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Research on Obtaining Nanocomposites Based on High-Density Polyethylene with the Use in Medicine

Shixaliyev Karam Sefi
Kurbanova Nusaba.I.,
Azerbaijan State Oil and Industry University Baku, AZ1010, Azerbaijan, 20 Azadlig Avenue

Abstract
Metal oxide (Cu_2O, ZnO) nanoparticles stabilized in high-pressure polyethylene matrix maleinated by mechanical-chemical method without using organic solvents were obtained and new composite materials based on industrial polymers were obtained by using them as a modifying agent. It has been shown that the properties of metal oxide nanoparticles located in the interphase layer of nanocomposites improve as a result of the interaction of maleinated polyethylene with maleic groups. In the obtained nanocomposites, nanoparticles play the role of a structure promoter and lead to the formation of a relatively small spherulite structure. Nanoparticles of copper (I) oxide and zinc oxide stabilized in a polymer alloy medium - maleinated high pressure polyethylene matrix - were obtained by mechanical-chemical method. Their phase composition and structure were determined by RFA and IR-spectroscopy methods and it was determined that they have bactericidal properties. Metal oxide-containing nanoparticles stabilized in a maleinated high-pressure polyethylene matrix were used as a modifying agent in order to improve the operational properties of industrial polymers (PMP, i-PP, PMP E/i-PP,). It is shown that the main characteristics of the resulting polymer nanocomposite make it possible to obtain various materials and equipment for medical equipment on its basis.фф

Keywords :metal oxide, nanoparticle, high pressure polyethylene, modifying agent

I. INTRODUCTION

Relevance of the topic and degree of development. Development of new polymer composite materials is one of the priority directions of development of modern techniques and technology. The combination of valuable properties of polymer matrixes, such as film formation, mechanical strength, resistance to chemical action and corrosion, and the functionality of nanofillers in one composite makes the obtained material even more promising. Currently, such materials are used in aviation, device manufacturing, medicine and other technological fields.

The study of the properties of systems containing nano-sized particles is very interesting and important both from the point of view of fundamental science and the practical application of such systems in a number of new technologies. Nanoscale objects (nanoobjects) occupy an intermediate position between bulk materials and atoms and show new physical and chemical properties that are characteristic only for the nanoscale state of matter. Studying the technology and properties of new nanocomposites is an urgent problem, and research dedicated to nanomaterials is constantly intensifying.

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The research object of the article is the preparation of metal oxide nanoparticles stabilized in maleinated high-pressure polyethylene matrix, determination of their structure, properties and fields of application. The subject of the research is the preparation and research of nanocomposites based on various industrial polymers using the received nanoparticles as fillers.

To achieve the set goal, the following issues were resolved:

- Preparation of copper (I) oxide and zinc oxide nanoparticles stabilized in maleinated high-pressure polyethylene matrix by mechano-chemical method, study of their structure and properties;
- Production of composites based on high pressure polyethylene using stabilized Cu_2O and ZnO nanoparticles in maleinated high pressure polyethylene matrix, study of their properties;
- Production of isotactic polypropylene-based composites using Cu_2O and ZnO nanoparticles stabilized in maleinated high-pressure polyethylene matrix, investigation of their properties;
- Production of isotactic polypropylene / high pressure polyethylene based composites using Cu_2O and ZnO nanoparticles stabilized in maleinated high pressure polyethylene matrix as fillers, study of their properties;
- Obtaining and studying the properties of isotactic polypropylene/butadiene nitrile rubber-based composites using Cu_2O and ZnO nanoparticles stabilized in a maleinated high-pressure polyethylene matrix;

II. METHODOLOGY

Metal oxide-containing nanoparticles were obtained by a mechanical-chemical method without using a solvent. Metal oxide nanoparticles stabilized in the studied, Maleinated high pressure polyethylene (MHPP) matrix were produced in a Brabender microextruder under nitrogen atmosphere. The structure and composition of polymer nanocomposites were determined by infrared spectroscopy (IR), scanning electron microscopy (SEM) and thermal analysis (TQA, DTA) methods. The phase composition and microstructure of the nanocomposite samples were studied using an X-ray phase diffractometer (RFA), the physical-mechanical properties of the samples were studied using the RMI-250 device, the fluidity index of the alloy was studied using the IIRT (Russia) device, and the heat resistance according to Vik was studied using the Vik device. The thermostability of the studied nanocomposite samples was studied with the help of a Q-1500D derivatograph (MOM, Hungary), and the SEM analysis was done with the help of a JEOL scanning microscope (Japan).

