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The influence of hollow iron oxide microspheres on polyethylene climate aging

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Abstract: Creation of biodegradable polymers is one of the most prospective trends aimed at solving problems of polymer waste accumulation and processing, and the development of effective oxo-additives for polyolefin raw materials. It is considered to be one of the most promising ways to ensure accelerated degradation of polymer waste in natural conditions. The present research work studies the effect of nanostructured iron oxide microspheres produced with ultrasonic aerosols pyrolysis on accelerated atmospheric aging of polyethylene. Two types of microspheres were used to modify polyethylene microspheres consisting of X-ray amorphous Fe_2O_3 (initial microspheres after synthesis) and microspheres, consisting of crystalline Fe_2O_3 (heat-treated). Samples of polyethylene modified with microspheres were aged by simulating cyclic climatic effects (temperature, UV, moisture). After the aging of polyethylene modified with microspheres, a higher degree of surface oxidation was discovered using the method of infrared spectroscopy. A strong surface erosion of polyethylene was observed with the addition of microspheres after aging at the same time, untreated polyethylene was preserved almost unchanged. The present study has shown that modification of polyethylene with iron oxide microspheres beyond the end of materials useful life provides its accelerated decomposition under the influence of the main components of atmospheric impact: light, temperature and humidity. At the same time, the complex of mechanical and technological properties of modified polyethylene remained at the acceptable level, which allows using the developed material for the production of packaging, agricultural and landscape films, which will decompose in natural conditions after the end of their lifetime.

Keywords: composites; microspheres; climatic aging; X-ray phase analysis; infrared spectroscopy; thermogravimetric analysis.

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Влияние полых микросфер оксида железа на климатическое старение полиэтилена

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Аннотация: Создание биоразлагаемых полимеров – одно из актуальных направлений в решении проблем накопления и переработки полимерных отходов. Разработка эффективных оксодобавок к полиолефиновому сырью рассматривается как один из наиболее перспективных способов обеспечения ускоренной деструкции полимерных отходов в природных условиях. Исследовано влияние наноструктурированных микросфер оксида железа, полученных методом пиролиза ультразвуковых аэрозолей, на ускоренное атмосферное старение полиэтилена. Для модификации полиэтилена были использованы микросферы двух типов: первый тип на основе рентгеноаморфного Fe_2O_3 (исходные микросферы после синтеза), второй тип на основе кристаллического Fe_2O_3 (термообработанные). Образцы полиэтилена, модифицированного микросферами, состаривали путем моделирования циклических климатических воздействий (температура, УФ, влажность). После ускоренного старения модифицированного микросферами полиэтилена методом инфракрасной спектроскопии обнаружена более высокая степень окисления поверхности. Показана сильная поверхностная эрозия полиэтилена с добавлением микросфер после старения, при этом необработанный полиэтилен сохранялся практически в неизменном виде. Представленное исследование показало, что модификация полиэтилена микросферами оксида железа после окончания срока службы материалов обеспечивает его ускоренное разложение под действием основных компонентов атмосферного воздействия: света, температуры и влажности. При модификации микросферами комплекс механических и технологических свойств полиэтилена остался на приемлемом уровне, что позволяет использовать разработанный материал для производства упаковочных, сельскохозяйственных и ландшафтных пленок, которые после окончания срока службы будут разлагаться в естественных условиях.

Ключевые слова: композиты; микросферы; климатическое старение; рентгенофазовый анализ; инфракрасная спектроскопия; термогравиметрический анализ.

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1. Introduction

Over the past few decades, the demand for plastics has increased significantly due to their low cost, excellent durability and processability. According to *The Economist*, between 1950 and 2015 about 8.3 billion tonnes of different types of plastics was produced worldwide. Currently, only 9 % of plastic materials are recycled and approximately 12 % are incinerated, while 79 % are thrown away as garbage into the environment [1]. This fact creates problems of plastic waste accumulation, which causes enormous damage to various ecosystems. Plastic accumulation is caused by its inability to decompose in natural conditions due to the presence of antioxidants and stabilizers in its composition [2].

The use of degradable materials can be a solution to reduce the accumulation of waste in the environment. These materials can be divided into two groups: those that are inherently biodegradable, whose chemical structure allows direct action by biological enzymes (such as amylase and cellulase), and those that become biodegradable after one or more physical and/or chemical processes, such as hydrolysis, photolysis or pyrolysis [2]. The latter group includes polymeric materials containing prooxidants/degradants known as oxobiodegradable polymers. These materials require oxidative degradation under UV light and heat to reduce their molar mass and form groups that are more easily assimilated by microorganisms [3].

