UDC 541.64:678.7

OBTAINING THE METAL-CONTAINING NANOPARTICLES IN POLYETHYLENE MATRIX BY MECHANO-CHEMICAL METHOD AND STUDY OF THEIR PROPERTIES**S.K.Ragimova***Institute of Polymer Materials, NAS of Azerbaijan**sevincrehimova71@gmail.com*

Received 24.04.2019

Accepted 14.10.2019

Metal-containing nanoparticles in the matrix of high-pressure polyethylene are obtained by the mechanochemical method without the use of organic solvents by high-speed thermal decomposition of salts of organic acids under conditions of high shear deformations. The phase composition and structure of the obtained nanocomposites were studied by X-ray phase, scanning electron microscope, and thermogravimetric analyzes. It is shown that the formation of nanoparticles of metal oxides in the polymer matrix, contribute to the stabilization of the composite, raising the temperature of the onset of its thermal-oxidative degradation. Micrographs of the obtained nanocomposites indicate the formation of layered structures that possess high fracture toughness.

Keywords: *metal-containing nanoparticles, high pressure polyethylene, mechano-chemical method, X-ray phase, scanning electron microscope and thermogravimetric analyzes.*

doi.org/10.32737/0005-2531-2020-2-20-25

Introduction

In recent years, considerable interest has been observed to 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 [1–4].

The most widely described in the literature is the preparation of nanoparticles of *d*-valence metals (copper, zinc, cobalt, nickel etc.) in various polymers [1, 4–6].

One of the methods for the formation of metal polymers is the high-rate thermal decomposition of precursors in a polymer melt solution. In the melt, the short-range order of the structure of the initial polymer is preserved, and the voids present in it become accessible for the localization of the formed particles [4].

The thermal method for producing nanoparticles, based on the decomposition of organic acid salts or organometallic compounds in a polymer medium (the Claspol method) [5], is simple; it can be carried out in a conventional heat-resistant glass flask at $t=300\text{--}350^{\circ}\text{C}$, however, a large amount of solvent is used, the yield of the nanocomposite is low. Vacuum oil (VO-1) is used as a solvent. The obtained samples are separated from the oil by repeated washing by benzene [6].

Due to the stringent requirements of the environmentalists for improving the safety of polymeric materials and the mandatory disposal of industrial waste, we propose an environmental mechano-chemical method for producing nanoparticles of metals without using organic solvents in an extruder – a closed type mixer [7].

The mechano-chemical approach (implementation of nanotechnology "bottom-up") to obtain nanocomposites provides the possibility of creating effective environmentally friendly and resource-saving technologies, since such technological processes are based on not dangerous chemical reactions in the solid phase, i.e. in the absence of solvents and technological operations, associated with their use. In addition, the mechano-chemical method is most suitable for industrial use.

In connection with the above, the use of a mechano-chemical method for the production of nanocomposites is an actual task.

The presented work is devoted to obtaining of metal-containing nanoparticles in the matrix of high-pressure polyethylene by environmental mechano-chemical method without using solvents by decomposing organic acid salts in the polymer medium under conditions of high shear deformations and studying the structure and properties of the obtained nanocomposites.

Experimental part

In the work were used: high-pressure polyethylene brand 10803-020 (PE) – "EP-300" (Azerbaijan), which has the following characteristics: the content of the crystalline phase 60±70%, density 0.94 g/cm³, melt index 1.3, melting point 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 were obtained in two stages by the method of high-speed thermal decomposition of salts of organic acids under conditions of 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 min [8, 9].

The phase composition and structure of the obtained nanocomposites were studied by XRD and SEM methods. For this, samples of the initial PE and the obtained nanocomposites in the form of 0.5–1.0 mm thick films were prepared by pressing at a temperature of 170°C and a pressure of 10 atm.

XRD – analysis of the obtained compositions was performed on the "D2 Phaser" instrument of Bruker (Germany).

SEM studies were performed on a "SEM HITACHIS 3400N" instrument (Japan).

