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Rheological and morphological analysis of irradiated high and low density polyethylene samples

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Abstract: The influence of intensity of the γ-irradiation on commercial high and low density polyethylene (LDPE and HDPE) granules (Kazanorgsintez PJSC, Kazan, Tatarstan, Russia) on their rheological and morphological properties at irradiation doses of 5 and 10 kGy was studied. Experiments in the oscillation mode revealed an increase in the dynamic moduli values with increasing radiation dose compared to the initial samples. At the same γ-irradiation doses, the HDPE samples compared to the LDPE ones showed the greatest changes in rheological properties, while the zero shear viscosity of HDPE increased by order of magnitude compared to the initial one at the irradiation dose of 10 kGy. Morphology analysis of supramolecular structures revealed an increase in cob-web-type structures for the irradiated sample in comparison with the initial sample, which may indicate the formation of branched structures under γ-irradiation.

Keywords: polyethylene; γ-irradiation; cobwebs structure.

INTRODUCTION

Polyethylene is the most usedr polymer material on the global market.[1–3] Most of the low-density polyethylene (LDPE) and high-density polyethylene (HDPE) are supplied to end-product manufacturers in the granular form. In comparison with the powdery and flaky forms, it has significant advantages: high bulk density; flowability, *i.e.*, when dosing, packing, moving, it is not accumulated in equipment units and does not form “dead zones” that lead to process instability and shutdowns; minimization of losses, since it is completely removed from feeding devices; less risk of destruction; no dust formation.

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Due of the growing demand for polymer products, as well as the emergence of new materials with improved characteristics, currently, modification of some properties of polyethylene is required, *i.e.*, improvement of only the necessary features while maintaining the others at the same level.[4–6] γ-Irradiation is one of the known methods for changing the properties of polymers.[7–11] For example,[12] when polypropylene was exposed to a low irradiation dose (up to 200 kGy), it was possible to achieve ~~a~~ higher melt strength and special rheological properties. El-Shamy *et al.* observed an increase in conductivity and improvement in the dielectric properties of polymer films after γ-irradiation.[10] An increase in the viscoelastic properties of polyethylene was observed after γ-irradiation in the range of irradiation doses from 7 to 103 kGy.[13]

As a result of ionizing radiation (irradiation doses of 20, 30 and 35 kGy),[14] some polymers, in particular, polyethylene, are prone to crosslinking, while others (*e.g.*, polypropylene and poly(methyl methacrylate) are more prone to chain breaking and decomposition. It was observed that under certain modes of ionizing radiation, the mechanical strength and hardness of LDPE and HDPE were increase by 40–60 %.[15] In addition, the effects of γ-irradiation on the electric properties of high-pressure polymer films have been studied.[16] The results of experimental studies showed that, after irradiation, cross-connections are formed inside the polyethylene, and carbonyl groups are formed on the surface. This leads to an insignificant increase in the degree of crystallinity and specific volumetric electrical resistance.

As a literature review showed, most of the studies present the results of γ-irradiation of finished polymer products (mainly films). For example, HDPE samples after hydraulic pressing were γ-irradiated in different atmospheres.[17] In another study, small samples were cut from LDPE sheets,[18] their dimensions were 12×50×2.5 mm^3, and then they were processed on industrial equipment; the values of the irradiation dose ranged from 100 to 2000 kGy. Polymer films 40 mm wide,[8] 0.6 and 1.2 mm thick were considered in the study. They were irradiated with a total dose of 25 kGy in a closed glass container. After γ-irradiation, prismatic specimens of 12.5×12.5×25.4 mm^3 for compression testing and specimens of 12.5 mm for tensile testing were extracted from a plate of industrial HDPE.[9]

The present work aims at studying the effect of γ-irradiation intensity on rheological and morphological properties of LDPE and HDPE granules produced by Kazanorgsintez PJSC (Kazan, Russia). Thus, unlike the majority of other authors, the irradiation of granules with subsequent production of disks (diameter 25 mm, thickness 1.2 mm) by pressing was considered. These disks were the objects for investigation in the present study.

