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INFLUENCE OF INJECTION MOULDING CONDITION AND ANNEALING ON THERMAL PROPERTIES, STRUCTURE, COLOR AND GLOSS OF COMPOSITE POLYAMIDE 6 WITH GLASS BEADS

Determination of the influence of processing and annealing on the change of thermal properties, structure, color and gloss for samples made of a polyamide 6 composite with glass beads was the aim of this work. Investigation of the crystallinity degree using the DSC method as well as investigation of the structure using optical microscopy have been made. The color change was determined by the CIELab method and the gloss by reflection at the angles of 20 and 60°. Investigations into the influence of the conditions of injection moulding on the properties of the PA 6 composite with glass beads, commercial name of Schulnamid 6 GB30H, have been conducted. The samples were injected using a KraussMaffei KM65-160C1 injection moulding machine. Investigations have been conducted for the samples before as well as after annealing. The highest value of the crystallization degree of the PA 6/glass beads composite was obtained at an injection temperature of 280°C and mold temperature of 100°C. During annealing, an increase in the crystalline phase content for the PA 6 composite with glass beads occurred. The increase in the lightness value after the annealing process of PA 6 filled with glass beads was obtained. The character of changes of the a* and b* coordinate values for the examined materials before and after the annealing process was evaluated, which proves the essential influence of the conditions of injection moulding and thermal treatment on the colour change.

Keywords: composites, thermal properties, structure, colour, gloss, polyamide 6, glass beads

WPŁYW PARAMETRÓW WTRYSKIWANIA I WYGRZEWANIA NA WŁAŚCIWOŚCI TERMICZNE, STRUKTURĘ, BARWĘ I POŁYSK KOMPOZUTU POLIAMIDU 6 Z KULKAMI SZKLANYMI

Obróbka cieplna kompozytów polimerowych pociąga za sobą zmianę właściwości termomechanicznych i struktury tych materiałów. Przewidywanie właściwości na skutek zmiany warunków przetwórstwa odgrywa dużą rolę w planowaniu składu, jak również w sporządzaniu kompozytów. W pracy przedstawiono wyniki badań zmiany właściwości termicznych, struktury, barwy i połysku po procesie wygrzewania kompozytu poliamidu 6 z kulkami szklanymi. Badania właściwości termicznych przeprowadzono metodą DSC. Strukturę obserwowano za pomocą mikroskopu optycznego do badań w świetle przechodzącym i spolaryzowanym. Zmiany barwy określono metodą CIELab, a połysku w zakresie kąta odbicia 20 i 60°. Badania przeprowadzono na próbkach wytworzonych metodą wtryskiwania przy zmiennej temperaturze wtryskiwania i temperaturze formy. Zarejestrowano wpływ temperatury wtryskiwania i temperatury formy na stopień krystaliczności, którego wartość rośnie przy wyższej temperaturze wtryskiwania i temperaturze formy oraz zmiany zakresu temperatury topnienia fazy krystalicznej. W pomiarach barwy uzyskano niewielkie zmiany jasności badanych próbek. Określono charakter zmian wartości współrzędnych a* i b* badanych materiałów, który wskazuje na wpływ temperatury wtryskiwania i temperatury formy na zmianę barwy. Stwierdzono wpływ wygrzewania na stopień krystaliczności, którego wartość rośnie po procesie wygrzewania oraz zmiany zakresu temperatury topnienia fazy krystalicznej. W pomiarach barwy stwierdzono wzrost wartości jasności po procesie wygrzewania. Określono charakter zmian wartości współrzędnych a* i b* badanych materiałów po procesie wygrzewania. Zarejestrowano istotny wpływ obróbki cieplnej na zmianę barwy.

