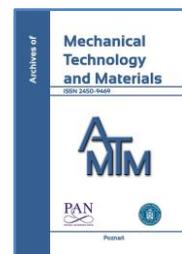


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Influence of heat treatment on the structure and properties of polyamide 6/ halloysite nanocomposites

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ABSTRACT

The nanocomposites of polyamide 6 (PA6) with halloysite nanotubes (HNT) were prepared by extrusion using co-rotating twin-screw extruder and then the standard test specimens were injected using a screw injection moulding machine. The content of HNT in the nanocomposites was 5 or 10 weight percent. The heat treatment of unmodified PA6 and nanocomposites was carried out in silicone oil in temp. $150 \pm 2^\circ\text{C}$. The samples were annealed for 3 hours and then cooled at a rate of 4 K/min. Differential scanning calorimetry (DSC) causes annealing to increase the crystallinity of the polyamide matrix. After an annealing treatment a nanocomposite with better mechanical properties was obtained. Halloysite nanotubes in polyamide matrix play the role of a nucleating agent.

1. INTRODUCTION

Heat treatment of semicrystalline polymers by heating them in a specific heat transfer medium and then cooling them to room temperature entails a change in the structure of these materials, and thus a change in their functional properties [1]. The direction of these changes is determined by the parameters of heat treatment as follows: the temperature and the heating time, the properties of the heating medium and the cooling rate [2].

In recent years, nanotube shaped fillers have aroused a great interest among scientists and industry. Due to their structure and specific physical and chemical properties, these can be widely used in various industries, such as electronics, electrotechnics, optics, etc., as well as in other

industries. Many different types of nanotubes are synthesized, but the most important are as follows: carbon, metallic and inorganic nanotubes [3]. Inorganic nanotubes include halloysite nanotubes (HNT - halloysite nanotubes) [4, 5].

Halloysite is a layered mineral with the formula $\text{Al}_2[\text{Si}_2\text{O}_5](\text{OH})_4 \cdot 2\text{H}_2\text{O}$ containing in its structure numerous natural nanotubes with high shape factor and packages of tiles [6]. The low content of hydroxyl groups on the surface causes that halloysite nanotubes disperse well in polymers, contrary to montmorillonite, and the nanocomposites produced are characterized by many specific properties [4, 6].

The influence of heat treatment on the structure and properties of polyamide 6 (PA6) and polyamide-

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montmorillonite nanocomposites has been extensively analyzed in many studies [7-9]. Xie et al. [1] after heating of polyamide/montmorillonite nanocomposites at 80°C for 6 hours, the degree of crystallinity and temperature of thermal deformation (HDT) of these materials was shown to increase. There are no literature data on the influence of heat treatment on the structure and properties of PA6 nanocomposites with halloysite nanotubes.

The aim of this paper was to evaluate selected physical properties and structure of heat-treated polyamide/halloysite nanocomposites by differential scanning calorimetry. Moreover, for comparison, unmodified PA6 was also studied.

2. EXPERIMENTAL

The following raw materials were used in the research:

- hydrolytic polyamide 6 (PA6) with the trade name Tarnamid® T-30 (natural colour), produced by Zakłady Azotowe w Tarnowie-Mościcach S. A.,
- halloysite nanotubes (HNT) with a diameter of approx. 20-30 nm and a length of approx. 1 µm to approx. 2 µm, manufactured by Sigma-Aldrich.

Nanocomposites PA6/HNT containing 5% weight and 10% weight of HNT were extruded using a co-rotating twin-screw extruder (type BTSK 20/40D by Bühler). The screw speed was 250 rpm. The temperature of the plastic in the head was 279°C and the pressure was 8 bar. The stamps were cooled in air and granulated. Samples were injected using a vertical pneumatic piston injection moulding machine (Birmingham model). Injection pressure was 1.2 bar, injection temperature 260°C and mould temperature 60°C. Before the extrusion of composites and injection molding the granules were dried in a thermal chamber at temp. 80± 2°C for 48 hours.

Heat treatment of unmodified PA6 and nanocomposites was carried out in silicone oil (POLASIL E-5, produced by Zakłady Chemiczne "Silikony Polskie" sp. z o.o. in Nowa Sarzyna) at 150 ± 2°C, heating the samples for 3 hours and then cooled in a heating medium at a rate of 0.4 K/min.

