INFLUENCE OF GAMMA IRRADIATION ON THE MORPHOLOGICAL PROPERTIES OF HDPE+\%ZrO$_2$ POLYMER NANOCOMPOSITES

A. NABIYEV$^{1,2}$, D. S. LINNIK$^3$, Y. E. GORSHKOVA$^2$, A. M. MAHARRAMOV$^1$, M. BALASOIU$^{2,4}$, A. OLEJNIczAK$^{2,5}$, A. I. IVANKOV$^2$, YU. S. KOVALEV$^{2,6}$, A. I. KUKLIN$^{2,6}$

$^1$ ANAS Institute of Radiation Problems, 9 B. Vahabzade str., AZ1143 Baku, Azerbaijan
E-mails: asifnebi@gmail.com; arifin56@yandex.ru

$^2$ Joint Institute for Nuclear Research, Joliot-Curie 6, 141980 Dubna, Moscow region, Russia
E-mails: asifnebi@gmail.com; Yulia.Gorshkova@jinr.ru; masha.balasoiu@gmail.com; aolejnicchem@gmail.com; ivankov@jinr.ru; kuklin@nf.jinr.ru

$^3$ Donetsk National University, Donetsk, Ukraine
E-mail: linnikus_911@mail.ru

$^4$ “Horia Hulubei” National Institute of Physics and Nuclear Engineering, P.O. Box MG-6, RO-077125 Bucharest-Magurele, Romania
E-mail: masha.balasoiu@gmail.com

$^5$ Faculty of Chemistry, Nicolaus Copernicus University, ul. Gagarina 7, 87-100 Torun, Poland
E-mail: aolejnicchem@gmail.com

$^6$ Moscow Institute of Physics and Technology, MIPT, 141701 Dolgoprudny, Russia
E-mail: kuklin@nf.jinr.ru

Received October 10, 2018

Abstract. The aim of the present work was to investigate the effects of gamma irradiation on the structural and morphological properties of pure high-density polyethylene (HDPE) and HDPE+\%ZrO$_2$ nanocomposites. The structural and morphological properties of the HDPE+ZrO$_2$ polymer nanocomposites were investigated using small-angle X-ray scattering, atomic force microscopy (AFM), and scanning electron microscopy (SEM). Topological studies by AFM are shown that the filler in the composite contains spherical aggregates covered with a layer of polyethylene. The formation of spherulites in the high-density polyethylene and nanocomposites with a low filler content has been established by the SAXS and SEM methods.

Key words: high-density polyethylene, zirconium dioxide, nanocomposite.

1. INTRODUCTION

The development of new multifunctional polymer nanocomposites based on metal oxide fillers, the study of their properties, is an important direction in the chemistry and physics of polymers, as well as in the field of new radiation-resistant materials [1]. Polymer nanocomposites are promising materials for the modern applications in smart microelectronics devices, capacitors, high voltage electrical insulation etc. Nano filler is one of the important additives to improve properties of polymers. High specific surface area of nano fillers induces more interfacial contacts.

Romanian Journal of Physics 64, 603 (2019)
between the molecular chain and the fillers in the nanocomposites. These contacts generate complex interfacial morphology in comparison with the neat polymers [2]. Other advantages of nano fillers are improvement or adjustment of the optical and thermal properties [3]. Addition of inorganic nanoparticles into polymer matrix shows novel and distinctive properties. Materials based on ZrO\textsubscript{2} have a wide range of potential applications in various fields of the economy due to their complex unique physical, chemical and biological properties. Polymer materials filled with ZrO\textsubscript{2} nano powders are extremely relevant and attractive from an economic point of view due to their high strength and functionality [4].

The protective effect of fillers is associated with a simple dilution of the polymer or with their involving in radiation-chemical processes. Filling polymers with nano fillers contributes to a more significant increase in the radiation resistance of composites. The effect of filler depends on these species. The crosslinking of polymers with high gamma radiation has led to many useful applications. It is very interesting to understand that radiation interacts with large molecules of polymers and their modification. In spite of the tremendous number of investigations devoted to this topic, remains great interest in due to radiation processing of polymer nanocomposites materials is a significant step in create of certain modern technologies [5].

The purpose of this work is investigation of the effects of γ-radiation on the morphological of pure HDPE and HDPE+\%ZrO\textsubscript{2} polymer nanocomposites.