Słowa kluczowe: kompozyty, właściwości termiczne, struktura, barwa, połysk, poliamid 6, kulki szklane

INTRODUCTION

Polymer composites play an important part in the development of technical polymer use. During the last twenty years, it is polymer composites that have been very popular as a group of polymer materials with interesting and sometimes very specific properties [1-3]. The reason for polymer composites manufacturing is the will to eliminate or to diminish the drawbacks that characterize polymers. Moreover, manufacturing composites from already known polymers is generally much faster than designing and manufacturing new polymers. Implementing the production of composites on a large industrial scale is also cheaper since it is based only on

the processes of mixing and, in contrast to the synthesis of new polymers, it requires much smaller investments [4-7]. Fillers added to plastics can modify the physical properties and structure. This way of obtaining specific materials, by physical modification, is carried out in highly industrialised countries, and in many papers it is included among the future methods of obtaining new generation constructional materials. Therefore, it is important to find such fillers which do not require excessive preliminary preparation - surface preparation, active compound removal before their addition to the composite, and filler introduction into the composite should be possible at low costs and with uncomplicated operations. The filler addition should also enable one to control the composite properties in the exactly determined way. Constructional polymer composites have good mechanical properties and resistance to many physical and chemical factors.

The composites properties depend on the structural factors of the polymer as well as on the processing conditions. The structural factors are for example: chemical structure of the macromolecules, molecular weight, physical structure of the polymer chain, crystallinity, molecular orientation and presence of additives [4-12]. The aim of this investigation was to determine the influence of annealing on the color and gloss of a dyed PA6/glass beads composite. The results of thermal properties testing as well as the structure of the tested composite before and after the annealing process are presented in this paper. The study was conducted on samples of composites prepared at different mold and injection temperatures.

MATERIALS AND INVESTIGATION METHODOLOGY

The Polyamide 6 composite with 30% glass beads, trade name Schulnamid 6 GB30H, manufactured by A. Schulman GmbH was used for the investigation. In the glass bead filled materials, compact beads were used, not hollow glass beads because of their mechanical properties. The beads had an average diameter of 20 μm. For good incorporation of the beads, beads with a surface treatment were used, which is additionally responsible for adhesion to the thermoplastic matrix. The samples for testing were injected using a Krauss-Maffei KM65-160C1 injection moulding machine, with a screw of 30 mm diameter, three heating zones, L/D = 23 and a constant pitch. The clamping force of the machine is 650 kN. The injection parameters are summarized in Table 1.

The polyamide composite before injection molding was dried in a heating cabinet ZELMET kc-100/200 at 80°C for 12 h. Annealing was conducted at the temperature of 170°C, the annealing rate being 0.015°C/s, annealing time 900 s per 1 mm of sample thickness, cooling rate of 0.010°C/s. The annealing parameters were defined on the basis of initial pre-tests [13-16].

TABLE 1. **Injection parameters of samples**
TABELA 1. **Parametry wtryskiwania próbek**

Parameters	a	b	c	d
melt temperature [°C]	250	250	280	280
mold temperature [°C]	100	50	50	100
pressure limit in plasticizing unit [MPa]	90	90	90	90
holding pressure [MPa]	70	70	70	70
holding time [s]	35	20	25	40
cooling time [s]	20	20	20	20

Tests of the thermal properties were made with the use of a scanning microcalorimeter PC 200, manufactured by Netzsch. DSC curves were acquired while heating the samples at the heating rate of 10°C/min, within the temperature range from 50 up to 250°C. In order to minimize the skin-core effect, the samples were cut parallel to the molten polymer flow direction in the injection mold cavity. The software of the DSC apparatus was used to calculate the crystallinity degree. The software allows investigation of the melting process of the sample in the considered temperature range and calculation of the area between the thermographic curve and the base line in the endothermic peak temperature range. The mass of the samples was in the range 7 to 10 mg. The samples were weighed using scales produced by SARTORIUS, with the accuracy of 0.01 mg, self-calibration and a closed measurement chamber. Investigation of the polymer structure was conducted in transmitted light with the use of an optical microscope, Nikon Eclipse E 200. The samples were microtomed slices, with a thickness of 10÷12 μm that were cut from the core of the injection moulded parts. A rotary microtome Thermo Shandon Finesse Me+ was used for this purpose. The study of the color was performed by means of the CIELab method using a SP60 colorimeter, manufactured by X-Rite. The results are presented in the form of chromaticity coordinates L*, a*, b*.