The content of crystalline phase and its melting point were determined by differential thermal analysis using the Netzsch DSC 204 scanning microcalorimeter. The samples were heated at a rate of 10 K/min to 250 °C and kept at this temperature for 5 minutes to eliminate their thermal history. The samples were then cooled to 40 °C at 5 K/min and reheated to 250 °C at 10 K/min. The studies were carried out in nitrogen atmosphere (20 ml/min). Melting point (T_m) and crystallinity degree (X_c) were determined on the basis of DSC curves recorded during the first and second heating of the samples. Crystallinity degree was calculated on the basis of the equation:

$$X_c = \frac{\Delta H_m}{(1-\phi)\Delta H_m^0} [\%] \quad (1)$$

Where: ΔH_m - melting enthalpy of the test sample (J/g), ϕ - weight share of HNT in the composite, ΔH_m^0 - melting enthalpy of PA 6 completely crystalline.

Melting enthalpy of crystallographic forms of PA 6 has similar values (ΔH_m^0 for α is J/g, however, ΔH_m^0 for γ — 239 J/g), therefore, the average enthalpy value equal to 240 J/g was assumed [10]. The DSC curves recorded during cooling were used to determine the temperature at which crystallization occurs at maximum rate (T_{kr}). Density tests were performed according to PN-92/C-89035 using AD 200 weight with hydro function, produced by AIX, Poland where the result was an arithmetic mean of 5 measurements.

Static tensile testing was carried out in accordance with PN-EN ISO 527-2:1998 using the Instron Model 4481 testing machine, which works in conjunction with the SERIE IX computer program, which records the results of the measurements. Standardized samples were stretched in the form of paddles at a speed of 50 mm/min, at a temperature of 20±3°C. The result was an arithmetic mean of 10 determinations.

3. RESULTS AND DISCUSSION

It is known that the density of polymeric materials depends on their chemical structure and crystalline structure - the density increases with raising degree of crystallinity [11]. Increased density also causes the introduction of fillers or nanofillers into the polymeric matrix, whereas nanofillers usually only slightly increase the density of the polymer. The higher the density of a polymer material, the higher the density of a filler (nanofiller) and its higher content [2]. The results of density determinations of the investigated materials are presented in Table 1.

Table 1: Density and yield point of materials tested before and after heat treatment

Sample determination	Density (g/cm ³)	Yield point (MPa)
PA6 – before OC	1,1162 ± 0,005	61,1 ± 2,3
PA6 – after OC	1,1189 ± 0,001	74,5 ± 3,0
PA6+5/HNT – before OC	1,1170 ± 0,011	62,7 ± 1,6
PA6+5/ HNT – after OC	1,1439 ± 0,013	71,3 ± 2,4
PA6+10/HNT– before OC	1,1531 ± 0,012	64,0 ± 1,6
PA6+10/ HNT– after OC	1,1659 ± 0,007	74,5 ± 2,1

On the basis of the analysis of the study results it was found that the density of the composites is slightly higher than that of unmodified PA6, with the composite containing 10% weight of HNT had a higher density than the composite

containing 5% weight of HNT. Moreover, it was found that as a result of heat treatment the density of the tested samples increased slightly, which is probably related to the increase in the degree of crystallinity of polyamide matrix.

Information on the crystalline structure of polymeric materials is provided, among others, by differential scanning calorimetry (DSC studies), which was conducted in the cycle: heating - cooling - heating. The aim of the second heating was to obtain a defined thermal history of the studied materials, because the method of preparation, thermal history and storage conditions of semicrystalline polymer samples affect the motility of macromolecular segments, as well as nucleation, growth and orientation of crystallites [12].

Figure 1 shows examples of DSC thermograms recorded during the first heating of the samples and Figure 2 shows them during cooling. Table 2 shows the values determined on the basis of registered DSC thermograms.

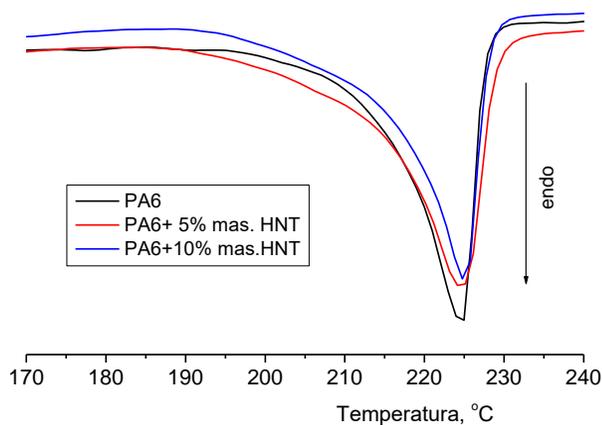


Fig. 1: Example of DSC thermograms recorded during the first heating of samples before heat treatment

