1. Introduction
The introduction of fillers into polymer matrix leads to improving the properties and applicability of materials. In this paper, the influence of filler on thermal behavior and thermal conductivity of polymer composites was studied.

Loading of the polymer with hybrid fillers and carbon nanomaterials leads to an improvement of thermophysical, electrophysical and mechanical properties. It was shown [1, 2] that introduction of high thermally conductive fillers leads to increase of thermal conductivity. In present work, carbon nanotubes (thermal conductivity coefficient of 3000 V/m K [3]) and aluminum nanopowder (230 V/m K [4]) were used. Also, despite the very low values of thermal conductivity, nanosized silicon dioxide is of interest as a filler for polymers. By advantage of its active and developed surface, when introduced into the polymer, it changes its structure, increases the density, and hence, the strength and thermal conductivity of the material may increase [5, 6].

2. Materials
The influence of type and concentration of the filler on melting and crystallization temperature, as well as thermal conductivity of the composites were investigated in the work. As a polymeric matrix for composite samples the polyamide 6 (PA) (by Branch «Khimvolokno Plant» JSC «Grodno Azot») was used. As a fillers the next materials were chosen: carbon nanomaterial (CNM) (obtained in the Laboratory of Disperse Systems of A. V. Luikov Heat&Mass Transfer Institute of NAS of Belarus) as well as Tarcosil T80 (SiO2) nanopowder and aluminum (Al) nanopowder (by Khristianovich Institute of Theoretical and Applied Mechanics SB of RAS).

The composition and density of the test samples are presented in Table 1. Density was measured by hydrostatic weighing method.

Samples of composite materials were prepared by solution mixing method in the Grodno branch of A. V. Luikov Heat&Mass Transfer Institute of NAS of Belarus. For thermophysical properties measurements the samples were made in the form of cylinders with a diameter of 12.8 mm and a height of ~ 1.5 mm.

Table 1 Composition of experimental samples based on PA

| sample № | type of sample          | density (kg·m⁻³) |
|----------|-------------------------|------------------|
| 1        | PA                      | 1100             |
| 2        | PA+20%CNM               | 1196             |
| 3        | PA+20%CNM+10%Al         | 1221             |
| 4        | PA+20%CNM+10% SiO2      | 1336             |

3. Methodology
The STA449 F3 Jupiter (NETZSCH) synchronous thermal analysis instrument was used to analyze thermal behavior of polymer composites. It was carried out in a temperature range from room temperature to 300 °C in
a nitrogen atmosphere. Heating/cooling rate was 5 K/min. The temperature research program includes five segments: heating - holding - cooling - holding - heating. The first segment is to remove thermal prehistory of the samples and for possible removal of moisture. Holding segments allow stabilizing the furnace temperature. Measurement error is 3%.

Thermal diffusivity $a$ and specific heat $C$ were determined using a laser flash method using an LFA457 MicroFlash instrument (NETZSCH) in the temperature range from room temperature to 150 °C (to avoid melting of the samples), thermal conductivity $\lambda$ was calculated by well-known formula:

$$\lambda = a \cdot \rho,$$

where $\rho$ is density.

Thermal conductivity measurement error is 8%.

4. Results and discussion

4.1. Thermal analysis

The results of thermal analysis of polymer composites are presented in Figure 1 and Table 2. For PA matrix one crystallization peak is observed at a temperature of 175.3 °C (see Table 2). Introduction of the filler shifts the temperature of crystallization peak to higher temperatures, which indicates that fillers act as nucleating agents and the growth of crystallites in polymer composites begins earlier than in a pure polymer. Filler introduction increases the temperature of crystallization peak by at least 21 °C. It should be noted that introduction of the filler into polymer matrix cause appearance of the second crystallization peak which position shifts to even higher temperatures by an average of 36 °C. The peak of double crystallization in nanocomposites can be interpreted by the formation of crystallites of various morphologies, degrees of defectiveness or sizes. [7, 8]. In addition, an increase in the width of the peak of crystallization indicates, apparently, a considerable scatter of crystallite sizes [7].

For pure PA the melting peak corresponds to a temperature of 227.7 °C. Filler loading causes a slight shift of melting peak temperature towards low temperatures (see Table 2) which indicates a decrease in the sample heat resistance. 10 wt.% SiO2 reduces melting peak temperature by almost 7 °C while 10 wt.% Al shifts the temperature by just 1 °C. It should be noted that introduction of a filler and increase in its concentration lead to enthalpy of fusion decreasing. This may indicate destabilization of the composite. Degree of crystallinity decreases due to 10 wt.% SiO2. Difference in melting point and enthalpy with addition of 10 wt.% Al or 10 wt.% SiO2 to the PA+CNM composite is related to the surface features of added particles and their interaction with the polymer.
4.2 Thermophysical properties

It is known that fillers influence on thermal and electrophysical characteristics of polymeric materials [9]. Figures 2 and 3 present measured thermal conductivity of investigated samples of composite materials.

Introduction of 20 wt.% CNM leads to increase of thermal conductivity by more than 2 times compared with pure PA. In samples with the same content of 20 wt.% of CNM and 10 wt.% of different fillers Al or SiO₂, respectively, thermal conductivity increases by about 3 times. That means, the fillers Al or SiO₂ have the same effect on thermophysical properties of materials, despite the fact that thermal conductivity of the fillers themselves differ by orders of magnitude. It can be assumed that this result is obtained due to nanosized and well-developed SiO₂ surface, and its addition contributes to additional compaction of the filler in the PA matrix, as seen in the SEM images (Figure 4). As a result, we observe an increase of thermal conductivity. Solid particles of Al have the same effect limiting the mobility of polymer macromolecules and thereby compacting its structure.

4. Conclusions

Thus, thermal behavior of PA based composites illustrates that introduction of fillers into the polymer matrix contributes to change of melting and crystallization peaks temperature. Increase of crystallization peak temperature by more than 20°C is observed, and melting peak temperature shifts towards lower temperatures as compared with the pure polymer. In addition, introduction of CNM leads to formation of second peak of crystallization which may be due to formation of crystallites of various morphologies, degree of imperfection or size. Melting enthalpy decreases with increasing filler concentration.

Thermal conductivity of polymer composites increases with increasing of filler content. Introduction of high thermally conductive fillers does not always have an obvious effect in terms of thermal conductivity increasing. Introduction of SiO₂ with high thermal conductivity has the same influence on thermophysical properties of the composite as the high thermally conductive Al filler. This is due to surface features of the filler particles and their interaction with the polymer.
Figure 4. AFM images of polymer composites:
a) pure PA;
b) PA+20 wt.% CNM;
c) PA+20 wt.% CNM+10 wt.% Al ;
d) PA+20 wt.% CNM+10 wt.% SiO2

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