The development of materials that are able to decompose under the influence of environmental factors with the assistance of oxo-additives at the end of their lifetime is one of the promising industrial approaches to the problem of polymer waste accumulation in the environment. As usual, transition metal compounds: Fe, Mn, Co added in stearates form or other organic complexes are used as oxo-additives whose function is to assist the degradation of the material [4, 5]. Inclusion of polar groups and reduction of molecular weight in polymer chains promotes interaction with microorganisms in the environment, turning them into biodegradable materials [3, 4].

The paper by Francisco J. Arráez and colleagues [5] considered the oxidation process of impact resistant polystyrene with the addition of 1.5 and 3 wt. % oxidizable raw material d2w as a pro-oxidant. The active components of this additive are Fe and Mn stearates (metal content (56.71 ± 0.41) and (6500 ± 200) ppm respectively). The authors showed that compositions with 1.5 % oxo-additive exhibited faster degradation than samples with 3 % oxo-additive at temperatures of 50 and 55 °C. A complete loss of mechanical properties of the pro-oxidant samples was noted and the changes were faster with increasing temperature.

The paper [3] investigated the effect of the pro-oxidant additive PDQ-H containing manganese at a concentration of 0.8 wt. % on the accelerated degradation of linear low density polyethylene (LLDPE) and low density polyethylene (LDPE). It was found that for both accelerated degradation and environmental degradation a complete loss of mechanical properties was obtained. Also, by FTIR spectroscopy it was found that due to the simultaneous presence of different degradation products containing carbonyl groups, the carbonyl band becomes wider with increasing degradation time, indicating a significant break in the polymer chains.

The analysis of the literature data shows that a common problem of using oxo-additives is the partial degradation during processing because of elevated temperatures [6, 7]. Thermal stability of samples with oxo additives, which in most studies / papers [8–10] was evaluated by TGA, naturally decreased due to oxodegradation processes leading to the formation of low molecular weight impurities. In this regard, the search for new materials that can perform the role of oxo-additives is an important scientific direction.

Not only the nature of the active metal and its compound, but also the dispersity and distribution of the additive as well as its morphology and specific surface area influence the effectiveness of oxo-degrading additives. In this case, hollow and porous oxide and metal microspheres are considered as a functional additive to various polymeric materials, characterized by a high specific surface area, processability and ease of creating composites with a uniform distribution in a wide range of concentrations and imparting a variety of functional properties [5, 11–16]. The introduction of microspheres based on metals and their compositions used as oxo-additives can provide a similar effect and reduce the period of natural decomposition of polymer composites.

In this regard, the purpose of this article is to investigate the effect of hollow iron oxide microspheres on the accelerated climatic aging processes and the basic mechanical properties of PE.

2. Materials and Methods

2.1. Sample production technology

LDPE in granules (LB7500N LP408294, LG Chem, South Korea) was used as a tested polymer matrix material.

Hollow iron oxide microspheres were obtained by ultrasonic spray pyrolysis at 900 °C. $Fe(NO_3)_3$-$9H_2O$ (chemical grade, RusChem, Moscow, Russia) was used to prepare a 20 % aqueous solution of iron nitrate. The solution was prepared and filtered using a paper filter, and then poured into the tank of a domestic ultrasonic atomizer. The flow rate of the dispersed solution through the steel tube reactor was maintained using an air compressor. A continuous supply of aerosol was carried out until the precursor in the tank was finished. After completion of the process and cooling down the plant elements, a dark red powder was extracted from the filter.

The resulting powder was divided into two equal parts for further removal of unreacted salt residues. The first part was placed in a muffle furnace for further afterburning of salts and recrystallization of microspheres. The second part of the powder was washed with distilled water; an ultrasonic homogenizer was used to better dissolve the iron nitrate in water. The resulting stable suspension was separated by centrifugation. Additionally, the powder was washed with acetone and air dried.

The compositions were prepared by rolling on the laboratory rollers UBL-6175-BL (PRC). The compositions of the tested samples are presented in Table 1.

The duration of mixing the composition was 15 min at roller temperatures of 150 and 140 °C and the gap between the rolls of 0.5–1.0 mm. Having mixed the composition, it was cooled and crushed on a rotary knife mill “Vibrotehnik” (Russia). Then the sample of the composition was dried in a drying cabinet for 30 min at $t = 90$ °C and pressed on a hand press RPA-12 at 180 °C and 150 MPa to obtain homogeneous films of thickness 1.2 mm. The samples of LDPE composites containing 1.25, 2.5, 5.0 wt. % of heat-treated and initial iron microspheres were prepared.