The thermal stability of of nanocomposite samples was studied on a Q-1500D derivatograph by MOM (Hungary). The tests were carried out in an air atmosphere in a dynamic

mode at heating of a sample of 5 deg/min from 20 to 500°C, test charge – 100 mg, the sensitivity of the DTA channels – 250 µV, TG – 100, DTG – 1 mV.

Results and discussion

Nanocomposite polymer materials based on PE 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. Phase identification was performed using interplanar spacing data using the ASTM card file. In the studied nanocomposites was shown that reflections from the planes of the crystal lattice of metals corresponding to the d_{hkl} copper oxide I (Cu₂O) and zinc oxide (ZnO) series were observed

Figures 1–3 show the diffraction patterns of the initial PE, as well as PE with zinc- and copper-containing nanoparticles. The reflexes corresponding to the initial PE are shown: d_{hkl} 4.46422, 4.11452, 3.72300, 2.46971 Å (Figure 1) and reflections characteristic of zinc oxide nanoparticles: d_{hkl} 2.82226, 2.61320, 2.47315, 1.90934, 1.62297, 1.37822 Å (Figure 2), which corresponds to the d_{hkl} zinc oxide (ZnO) series for ASTM files and for copper (I) oxide nanoparticles: d_{hkl} 3.02865, 2.46621, 2.13467, 1.74139, 1.51044, 1.28865 Å (Figure 3), which corresponds to the d_{hkl} series of copper oxide I (Cu₂O) according to the ASTM file [*d*-Spacings (20) – 01-071-3645 (Fixed Slit Intensity) – CuK_{α1} 1.54056 Å. Entry Date: 11/19/2008 Last Modification Date: 01/19/2011].

Fig. 1. Diffractograms of the original PE.

Fig. 2. Diffractograms of PE with zinc-containing nanoparticles.

Fig. 3. Diffractograms of PE with copper-containing nanoparticles.

The size of the nanoparticles was determined using the Create Area command using the program (DIFFRAC.EVA.V3.2) (34 ± 1.0) nm for Cu_2O and (39 ± 1.0) nm for ZnO .

Crystallinity for: PE – 53.2; PE/NP Cu_2O – 48.8; PE/NP ZnO – 49.4.

Figures 4–8 show the SEM-images of original PE and PE with zinc- and copper-containing nanoparticles.

As can be seen from Figure 4, the micrograph of the initial PE is a loose shapeless structure.

From Figure 5 it can be seen how bright formations are present on the background of the polymer matrix – metal nanoparticles, spherical in shape or close to the latter. The particle size distribution is not very wide (2.78, 4.05, 17.1 nm).

As can be seen from Figure 6, a micrograph with copper-containing nanoparticles (5%) indicates the formation of a layered structure. The particle size distribution is not wide (49.3 nm).

In Figure 7, it is seen how on the background of the dark part – the polymer matrix – there are light formations – metallic nanoparticles, spherical in shape or close to spherical. Particle size distribution is not very wide (2.33, 3.5, 3.91, 7.01 nm).

On the Figure 8, a micrograph with zinc-containing nanoparticles (5.0 %) also indicates the formation of a layered structure, which has a high fracture toughness [10]. The particle size distribution is quite wide (17.0, 36.5, 59.7 nm).

Fig.4. SEM image of original PE

Fig.5. SEM image of PE with copper-containing nanoparticles (3%).

Fig.6. SEM image of PE with copper-containing nanoparticles (5%).

Fig.7. SEM image of PE with zinc-containing nanoparticles (3%).

Fig.8. SEM image of PE with zinc-containing nanoparticles (5%).

Figures 5 and 7 demonstrated that with a low content of nanoparticles (3.0 %), they do not interact with each other, since they are separated by a polymer matrix. With an increase in the concentration of nanoparticles (5.0 %) – Figures 6 and 8 – percolation occurs – a charge exchange between particles. When this occurs, the agglomeration of nanoparticles takes place, as well as their interaction with the polymer matrix at the nanoscale, as a result of which its supramolecular structure changes. Micrographs of the obtained nanocomposite indicate the formation of layered structures that have a high fracture toughness [10, 11], that is not characteristic of the initial PE.