2. MATERIALS AND METHODS

New high density polyethylene matrix samples (HDPE+ZrO\textsubscript{2}) were obtained using a crystal zirconium dioxide (ZrO\textsubscript{2}) particles with spherical morphology by thermal pressing method under pressure of 15 MPa and at a temperature of 165°C and then an abrupt cooling in the water-ice system. As a filler it has been used a crystal zirconium dioxide ZrO\textsubscript{2} spherical particles (Sky Spring Nanomaterials, Inc. Houston, USA) with size of 20–30 nm, specific surface area of $S = 35 \text{ m}^2\cdot\text{g}^{-1}$ and density of 5.68 g·cm\textsuperscript{-3}. As a polymer matrix, it has been chosen powdered high-density polyethylene (powder-shaped stamps 20806-024). Its has an average molecular weight of $95 \cdot 10^3$ g·mol\textsuperscript{-1}, crystallinity degree of 60%, melting point of 130°C, and density of 958 kg·m\textsuperscript{-3}. The samples were made as thin film, the thickness and the diameter were 80–100 μm and 5 cm, respectively. The volume fraction of the nano filler was 1, 5, 10, and 20% in the polymer matrix. The thickness and the diameter of the samples were 80–100 μm and 5 cm, respectively.

The samples were irradiated by γ-rays. The irradiation were performed at room temperature with γ-radiation $\text{^{60}}$Co isotope source on the facility PX-γ-30 (ANAS Institute of Radiation Problems, Baku, Azerbaijan). The samples were subjected to various doses from 100 kGy to 500 kGy. The dose rate was 2.7 kGy·h\textsuperscript{-1} during the irradiation [6].
Small-angle X-ray scattering (SAXS): Small angle X-ray scattering experiments were carried out on a Rigaku X-ray instrument with high-speed Cu rotating anode (SMAXS 3000 Point SAXS system, at MIPT, Dolgoprudniy, Russia) using a standard transmission configuration. An X-ray wavelength of $\lambda = 1.54 \, \text{Å}$ was used, resulting a momentum transfer $Q$ in the range of $0.005 – 1.4 \, \text{Å}^{-1}$. SAXS measurements have been carried out at room temperature [7].

Atomic force microscopy: The morphological features of HDPE+ZrO$_2$ polymer nanocomposite films were analyzed by NTEGRA PRIMA microscope at tapping mode with commercial NSG01_Au tips of 10 nm curvature radius (NT-MDT Spectrum Instruments, Zelenograd, Russia) at room temperature. Scan size was $10 \times 10$ microns. Images were taken continuously at a scan rate of 0.3–0.5 Hz.

Scanning electron microscopy: The surface fracture of composite morphology has been studied using cryogenically fractured samples. By immersing the samples in liquid nitrogen, a brittle fracture have been obtained avoiding large deformations in the surface. Distribution of zirconium dioxide nanoparticles in the polymer matrix has been studied by scanning electron microscopy. Morphological studies were performed using JEOL JSM-6490LV SEM instrument, operating at an accelerating voltage of 10–20 kV and EDX analyzer INCA Penta FETx3.

### 3. RESULTS AND DISCUSSION

Before the study of the morphology of high-density polyethylene and HDPE+$\%$ZrO$_2$ nanocomposites, the $\gamma$-radiation induced changes have been studied for the degree of crystallinity, as well as the dimensions and morphology of the crystallites of the polymer. Thus, according to the small-angle X-ray scattering results, it has been observed crystallites of spherical polyethylene with an average size of $19.5 \, \text{nm}$ at an irradiation dose of $0 \, \text{kGy}$ (Fig. 1). Irradiation of pure polyethylene with a dose of $100 \, \text{kGy}$ leads to an increase in the degree of crystallinity of polyethylene. This also indicates an increase in the scattered intensity at small X-ray scattering vectors. The average size of spherulites decreases to $12.5 \, \text{nm}$. Meanwhile, changes in the structure of the composite containing the maximum amount of filler have not observed even at a dose of $300 \, \text{kGy}$. The filler has been monodisperse distributed in the volume of the composite in the range of the scattering vector from $0.015$ to $0.8 \, \text{Å}^{-1}$. The formation of aggregates of the filler particles has been observed only for $Q < 0.015$. The logarithm of the slope of the rectilinear portion of the scattering curve is $-4$, which indicates the absence of a diffuse region between the polymer and the filler. The average particle size of the aggregate particles is about $80 \, \text{nm}$.

