NANO-SIZE FILLERS AS THEY INFLUENCE THE PROPERTIES OF A NANOCOMPOSITE BASED ON POWDER POLYPROPYLENE

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ABSTRACT

Specific features of the technology to produce a nanocomposite on the basis of a powder polypropylene (PP) and its properties are considered. It has from 0.05 up to 2 % of nanosize fillers. Montmorillonite, ultradisperse diamonds and a concentrate from the mutual activation of a polypopylene and montmorillonite using planetary MPF-1 mechanoactivator were used as fillers. Bulk billets were made by a method of indirect pressing at a hydraulic press.

Properties of the produced materials were studied. Dependencies between the density of the material, its elongation properties, its tribological behavior and the concentration of a nanofiller in the material were described. It was shown that physical-mechanical properties do not depend on the kind of the filler, but come from the concentration values.

INTRODUCTION

Polypropylene is a linear, partly crystalline thermoplastic material. It is widely used and efficient, and easily processed. Its melting temperature is 164-170ºC.

Many authors say that introduction of nanofillers into the polymers in low concentrations, opposite to microparticles, improves physical and mechanical, and tribological properties of the produced composite, as well as its thermal stability, and protective properties against UV and IR radiation.

To make nanocomposites the developers of nanocomposite materials introduce various materials into the polymer matrix, including nanodiamonds [1-3]. Nanodiamonds are highly efficient active fillers of polymer nanocompositions that upgrade mechanical and tribological properties of the produced composites. However, we failed to find any information on introduction of nanodiamonds into the PP.

There is mush interest of the researchers to the organic clays [4-9]. However, the enlisted works do not specify if the samples on the basis of PP for particular tests were produced in a bulk or film condition. We may suppose that they speak about films but not about bulk samples. The goal of this work is to make bulk samples of nanocomposites on the basis of PP to reveal the behavior of values of various properties of the produced materials.

THE MATERIALS

Powder polypropylene PPK by process requirements 2211-017-4260962-2000 made at ALGOL Ltd (Kirov) in 2006 was used as a filler.

Ultra disperse diamonds produced by detonation techniques in RFNC-VNIIEF were used as nanodiamonds.

Montmorillonit, which is a nanoclay from a certain field, was provided by the Institute of the Oil Chemical Synthesis of the Russian Academy of Science, Moscow.

The concentrate on the basis of powder polypropylene and montmorillonite in the ratio of 50:50 was prepared my mechanoactivation in MISA, Moscow.

PRODUCTION AND TESTING TECHNIQUES

When developing a technology to produce the material we used a composite on the basis of polypropylene and a nanofiller – montmorillonite (nanoclay), nanodiamonds and a concentrate on the basis of polypropylene and montmorillonite produced by mechanoactivation. The concentration of fillers in the composite was from 0.05% wt. Up to 2.0% wt.

The composite material was produced in the following way: at first some press-material was made, which was a mechanical mixture of powders of polypropylene and nano-fillers in a certain ratio, and then this press-material was processed by direct pressing to make bulk billets in the form of plates 150×150×6 mm.

The technological process to make a composite comprised the following operations:

- preparing the portions of initial components in compliance with the formula;
- mixing of the components;
- preparing the portions of the press-composition for processing;
- pressing of the billets (samples).

Preparation of a press-composition was performed in the following stages: the amount of powder components – polypropylene and a nanofiller (montmorillonit, nanodiamonds or a concentrate) – in the amount calculated in compliance with the formula were fed into the drum of the mixer of barrel type. Mixing was done with metal balls. The ratio of the total weight of the components to the total weight of the balls was from 1:3 to 1:5. The volume of the loaded components with the balls was not less than 1/2 and not more than 2/3 of the volume of the drum.

The time of mixing of the components in the mixer until the uniform condition was selected experimentally and it made actually 6.0 hours.