CIELab is the most complete color space specified by the International Commission on Illumination. The L*a*b* is a three-dimensional model (Fig. 1).
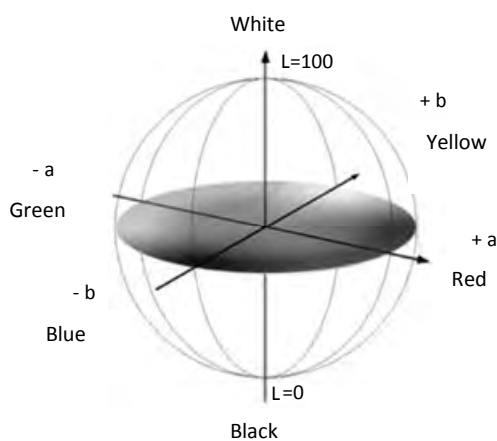

Fig. 1. CIELab space
Rys. 1. Przestrzeń CIELab

The lightness of a sample is represented by the symbol L* and this value is based on the percent of light reflectance. If the L* value is zero, the sample is black. If the value is 100, the sample is white. Any sample that is void of hue and falls somewhere between 0÷100% reflectance will be a variation of gray. The a* and b* coordinates have no specific numerical limits. Positive a* is red. Negative a* is green. Positive b* is yellow. Negative b* is blue.

The gloss was determined using a Gloss Meter. The Gloss Meter comprises a light source which is directed at the test surface at a specified incidence angle and a receptor which is located at the mirror reflection of the incident beam. Gloss change was determined by the reflection angles of 20 and 60° on the device, Elcometer 406L Statistical Gloss Meter. The investigations have been conducted according to conventional standards (ISO).

INVESTIGATION RESULTS AND DISCUSSION

The investigations have been performed in order to estimate the processing capability and usability of PA 6 composites with glass beads addition. The structure and properties of the composite were determined on the samples in the form of injection moulds. As a result of such a method of sample preparation, the structure and properties were conditioned by the processing parameters. The results of differential scanning calorimetry investigations of the polyamide with glass beads composite before and after annealing were presented in the form of thermographic curves (Fig. 2). The values calculated on the base of DSC thermographic curves are listed in Table 2.

TABLE 2. **Results of DSC investigations obtained from calculations by Netzch programme**
TABELA 2. **Wyniki badań metodą DSC uzyskanych z obliczeń programu Netzch**

Parameters	Enthalpy [J/g]	Melt temperature range [°C]	Melt temperature – peak maximum [°C]	Crystallinity degree [%]
Before annealing				
a	38.37	218.9÷226.2	222.4	20.2
b	29.12	217.2÷226.3	223.3	15.3
c	28.61	218.9÷225.9	223.6	15.1
d	40.78	219.1÷226.9	223.7	21.5
After annealing				
a	41.81	215.7÷227.8	224.0	22.0
b	38.28	215.8÷227.3	224.1	20.2
c	37.92	217.1÷226.6	222.8	19.9
d	42.31	217.0÷226.7	223.6	22.3

The DSC investigations prove the increase in the crystallinity degree of the PA 6/glass beads composite after the annealing process. However, the shape of the thermograms is insignificantly changed. This result was expected, considering the fact that PA6 is an semi-crystalline polymer, and an increase in crystalline phase can be expected.

