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COPPER-CONTAINING NANOCOMPOSITES BASED ON ISOTACTIC POLYPROPYLENE AND HIGH PRESSURE POLYETHYLENE

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The effect of nanofillers additives containing copper oxide nanoparticles stabilized by a polymer matrix of high-pressure polyethylene obtained by the mechanochemical method on features of the structure and properties of metal-containing nanocomposites based on isotactic polypropylene and high-pressure polyethylene was studied using differential thermal (DTA) and X-ray phase (XRD) analyzes. The improvement of strength, deformation and rheological parameters, as well as thermal-oxidative stability of the obtained nanocomposites was revealed, that apparently, is associated with the synergistic effect of interfacial interaction of copper-containing nanoparticles in the PE matrix with the components of the PP/PE polymer composition.

Keywords: *isotactic polypropylene; high pressure polyethylene, copper oxide nanoparticles, thermal properties, DTA and XRD analysis.*

doi

Introduction

For the directed improvement of the properties of polypropylene (PP), the modification method is widely used, which consists in creation of polymer–polymer compositions [1].

Isotactic polypropylene (PP) and high pressure polyethylene (PE) are known to be immiscible polyolefins. To improve their compatibility existence functional groups in their composition or introduction of nanofillers (NF), which are an interphase additive, to the composition to improve both the compatibility of components and the operational properties of the obtained materials, is necessary [2–8].

The use of dispersed nanofillers allows one to control the structure and properties of materials due to nucleating and orientational effects, changes in the conformation of macromolecules, their chemical bonding to the surface of nanoparticles, and "healing" of structural defects [9, 10]

The development of research on nanoscale and cluster metal-containing particles in polymer matrices was largely facilitated by the creation of metal–polymer composite materials with specific physico-[mechanical and operational properties: increased thermal and electrical conductivity, high magnetic susceptibility, the ability to shield ionizing radiation, etc. [11, 12].

It is known that the use of *d*-valence metal nanoparticles (copper, zinc, cobalt, nickel, etc.) in polymers allows one to obtain fundamentally new materials which are widely used in radio and optoelectronics as magnetic, electrically conductive, and optical media [12, 13].

The purpose of this work was to obtain and study the structure and properties of composites based on PP and PE with copper-containing nanofillers NF stabilized by a polymer matrix.

Experimental part

In the work were used: isotactic PP "Kaplen" (Russia) of brand 01 030 with a molecular mass of $\sim(2-3) \cdot 10^5$, polydispersity index 4.5, MFI (2.3–3.6) g/10 min; High-pressure polyethylene (PE) of brand 15803-020 (Azerbaijan, SOCAR Polymer), $\rho = 0.917-0.921$ g/cm³, MFI (1.5–2.5) g/10 min.

The nanoparticles (NP) of copper(I) oxides stabilized by a high-pressure polyethylene polymer matrix obtained by the mechanochemical method in a polymer melt were used as NF. The content of nanoparticles is 5 mass%, size 25 ± 1.0 nm, crystallinity 35–45% [14, 15]. The ratio of the components of the composition (mass %): PP/PE/NF = 50/50 / (0.5, 1.0, 2.0).

Nanocomposite polymeric materials were obtained by mixing PE with copper-containing

nanofillers on laboratory rollers at a temperature of 160–165°C for 15 minutes. For mechanical testing, the resulting mixtures were pressed in the form of plates 1 mm thick at 190°C and a pressure of 10 MPa for 10 minutes.

Physical-mechanical parameters of the obtained compositions were determined on a RMI-250 device.

The melt flow index (MFI) was determined on a CEASTMF50 capillary rheometer from INSTRON, Italy, at a temperature of 190°C and a load of 5 kg.

X-ray phase analysis (XRD) of the obtained compositions was performed on a "D2 Phaser" instrument from Bruker, Germany.

The thermal stability of the studied samples of nanocomposites was studied on a Q-1500D derivatograph manufactured by MOM, Hungary. The tests were carried out in an atmosphere of air in a dynamic mode at a sample heating of 5 deg/min from 20 to 500°C, 100 mg sample load, channel sensitivity DTA-250 μ V, TG-100, DTG-1 mV.

Results and discussion

Nanocomposite polymer materials based on PP/PE with a copper-containing nanofiller were obtained. Ratio of initial components (mass %): PP/PE/NF = 50/50/(0, 0.5, 1.0, 2.0).