After mixing the blend was recovered from the drum and sieved through 063 or 1. mesh to separate the balls and destroy the aggregated clusters (conglomerates) of the material of various sizes when they are friable.

When pressing the portion of the material to make a billet, it was loaded into the prepared press-form. The assembled press-form was put onto the press plates with the electric heating. The applied pressure made up (5.0±0.5) MPa and at this value of pressure the press-form was heated up to the temperature of (190 – 200)ºC.

After reaching the preset temperature the exposure time kept was calculated from (2.0 – 3.0) min per 1 mm of the thickness of the billet. The press-form was disassembled and the billet was recovered at the temperature not higher than 60ºC.

The sample for tests was mechanically cut out of the pressed billets in the form of plates (150×150×6) mm in size.

Before tests each sample was visually examined and its density was determined. The samples for tests should have even and smooth surface without spallation, cavities or other defects. The density of the samples was evaluated by hydrostatic weighing.

Mechanical tests of the samples was performed in compliance with the valid standards of the Russian Federation. Not less than 5 samples were taken for tests; before the tests they were conditioned for not less than 16 hours at the temperature of 296±2K (23±2ºC) and relative humidity of 50±5 %. The tests were carried out using the testing instruments by INSTRON Company that provide the load measurements with the error of not more than 1% of the value being measured.

Statistic processing of the produced data was done following the method described in [10].

THE PRODUCED RESULTS AND THEIR DISCUSSION

When making the material we used the composite on the basis of polypropylene and a nanofiller – montmorillonite (nanoclay), nanodiamonds, and the concentrate on the basis of polypropylene and montmorillonite taken in the ratio of 50:50 and produced by mechanoactivation during 15 minutes. The concentration of the nanofillers introduced into the composition was 0; 0.05; 0.1; 0.5; 1.0 and 2.0 % wt taken by the basic filler.

As it comes from the data in Figure 1, with the growth of the amount of the filler from 0 up to 2 % wt. the density of the produced nanocomposite grows inconsiderably, and the density changes do not depend here on the nature of the filler and result only from its concentration.

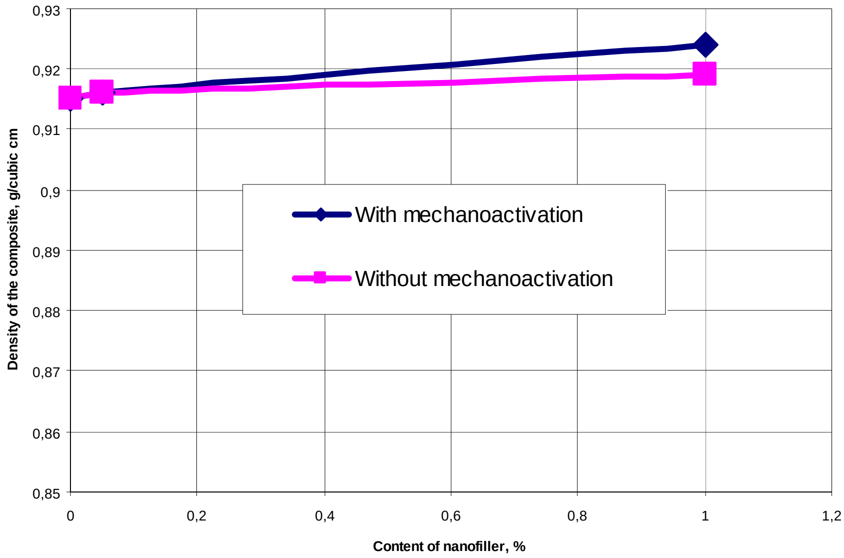

Figure 1: Density of the composite as a function of the content of the nanofiller (in case of no activation - PP with nanoclay, with mechanoactivation – PP with the content concentrate of PP and nanoclay)

Besides, we can make a conclusion that the worked out technology results into the uniform distribution of the nanofiller in the composite. Figure 2 shows how intensity of the color changes in the made samples as a function of growth of the content of the filler. All produced billets have a uniform color without any whitening or darkening.

