

A. GNATOWSKI^{1*}, R. GOŁĘBSKI¹, K. STACHOWIAK¹**EFFECT OF PROCESSING CONDITIONS ON SELECTED PROPERTIES OF POLYAMIDE 6 COMPOSITES FILLED BY MODIFIED BENTONITE**

The aim of this study was to present the results of the examinations of the structure and thermomechanical properties of PA6/NanoBent composite. NanoBent composites composed of minerals from the smectite group (mainly montmorillonite) were used for modification of polyamide 6. PA6 composite with content of 1, 3, 5% of NanoBent was prepared in a Theysohn TSK 75-N twin screw extruder. The samples were prepared using the injection technology by means of a Krauss-Maffei KM65-160 C1 injection molding machine. The samples of composites obtained at different injection temperatures and injection mold temperatures were used for the examinations. Degree of crystallinity was examined using the DSC method whereas the material structure was examined with an optical microscope. DSC studies showed a reduction in the value of the degree of crystallinity with the increasing content of nanofiller in the polymer material. The narrowing of the peak was recorded in the DSC thermograms for nanocomposites with greater percentage of the nanofiller. Dynamical properties of polyamide 6 nanocomposite were also determined in relation to temperature and frequency. The samples were bended at frequencies of 1 Hz and 10 Hz over the temperature range from -100°C to 180°C and the heating rate of 2K/min. A significant increase in storage modulus was observed for PA6 samples with the content of 5% of NanoBent obtained at the injection temperature of 270°C and mold temperature of 70°C . Smaller size of spherulites and arrangement of structural elements in clusters along the line of polymeric material flow in the mold cavity at higher contents of NanoBent were observed during structural examinations of the composites.

Keywords: polyamide 6, composites, bentonite, structure, thermomechanical properties.

1. Introduction

Mixing of polymers with fillers and nanofillers has been used to obtain polymeric materials with specific mechanical and thermal properties. Nowadays, the amount of polyamide composites in polymer materials is increasing. This is justified by a number of advantages of the manufacturing methods used, expanded possibilities of their use, and specific operating conditions. Properties of products manufactured from polymer materials depend on the nature of the filler, structural factors of the polymer, and processing conditions. Studies published by Jakubowska et al. (2010), Mészáros et al. (2013) and Gnatowski et al. (2005) have enumerated structural factors such as molecular weight, chemical structure of macromolecules, physical structure of the chain, crystallinity, molecular orientation. Among the functional conditions are temperature, load duration, pressure, strain, etc. [1-4]. Nanotechnology offers great opportunities for obtaining new materials with improved properties and a much greater range of applications. Pramoda et al. (2004) argue that

the improvement in thermal stability of the polymer matrix occurs only when the modifier particles are dispersed at the level of nanometers [5]. Modern nanomaterials are characterized by improved mechanical, thermal, and electrical properties. Inorganic nanofillers such as nanosilica and natural phyllosilicates are becoming increasingly popular (montmorillonite, smectite) and have been successfully applied as nanofillers for thermoplastics. The problems with modification of this polymer have been studied by Yang et al. (2007), Manias (2001), Ajayan et al. (2003), Zhang et al. (2004), Leite et al. (2009), Ch. Zhang et al. (2019), Z. Huang et al (2015) and G. Zhu (2011) [6-13]. The study [14] compared the results obtained from dynamic-mechanical thermal analysis (DMTA) curves for PA6/OMMT nanocomposites (NC) and PA6/TPU/OMMT nanocomposite blends (NCB), containing 2 and 4 wt % of organically modified montmorillonite. Stankowski et al. (2008) found that compared to polyamide 6, dynamic storage modulus of the PA6 nanocomposites and nanocomposite blends is higher in the temperature ranges below and above the glass transition. Polymer composites

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containing suitably modified fillers exhibit much better properties than achievable when using conventional fillers. A smaller amount of nanofillers allows for better performance, i.e. greater elasticity, reduced flammability, improved barrier properties, e.g. less vapour and gas permeability, better thermal stability, and flexibility and resistance to fatigue [5-17]. The possibility of obtaining products with desired properties of the band opens up new prospects for application. The purpose of this study is to analyse thermomechanical properties and structure of composite polyamide 6 with NanoBent.

