree the injection temperature, have a significant influence on the crystallinity degree of high-density polyethylene (HDPE), whereas the injection velocity is much less affected. The increase in values of these parameters causes a rise in the values of crystallinity degree and better ordering the material structure.
- These changes in the degree of crystallinity make the values of strength properties, i.e. tensile strength and hardness, rise at higher mould and injection temperatures.
- In turn, the impact strength decreases with an increasing degree of crystallinity, hence the highest values of this parameter were obtained by samples injected at the lowest injection conditions.

Furthermore, from research on the impact of the multiplicity of the processings on the properties tested, we can state that:

- The introduction of subsequent granulation and injection processes decreases the values of the crystallinity degree significantly, which causes a drop in tensile strength and hardness and an increase in the impact strength. In addition, the HDPE structure was changed – it is more branched and irregular, and the spherulites are smaller.
- Furthermore these processes cause a decrease in the MFR value, which is related to the thermal and mechanical degradation of polymer chains of macromolecules, i.e. their tearing during subsequent thermal cycles.

References

1. Kurtz SM. *UHMWPE Biomaterials Handbook*, Second Edition. San Diego: Elsevier Inc; 2009.
2. Peacock AJ. *Handbook of polyethylene. Structures, properties and applications.* New York: Marcel Dekker, Inc; 2000.
3. Ratner BD, Hoffman AS, Schoen FJ, Lemons JE, editors. *Biomaterials Science: An Introduction to Materials in Medicine*. San Diego: Academic Press; 2013.
4. Nowacki J, Dobrzański L, Gustavo F. *Implanty śródszpikowe w osteosyntezie kości długich*. Gliwice: International OCSCO WordPress; 2012.
5. Saechtling H. *Tworzywa sztuczne*. Poradnik. Warszawa: WNT; 2000.
6. Bociąga E. Wpływ temperatury formy wtryskowej i prędkości wtryskiwania na wybrane właściwości wyprasek polietylenowych. *Polimery* 2000; 45(11-12): 830-836.
7. Greener J, Wimberger-Friedl R. *Processing Injection Molding. Process, Materials and Applications*. Munich: Hanser Publisher; 2006.
8. Smorawiński A. *Technologia wtrysku*. Warszawa: WNT; 1989.
9. Rosato D. *Injection molding handbook*. Boston: Kluwer Academic; 2000.
10. Polyethylene. Caps, Closures and Tubes Applications [homepage on the Internet]. No date [cited 2018 Apr 26]. Available from: http://basellorlen.pl/assets/produkty/aplikacje/2014E_PE_CCT.pdf
11. Polietylen Purell. Do zastosowań w medycynie i farmacji. Applications [homepage on the Internet]. No date [cited 2018 Apr 26]. Available from: http://www.basellorlen.pl/assets/produkty/aplikacje/2014_PE_Purell.pdf
12. Purell GB7250. Applications [homepage on the Internet]. No date [cited 2018 Apr 26]. Available from: https://www.lyondellbasell.com/en/polymers/p/Purell-GB-7250/2a2de9d2-d83b-49b2-9297-3768155fbc74
13. HDPE processing conditions [homepage on the internet] No date [cited 2018 Apr 26]. http://www.viewmold.com/sources/Plastic_resin_injection_molding_processing_condition/HDPE_injection_molding_processing_condition.html
14. EN ISO 527-1:2012. Plastics – Determination of tensile properties – Part 1: General principles.
15. EN ISO 527-1:2012. Plastics – Determination of tensile properties – Part 2: Test conditions for moulding and extrusion plastics.
16. Pietraszek J. Planowanie doświadczeń-możliwość czy konieczność [homepage on the Internet]. No date [cited 2018 Apr 26]. Available from: https://media.statsoft.pl/_old_dnn/downloads/doe.pdf
17. Korzyński M. *Metodyka eksperymentu planowanie, realizacja i statystyczne opracowanie wyników eksperymentów technologicznych*. Warszawa: Wydawnictwo Naukowo Techniczne; 2006.
18. Dobosz M. *Wspomagana komputerowo statystyczna analiza wyników badań. Warszawa*: Akademicka Oficyna Wydawnicza EXIT; 2004.
19. Kosmol J. *Wybrane zagadnienia metodologii badań*. Gliwice: Wydawnictwo Politechniki Śląskiej; 2010.
20. Polański Z. *Planowanie doświadczeń w technice*. Warszawa: PWN; 1994.
21. Design of experiments: science, industrial DOE [homepage on the Internet]. C2018 [cited 2018 Apr 23]. Available from: http://www.statsoft.com/Textbook/Experimental-Design#centralc
22. STATISTICA [computer program]. Version 13.3. Kraków: StatSoft Polska; 2018.
23. Bociąga E. Effect of Manufacturing Conditions on the Properties of Injection Molded Polyethylene Test Specimens. *The Journal of Injection Molding Technology* 2001; 5(1): 15-22.
24. Bociąga E, Palutkiewicz P. The Influence of Injection Molding Parameters and Blowing Agent Addition on Selected Properties, Surface State, and Structure of HDPE Parts. *Polymer Engineering and Science* 2013; 53(4): 780-791.
25. Bociąga E. Wpływ temperatury formy wtryskowej i prędkości wtryskiwania na wybrane właściwości wyprasek polietylenowych. *Polimery* 2000; 45(11-12): 830-836.
26. EN ISO 179-1:2010. Plastics – Determination of Charpy impact properties – Part 1: Non-instrumented impact test.
27. EN ISO 2039-1:2010. Plastics- Determination of hardness- Part 1: Ball identation method.
28. EN ISO 113570-1:2016. Plastics- Differential scanning calorimetry (DSC) – Part 1: General principles.
29. Porowski R. Wprowadzenie do analizy termicznej polimerów. *Zeszyty Naukowe SGSP* 2017; 64(4): 67-90.
30. EN ISO 1133-1:2011. Determination of the melt mass – flow rate (MFR) and the melt volume – flow rate (MVR) of thermoplastics – Part 1: Standard method.
31. Ciesińska W. Liszyńska B. Zieliński J. Makomaski G. Badania reologiczne poliolefin. *Czasopismo techniczne – Mechanika* 2009; 3(106): 57-60.
32. Krzyżak A, Sikora R. Wskaźnik szybkości płynięcia – czynniki wpływające na jego zmianę. *In: Koszkul J., editor. Materiały polimerowe i ich przetwórstwo*. Częstochowa: Wydawnictwo Politechniki Częstochowskiej, 2000; p. 19-26.
33. Frącz W. Wpływ wielokrotnego przetwórstwa polimerów na parametry stanu tworzywa w formie wtryskowej. *Zeszyty Naukowe Politechniki Rzeszowskiej – Mechanika* 2012; 84(3/12): 15-29.
34. Kowalska B. Problematyka krystalizacji polimerów w procesie wtryskiwania. *Polimery* 2007; 52(7): 83-87.

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