For the composite samples, as a result of the annealing process, the temperature of the highest melting rate was not reduced but the range of melting temperature was changed significantly.
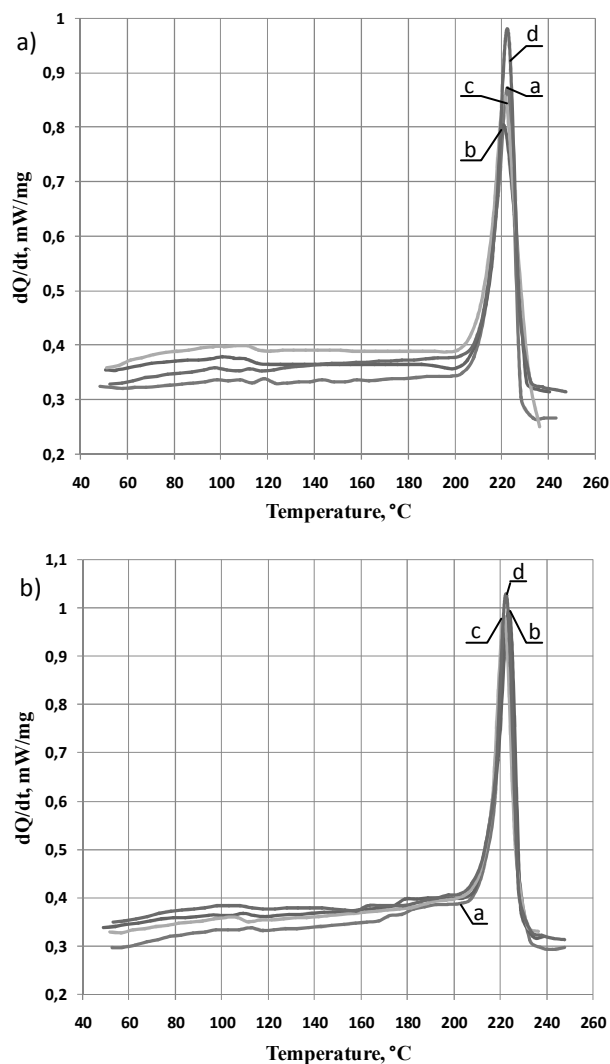

Fig. 2. Thermograms DSC of polyamide 6 composite with glass beads: a) before annealing, b) after annealing; a, b, c, d - injection parameters of samples

Rys. 2. Termogramy DSC: kompozytu PA 6 z kulkami szklanymi: a) przed wygrzewaniem, b) po wygrzewaniu; a, b, c, d - parametry wtryskiwania próbek

In the case of composite samples produced at a lower injection and mold temperature, the amount of energy absorbed by the polymer is decreased. The lowest values of melting enthalpy were obtained for the samples of PA6/glass beads composite produced at the melt temperature of 280°C and mold temperature of 50°C.

Rapid cooling of the composite to a temperature much lower than the melting temperature causes too small a chain mobility, so that they can create areas

with maximum ordering, which leads to a reduction in the degree of crystallinity. However, slight undercooling favors the formation of more structured composite structures.

In Figures 3 and 4, pictures of the structures for the composite before and after annealing have been presented.
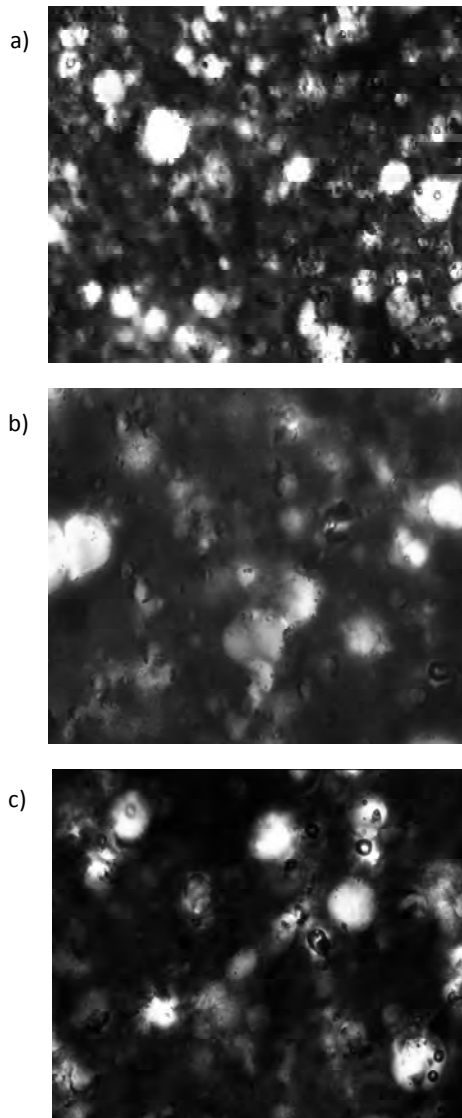