2.2. Analytic methods

The structure of microspheres and composite was studied by scanning electron microscope (SEM) Tescan Vega 3, TESCAN, Brno, Czech Republic with EDX analyzer.

In this paper, the X-ray phase analysis (XRD) was performed on an ARL X'TRA diffractometer (Thermo Scientific, Switzerland) using CuKα radiation ($\lambda CuK\alpha = 0.15412$ nm) in the 2θ angle range (5–60 degrees). Bregg-Brentano measurement

Table 1. LDPE-based composites modified with iron oxide microspheres

Microsphere type	Microsphere content, wt. %		
Initial	1.25	2.5	5.0
Heat-treated	1.25	2.5	5.0

Table 2. Physical and mechanical properties of composites

Tested materials	Microsphere content, wt. %	Relative elongation at the point $F_{\max}$ ($\varepsilon_{\max}$), %	Yield strength σ_s, MPa	Modulus of elasticity E, MPa
Initial LDPE	0.00	576	8.00	128
LDPE filled with heat-treated microspheres Fe_2O_3	1.25	294	5.90	184
	2.50	267	5.86	200
	5.00	140	5.84	162
LDPE filled with initial microspheres Fe_2O_3	1.25	255	5.90	167
	2.50	376	5.90	139
	5.00	411	6.00	168

geometry, step scanning mode (0.02 degree step) at 1.2 was used. XRD based on CuKα radiation and Bregg-Brentano geometry is the most popular of the X-ray phase spectroscopy methods.

The accelerated weathering test was performed via three-factor climatic chamber ATLAS UV-Test (USA) according to ASTM D5208 (cycle B). The single 12-hours test cycle consisted of 4-hour condensation at 50 °C, and then irradiation with UV light for 8 hours at 70 °C. The wavelength of UV lamp was 340 nm and the irradiance was 1.35 $W \cdot m^{-2}$ with humidity of 90–100 %. The total time of weathering was 168 hours (14 cycles).

The IR spectra of the compositions and the initial LDPE before and after exposure in an environmental chamber were recorded using a Bruker Lumos FT-IR microscope macromodule in the spectral range of 4000–600 cm^{-1}.

The thermogravimetric analysis (TGA) was carried out using a synchronous thermal analysis device (TGA/DSC3+, Mettler Toledo, Greifensee, Switzerland) in the temperature range of (+25–+800) °C at a heating rate of 10 $deg \cdot min^{-1}$ in air (100.0 $mL \cdot min^{-1}$). For measurements, a 150 µL aluminum oxide crucible was used; the sample weight was 4–6 mg. The results were processed using the Star SW Lab Mettler software version 16.10 (Greifensee, Switzerland).

The processes of glass transition, cold crystallization, and melting of LDPE and composites were studied by a differential scanning calorimeter DSC 214 Polyma (NETZSCH-Geratebau GmBH, Selb, Germany) according to ISO 11357-3:2018. The heating of the samples was carried out in the temperature range of 20–200 °C at a scanning speed of 10 $°C \cdot min^{-1}$. The weight of the samples was (8 ± 0.5) mg. A temperature scale and an enthalpy of melting were calibrated against indium, zinc, and stannic standard samples.

The analysis of physical and mechanical properties of the compositions was carried out using a universal testing machine DVT (Devotrans, Turkey). For the tests on the pneumatic punching press GT-7016-AR (Gotech testing Machines Inc., Taiwan) the samples of compositions with size 100×10 mm were cut out. A total of 21 samples were prepared: 3 samples for each composition (n = 7). The results of relative elongation, yield strength and modulus of elasticity were obtained automatically from geometrical parameters of samples in Devotrans CKS v2.1.4 software system by a series of at least 5 measurements (samples) as shown in Table 2.

3. Results and Discussion

The phase composition and structure of microspheres powder was investigated with the X-ray diffraction technique (Fig. 1).

The diffractogram of microspheres without annealing does not contain sharp peaks (Fig. 1 – curve *a*), which indicates that the material of the microspheres is amorphous. The diffractogram of annealed microspheres shows high crystallinity of the material (Fig. 1 – curve *b*). The interpretation of the XRD data showed the presence of one phase – hematite Fe_2O_3.