In the presented study, nanocomposites containing high pressure polyethylene ((HPP)) and zinc oxide were obtained analogously to nanocomposites containing (HPP) and copper (I) oxide, and their structure, physical-mechanical properties, fluidity index, and thermal properties of the alloy were studied. The ratio of the components of the nanocomposition is (HPP) /nanofiller (wt.%) = 100/(0.3; 0.5; 1.0). As a nanofiller, zinc oxide nanoparticles stabilized in a maleinated high-pressure polyethylene matrix obtained by a mechanical-

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chemical method in a polymer alloy environment were used. Filler nanoparticles were obtained in an analytical mill of A-11 basic (IKA, Germany) brand. The maximum rotation speed of the mill is 28000 revolutions/min, processing and its duration was 30 seconds.

Determination of the size of the obtained nanoparticles was carried out using a laser analyzer called Mastersizer 3000 (Malvern Instruments, England). The laser diffraction method is used to determine the particle size. The measuring range of the device is from 10 nm to 3500 μm, and the frequency of recording the obtained results is 10 kHz.Production of metal oxide nanoparticles (copper oxides) stabilized in maleinated high-pressure polyethylene matrix by mechanical-chemical method, under conditions of high bending deformation of organic acid salts, by high-speed thermal expansion method, was investigated in two stages.

In the first stage, a binary mixture of polymer and recursor was prepared in laboratory rollers at a temperature of 100-120 °C. For this purpose, the roller is first heated to the required temperature, then maleinated high-pressure polyethylene is gradually added between the rollers of the roller. After melting maleinated high-pressure polyethylene, the reaction mixture is gradually added to the mixture by continuing stirring, and the process is continued for 20 minutes.

In the second stage, after raising the temperature of the used extruder to 120°C, the mixture obtained in the first stage is fed to the extruder in a nitrogen atmosphere. After mixing the mixture for 20 minutes, the temperature of the extruder is raised to 240°C and mixed for an additional 15 minutes. . The work of the extruder is stopped and the received corrosion is removed. The structure and properties of copper metal oxide (Cu_2O, ZnO) nanoparticles in maleinated high-pressure polyethylene matrix were studied.

III. RESULTS AND DISCUSSION

Phase composition and microstructure of HPP -based nanocomposite samples were studied by X-ray phase analysis (RFA). The diffractograms of (HPP) -based nanocomposites containing primary high-pressure polyethylene and zinc oxide were drawn. The primary HPP diffractogram is presented in figure 1,

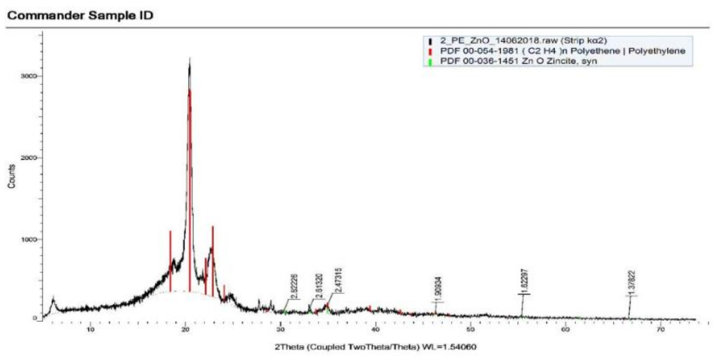

Fig. 1 RFA diffractogram of high-pressure polyethylene-based ZnO-containing nanocomposites

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Reflexes appearing in the diffractogram: reflexes corresponding to polyethylene macromolecule: dhkl 4.11616; 3.73572; 2.97165; 2.48033; 2.34787; 2.25572; 2.22098; 2.17096; 2.10536; 1.93822; 1.71736; 1.66867 A° and reflexes characteristic of zinc oxide nanoparticles according to the dhkl order of the ASTM card: dhkl 2.82266; 2.61320; 2.47315; 1.90834; 1.62297 A° (figure 3.9.) [d -Spacings (20) – 01-071-3645 (Fixed Slit Intensity) - Cu Kα1 1.54056 A. Entry Date: 11/19/2008 Last Modification Date: 01/19/2011]

Thus, the RFA diffractograms confirm the presence of zinc oxide nanoparticles in the YTPE-based zinc oxide-containing nanocomposites we obtained.

Strength limit, relative elongation at break, fluidity index and thermal properties of the studied nanocomposite samples were studied.

Physical and mechanical properties of zinc oxide nanocomposites based on high-pressure polyethylene, heat resistance and fluidity index of the alloy are presented in Table 1.