Thermo-oxidative properties of metal-containing nanocomposites are studied. Thermal stability of the obtained samples of metal-containing nanocomposites was estimated by the activation energy (E_a) of thermal oxidative degradation, calculated using double logarithmization according to the TG curve [12], by the temperature of 10% (T_{10}), 20% (T_{20}) and 50% (T_{50}) decomposition of the studied samples, and also by their half-life time – $\tau_{1/2}$. The data obtained as a result of thermogravimetric studies are given in the table.

Thermal properties of the studied samples

Composition	Parameters				
	Temperature, °C			Half-life time, min	Activation energy, kJ/mol
	T_{10}	T_{20}	T_{50}		
PE	290	340	380	72	129.35
PE+nanoparticles Cu ₂ O (5%)	300	350	400	76	140.86
PE+nanoparticles ZnO (5%)	310	360	410	78	145.57

As can be seen from the table data, the introduction of nanoparticles of copper and zinc oxides into the matrix of the polyethylene composition contributes to an increase in the decomposition temperature of the samples: T_{10} and T_{20} at 10–20°C, T_{50} at 20–30°C; the half-life time $\tau_{1/2}$ increases from 72 to 76–78 min, the activation energy (E_a) of the decomposition of the thermal-oxidative destruction of the ob-

tained nanocomposites increases by 11.5–16.2 kJ/mol.

It is shown that the introduction of metal nanoparticles into the structure of PE stabilizes the composition, increasing the temperature of the onset of thermal-oxidative degradation by 20–30°C, while the melting point remains almost unchanged and makes up 100°C.

Derivatographic studies have shown that the introduction of metal oxide nanoparticles into PE contributes to the improvement of the thermal-oxidative stability of the obtained nanocomposites.

Summary

Metal-containing nanoparticles in the matrix of high-pressure polyethylene (PE) are obtained by the mechano-chemical method without using organic solvents.

The composition and structure of the obtained nanocomposites were studied using XRD and SEM methods. XRD diffractograms confirm the presence of nanoparticles of zinc and copper oxides on the PE matrix.

Micrographs of the obtained nanocomposites indicate the formation of layered structures that possess high fracture toughness.

Thermogravimetric studies have shown that the introduction of nanoparticles of metal oxides into PE stabilizes the composition, increasing the temperature of the onset of thermal-oxidative degradation by 20–30°C.

References

- Gubin S.P., Yurkov G.Yu., Kosobudsky I.D. Nanomaterials based on metal-containing nanoparticles in polyethylene and other carbon-chain polymers. *Int. J. Materials and Product Technology*. 2005. V. 23. No 1–2. P. 2–25
- Pomogailo A.D. Molekuliarnye polimer-polimernye kompozitsii. *Sinteticheskie aspekty. Uspehi himii*. 2002. T. 71. No 1. S. 5–38.
- Mihailin Iu.A. Polimernye nanokompotcionnye materialy. *Polimernye materialy*. 2009. No 7. S. 10–13
- Gubin S.P. Chto takoe nanochastitcy? *Tendentsii razvitiia nanohimii i nanotekhnologii*. Ros. him. zhurn. 2000. XLIV. No 6. S. 23–31.
- Kosobudskii I.D., Gubin S.P. Novyi tip metallopolimerov – metallicheskie clastery v polimernykh matritsakh. *Vysokomolek. soedineniia*. 1985. A. T. 27. No 3. S. 689–695.