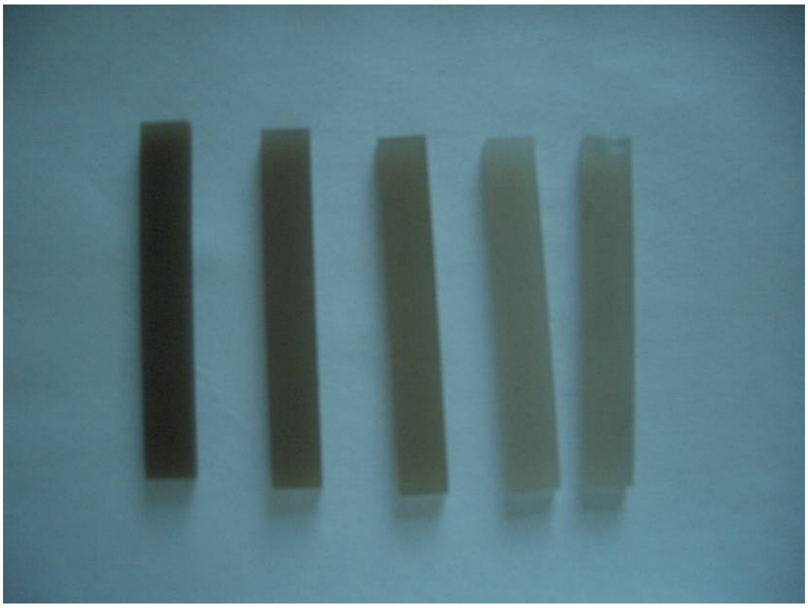

Figure 2: Samples on the basis of powder polypropylene with a various content of montmorillonite (from the right to the left from 0.05 up to 2 %)

After mechanical stretching tests and general evaluation of the produced results we may make the following conclusions.

Only brittle destruction of the samples is characteristic for the samples of pure polypropylene. Figure 3 shows the sample of pure polypropylene after mechanical tests. As you can see in the Figure, there is no neck characteristic for plastic destruction of the sample. The sample with the introduced nanofiller can have the same character of destruction.

However, for a considerable number of compositions with the introduced nanofillers mixed the destruction of the samples is characteristic after mechanical tests for stretching. A part of samples gets destroyed in a brittle way, and another part in an elastic way (see Figure 4). And specific elongation at rupture of the samples may vary a lot – from 3-4% at the brittle destruction and up to 120% at the elastic one.

Similar effect is revealed practically for all the compositions under study, and it does not depend on the kind of the filler, but is determined only by the nanofillers introduced into the composition.