2. Methods and materials

Polyamide 6 with commercial name of Tarnamid T-27 was used in the study. Modification of polyamide 6 was performed using NanoBent composed of minerals from the smectite group, mainly montmorillonite (aluminosilicate modified with quaternary ammonium salt with alkyl and alkylaryl substituents). The NanoBent composites were developed at Rzeszów University of Technology and were obtained from ZGM Zębiec (Poland) [18,19]. Composites of polyamide 6 with addition of 1, 3, 5% of NanoBent were obtained in POLIMARKY (Poland) using a Theysohn TSK 75-N twin screw extruder. The Theysohn TSK 75N represents an advanced design based on a combination of various types of co-rotating extruders. The Theysohn TSK 75N was designed specifically to suit the needs of flexible high-performance extrusion systems. The use of co-rotating twin screw kneader allowed for good mixing of the components. Such systems have been used for preparation of composites in previous studies [16]. Before processing and injection molding, polyamide composites were dried in a ZELMET kc-100/200 heating cabinet at 80°C for 4 h. The test samples were prepared using a Krauss Maffei KM65 – 160C1 injection molding machine with a screw diameter of 30 mm, and L/D ratio of 23, with three zones and constant pitch throughout the length, and clamping force of 650 kN. The parameters of injection molding process that ensured optimum values of the properties studied were as follows: injection temperature of 270°C, maximum allowable pressure in the plasticizing system of 120 MPa, clamping pressure of 60 MPa, clamping time of 20 s, cooling time of 20s, mold temperature of 70°C. In order to compare changes in the degree of crystallinity and thermomechanical properties, the results of tests were summarized for samples obtained at injection temperature of 250°C and mold temperature of 45°C, and injection temperature of 230°C and mold temperature of 20°C.

The testing of thermal properties using the DSC method for polyamide 6 composites with NanoBent was performed using a PC 200 Netzsch scanning microcalorimeter. The DSC curves were recorded during heating of the samples at 10°C/min at the temperature range from 50 to 270°C. Preparations for DSC testing were cut out perpendicularly to the direction of flow of the polymeric material from the samples obtained through injection. The PC 200 Netzsch software was used to evaluate the degree of crystallinity depending on the content of NanoBent.

The software enabled analysis of the sample melting process and evaluation of the area between the thermographic curve and the baseline for the occurrence of endothermic reflex. Indium was used as a model, with the sample weight ranging from 7 to 10 mg. The test samples were weighed with a SARTORIUS balance with weighing accuracy of 0.01 mg, internal calibration and a closed measuring chamber. The tests of dynamic mechanical properties were performed with the use of a Netzsch DMA 242 apparatus with a holder for three-point free bending of beam-shaped samples. The samples of the PA6/NanoBent composite put in the holder were subjected to sinusoidally changing force, at the frequency of 1 Hz and 10 Hz, with constant amplitude and sample heating from temperature of –100°C to 180°C. Structural studies were performed using a Nikon optical microscope Eclipse E 200. The samples for testing with thickness of 10 to 16 microns were cut out using a Thermo Electron Corporation microtome.

3. Results

Fig. 1 shows the DSC thermograms for polyamide 6 and the polyamide 6 composite with NanoBent at variable injection temperature and mold temperature. Table 1 shows the values determined based on the recorded DSC thermographic curves. In the case of polyamide 6 samples obtained at lower injection and mold temperatures, the amount of energy absorbed by the polymer decreased. The lowest values of melting enthalpy were reached for the samples of polyamide and composites obtained at injection temperature of 230°C and a mold temperature of 20°C (Table 1). With rapid cooling of the composite to the temperature much lower than the melting point, chain mobility becomes too small to form areas with maximum arrangement, leading to a reduction in the degree of crystallinity. However, small undercooling favours formation of more organized composite structures. The temperature of the beginning and the end of crystallization for the composite samples obtained in different temperature conditions changed proportionally to changes in the value of melting enthalpy. Analysis of DSC thermograms reveals a narrowing and shift in the peak towards the lower temperature range for the composite containing 1% of NanoBent (Fig. 1(b), Table 1).

An increase in the content of NanoBent in polyamide 6 composites to 5% led to peak narrowing and its shift towards higher temperatures (Fig. 1(a), (b), Table 1). Lower values of melting enthalpy were recorded for the composites containing 1, 3, and 5% of NanoBent. Presence of a double melting peak on thermograms in the case of composites may result from a transformation taking place in the PA matrix. The high-temperature and narrow melting range for the crystalline phase of PA6 composites containing 3 and 5% is likely to be related to a higher degree of macromolecule arrangement, leading consequently to a greater heat resistance of the polymer.

The results of the DMTA tests for polyamide with NanoBent composites for samples prepared at different injection and mold temperatures are presented in a graph showing the storage modulus E' vs. temperature (Fig. 2).