The physical-mechanical, rheological, thermophysical and thermal properties of the obtained nanocomposites are studied.

Table 1 shows the physical, mechanical and rheological parameters of the obtained composite materials.

As can be seen from the data in Table 1, the introduction of 0.5–1.0 mass % NF into the composition leads to an increase in the strength index from 13.15 to 16.87 MPa. An increasing the NF concentration of more than 1.0 mass % leads to a decrease in the strength of the composite (13.83 MPa), that is probably due to the aggregation of NP, that leads to the formation of microdefects in the bulk of the polymer matrix. The introduction of 0.5 – 1.0 mass % NF into the composition leads to an increase in the strain at break of the composite by a factor of 1.2, that is apparently connected with the synergistic effect of interfacial interaction of copper-

containing nanoparticles in the PE matrix with the components of the polymer composition PP/PE the mutual influence of which contributes to an increase in both the degree of deformation and the strength index.

A study of Vicat softening temperature of the obtained compositions showed that the introduction of a nanofiller into the composition of PP/PE practically does not affect the heat resistance index.

At the same time, an increase in the content of the nanofiller (1.0–2.0 mass %) contributes to an increase of MFI to 18.5 (1.0 mass. %) and 25.4 (2.0 mass.%) g/10 min, that indicates an improvement in the fluidity of the composition and the possibility of processing it by injection molding and extrusion.

Figures 1 and 2 show the XRD patterns of the initial PP/PE and PP/PE with a copper-containing nanofiller.

The reflexes corresponding to the initial PP/PE are shown in Figure 1 and the reflexes characteristic of copper-containing nanoparticles: d_{hkl} 3.02053, 2.46466, 2.13683, 1.74331, 1.51025, 1.28812 Å (Figure 2), which corresponds to the ASTM d_{hkl} series of copper oxide(I). [d-Spacing (20) – 01-071-3645 (Fixed Slit Intensity) – CuK α 1 1.54056 Å. Entry Date: 11/19/2008 Last Modification Date: 01/19/2011].

The thermal stability of the studied samples based on PE containing NF with NP of copper oxide was estimated by the value of mass loss, activation energy (E_a) of thermal-oxidative degradation, calculated by double logarithming of the TGA curve according to the method [16], by the temperature of 10% (T_{10}), 20% (T_{20}) and 50% (T_{50}) of the decay of the studied samples, as well as by their half-life time – $T_{1/2}$. The data obtained as a result of derivatographic studies are shown in Table 2.

It is shown that the introduction of NF containing NP of copper oxide into the composition contributes to an increase in the half-life temperature of samples: T_{50} from 325 to 390°C; the half-life time $t_{1/2}$, increases from 55.6 to 74.8 min., the activation energy (E_a) of the thermal-oxidative degradation of the obtained nanocomposites increases from 191.4 to 248.9 kJ/mol.

Table 1. Physico-mechanical and rheological parameters of the obtained nanocomposites

Composition (mass. %) PP/PE/NF	Breaking strength, MPa	Specific elongation, %	Vicat softening, °C Point, °C	MFI, g/10 min
50/50/0	13.15	20	160	9.5
50/50/0.5	16.87	24	160	13.8
50/50/1.0	14.96	24	160	18.5
50/50/2.0	13.83	22	160	25.4

Fig.1. Diffractogram of the sample PP/PE. **Fig.2.** Diffractogram of the sample PP/PE/NF.

Table 2. Thermal properties of studied nanocomposites samples

Composition, mass. % PP/PE/NF	$T_{10}, ^\circ\text{C}$	$T_{20}, ^\circ\text{C}$	$T_{50}, ^\circ\text{C}$	$\tau_{1/2}, \text{min}$	$E_a, \text{kJ/mol}$
50/50/0	200	275	325	55.6	191.4
50/50/0.5	300	335	380	71.2	230.5
50/50/1.0	335	355	390	74.8	248.9
50/50/2.0	290	320	360	69.1	220.7

Derivatographic studies have shown that the introduction of NF containing NP of copper oxides into the composition improves the thermal-oxidative stability of the obtained nanocomposites.