Table 1. Physico-mechanical properties(PMP) of high-pressure polyethylene-based zinc oxide nanocomposites

Composition of nanocomposites (wt.%) PMP /ZnOMPE	strength limit, σ_q, MPa	Relative elongation at break , ε_q, %	Heat resistance according to Vik, °C	Melt flow index q/10 min.
100/0	11.39	400	130	9.9
100/0.3	12.07	720	140	10.8
100/0.5	13.56	660	135	11.7
100/1.0	11.67	637	128	15.4

As can be seen from the table, the maximum value of the strength index of the nanocomposite containing zinc oxide was observed in the amount of 0.5% by mass of nanofiller, the maximum value of the relative elongation at break and heat resistance according to Vic was observed in the amount of 0.3% by mass of nanofiller, and the maximum value of the fluidity index of the alloy was observed in the amount of 1.0% by mass of nanofiller. Based on the improvement of the strength index and the value of the relative elongation at break in nanocomposites, on the other hand, taking into account that the excessive increase of the TP is unacceptable, the optimal amount of nanofiller was considered to be 0.5% by mass. In the nanocomposite containing zinc oxide, at the optimal amount of nanofiller (0.5% by mass), the strength index is from 11.30 to 13.56 MPa, the relative elongation at break is from 400 to 660%, and the heat resistance according to Vic is from 130 to 135°C. , and the fluidity index of the alloy increased from 9.9 to 11.7 g/10 min. Such improvement in physical and mechanical properties can be explained by the synergistic effect caused by the interaction of MPE and nanoparticles.

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The study of the heat resistance of the obtained nanocomposites according to Vic showed that the inclusion of nanofiller in the optimal amount (0.5% by mass) in the composition of high-pressure polyethylene leads to an increase in the heat resistance index from 130ºC to 135ºC in nanocomposites containing zinc oxide. Further increase of nanofiller leads to decrease of heat resistance index.

At the same time, the amount of nanofiller in the amount of 0.5 wt.% causes an increase in the flow rate of the alloy up to 11.7 g/10 min in nanocomposites containing zinc oxide compared to the initial high pressure polyethylene (9.9 g/10 min). The reason for the improvement of the AAC can be explained by the presence of MPE in the nanocomposite. The improvement of the fluidity index of the alloy of the composition allows it to be processed by pressure casting and extrusion methods.

The effect of the amount of nanofillers with zinc oxide nanoparticles on the thermal properties of nanocomposites obtained on the basis of PMR was studied by the method of thermogravimetric analysis and the experimental results are presented in Table 2.

Table 2 Thermal properties of PMP-based zinc oxide nanocomposites

Composition of nanocomposites (wt.%), PMP /ZnOMPE	$T_{10\%}$, ºC	$T_{20\%}$, ºC	$T_{50\%}$, ºC	$\tau_{1/2}$, dəq.	E_a, kC/mol
100/0	325	350	400	72	120.4
100/0.3	340	365	425	75	130.8
100/0.5	360	370	450	81	135.9
100/1.0	337	360	420	74	132.7

It has been shown that the inclusion of an optimal amount (0.5 wt.%) of zinc oxide nanofiller in the composition, the decomposition temperature T10 corresponding to 10% mass loss is from 325 to 360 ºC; Decomposition temperature T20 corresponding to 20% mass loss is from 350 to 370 ºC; T50 of decomposition temperature corresponding to 50% mass loss is from 400 to 450ºC; causes an increase in half-life ($\tau_{1/2}$) from 72 to 81 min. The activation energy (Ea) of the thermooxidation destruction reaction of the obtained nanocomposites increases to 135.9 kC/mol compared to the activation energy of the thermooxidation destruction reaction of the original high-pressure polyethylene (EaPE=120.4 kC/mol). The improvement of the thermal stability of nanocomposites can be explained analogously to that shown in HPP - based copper (I) oxide-containing nanocomposites. As can be seen from the obtained experimental evidence, the thermal properties of zinc oxide-containing nanocomposites increase up to 0.5 wt.% of nanofiller, and a relative decrease is observed with the subsequent increase of nanofiller. The decrease in the properties of the composites with the increase in the amount of nanofiller can be explained by the fact that the nanoparticles lose their activity to a certain extent by forming agglomerations.

Based on the results of derivative studies, we can say that the inclusion of a metal oxide-containing nanofiller in the composition of the composition leads to an increase in the

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thermal oxidation stability of the obtained nanocomposites, in other words, the inclusion of metal nanoparticles in any polymer matrix increases its resistance to thermal oxidation destruction in air compared to the unfilled polymer.

Comparing the experimental evidence given in Tables 1 and 2, it is known that the thermal indicators of copper(I) oxide-containing and zinc oxide-containing nanocomposites are close to each other, however, the indicators of zinc-containing nanocomposites are relatively high.

As for the physical-mechanical properties, comparing the above (Tables 1. and .2) physico-mechanical and mechanical properties of MHPP -based copper(I) oxide and zinc oxide nanocomposites, it is clear that the copper(I) oxide nanocomposite has better performance.