EXPERIMENTAL

Materials

LDPE and HDPE granules produced by Kazanorgsintez PJSC, the largest Russian producer of ethylene polymers and copolymers, were taken as the objects of research. LDPE of 15313-003 grade (hereinafter – 153) meets the requirements of GOST 16337-77 (Russia). Technical characteristics of this polyethylene grade: density 0.9185–0.922 kg m^{-3}, melt flow index 0.21–0.39 g per 10 min (measured at the load of 2.16 kg and at the temperature of 463 K); tensile yield limit not less than 9.8 MPa. HDPE of PE2HT76-17 grade (hereinafter referred to as 2HT) corresponds to technical specifications TU 2243-174-00203335-2007 (Russia). Technical characteristics of this polyethylene grade: density 0.955–0.961 kg m^{-3}, melt flow index 2.3–3.3 g per 10 min (measured at a load of 5 kg at a temperature of 463 K); tensile yield limit not less than 26 MPa. For both samples (LDPE and HDPE), the tensile tests were performed using dumbbell-shaped plate specimens with the following dimensions: thickness – 1 mm; the width – 3 mm and length of the narrow part – 40 mm. The dimensions of the current specimens were calculated as the average value of triple measurements.

γ-Irradiation

Irradiation of LDPE and HDPE granules was realized using a RV-1200 radiation unit (Russia). The Co^{60} isotope was the source of γ-radiation. The maximum activity of the irradiator was 2.3×1016 Bq (600 kCi). The installation contained a mechanism for rotating tape blocks, an irradiation chamber, extracted irradiator traverse, ~~a~~ feeding device, tubular elements with radiation sources, ~~a~~ plane irradiator, an assembly chamber, a backup storage, an operator's room, an irradiator storage, ~~a~~ transport device for tape blocks, ~~an~~ annular transport channel, and concrete walls. The samples were placed in an RV-1200 chamber at certain distances from the radiation source. Since these distances were different, the dose of irradiation was also different. Thus, polymers with irradiation doses of 5 and 10 kGy were obtained in the course of the irradiation. During irradiation, polyethylene granules were in 2 kg tissue bags; 2 bags, 2 kg each, were exposed to one dose.

Sample preparation

Before pressing, LDPE and HDPE granules weighing 60–70 g were prepared. The process of manufacturing polymer products by pressing was based on filling a mold cavity with a melt, followed by its compaction due to pressure and cooling. The pressed samples were prepared using a YT-30 RS press. Pressing mode: the temperature was 403.15 K for LDPE and 433.15 K for HDPE; pressure – 100 atm.; process duration – 10 min. When preparing the samples, pre-compaction was performed (*i.e.*, when the pressure dropped, it was increased to 9.806 kPa). Cooling time to the temperature of 303.15–313.15 K was 3–4 min. Plates with the size of 150×150 mm^2 and thickness of 1.2 mm were obtained in sets of five.

Morphology observation

The morphology study of the supramolecular structures of the polyethylene samples was performed on cleaved discs. To prepare the cleavage, the specimens (discs with a diameter of 25 mm and a thickness of 1.2 mm) were submerged in liquid nitrogen for 40 s, after which they were removed and cleaved. The samples fixed on the holder were placed in the chamber of a Quorum Q 150T ES vacuum unit (Quorum, Great Britain). The conductive layer was deposited by cathode sputtering of Au/Pd alloy at a ratio of 80/20. The thickness of the applied layer was 10 nm. The morphology of samples was observed with a Merlin field-emission scanning electron microscope (Carl Zeiss, Germany). The surface morphology was surveyed at an accelerating voltage of primary electrons of 5 kV and a probe current of 300 pA for minimal impact on the object of study.

Parallel plate rheology

The frequency sweep and rotary tests were performed to identify the rheological properties through dynamic modulus (G', G'' / Pa), viscosity curve, and 1st normal stress coefficient of pure and γ-irradiated samples. Rheological measurements were made using a Physica MCR-102 (Anton Paar) instrument at 473.15–493.15 K. The study was performed in an inert environment (nitrogen) to avoid polymer destruction. The predetermined temperature of the sample was controlled and maintained by the lower heating system based on Peltier elements P-PTD200 and the active casing based on Peltier elements H-PTD200 (maintenance error – 0.01 K); a P-ETD400 device was used for temperatures above 473.15 K. This method minimizes temperature gradients in the samples (Anton Paar Physical MCR technical specifications). The PP25 "plate-plate" system was used in the studies; the diameters of the upper and lower plates were 25 mm.

RESULTS AND DISCUSSION

Rheological analysis

The curves of effective viscosity (η), storage (G'), and loss (G'') moduli are shown in Fig. 1. The frequency range (ω) of 0.05-200 rad s^{-1} corresponds to the linear viscoelastic regime when the strain is equal to 5 %.