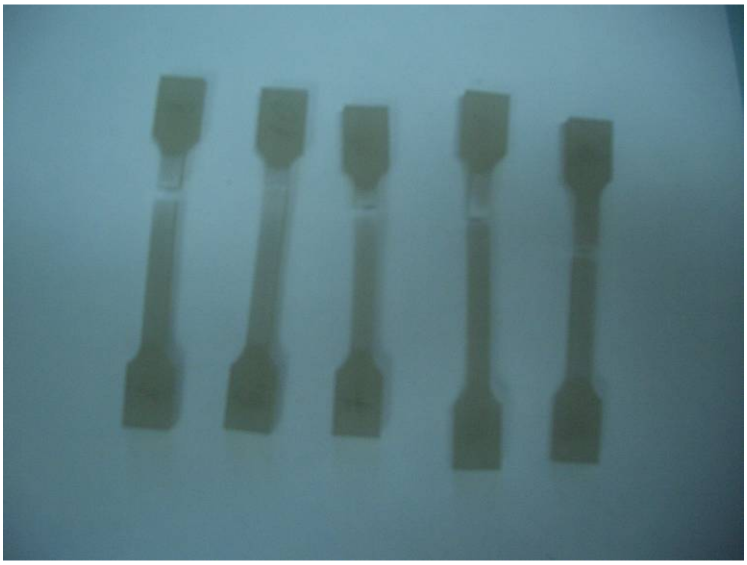

Figure 3: Samples of pure polypropylene after mechanical tests

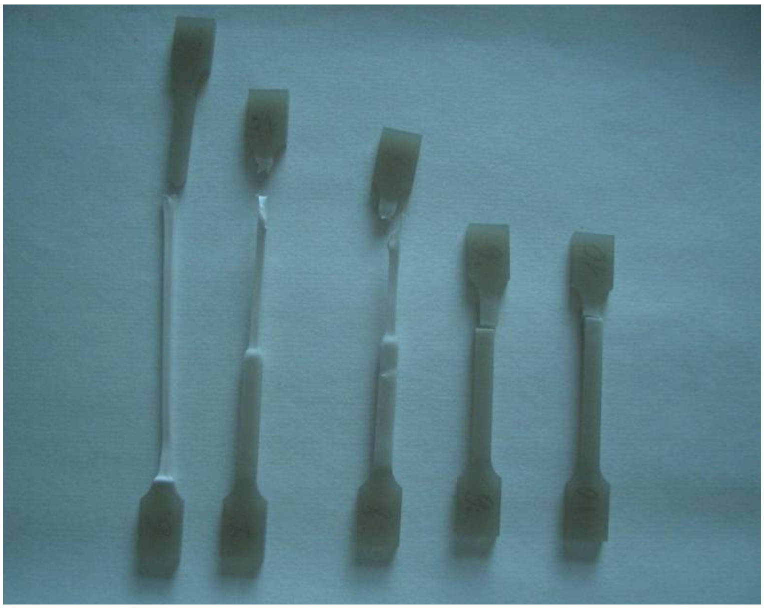

Figure 4: Samples of nanocomposite on the basis of polypropylene and 0.05% of nanodiamonds after mechanical tests

Breaking point behavior at stretching of the brittle samples of various composition as a function of the filling degree with various fillers is given in Figure 5.

