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PREPARATION OF METAL CONTAINING NANOCOMPOSITES BASED ON HIGH PRESSURE POLYETHYLENE AND RESEARCH INTO THEIR BACTERICIDAL PROPERTIES

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Abstract: *Metal-containing nanocomposites based on high-density polyethylene (PE) were obtained by a mechanical-chemical method without using organic solvents by high-speed thermal decomposition of organic acid salts in terms of high shear deformations. The phase composition and structure of the obtained nanocomposites were studied by the method of X-ray phase analysis (XRD). XRD diffraction patterns confirm the presence of nanoparticles of zinc and copper oxides on the PE matrix. High antibacterial activity of zinc and copper-containing nanocomposites in respect of gram-positive and gram-negative bacteria was revealed: Aspergillus niger, A.ochraseus, Penicillium cuclopium, Cladosporium herbarium, Fusarium moniliforme and F.oxysporium. This testifies to the possibility of their use as antimicrobial additives for purifying drinking water from harmful microbes, as well as additives to plastics for imparting bactericidal properties.*

Keywords*: metal-containing nanocomposites; high pressure polyethylene; nanoparticles of zinc and copper oxides; XRD analysis; bactericidal properties*
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Introduction

One of the promising areas in the science of polymers and materials science in recent years is the development of principles of polymer nanocomposites production which are the newest type of functional materials and can be used in a wide variety of applications [1, 2].

In recent years, considerable interest has been shown in composite materials based on polymer matrices and nanoscale metal particles which is caused by a wide range of their application - from catalysis to nanotechnology in information technology [1].

Metal-polymer composite materials are mainly used in the electronic and radio engineering industry, as well as in aircraft and rocket production [2].

The use of nanoparticles of metals of variable valence (copper, cobalt, nickel, etc.) in polymers allows obtaining fundamentally new materials that are widely used in radio and optoelectronics as magnetic, electrically conductive and optical media [1, 3].

It has long been known that noble metals - gold, silver - have bactericidal properties against many disease-causing bacteria and viruses. And their nanoparticles are hundred-fold higher than these figures. In recent years, it has been found that nanoparticles of some transition metals obtained through the use of different methods and stabilized on polymer matrices have bactericidal properties [4-6].

One of the methods for the formation of metal polymers is the high-speed thermal decomposition of precursors in a dissolved polymer melt. All necessary components are available to get access to the particles. In the melt, the short-range order of the structure of the initial polymer is preserved, and the voids

in it became accessible for localization of particles formed. First of all, they are embedded in the inter-spherolite regions of the polymer matrix, in the space between the lamellae and further into centers of spherulites. In this case, there is a strong interaction between nanoparticles and polymer chains [7].

The thermal method for producing nanoparticles based on the decomposition of organic acid salts or organometallic compounds in a polymer medium (the Claspol method) [8] is simple; it can be carried out in a conventional heat-resistant glass flask at t = 300-350 ° C, however, a large amount of solvent is used; the yield of nanocomposite is not high. Vacuum oil is used as a solvent. The obtained samples were separated from the oil by repeated washing out with benzene [9].

Allowing for stringent environmental requirements to improve the safety of polymeric materials and the mandatory disposal of industrial waste, we propose an environmental mechanical-chemical method for producing metal nanoparticles without using organic solvents in an extruder — a closed type mixer [10].

The mechanical-chemical approach (implementation of the "bottom-up" nanotechnology) to obtain nanocomposites allows you creating effective environmental and resource-saving technologies, since such technological processes are based on chemical reactions in the solid phase, i.e. in the absence of solvents and technological operations associated with their use. In addition, the mechanochemical method is most suitable for industrial use.

In connection with the above, the use of the mechanical-chemical method for producing nanocomposites seems to be an urgent task.

The presented work is mainly concerned with obtaining metal-containing nanoparticles in a polyethylene matrix without using solvents by decomposing organic acid salts in a polymer medium in terms of high shear deformations and research into bactericidal properties of the obtained nanocomposites.

Experimental part

In the work were used a high-pressure polyethylene of the brand 10803-020 (PE) with characteristics as follows: the content of the crystalline phase 60÷70%, density 0.94 g/cm^3, melt index 1.3, melting temperature determined by the DTA method, 100°C; as metal – containing compounds (precursors) - copper and zinc acetates obtained by us through the interaction of metal oxides with acetic acid.