Fig. 3. Structures observed with optical microscope at magnification 400x of polyamide 6 composite with glass beads before annealing; a), b), c) injection parameters of samples

Rys. 3. Struktura obserwowana pod mikroskopem optycznym przy powiększeniu 400x kompozytu PA 6 z kulkami szklanymi przed wygrzewaniem; a), b), c) parametry wtryskiwania próbek

Crystallization of the composite proceeds through a process of nucleation, it is the thermodynamically stable formation of embryos, and through a process of growth of the crystalline phase. The crystals grow much faster in the pre-embryos created than evenly distributed throughout the amorphous phase. The emergence of any crystal growth process is initiated by earlier formation of the embryo having a large surface area in relation to its mass. The results of microscopic examination indicate that the nucleation is a heterogeneous composite produced by the presence of glass beads. The size of the crystal structures in the samples prepared at a higher mold temperature are larger compared to samples prepared at a lower mold temperature. Annealing causes the development of crystalline structures. For the structure of a composite after annealing, characteristically the size of the crystal structures increases while the number of them decreases.
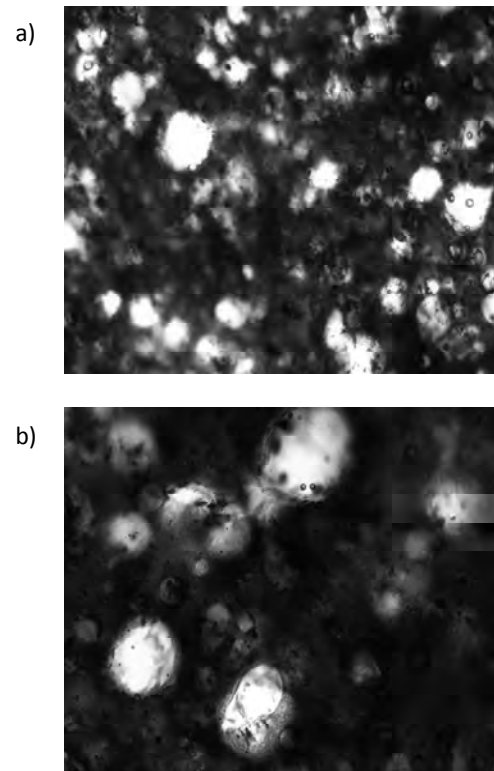

Fig. 4. Structures observed with optical microscope at magnification 400x: a) composite before annealing, b) composite after annealing; melt temp. 280°C, mold temp. 100°C

Rys. 4. Struktura obserwowana pod mikroskopem optycznym przy powiększeniu 400x: a) kompozyt niewygrzewany, b) kompozyt po obróbce cieplnej; temp. wtrysk. 280°C, temp. formy 100°C

The results of the gloss tests of composite samples prepared with variable temperature conditions are shown in Figure 5. Higher gloss values were recorded for the composite samples prepared at a higher mold temperature, and both the reflection angles of 20° and 60° recorded a similar trend of change. Higher gloss values were also recorded for the composite samples after annealing.

Table 3 summarizes the recorded a*, b* and L* coordinate values of the test composite before and after annealing. The character of the changes in the a* and b* coordinate values of the composite demonstrates the effect of temperature conditions of the process to change the color. Samples of the composite produced at higher melt and injection mold temperature were characterized by a smaller a* coordinate value and greater b* coordinate value. This increased the saturation of the green - yellow shade of polyamide 6 with glass beads