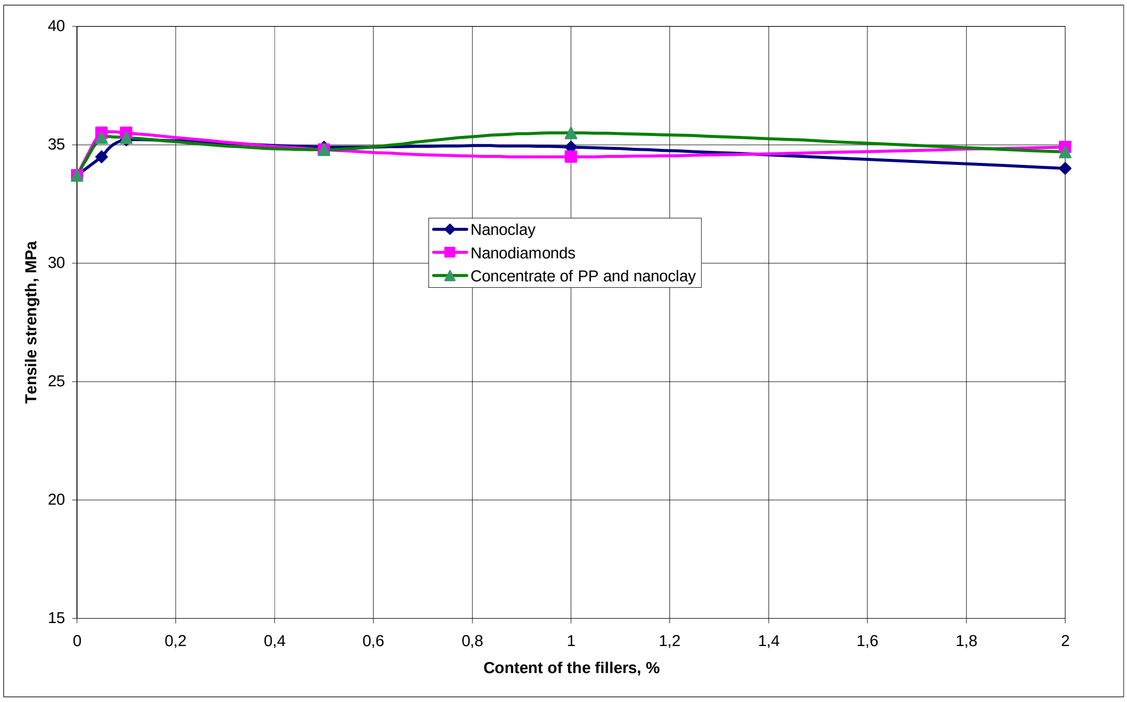

Figure 5: Tensile strength at rupture for the samples made of nanocomposites on the basis of polypropylene and various nanoadditives as a function of the content of the nanoadditives

As it comes from the Figures, at brittle destruction of the samples of polypropylene with the introduced nanofillers at the concentration of any nanofiller of already 0.05% there is a growth (though inconsiderable) of the strength at rupture of the sample. Similar effects were observed by other authors. Though from the data given in the enlisted publications it is not clear if the authors studied bulk or film samples, we may suppose that the results they got refer to the film samples, as there was no any information found in the literature on production of the bulk nanocomposites on the basis of polyolefins.

Figure 6 below shows that at brittle destruction of the samples of polypropylene with nanofillers introduced into the composition at the concentration of any nanofiller from 0.05% we observe the growth, though the non-linear one, of the relative elongation at rupture. So, we may say that when nanofillers are introduced into the composition the general tendency is the growth of the relative elongation at rupture of the samples.