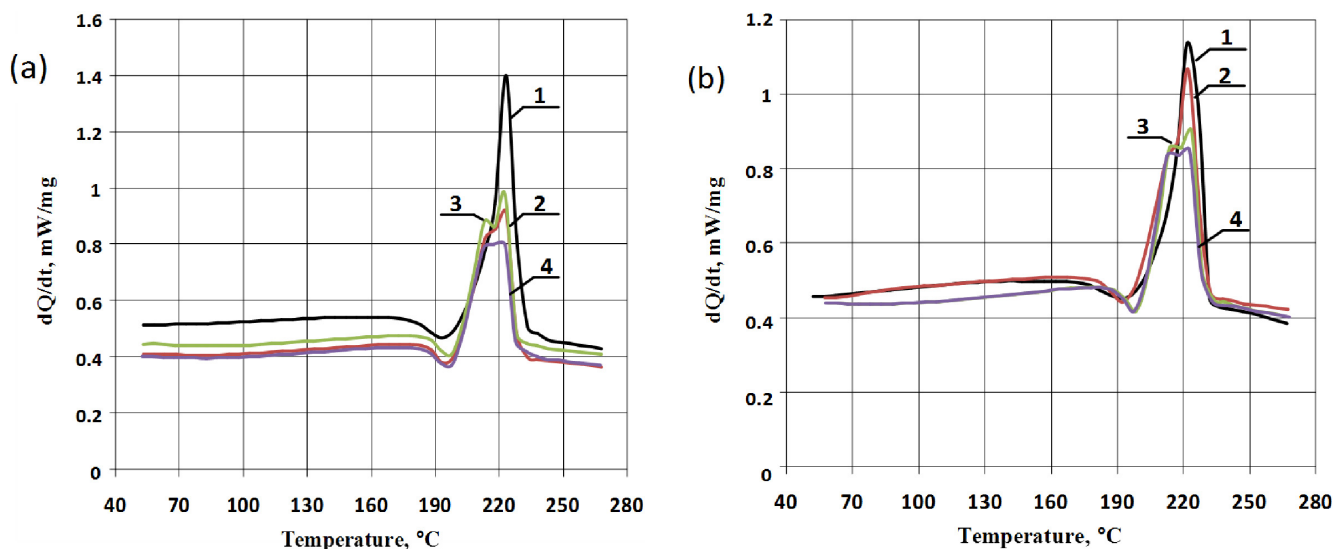


Fig. 1. DSC thermograms: (a) samples prepared at injection temperature of 270°C and mold temperature of 70°C, (b) samples prepared at injection temperature of 250°C and mold temperature of 45°C; (1) PA6, (2) PA6 composite with 1% NanoBent, (3) PA6 composite with 3% NanoBent, (4) PA6 composite with 5% NanoBent

TABLE 1

Results of DSC examinations

Samples		Degree of crystallinity, %	Melt temperature range, °C	Melt temp. – peak max., °C
Obtained at injection temp. of 270°C and mold temp. of 70°C	PA6	34.3	193.2-243.3	223.3
	PA6 + 1% NanoBent	30.8	193.5-233.4	222.2
	PA6 + 3% NanoBent	28.3	197.8-237.8	223.1
	PA6 + 5% NanoBent	24.7	198.1-238.2	222.8
Obtained at injection temp. of 250°C and mold temp. of 45°C	PA6	31.7	192.2-236.1	222.2
	PA6 + 1% NanoBent	29.6	192.7-232.8	222.7
	PA6 + 3% NanoBent	27.1	199.1-234.2	224.1
	PA6 + 5% NanoBent	24.4	198.9-233.6	223.1
Obtained at injection temp. of 230°C and mold temp. of 20°C	PA6	29.4	193.5-234.9	223.4
	PA6 + 1% NanoBent	27.1	191.5-233.5	218.5
	PA6 + 3% NanoBent	25.4	198.5-233.8	223.0
	PA6 + 5% NanoBent	22.3	197.2-232.2	222.2

