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METAL-CONTAINING NANOPARTICLES IN A MALEINIZED POLYETHYLENE MATRIX AS NANOFILLERS FOR POLYPROPYLENE**N.I.Kurbanova, Z.N.Huseynova, N.Y.Ishenko, A.T.Aliyev, T.M.Guliyeva,
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The effect of additives of metal-containing nanofillers including nanoparticles of zinc oxide stabilized on a polymer matrix of maleinized polyethylene on the properties of nanocomposites based on isotactic polypropylene by methods X-ray phase and thermogravimetric analyses was studied. The improvement of the strength and rheological indexes, as well as the thermooxidative stability of the nanocomposites obtained was revealed.

Keywords: *isotactic polypropylene, metal-containing nanofillers, maleinized polyethylene matrix, physical and mechanical properties.*

Introduction

One of the most promising trends for the development of modern science is nanotechnology – the production and use of materials containing nanoparticles (NP).

In recent years, there has been a significant interest in composite materials on the basis of polymer matrices and metal nanoscale particles, which is due to a wide range of their applications – from catalysis to nanotechnology in information techniques.

The development of nanotechnology has opened the possibility of carrying out research in the field of composite nanomaterials, and has now made it possible to proceed to the development and use of promising polymeric materials for sensors, catalysis, nanoelectronics, etc. Metallopolymer composites are used mainly in the electronic and radio engineering industries, as well as in aviation and rocket construction [1–3].

It is known that in order to improve the performance of plastics, fillers are used in an amount of 30–50 mass % by weight. Filled plastics are used, mainly, as a structural material [4].

In the world today, various types of polymer composite materials based on nanofillers actively replace the traditional materials [5]. Polymeric nanocomposites can be obtained in situ, i.e. by polymerization of the monomer in the presence of a nanofiller previously dispersed in the reaction medium [6]. The method

of introducing a nanofiller in the melt of polymers is more preferable. This method is most suitable for use in modern industry. It makes it possible to obtain nanocomposite polymers for a wide cross-section of producers, what makes this method promising and cost-effective [7].

The modification of polypropylene (PP) by the creation of various composite materials makes it possible to significantly expand the field of its application. The filled polypropylene ranks one of the first places among the filled thermoplastics. At present more attention is paid to the development of composites with nanosized fillers. Such composite materials have higher characteristics than composite materials with micro- and macrofillers. The introduction of even a small amount of nanosize filler into polypropylene can significantly change the physical properties, enhance barrier qualities, thermal stability, electrical conductivity, etc. [8, 9].

The use of nanoparticles of *d*-valence metals (zinc, cobalt, nickel etc.) in polymers makes it possible to obtain fundamentally new materials that are widely used in radio and optoelectronics as magnetic, electrically conducting and optical media [2, 9].

The purpose of this work is to study the effect of additives of metal-containing nanofillers (NF) on the physicomechanical, rheological, thermophysical and heatphysical properties of composites on the basis of isotactic PP.

Experimental part

In the work isotactic PP of TPPF79FB brand (Russia) with a melt flow limit of 10–15 g/10 min, Vicat softening (10N) no more than 150°C are used.

As NF there was used zinc oxide NP stabilized on a polymer matrix of maleinized high-density polyethylene, obtained by mechanochemical method in a polymer melt. The content of nanoparticles is 5 mass % the size is 11–17 nm, the degree of crystallinity is 35–45% [10]. The ratio of components of polymer mixtures (mass %): PP/NF = 100/(0.5, 1.0, 3.0).

Nanocomposite polymeric materials were obtained by mixing PP with zinc-containing NF on the laboratory mill at a temperature of 160–165°C. To carry out the mechanical tests, the obtained mixtures were pressed in the form of plates 1 mm thick at 190°C for 15 min and 10 MPa pressure.

The physico-mechanical properties of the obtained compositions were determined on the RMI-250 instrument, and the melt flow index (MFI) on the index of thermoplasts melt (IIST) instrument at a temperature of 200°C, at a load of 5.00 kg.

X-ray phase analysis (XRD) of the obtained compositions was carried out on a "D2 Phaser" device from Bruker (Germany).

The thermostability of the test samples of thermoplastic elastomers was studied on a Q-1500D derivatograph manufactured by MOM (Hungary). The tests were carried out in an air atmosphere in a dynamic mode when the sample was heated to 5 deg/min from 20 to 500°C, weighed portion 100 mg, the sensitivity of the channels DTA-250 μ V, TG-100 mg, DTG-1 mV.