Metal-containing nanoparticles in the matrix of high-pressure polyethylene in two stages were obtained by the method of high-speed thermal decomposition of salts of organic acids under high shear deformations. In the first stage, at a temperature of 130-140 ° C, a binary mixture of polymer and precursor was prepared on laboratory rolls. In the second stage, the mixture was heated in a Brabender microextruder in a nitrogen atmosphere at a temperature of 190-200 ° C for 10-12 minutes. [11,12].

The phase composition of the obtained nanocomposites was studied by XRD method. Samples of the initial PE and obtained nanocomposites in the form of films with a thickness of 0.5 – 1.0 mm were prepared for XRD analysis and study into bactericidal properties by pressing at a temperature of 170°C and a pressure of 10 atm.

Note that the X-ray phase analysis (XRD) of the obtained compositions was performed on the “D2 Phaser” instrument of Bruker (Germany).

Results and discussion

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

The phase composition of the obtained nanocomposites was studied by X-ray structural analysis. Figure 1 shows the diffraction patterns of the original PE, as well as PE with zinc and copper-containing nanoparticles. Phase identification was carried out according to the data on inter-planar distances through the use of ASTM card file. It revealed that reflections from the planes of the crystal lattice of metals corresponding to the ASTM series d_{hkl} of copper oxide I (Cu_2O) and zinc oxide (ZnO) were observed in the studied nanocomposites.

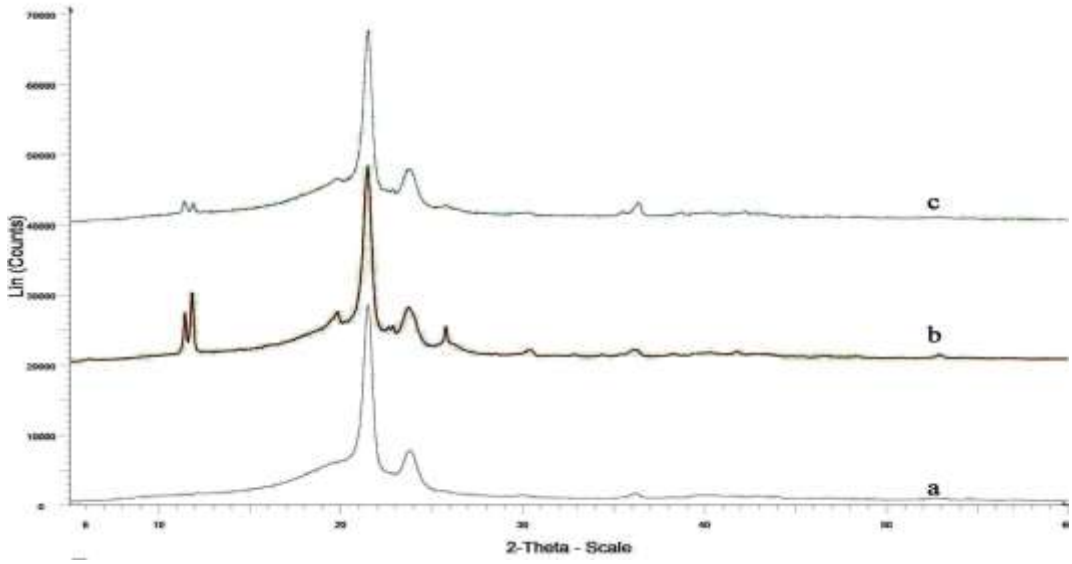

Fig. 1. Diffraction patterns of the initial PE (a), PE with zinc (b) and copper (c) containing nanoparticles

To study the bactericidal properties of obtained composites based on PE containing copper and zinc nanoparticles, micromycetes such as *Aspergillus niger*, *A.ochraseus*, *Penicillium cuclopium*, *Cladosporium herbarium*, *Fusarium moniliforme*, and *F.oxysporium* were used as test cultures. Within two months, metal-containing nanocomposites were placed in a nutrient medium where they were sown with various fungi. After the set time had elapsed, these composites were subjected to microscopic examination for comparison with the surface of the original metal-containing nanocomposites. It found that the metal-containing nanocomposites exposed to the sowing of fungi did not differ from the original composites and no changes were recorded either visually or by microscopic methods. The explorations made are illustrative of long-term resistance of metal-containing nanocomposites to the fungi effects.