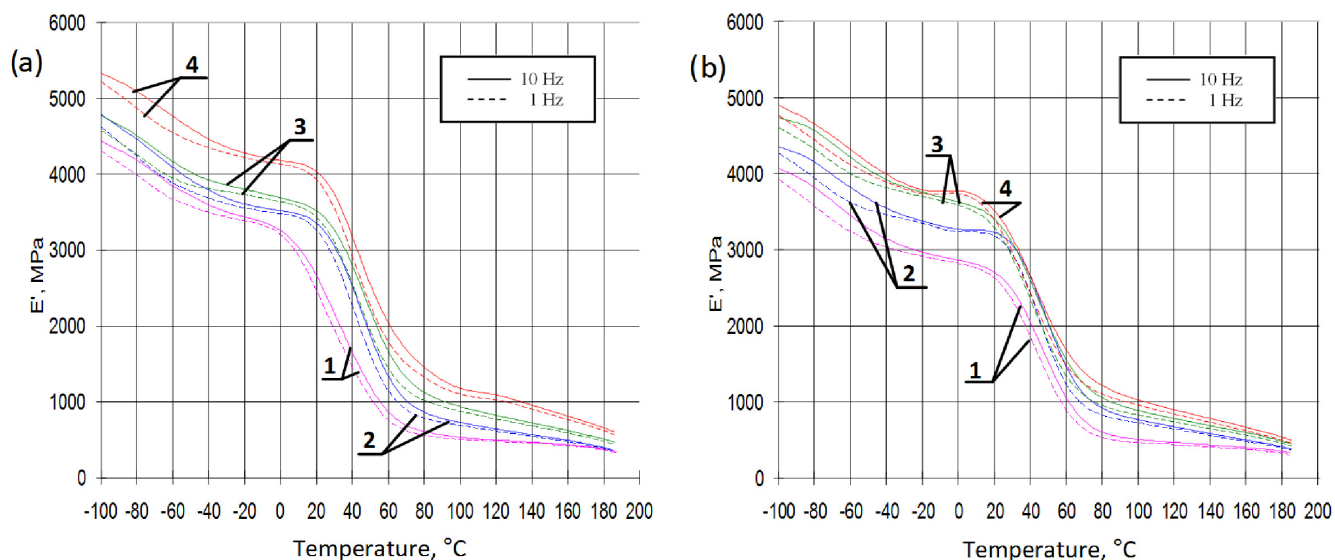


Fig. 2. Value of storage modulus vs. temperature: (a) samples prepared at injection temperature of 270°C and mold temperature of 70°C, (b) samples prepared at injection temperature of 250°C and mold temperature of 45°C; (1) PA6, (2) PA6 composite with 1% NanoBent, (3) PA6 composite with 3% NanoBent, (4) PA6 composite with 5% NanoBent

The thermomechanical curves obtained during the DMTA tests for the composite with 1, 3 and 5% of NanoBent are presented in Fig. 2. The test showed that the addition of NanoBent to PA6 causes an increase in storage modulus E' . The analysis of the values recorded for storage modulus shows differences for the material prepared at different injection temperatures and mold temperatures. The diagrams of the recorded values are presented in Figures 2(a) and 2(b). The lowest values of storage modulus for the samples of polyamide and composites were obtained at the injection temperature of 250°C and mold temperature of 45°C. In the range of temperature values lower than the glass transition temperature, the polyamide composite is in a glassy state and becomes hard and brittle. With the increase in temperature, the values of the modulus for the composite with 5% of NanoBent decrease less intensively than for polyamide 6.

The results of structural studies are shown in Figure 3.

Crystallization of the polymeric material occurs through nucleation, i.e. thermodynamically stable formation of nuclei, and through the growth of the crystalline phase. The crystals grow much faster on the previously formed nuclei than from the

evenly distributed amorphous phase. The emergence of a crystal during the growth process is initiated by the previous formation of a nucleus having a large surface area compared to its mass. The results of microscopic examinations indicated that composite nucleation process is heterogeneous, caused by the presence of aluminosilicate-modified quaternary ammonium salt with alkyl and alkylaryl substituents. It is characteristic for change of the structure of polyamide 6 composite with NanoBent that spherulite size is reduced, with higher number and arrangement in clusters.

4. Conclusions

The analysis of DSC tests reveals a significant effect of the addition of NanoBent on thermal properties of polyamide 6. It was found based on the analysis of DSC thermograms that addition of NanoBent leads to changes in the melting point of crystalline phase, initial crystallization temperature and small changes in temperature at which crystallization takes place