6. Iurkov G. Iu., Kozinkin A.V., Nedoseikina T.I., Shuvaev A.T., Vlasenko V.G., Gubin S.P., Kosobudskii I.D. Nanochastitcy medi v polietilenovoi matritse. Neorgan. materialy. 2001. T. 37. No 10. S. 1175–1179.
7. Tarasova N.P., Nefedov O.M., Lunin V.V. Himiia i problemy ustoichivogo razvitiia i sokhraneniia okruzhaiushchei sredy. Uspehi himii. 2010. T. 79. No 6. S. 491–492.
8. Kurbanova N.I., Alimirzoeva N.A., Guseinova Z.N., Nurullayeva D.R. Ecological Method of Preparation of Metal-Containing Nanoparticles in Polyethylene Matrix. 3st International Turkic World Conference on Chemical Sciences and Technologies. Azerbaijan, Baku. 2017. 10–13 Sept. Book of Proceedings. P. 24–26.
9. Kurbanova N.I., Kuliyeu A.M., Alimirzoeva N.A., Aliyev A.T., Ichenko N.Ya, Nurullayeva D.R. Preparation of copper-containing nanoparticles in polyethylene matrix. 5th Int. Caucasian Symposium on Polymer & Advanced Materials. Georgia, Tbilisi 2017. 2–5 July. P. 91.
10. Berlin A.I. Nekotorye perspektivy razvitiia polimernykh konstruktsionnykh materialov. Vysokomolek. soed. 2010. A. T. 52. No 9. S. 1541–1550.
11. Chvalun S.N. Polimernye nanokompozity. Priroda. 2000. No 7. S. 1–12.
12. Praktikum po himii i fizike polimerov. Pod red. V.F.Kurenkova. M.: Himiia, 1990. 299 s.

MEXANİKİ-KİMYƏVİ METODLA POLİETİLEN MATRİSİNDƏ METALTƏRKİBLİ NANOHISSƏCİKLƏRİN ALINMASI VƏ ONLARIN XASSƏLƏRİNİN TƏDQIQI

S.K.Rəhimova

Yüksək təzyiq polietileni matrisində mexaniki-kimyəvi metodla üzvi həlledicilərdən istifadə etmədən yüksək hərəkət deformasiyası şəraitində üzvi turşu duzlarının yüksək sürətli termiki parçalanması yolu ilə metaltərkibli nanohissəciklər alınmışdır. Alınmış nanokompozitlərin faza tərkibi və quruluşu rentgen faza analizi, skanedic elektron mikroskopu, və termogravimetrik analiz metodları ilə tədqiq olunmuşdur. Müəyyən edilmişdir ki, polimer matrisdə metal oksidi nanohissəcikləri əmələ gəlir ki, onlar da kompozitin stabilliyini artırmaqla onun termooksidləşmə destruksiyasının başlanğıc temperaturunu yüksəldir. Alınan nanokompozitlərin mikrofotografiyaları sübut edir ki, yüksək parçalanma özlülüyünə malik təbəqəli struktur yaranır.

Açar sözlər: metaltərkibli nanohissəciklər, yüksəktəzyiq polietileni, mexaniki-kimyəvi metod, rentgen faza, skanedic elektron mikroskop və termogravimetrik analizlər.

ПОЛУЧЕНИЕ МЕТАЛЛСОДЕРЖАЩИХ НАНОЧАСТИЦ В ПОЛИЭТИЛЕНОВОЙ МАТРИЦЕ МЕХАНО-ХИМИЧЕСКИМ МЕТОДОМ И ИССЛЕДОВАНИЕ ИХ СВОЙСТВ

С.К.Рагимова

Получены металлсодержащие наночастицы в матрице полиэтилена высокого давления механо-химическим методом без использования органических растворителей путем высокоскоростного термического разложения солей органических кислот в условиях высоких сдвиговых деформаций. Фазовый состав и структура полученных нанокomпозитов исследованы методами рентгенофазового, сканирующего электронного микроскопа и термогравитометрического анализов. Показано образование наночастиц оксидов металлов в полимерной матрице, которые способствуют стабилизации композита, повышая температуру начала термоокислительной деградации. Микрофотографии полученных нанокomпозитов свидетельствуют об образовании слоистых структур, которые обладают высокой вязкостью разрушения.

Ключевые слова: металлсодержащие наночастицы, полиэтилен высокого давления, механо-химический метод, рентгенофазовый, сканирующий электронно-микроскопический и термогравитометрический анализы.