Figure 2 shows micrographs of PE-based composites containing copper and zinc nanoparticles: initial and 2 months after seeding. The obtained composites based on PE containing copper and zinc nanoparticles were notable for strong bactericidal properties against gram-positive and gram-negative bacteria: *Aspergillus niger*, *A.ochraseus*, *Penicillium cuclopium*, *Cladosporium herbarium*, *Fusarium moniliforme* and *F.oxysporium.* This apparently makes it possible to use them as antimicrobial additives to purify drinking water from harmful microbes, as well as additives to plastics to impart them bactericidal properties and thus open up new perspectives in the field of packaging materials [13].

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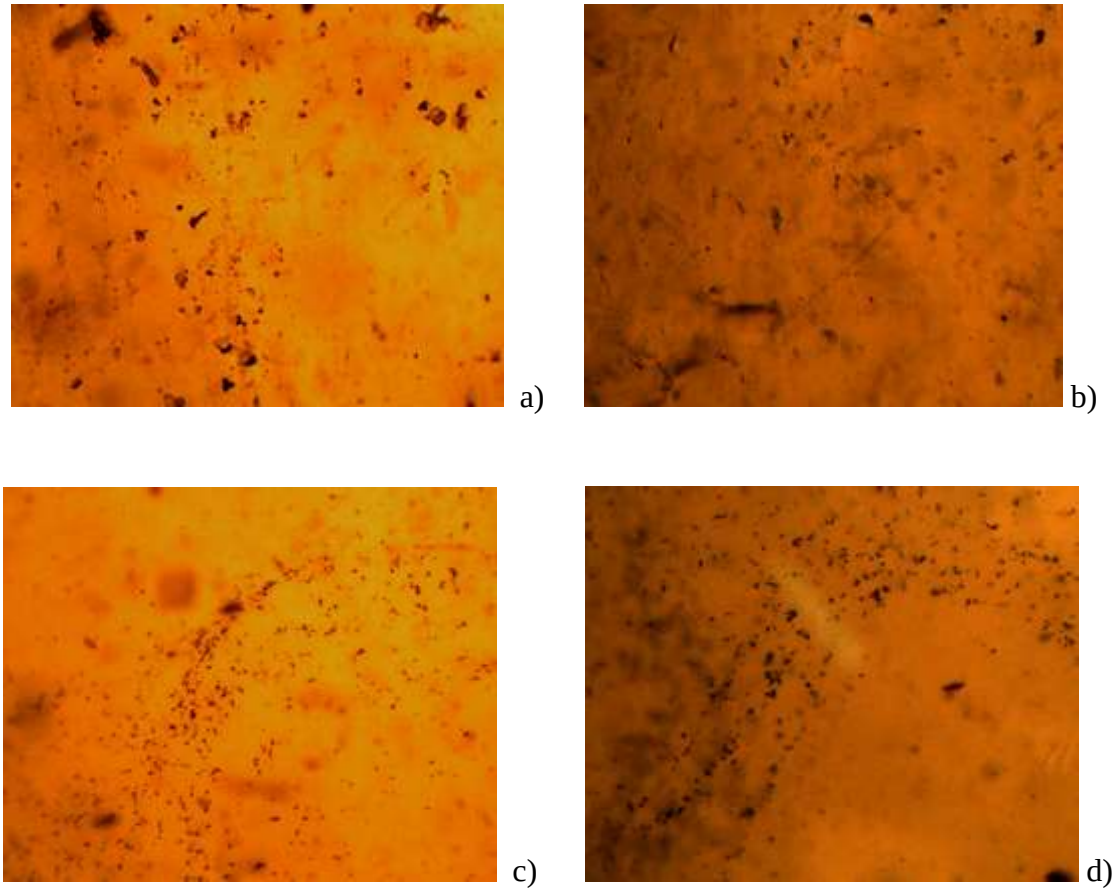

Fig.2 Micrographs of composites based on PE containing copper (a, b) and zinc (c, d) nanoparticles: initial - (a,c) and 2 months after seeding - (b,d).