Small-angle neutron scattering (SANS) experiments showed that at ambient conditions ZrO$_2$ nanoparticles are mainly distributed as monomers in the polymer matrix and separated by a high-density polyethylene interlayer for all concentrations of filler [8].
Surface morphology changes of polyethylene and composites films have been investigated after gamma irradiation by the AFM method. This method has been chosen not only for the analysis of the filler distribution in the composite, but also for studying the change in polymer viscosity with increasing radiation dose. Figure 2 shows the AFM images of pure HDPE, HDPE+5%ZrO₂ and HDPE+20%ZrO₂ polymer nanocomposite films. Before irradiation, the surface of pure polyethylene has been characterized by the presence of banded texture, which is a replica of the surface of the metal mold. The introduction of 5% filler leads to the formation of oval-shaped cluster structures with an average size of 240 nm and a decrease in the surface roughness of the composite. An increase in the content of the filler affects the increase in the size of cluster structures with an average size of 460 nm and a change in the surface roughness. Irradiation of a pure polymer with a dose of 100 kGy results in a decrease in the surface viscosity of the polymer. This decrease and an increase in the crystallinity of the polymer lead to observation of low-molecular products of radiation and radio-stimulated oxidative degradation of the polymer matrix. Low molecular weight degradation products of the polymer are characterized by greater segmental mobility of the moieties. These type of units affects the decrease in the hardness of the polymer surface. A similar situation has been observed at a dose of 300 kGy. A further increase in the dose of gamma irradiation leads to an increase in the number of cracks and holes on the surface formed during the mechanical destruction of the polymer. It should be noted that after irradiation, the mechanical strength of the polymer has been reduced by a factor of hundreds and the use of the polymer is no longer possible.

The introduction of filler allows eliminating this drawback. The density of the filler is more than 5 times higher than the density of the polymer. Therefore, the filler absorbs more of the γ-radiation. Considering the chemical inertness of zirconium oxide and the absence of transition degrees of zirconium oxidation, the introduction of the filler has a positive effect on the properties of the polymer after irradiation.
Thus, the introduction of 5 wt% of zirconium oxide does not lead to a change in the morphology of the composite after 100 kGy irradiation. The hardness of the surface of the film material decreased for a composite with a filler content of 5 wt. % after 300 kGy and higher irradiations. An increase in the content of ZrO₂ to 20 wt. % allows to retain not the hardness of the composite, but also the morphology of the composite. The size of the cluster structures increases insignificantly from 500 nm (the non-irradiated composite) to 650 nm at an irradiation dose of 500 kGy.

<table>
<thead>
<tr>
<th>Dose (kGy)</th>
<th>HDPE pure</th>
<th>HDPE+5%ZrO₂</th>
<th>HDPE+20%ZrO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
</tr>
<tr>
<td>100</td>
<td><img src="image4.png" alt="Image" /></td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
</tr>
<tr>
<td>300</td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
<td><img src="image9.png" alt="Image" /></td>
</tr>
<tr>
<td>500</td>
<td><img src="image10.png" alt="Image" /></td>
<td><img src="image11.png" alt="Image" /></td>
<td><img src="image12.png" alt="Image" /></td>
</tr>
</tbody>
</table>

Fig. 2 – AFM images of pure HDPE, HDPE+5%ZrO₂ and HDPE+20%ZrO₂ polymer nanocomposite films.
A change in the bulk morphology of HDPE and HDPE+\%ZrO\textsubscript{2} composites before and after irradiation was studied for cleavage of film materials by the SEM method. Figure 3 presents SEM images of pure HDPE, HDPE+5\%ZrO\textsubscript{2} and HDPE+20\%ZrO\textsubscript{2} polymer nanocomposites.

![SEM images of pure HDPE, HDPE+5\%ZrO\textsubscript{2} and HDPE+20\%ZrO\textsubscript{2} polymer nanocomposites.](image)