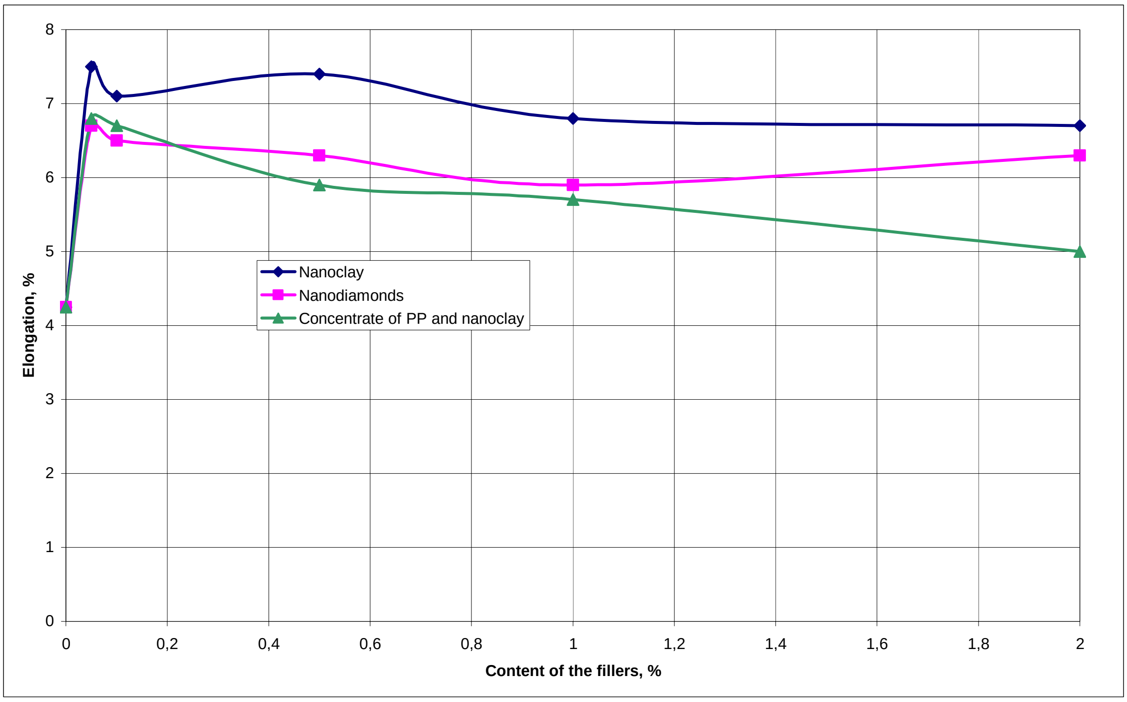

Figure 6: Relative elongation at rupture of the samples of nanocomposites on the basis of polypropylene and various nanoadditives as a function of the content of the nanoadditives

Figure 7 shows the plot of the coefficient of elasticity at stretching of the nanocomposite as a function of the content of the filler; the plot of the constant of friction for the nanocomposite as a function of the content of the filler is given in Figure 8; the plot of the wear-out rate of the nanocomposite as a function of the content of the filler is given in Figure 9.

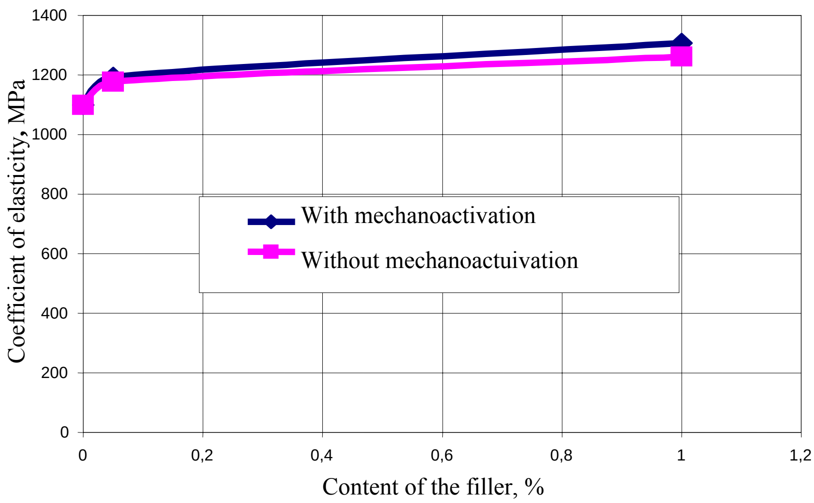

Figure 7: The coefficient of elasticity at stretching of the nanocomposite as a function of the content of the nanofiller (in case of no activation - PP with nanoclay, with mechanoactivation – PP with the content concentrate of PP and nanoclay)

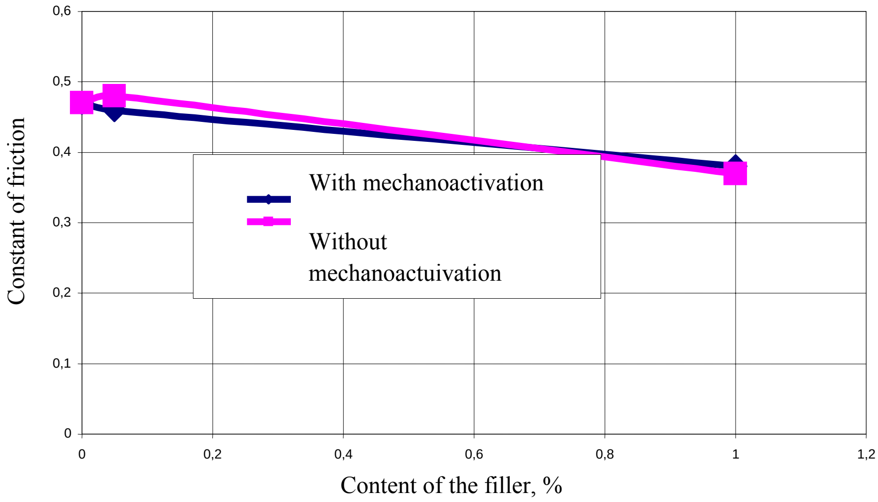

Figure 8: The constant of friction for the nanocomposite as a function of the content of the nanofillers (in case of no activation - PP with nanoclay, with mechanoactivation – PP with the content concentrate of PP and nanoclay)