It is noteworthy that with an increase in the absorbed dose of γ-irradiation, the values of the storage modulus and loss modulus increase, including their position relative to each other. Moreover, the influence of γ-irradiation on HDPE is more significant than that on LDPE. For HDPE, the values of G' and G'' at low frequencies increase by an order of magnitude at the irradiation dose of 10 kGy. For the initial unirradiated LDPE sample, the processing of the obtained data revealed that at the temperature of 473.15 K, the cross over point of G' and G'' is ω^* = 1.26 rad s^{-1}, *i.e.*, $G' > G''$ at $\omega > 1.26$ rad s^{-1} and $G' > G''$ at $\omega < 1.26$ rad s^{-1}; for HDPE this value is ω^* = 36.75 rad s^{-1} (Table I), which is different by an order of magnitude. The table shows the angular frequency values corresponding to the cross over points of G' and G'' distribution for the studied samples at 473.15, 483.15 and 493.15 K. According to the table, for HDPE, there is a sharp shift of the cross over point to the region of low angular velocity, *i.e.*, the material acts as elastic over a wider range of angular velocity.

As expected, exposure to γ-irradiation led to an increase in the effective viscosity, in particular η_0 (Fig. 1a and c). Note that the range of shear rates is limited to 0.4 s^{-1} due to extrusion of the sample through the gap at high shear rates. As illustrated in the figure, for HDPE, the increase in the irradiation dose by 10 kGy led to an increase in η_0 by an order of magnitude, compared to LDPE, despite the fact that the viscosity of the initial samples differed insignificantly. Thus, the obtained results indicate that γ-irradiation is more effective for HDPE-type polymers, which is accompanied by a more pronounced increase in both the values of dynamic moduli and the value of the effective viscosity.

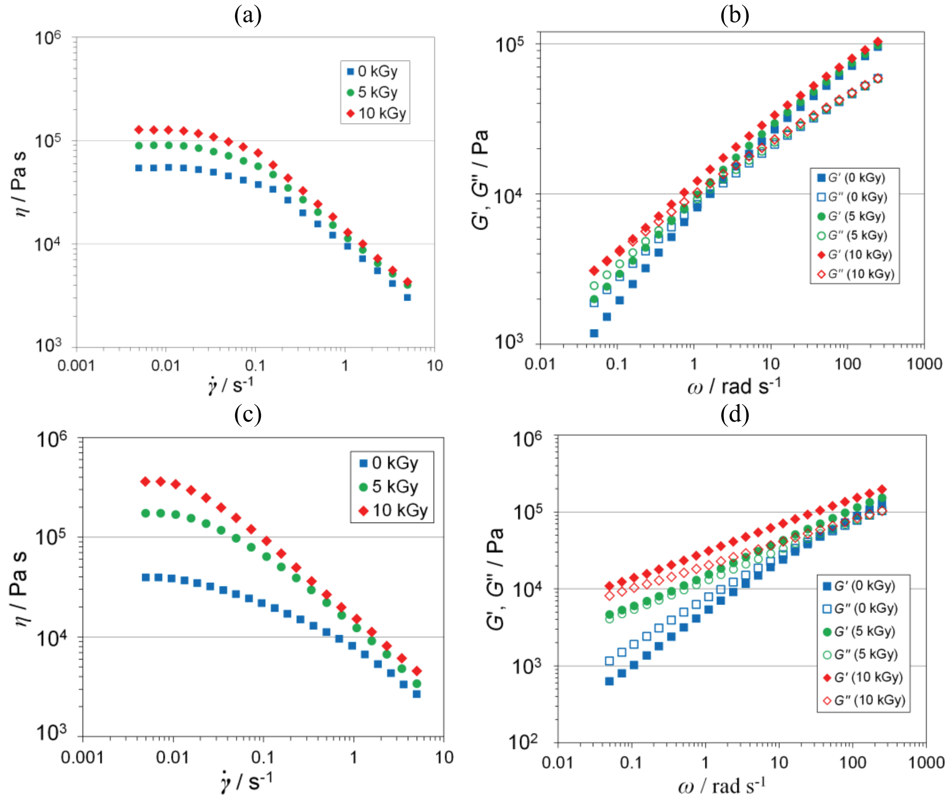

Fig. 1. Viscosity curves (a, c) and dynamic moduli (b, d) for 153 (LDPE, a, b) and 2HT (HDPE, c, d) at a temperature of 473.15 K.