This apparently makes it possible to use them as antimicrobial additives to purify drinking water from harmful microbes, as well as additives to plastics to impart them bactericidal properties and thus open up new perspectives in the field of packaging materials [13].

Summary

-The conditions for preparation of metal-containing nanoparticles in the matrix of high-pressure polyethylene (PE) through the use of the mechanical-chemical method without the use of organic solvents were presented.

-The composition and structure of the obtained nanocomposites were studied by XRD method. XRD diffraction patterns confirmed the presence of nanoparticles of oxides of zinc and copper on the PE matrix.

-High bactericidal properties of obtained composites based on PE-containing copper and zinc nanoparticles were revealed to suggest that they can be used as antimicrobial additives for purifying drinking water from harmful microbes, as well as additives to plastic masses for imparting bactericidal properties to them.

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YÜKSƏK TƏZYİQ POLİETİLENİ ƏSASINDA METALTƏRKİBLİ NANOKOMPOZİTLƏRİN ALINMASI VƏ ONLARIN BAKTERİSİD XASSƏLƏRİNİN TƏDQİQİ

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Yüksək təzyiq polietileni(PE) əsasında mexaniki-kimyəvi metodla üzvi həlledicilərdən istifadə etmədən üzvi turşu duzlarının yüksəksürətli termiki parçalanması yolu ilə yüksək hərəkət deformasiyası şəraitində metaltərkibli nanokompozitlər alınmışdır. Alınmış nanokompozitlərin faza tərkibi və strukturu rentgen-faza analizi (RFA) metodu ilə öyrənilmişdir. RFA-nın alınmış difraktoqramları polietilen (PE) matrisində sink oksidi (ZnO) və mis(I) oksidi (Cu_2O) nanohissəciklərinin varlığını təsdiq edir.

Sink və mis tərkibli nanokompozitlərin γ-müsbət və γ-mənfi bakteriyalara: Aspergillus niger, A.ochraseus, Penicillium cuclopium, Clodosporium herbarium, Fusarium moniliforme and F,oxysporium. və.s. nəzərən yüksək antibakterial aktivliyi aşkar edilmişdir. Bu onu göstərir ki, onlardan içməli suyun zərərli mikroblardan təmizlənməsi, həmçinin plastik kütlələrə bakterisid xassə vermək üçün əlavə kimi istifadə etmək olar.

Açar sözlər: *metaltərkibli nanokompozitlər, yüksək təzyiq polietileni (PE), sink- və mis oksid nanohissəcikləri, RFA analizi, bakterisid xassələr*

ПОЛУЧЕНИЕ МЕТАЛЛСОДЕРЖАЩИХ НАНОКОМПОЗИТОВ НА ОСНОВЕ ПОЛИЭТИЛЕНА ВЫСОКОГО ДАВЛЕНИЯ И ИССЛЕДОВАНИЕ ИХ БАКТЕРИЦИДНЫХ СВОЙСТВ

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Получены металлсодержащие нанокомпозиты на основе полиэтилена высокого давления (ПЭ) механо-химическим методом без использования органических растворителей путем высокоскоростного термического разложения солей органических кислот в условиях высоких сдвиговых деформаций. Фазовый состав и структура полученных нанокомпозитов исследованы методом рентгено-фазового анализа (РФА). Дифрактограммы РФА подтверждают наличие наночастиц оксидов цинка и меди в матрице ПЭ. Выявлена высокая антибактериальная активность цинк- и медьсодержащих нанокомпозитов по отношению к грамм-положительным и к грамм-отрицательным бактериям: Aspergillus niger, A.ochraseus, Penicillium cuclopium, Cladosporium herbarium, Fusarium moniliforme и F.oxysporium. Это свидетельствует о возможности использования их в качестве антимикробных добавок для очищения питьевой воды от вредных микробов, а также добавок к пластическим массам для придания им бактерицидных свойств.

Ключевые слова: *металлсодержащие нанокомпозиты, полиэтилен высокого давления, наночастицы оксидов цинка и меди, РФА-анализ, бактерицидные свойства*