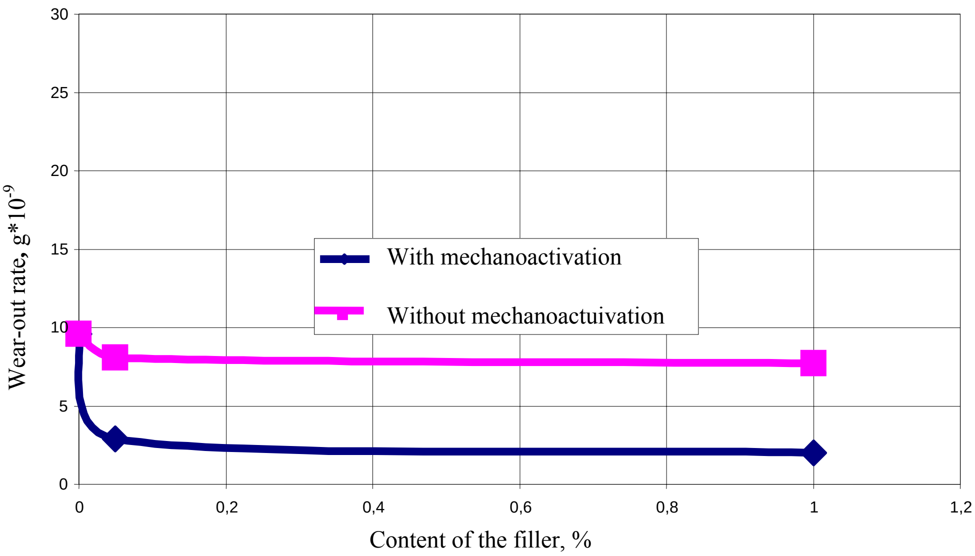

Figure 9: The wear-out rate of the nanocomposite as a function of the content of the filler (in case of no activation - PP with nanoclay, with mechanoactivation – PP with the content concentrate of PP and nanoclay)

The produced results make it possible to summarize the following:

- At tensile tests of the samples of the powder polypropylene with the introduced nanoadditives into the composition (up to 2%) we observe considerable spread in values produced,
- Introduction of nanoadditives into the composition results into the improvement in the properties of the produced nanocomposites (physical, mechanical, and tribological), and we may note that this effect does not depend on the kind of the filler but is determined by its concentration.

CONCLUSIONS

Bulk billets of nanocomposites on the basis of powder polypropylene of PPK brand were produced by direct pressing using montmorillonite (nanoclay), nanodiamonds, and the concentrate produced by mechanoactivation of polypropylene and montmorillonite as nanofillers. The content of the fillers in the composites varied from 0 up to 2 % wt.

The tests of the bulk samples showed that the introduction of the nanofillers into the composite results into the following:

- Inconsiderable increase of the density of the produced material;
- Changes in the destruction character of the composite from the brittle one for the pure polymer to a partly plastic for a nanocomposite even at the introduction of 0.05% of the nanofiller;
- Inconsiderable upgrading of the breaking point at stretching;
- Growth of relative elongation at rupture;
- Reduction of the constant of friction;
- Reduction of the wear-out rate.

Introduction of the nanoadditives into the composite results into the upgrading of the properties of the produced nanocomposites – physical, mechanical and tribilogical ones, and this effect does not depend on the kind of the filler used, but is determined by its concentration.

ACKNOWLEDGEMENTS

The work was done under Federal Purpose Program “Research and Development in he Priority Areas of the Scientific and Technological Complex of Russia for the years 2007-2012” within State Contract №02.513.11.3222.

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