composites. Annealing causes an increase in the composite polyamide 6 with glass beads L* value, which means that the sample has become clearer. Samples of the composite obtained at the melt temperature of 280°C and mold temperature of 100°C after annealing are characterized by smaller a* and b* coordinate values. Heat treatment of composite polyamide 6 with glass beads increased the saturation of the green shade. For a sample obtained in other conditions, annealing causes an increase in the saturation of the green - yellow shade.
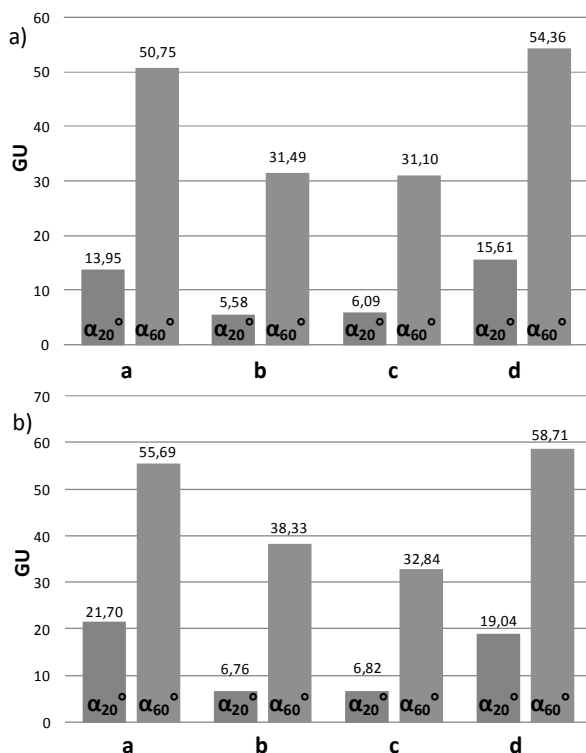

Fig. 5. Gloss of examined polymer materials: a) composite before annealing, b) composite after annealing; a, b, c, d - injection parameters of samples

Rys. 5. Połysk badanych materiałów: a) kompozyt przed wygrzewaniem, b) kompozyt po wygrzewaniu; a, b, c, d - parametry wtryskiwania próbek

TABELA 2. **Jasność L*, współrzędna a* oraz b* badanego kompozytu przed oraz po procesie wygrzewania**

TABLE 2. **Lightness L*, a* and b* coordinate values for examined composite before and after annealing**

Before annealing			
Parameters	L*	a*	b*
a	26.43	−0.17	−0.53
b	26.25	−0.23	−0.28
c	25.88	−0.23	−0.35
d	25.41	−0.29	−0.20
After annealing			
a	28.1	−0.18	−0.45
b	26.8	−0.27	−0.30
c	27.3	−0.26	−0.32
d	27.9	−0.49	−0.38

CONCLUSIONS

The analysis of DSC studies show a significant effect of the processing temperature conditions on the thermal properties of the composite polyamide 6 with glass beads. Based on DSC thermograms, changes in the melting range of the crystalline phase and the beginning of the crystallization temperature of the samples prepared at different temperatures of the mold and injection were revealed. No significant change in temperature was registered at which crystallization occurs at maximum speed. The DSC results show an increase in the degree of crystallinity of the composite samples prepared at a higher mold temperature, which influences the change of the performance of the material. Significant changes were observed in a study of the composite structures under an optical microscope. Growth of structural elements for samples prepared at higher temperatures of mold and changes of the amorphous phase in the composite were registered. In a study of the color and gloss of the composite polyamide 6 with glass beads, it was observed that they change, depending on the temperature conditions of the process. Samples of the material produced at a higher mold temperatures were characterized by a greater gloss and a different color. Based on the analysis of DSC thermograms, it was found that annealing causes changes in the scope of the melting of the crystalline phase and the beginning of the crystallization temperature. There was no significant change in the temperature at which crystallization occurs at maximum speed. The DSC results show an increase in the degree of crystallinity for the composite after heat treatment. There were significant changes in the structure during the tests of the composite under an optical microscope. The growth of structural elements and changes of the amorphous phase in the composite after annealing, as well as the irregular arrangement of structural elements in the clusters in a random manner unrelated to the direction of the flow line of the polymeric material in the mold cavity was registered. In a study of color and gloss of the composite polyamide 6 with glass beads, significant changes after the annealing process were recorded. Samples of the material after the heat treatment process were characterized by a greater gloss and other colors. The change in the value of coordinates a*, b*, and lightness L*, and the gloss value can be explained by the different structure of the composite before and after heat treatment (crystallinity, amorphous), and thermomechanical properties.

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