Results and its discussion

Nanocomposite polymer materials based on PP with metal-containing nanoparticles were obtained. The composition and structure of the obtained nanocomposites are studied.

The phase composition of the obtained nanocomposite was studied by X-ray diffraction analysis (RPhA). Phase identification was carried out from the data on interplanar distances, using the ASTM card file. It is shown that in the studied nanocomposites reflections from the planes of the crystal lattice of metals were observed, corresponding to the d_{hkl} series of zinc oxide (ZnO), according to the ASTM file (Figures 1, 2).

The effect of additives of metal-containing nanofillers on the physico-mechanical, rheological, thermophysical and thermal properties of composites on the basis of isotactic PP has been studied. The physico-mechanical and rheological properties of the composites obtained are presented in Table 1.

As can be seen from the data in Table 1, the introduction into the composition 0.5–1.0 mass % of NF leads to a slight increase in the strength index from 21.6 to 32.7 MPa. Increase in the concentration of NF more than 1.0 mass % leads to a decrease in the strength of the composite (11.8 MPa), which is probably due to the aggregation of nanoparticles, which leads to the formation of microdefects in the bulk of the polymer matrix. An increase in the concentration of NF leads to a decrease in the strain at break of the composite, which, apparently, is due to blocking of the mobility of polymer segments by nanoparticles at the nanolevel.

The study of the by Vicat heat resistance by of the obtained compositions showed that the

Table 1. The physico-mechanical and rheological properties of the obtained composites

Composition	Tensile strength, σ_p , MPa	Tensile strain, ϵ_p , %	Vicat softening point, °C	Melt flow index (MFI), g/10 min
PP	21.6	46	165	9.5
PP/NF(0.5)	28.1	22	165	15.1
PP/NF(1.0)	32.7	80	165	19.7
PP/NF(3.0)	11.8	20	165	41.2

Fig.1. Diffractograms of the sample PP.

Fig.2. Diffractograms of the sample PP/NF.

introduction of a nanofiller into the PP composition leads to the preservation of the heat resistance index at 165°C.

The study of the melt flow index (MFI) showed that increase in the NF content (1–3 mass %), contributes to the increase of MFI to 19.7 (1 mass %) and 41.2 g/10 min (3 mass %), what testifies to improvement of fluidity of the composition and the possibility of processing it by injection molding and extrusion.

The thermal stability of the test samples based on PP containing NF with NP of zinc oxide was estimated from the mass loss, destruction activation energy (E_a) of the decomposition of thermooxidative destruction, calculated by the double logarithm of the TG curve no the methods [11], and a temperature of 50% (T_{50}) decay of the samples under study, and also by the time of their half-life – $\tau_{1/2}$. The data obtained from derivatographic studies are shown in the Table 2.

Table 2. Thermal properties of the resulting composites

Composition	T_{50} , °C	$\tau_{1/2}$, min.	Melting point, °C	E_a , kJ/mol
PP	340	64	145	122.49
PP/NF(0.5)	360	68	145	170.23
PP/NF(1.0)	370	71	145	175.53
PP/NF(3.0)	360	69	145	173.12

As can be seen from the data in Table 2, the introduction of NF containing NP of zinc oxide into the composition contributes to an increase in the half-life temperature of the samples: T_{50} at 20–30°C; the half lifetime $\tau_{1/2}$ increases from 64 to 71 min., the activation energy (E_a) of the decomposition of the thermooxidative degradation of the resulting nanocomposites rises from 122.49 to 175.53 kJ/mol.

Derivatographic studies have shown that the introduction of NF containing NP of zinc oxide into the composition contributes to the enhancement of thermooxidative stability of the obtained nanocomposites.

Conclusions

The influence of a nanofiller containing nanoparticles of zinc oxide on the properties of composites on the basis of isotactic PP has been studied.

X-ray diffraction patterns confirm the presence of zinc oxide nanoparticles on the PP matrix.

The improvement of strength and rheological parameters, as well as thermooxidative stability of nanocomposites obtained, was revealed.

It is shown that nanocomposites based on PP can be processed both by pressing and injection molding method as well as extrusion method.