Numerous experimental data on the mechanical, strength, relaxation, and other properties of polymer–polymer, polymer–filler mixtures are explained in within a frame of concepts on existence of interphase layer [17].

The properties of polymer composites are significantly affected by the supramolecular structure of the polymer (the size of spherulites, the degree of crystallinity, the presence of C=O groups, different branchings, etc.) the interfacial interaction at the phase boundary [18].

The copper-containing nanoparticles used in this work, located at the interface between the structural elements of PP and PE, contribute to the formation of heterogeneous nucleation centers in the composition of the melt, which, in the process of stepwise cooling of the nanocomposite, contribute to the increase of crystallization centers, which generally lead to an improvement in the crystallization process and the formation of a relatively fine spherulite structure.

The results testify to that small amounts of nanofiller (0.5–1.0 mass %) introduced into the polymer obviously play the role of structure-forming agents – artificial crystallization nuclei, which contributes to the formation of a fine-spherulite structure in the polymer, characterized by improved physical-mechanical, rheological and thermal properties of the resulting nanocomposite [19].

Conclusion

The effect of a nanofiller containing copper oxide nanoparticles stabilized by a polyethylene matrix obtained by the mechanochemical method on composites properties based on PP/PE is studied.

X-ray diffraction patterns confirm the presence of copper oxide nanoparticles in the composition of PP/PE based composites

The improvement of strength, deformation and rheological indicators, as well as thermo-oxidative stability of the obtained nanocomposites was revealed.

It is shown that PP/PE based nanocomposites can be processed both by pressing and by injection molding and extrusion.

The prospects of using a nanofiller containing NP of copper oxides stabilized by a polyethylene matrix obtained by the mechanochemical method as an additive to PP/PE has been shown, which contributes to the creation of a fine-crystalline structure of the composition, and therefore its properties are improved and thereby the field of application of the obtained nanocomposite is expanded.

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İZOTAKTİK POLİPROPİLEN VƏ YÜKSƏK TƏZYİQLİ POLİETİLEN ƏSASINDA MİSTƏRKİBLİ NANOKOMPOZİTLƏR

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Mexaniki-kimyəvi üsulla alınmış polietilen matrisində stabiləşdirilmiş mis oksid nanohissəcikləri (NH) saxlayan nanodoldurucuların (ND) izotaktik polipropilen (PP) və yüksək təzyiqli polietilen (PE) əsasında nanokompozitlərin xassələrinə təsiri rentgenfaza (RFA) və termogravimetrik analiz (TQA) metodları ilə tədqiq olunmuşdur. Alınan nanokompozitlərin möhkəmlik, deformasiya və reoloji xassələrinin, həmçinin termooksidləşmə stabilliyinin yaxşılaşması müəyyən edilmişdir. Görünür, bu da yüksək təzyiq polietilenindəki mistərkibli nanohissəciklərin PP/PE kompozitin komponentləri ilə qarşılıqlı təsirinin sinergetik effekti ilə əlaqədardır.

Açar sözlər: izotaktik polipropilen, yüksək təzyiqli polietilen, mis oksid nanohissəcikləri, termiki xassələr, RFA, TQA analizi.

МЕДЬСОДЕРЖАЩИЕ НАНОКОМПОЗИТЫ НА ОСНОВЕ ИЗОТАКТИЧЕСКОГО ПОЛИПРОПИЛЕНА И ПОЛИЭТИЛЕНА ВЫСОКОГО ДАВЛЕНИЯ

С.К.Рагимова

Исследовано влияние добавок нанонаполнителей (НН), содержащих наночастицы оксидов меди, стабилизированные полимерной матрицей полиэтилена высокого давления, полученные механо-химическим методом, на особенности структуры и свойств металлсодержащих нанокмпозитов на основе изотактического полипропилена и полиэтилена высокого давления методами дифференциально-термического (ДТА) и рентгенфазового (РФА) анализов. Выявлено улучшение прочностных, деформационных и реологических показателей, а также термоокислительной стабильности полученных нанокмпозитов, что, по-видимому, связано с синергетическим эффектом межфазного взаимодействия медьсодержащих наночастиц в матрице ПЭ с компонентами полимерной композиции ПП/ПЭ.

Ключевые слова: изотактический полипропилен; полиэтилен высокого давления; наночастицы оксидов меди; термические свойства, ДТА и РФА анализы.