The chips of the polymers were prepared by cooling in liquid nitrogen, followed by a transverse fracture of the films. SEM results show that a large amount of polyethylene screeds are formed after cooling and fracture of non-irradiated polymer and composites. This indicates the high elasticity of polyethylene even in a glass condition. Introduction of the filler with 1 wt. \% does not lead to the appearance of cluster formations, but leads to morphological changes in the polymer. In this case, the size of the screeds decreases with increasing filler content. The formation of cluster structures is observed for the introduction of 5 wt. \% ZrO\textsubscript{2} and more. Cluster structures are spherical objects consisting of aggregates of zirconium oxide coated with polyethylene in the filler content of 5 wt. \%. In HDPE+20\%ZrO\textsubscript{2}, however, these cluster structures are open cavities of polyethylene containing a filler powder. The rupture of spherical formations in a composite of HDPE+5\%ZrO\textsubscript{2} is not possible due to their low size.
Crucial morphological changes are observed in pure polyethylene with increasing the irradiation dose. Irradiation with a dose of 100 kGy leads to a decrease in the elasticity of the polymer. The formation of sreeds from the amorphous phase is observed only between lamellar structures containing a greater number of crystallites of polyethylene. A further increase in the irradiation dose leads to the fact that the proportion of the amorphous phase decreases and the elasticity of the polyethylene. As shown in the microphotography of HDPE with a dose of 300 kGy, sreed formation on the cleavage surface is not observed. Meanwhile, spherulites of polyethylene with a size of 20 to 70 nm and crystallites with thickness of about 30 nm and a length up to 200 nm are formed. A further increase in the irradiation dose mainly leads to an increase in the content of polyethylene spherulites without a significant change in their size.

A composite with a minimum amount of filler retains the plastic phase of polyethylene only at an irradiation dose of less than 100 kGy. It should be noted that at 300 kGy dose the amount of polyethylene spherulites is much higher than in a pure polymer. The formation of larger crystallites is not observed. An analogous situation is observed for composites with 5 wt. % filler content irradiated with dose of less than 100 kGy. The formation of spherulites and crystallites is no longer observed on the cleavage surface of polyethylene at higher doses. This is due not only to the more significant effect of the absorption of gamma radiation by zirconium oxide, but also to the plasticizing effect of the filler on the polymer matrix. The another reason is related to the high difference in dielectric permittivities of polyethylene and filler ($\varepsilon_{\text{HDPE}} = 2.1$ and $\varepsilon_{\text{ZrO}_2} = 25$). During the formation of composite films, the filler interferes with the crystallization of polyethylene, which are the centers of further growth of crystallites. A further increase in the irradiation dose leads to a mechanical destruction of the filler-polymer cluster structures upon fracture of the composite film. The composites with the filler content of HDPE+20%ZrO$_2$ are subject to the smallest morphological changes. In this case, the presence of the plastic phase is maintained even at the maximum radiation dose. The spherulites and crystallites are not formed. It should be noted that there is a physical interaction of the filler with the polymer at an irradiation dose of more than 300 kGy. In addition to the radiation destruction of the polymer matrix its oxidation is also occurred due to irradiation in air. Meanwhile, oxidation leads to the appearance in the structure of the polymer unit of more polar hydroxy, aldo, keto and carboxy groups, which increase the dielectric constant of the polymer.

4. CONCLUSION

The structural studies by the SEM method of HDPE–ZrO$_2$ based composites showed that the introduction of a polar filler leads to the formation of cluster structures in cellular forms. Inside the cells, there was mainly zirconium oxide, and the clusters were separated by a polymer matrix [8]. An increase in the content of the filler leads to an increase in the dimensions of these structures. It should be noted that
there are no inclusions of filler particles in the bulk of the polymer matrix in the composites. This was related to the permittivity difference between zirconium oxide and polyethylene. The SAXS results show that γ-irradiation of polyethylene leads to an increase in the content of its crystallites. A significant change was not observed even at irradiation doses of 500 kGy in the structure of the polymer of the composite.

Thus, it should be indicated that pure polyethylene under gamma irradiation with a dose of 100 kGy undergoes not only structural but also morphological changes. The structural changes included an increase in the degree of crystallinity, which affects the morphology of polyethylene in the form of reduced elasticity. An increase in the irradiation dose leads to the formation of more polyethylene spherulites and a complete loss of the elastic properties of polyethylene. Introduction 1 wt. % of zirconium oxide changes only the morphology of the composite at low irradiation doses without increasing the radiation resistance of the polymer. Composites with a 5 wt. % of the filler content do not differ morphologically from composites with 1 wt. % filler. However, there is no formation of polyethylene spherulites in the volume of the composite after irradiation with doses above 300 kGy. In addition to the elasticity of polyethylene, the smallest morphological changes in the composite with the filler content of 20 wt. % were observed with increasing irradiation dose. It should be noted that morphological changes were not observed only in the volume of the composite, but also on the surface of the film material. In addition to radiation destruction, processes of polymer oxidation and the formation of plastic low-molecular decomposition products occurred.

Acknowledgements. The work was supported through the JINR-Romania Cooperation Programme Project of 21.05.2018 Order No. 323/92. AFM study was partially supported by JINR-Romania grant No. 321, item 15 from 21.05.2018.

REFERENCES