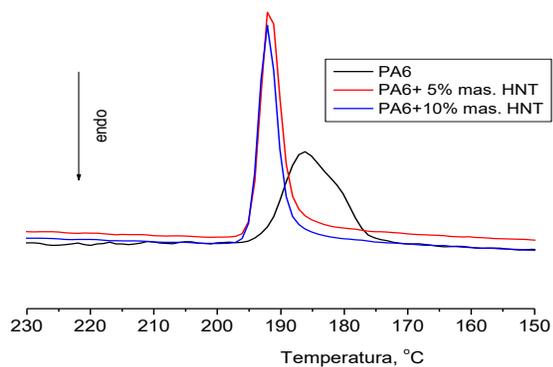


Fig.2: Example of DSC thermograms recorded during sample cooling prior to heat treatment

Table 2. Values determined by DSC thermograms (accuracy of temperature measurement $\pm 0,5^{\circ}\text{C}$)

Sample determination	First heating			Cooling	Second heating		
	T_m (°C)	ΔH_m (J/g)	X_c (%)	T_{kr} (°C)	T_m (°C)	ΔH_m (J/g)	X_c (%)
PA6 – before OC	225,0	60,74	25,3	186,0	221,0	45,87	19,1
PA6 – after OC	226,0	63,08	26,3	186,0	221,5	51,7	21,5
PA6+5/HNT – before OC	225,0	60,1	26,4	192,0	220,0	48,69	21,3
PA6+5/ HNT – after OC	225,0	65,97	28,9	192,0	220,0	53,95	23,7
PA6+10/HNT – before OC	225,0	56,93	26,4	192,0	220,0	43,86	20,3
PA6+10/ HNT – after OC	223,0	62,55	28,9	192,0	220,0	51,14	23,7

Symbols in the table: OC- heat treatment, T_m - melting temperature, T_{kr} - temperature at which crystallization occurs at maximum rate, ΔH_m – melting enthalpy of the tested sample (J/g), X_c –calculated crystalline phase content

On the basis of the analysis of the test results it was found that both the composition of the tested sample and the applied heat treatment had no significant influence on the melting temperature (T_m), which during the first heating amounted to approx. 223°C – 225°C (Table 2). After the second heating of the samples, i.e. for the same thermal history of the tested materials, it was found that the polyamide matrix melts at a temperature of approx. 220°C – 221°C (Table 2).

Calculated from formula (1), the crystalline phase content (Table 2) confirmed the assumption that as a result of the applied heat treatment (heating the samples for 3 hours in silicone oil at the temperature of 150°C and then cooling them slowly), the order of the macromolecular segments is increased. During the slow cooling of samples, macromolecular segments had more time to organize themselves and hence a higher content of crystalline phase in the materials tested after heat treatment. This type of heat treatment is called annealing [2, 8]. Moreover, it was found that the content of crystalline phase in both nanocomposites was higher than in unmodified PA6.

Based on the analysis of DSC thermograms recorded during sample cooling, it was found that the heat treatment had no effect on the temperature at which crystallization takes place at maximum rate (T_{kr}), (Table 2). However, it was found that the T_{kr} value of both nanocomposites (before heat treatment and after heat treatment) is by 6°C higher than unmodified PA6. The higher T_{kr} value and higher content of crystalline phase in nanocomposites prove that halloysite nanotubes act as a nucleating factor on which heterogeneous embryos of crystallization are formed [13]. Higher crystallization temperature (T_{kr}) is important from

the point of view of the processing of these materials, as it allows to shorten the injection process cycle.

The values of yield stress before and after heat treatment are a reflection of the observed changes in crystallinity degree. It is known that the higher the content of the crystalline phase, the higher the strength of the polymeric material.

4. CONCLUSIONS

Heat treatment applied in the tests consists on heating the samples for 3 hours in silicone oil at the temperature of 150°C and then the samples slow cooling increased the arrangement of macromolecular segments - increasing the content of crystalline phase in the studied materials. Heat treatment did not affect the temperature at which crystallization takes place at maximum speed (T_{kr}). The T_{kr} value of both composites (before heat treatment and after heat treatment) was 6°C higher than that of unmodified PA6. Higher T_{kr} value and higher content of crystalline phase in nanocomposites prove that halloysite nanotubes are nucleants for polyamide matrix. After heat treatment, the density and yield point of the tested materials were higher than that of the samples before heat treatment.

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