It was determined that nano-sized metal oxides change the molecular and crystalline structure of thermoplastic MHPP, as a result of which the hardness and heat resistance of nanocomposites increase. The main reason for the increase in hardness and heat resistance of thermoplastic nanocomposites is the formation of chemical bonds between the components of the system - polymer macromolecules and nanoscale metal oxides. Such connections are formed as a result of thermomechanical effect when introducing nano additives into the polymer alloy. Crystallization of the chemically constructed macromolecule occurs at a higher temperature than the original MHPP and results in the formation of a superior crystalline structure of the polymer. At the same time, a new network structure is formed as a result of intermolecular construction in polyethylene. Such transformations in the crystalline structure of the thermoplastic cause an increase in the hardness and heat resistance properties of the nanocomposite.

Thus, analyzing the results of our research on the effect of copper(I) oxide and zinc oxide nanoparticles stabilized in the MHPP matrix on the structure and properties of metal oxide-containing nanocomposites based on high-pressure polyethylene, we can show the following:

- RFA diffractograms confirm the presence of copper(I)- and zinc oxide nanoparticles in composite samples obtained on the basis of high-pressure polyethylene;
- fillers containing copper(I) and zinc oxide nanoparticles stabilized in the maleinated polyethylene matrix were found to have a positive effect on the physical-mechanical, thermal and operational properties of high-pressure polyethylene-based composites;

improvement of strength, deformation and fluidity indicators of the obtained nanocomposites, as well as thermooxidation stability was found. This can be explained by the synergistic effect and the formation of a network structure in the nanocomposite as a result of the interaction of metal oxide-containing nanoparticles with maleic groups in MHPP;

it has been shown that nanocomposites obtained on the basis of MHPP can be processed not only by pressing, but also by casting and extrusion methods under pressure;

-in addition to the promising application of nanofillers containing copper(I) and zinc oxide nanoparticles, stabilized in maleinated high-pressure polyethylene matrix obtained by mechanical-chemical method, as an addition to MHPP, it also expands the application possibilities of obtained nanocomposites;

Nanocomposites obtained on the basis of MHPP have high serviceability, strong deformation, thermophysical properties, and can be recommended as construction materials for the following purposes: as a high-performance material in the manufacture of vehicles, as

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an insulating material for electronics and electrical devices, in packaging of food products, as well as construction materials, for example, barrier materials, weatherproof materials, etc. can be used as

In addition to the above, considering the bactericidal and catalytic properties of nanocomposites containing copper(I) oxide and zinc oxide based on high pressure polyethylene, highly selective catalysts based on them, as well as medical materials, including implants, drug delivery systems, antibacterial for biological medical devices coatings, antimicrobial packaging agents, etc. can be obtained.As can be seen from the obtained experimental results, the thermal and flow properties of nanocomposites containing Cu_2O and ZnO also increase up to 0.5% by mass of nanofiller, a noticeable decrease in the ratio is observed with the further increase of nanofiller. increases and prevents the diffusion of air oxygen.

Thus, the effect of copper and zinc oxide nanoparticles stabilized in the maleinated high-pressure polyethylene matrix on the structure and properties of HPP-based metal-containing nanocomposites showed that the physical-mechanical and thermal properties of the nanocomposites in the maleinated high-pressure polyethylene matrix increased twice.

IV. CONCLUSION

1. It has been shown that the received modified nanocomposites have high performance, deformation, strength, thermophysical properties, can be processed by pressing, as well as pressure casting and extrusion methods, which further expands their application areas.
2. It was determined that the physical-mechanical properties of the obtained nanocomposites increase compared to the initial polymer matrix, the thermal resistance increases by 1.5-2 times, and the fluidity index of the alloy increases by 1.3-1.8 times, which means that copper (I)- and zinc oxide-containing nanoparticles are highly maleated due to the interaction with maleic groups in the pressurized polyethylene matrix, it is related to the creation of a synergistic effect.
3. SEM analysis showed that the metal oxide nanoparticles stabilized in the MPE matrix form a relatively small spherulite structure in the modified nanocomposites by playing the role of structuring agent, and as a result, the physical-mechanical, thermal and operational properties of the obtained nanocomposites are improved.
4. The study of the thermophysical and thermal properties of the obtained nanocomposites showed that when a metal-containing nanofiller of 0.3-0.5 k.h. is included in their composition, the activation energy of the thermooxidation destruction process increases by 1.4-1.7 times, the temperature range of their operation is expanded by significantly increasing the thermostability.
5. Obtained nanocomposites with improved properties are used in mechanical engineering, electrical engineering, medicine, food industry, petrochemical industry, construction, etc. can be recommended for application as a promising material.
6.The main characteristics of the resulting polymer nanocomposite make it possible to obtain various materials and medical equipment on its basis.

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Shixaliyev Kerem Seyfi
Doctor of Technical Sciences
Professor-Academician of the European Academy of Natural Sciences Professor,
Department of Organic Substances and Technology of Macromolecular Compounds Azerbaijan State Oil and Industry University, Baku, Azerbaijan author of 400 scientific articles, 30 textbooks and study guides, 25 discoveries and more than 15 monographs