References

1. Suzdalev I.P., Suzdalev P.I. Nanoclusters and nanocluster systems // Adv. Chem. 2001. V. 70. No 3. P. 203–240.
2. Pomogailo A.D., Rosenberg A.S., Uflyand I.E. Nanoparticles of metals in polymers. M.: Chemistry. 2000. 672 p.
3. Tretyakov A.O. Polymer nanocomposites – materials of the XXI century. Equipment and tools for professionals. 2003. V. 37. No 2. P. 18–20.
4. The encyclopedia of polymers. M.: The Soviet Encyclopedia. 1974. V. 2. P. 328.
5. Foster L. Nanotechnology. Science, innovation and opportunities. M.: Technosphere, 2008. 352 p.
6. Antipov E.M., Barannikov A.A., Gerasin V.A. et al. The structure and deformation behavior of nanocomposites based on polypropylene and modified clays // High-mol. comp., 2003. A. V. 45. No 11. P. 1885–1898.
7. Kovalchuk A.A., Shchegolikhin A.N., Dubnikova I.L. et al. Nanocomposites polypropylene/ multi-walled carbon nanotubes: in situ polymerization and properties // Plast. masses. 2008. № 5. P. 27–30.
8. Sister V.S., Ivannikova E.A., Lomakin S.M. Comparative analysis of thermal stability of polymer nanocomposites based on polypropylene // Nanomater. nanotechnol. 2012. № 3. P. 13–28.
9. Gubin S.P., Yurkov G.Yu., Kosobudsky I.D. Nanomater. based on metal-containing nanoparticles in polyethylene and other carbon-chain polymers // Int. J. Mater. Product Technol. 2005. V. 23. No 1–2. P. 2–25.
10. Kurbanova N.I., Alimirzoeva N.A., Guseinova Z.N., Nurullayeva D.R. Ecological Method of Preparation of Metal-Containing Nanoparticles in Polyethylene Matrix // 3rd Int. Turkic World Conf. Chem. Sci. and Technol. (ITWCCST 2017). Baku. 10–13 Sept. 2017. Abstract. P. 98.
11. Technic. properties of polymeric materials: Educational-reference manual // Under the general ed. prof. Kryzhanovsky V.K. SPb.: The profession, 2007. 240 p.

MALEİNLƏŞDİRİLMİŞ POLİETİLEN MATRİSİNDƏ STABİLLƏŞDİRİLMİŞ METALSAXLAYAN NANOHISSƏCİKLƏR – POLİPROPİLENİN NANODOLDURUCUSU KİMİ**N.İ.Qurbanova, Z.N.Hüseynova, N.Y.İşenko, A.T.Alyev, T.M.Quliyeva, S.K.Rəhimova, S.A.Rzayeva**

Tərkibində maleinləşdirilmiş polietilen matrisində stabilləşdirilmiş sink oksid nanohissəciyi saxlayan nanodoldurucunun izotaktik polipropilen əsaslı nanokompozitin xassələrinə təsirini rentgenfaza və termogravimetrik analiz metodları ilə tədqiq edilmişdir. Alınan nanokompozitlərin möhkəmlik və reoloji göstəricilərin həmçinin termooksidləşdirici stabilliyinin yaxşılaşması aşkar edilmişdir.

Açar sözlər: izotaktik polipropilen, metalsaxlayan nanodoldurucu, maleinləşdirilmiş polietilen matrisi, fiziki-mexaniki xassələr.

МЕТАЛЛСОДЕРЖАЩИЕ НАНОЧАСТИЦЫ В МАЛЕИНИЗИРОВАННОЙ ПОЛИЭТИЛЕНОВОЙ МАТРИЦЕ – НАНОНАПОЛНИТЕЛИ ПОЛИПРОПИЛЕНА**Н.И.Курбанова, З.Н.Гусейнова, Н.Я.Ищенко, А.Т.Алыев, Т.М.Гулиева, С.К.Рагимова, С.А.Рзаева**

Исследовано влияние добавок металлсодержащих нанонаполнителей, включающих наночастицы оксида цинка, стабилизированного на полимерной матрице малеинизированного полиэтилена на свойства нанокomпозитов на основе изотактического полипропилена (ПП) методами рентгенофазового и термогравиметрического анализа. Выявлено улучшение прочностных и реологических показателей, а также термоокислительной стабильности полученных нанокomпозитов.

Ключевые слова: изотактический полипропилен, металлсодержащие нанонаполнители, матрица малеинизированного полиэтилена, физико-механические свойства.