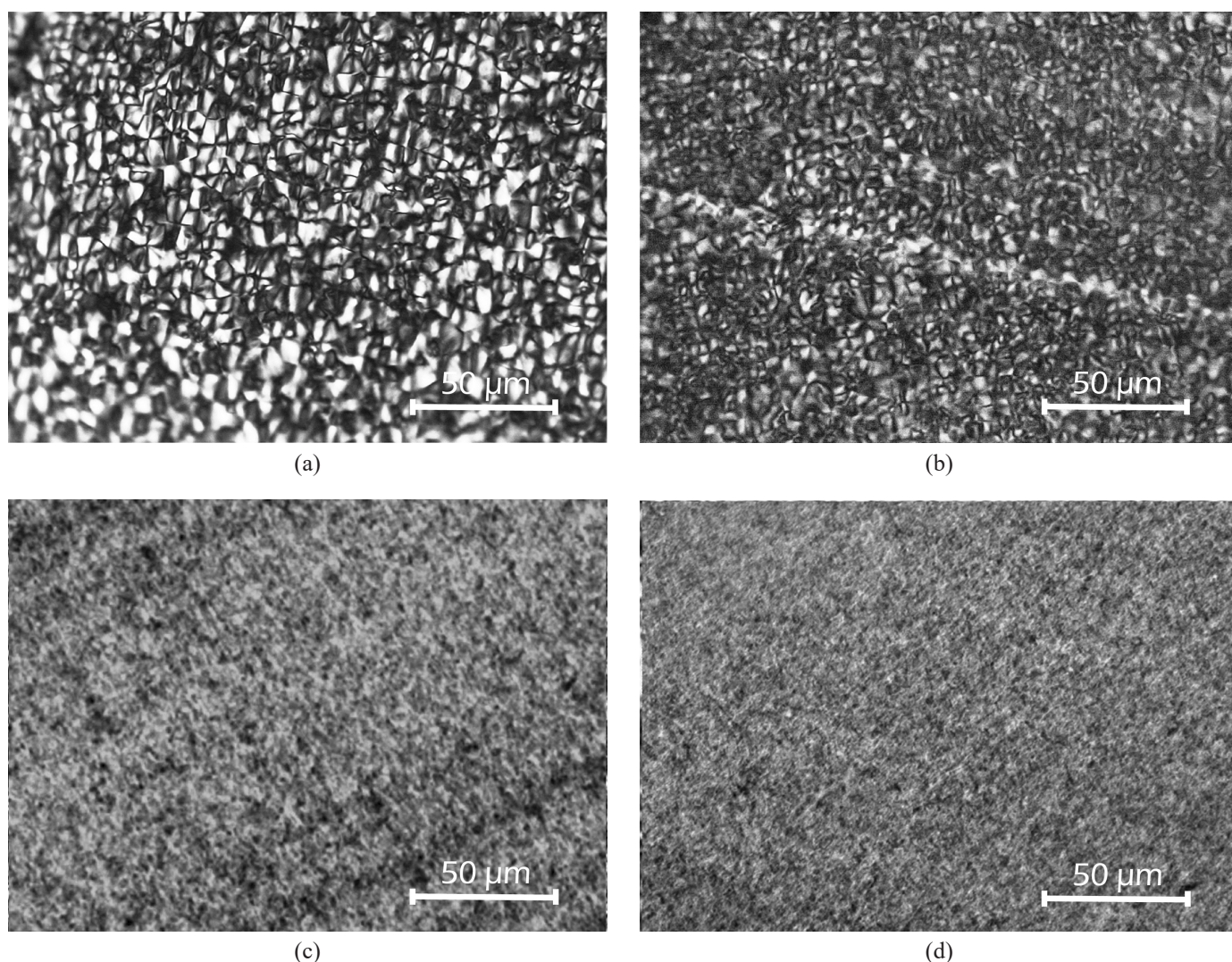


Fig. 3. The structures (samples prepared at an injection temperature of 270°C and mold temperature of 70°C) observed with an optical microscope with magnification of 400x: (a) PA6, (b) PA6 composite with 1% NanoBent, (c) PA6 composite with 3% NanoBent, (d) PA6 composite with 5% NanoBent

at maximum speed. The results of DSC tests show a decrease in crystallinity of the composites containing 1, 3 and 5% of NanoBent, which impact on functional properties of the composites. Dynamic properties of nanocomposites depend on the content of NanoBent. The highest values of storage modulus were recorded for the composites obtained at the injection temperature of 270°C and mold temperature of 70°C.

It was observed that all storage modulus curves (for polyamide and composite, samples obtained at different injection and mold temperatures) were close to each other but their maximum values differed. Significant changes in the structure were observed during examinations of composites using an optical microscope. Smaller size of spherulites and arrangement of structural components in clusters along the line of polymeric material flow in the mold cavity were observed at higher contents of NanoBent.

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