TABLE I. Influence of irradiation dose on cross over point (ω^* / rad s^{-1}) of G' and G''

Sample	Temperature, K	γ / kGy		
		0	5	10
LDPE (153)	473.15	1.26	0.58	0.05
	483.15	1.65	0.59	0.08
	493.15	2.04	0.64	0.13
HDPE (2HT)	473.15	36.75	0.04	$G'>G''$
	483.15	39.5	5.73	0.13
	493.15	46.1	6.27	0.42

Morphological analysis

Changes in the morphology of supramolecular structures after exposure to intense radiation were studied using the HDPE as an example. The photographs were taken at 20000× uniform magnification. The measurements were performed for the cleavages of the initial samples. shows The fibrous objects visible in Fig. 2 could not be attributed to structures such as a mixture of "nodules" and "cobwebs".[19] It was observed that, in the absence of irradiation, during the sample crystallization after pressing, "nodules" and "cobwebs" of a uniform type were formed with an average "cobwebs" diameter of 117.6 nm and a small number of "cobwebs" of small diameter (Fig. 2a). An irradiation dose of 5 kGy leads to the decrease in the average diameter of the "cobwebs" down to 56.4 nm and the increased content of "cobweb" structures. This could be explained by the formation of branched structures on irradiation of polyethylene, which interferes with the structuring of the macromolecules.[20]

(a) (b)

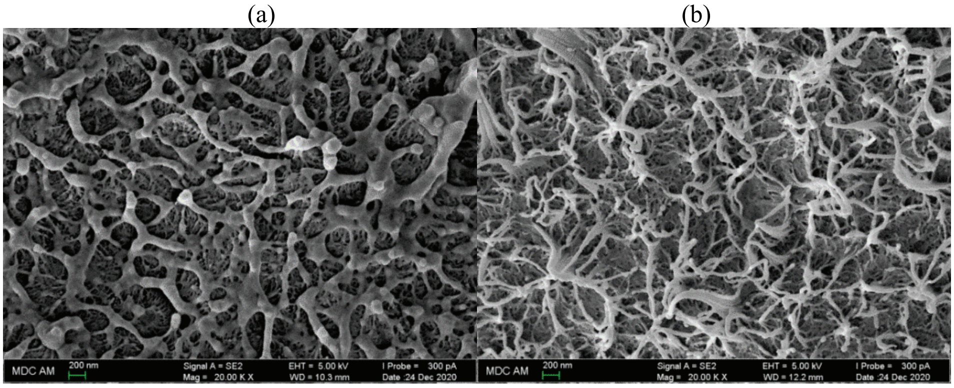

Fig. 2. SEM micrographs of HDPE samples (cleavages) under different irradiation doses: 0 (a) and 5 kGy (b).

CONCLUSIONS

In this work, the rheological and morphological properties of commercial polyethylene samples of LDPE and HDPE grades were analyzed. The studies were performed on samples made by pressing granules that had been exposed to γ-irradiation from the Co^{60} isotope. Experiments in the oscillation mode revealed an increase in storage and loss moduli with increasing radiation dose. The increase in dynamic moduli and effective viscosity for HDPE were more significant, especially at low angular frequencies and shear rates. For both samples (LDPE and HDPE), an increase in the radiation dose was found to lead to a shift in the cross over point for G' and G'' to lower values, *i.e.*, treated samples behave like a solid body at lower angular velocities. Morphology analysis of the supramolecular structures revealed an increase in the cobweb-type structures for the irradiated sample compared to the original one. In this case, the original sample has a structure consisting of nodules and cobwebs. Thus, irradiation of polyethylene granules leads to the formation of branched structures, which seem to interfere with the structuring of the macromolecules on their further path to the final products.

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ИЗВОД

РЕОЛОШКА И МОРФОЛОШКА АНАЛИЗА ЗРАЧЕНИХ HDPE И LDPE УЗОРАКА

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Проучаван је утицај интензитета зрачења комерцијалних гранула LDPE и HDPE (Kazanorgsintez PJSC, Казан, Татарстан, Русија) на њихова реолошка и морфолошка својства у дозама озрачености од 5 и 10 kGy. Експерименти у режиму осцилација открили су повећање вредности динамичког модула са повећањем дозе радијације у поређењу са почетним узорцима. У истим дозама зрачења, HDPE узорци у поређењу са LDPE показали су највеће промене у реолошким својствима, док се вискозност при малим брзинама смицања HDPE повећала за ред величине у поређењу са почетном са дозом озрачености од 10 kGy. Морфолошка анализа супрамолекуларних структура открила је повећање структура типа паукове мреже за озрачени узорак у поређењу са почетним, што може указивати на формирање разгранатих структура под зрачењем.

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