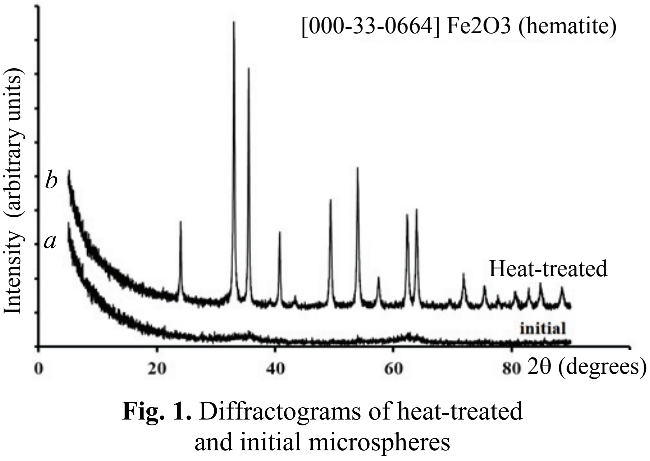
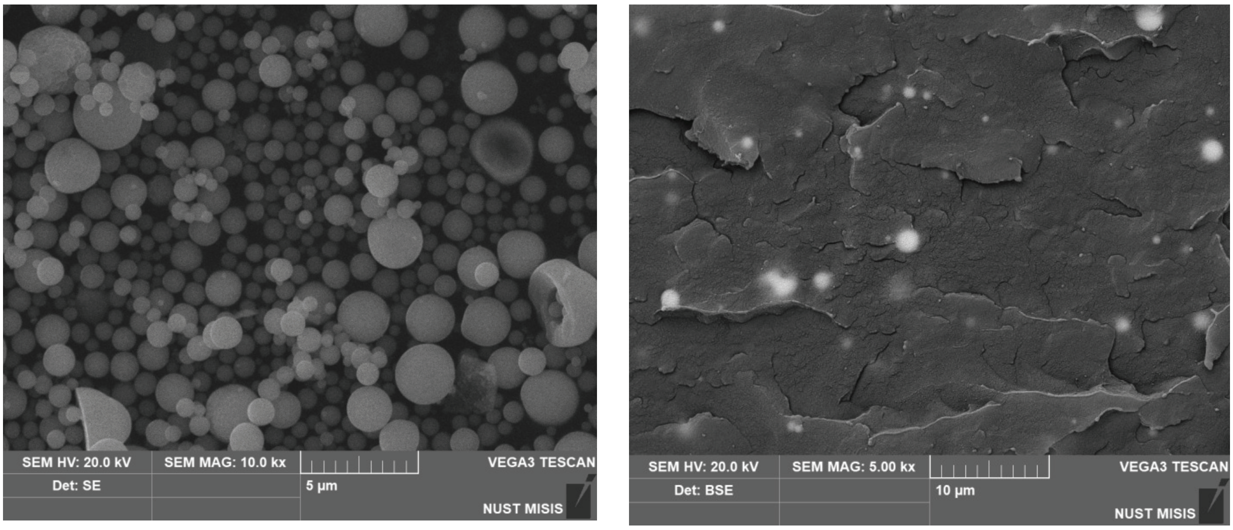


Fig. 1. Diffractograms of heat-treated and initial microspheres



(*a*) (*b*)

Fig. 2. Structure of Fe_2O_3 microspheres (*a*)
and LDPE-based composite (*b*) containing 5.0 wt. % Fe_2O_3 microspheres (brittle fracture)

The obtained microspheres had a hollow structure and an average size from 1 to 4 microns (Fig. 2*a*). In the composite, the spheres were well blended with the binder and, when examining the brittle chip surface (Fig. 2*b*), they cannot be practically detected on the surface. The analysis of the SEM data also did not reveal the presence of aggregates of microspheres. Individual particles are statistically distributed throughout the composite.

The introduction of functional fillers often leads to a decrease in the complex of mechanical properties, so the study of strength properties of the investigated composites was carried out (Table 2). According to the Table 2 it was found that the introduction of microspheres in the whole investigated range of concentrations (from 1.25 to 5 wt. %) does not significantly affect the strength characteristics of polyethylene. Considering the preservation of standard values of physical and mechanical properties when introducing microspheres into the composition of LDPE, as well as their small size and lack of aggregates, the obtained compositions can be used in the production of consumer goods, for example, packaging films, bags.

The main negative influence of traditionally used oxo additives is the reduction of properties and degradation at elevated temperatures during the processing of composites and manufacturing of products from them. Thus, the influence of microsphere-based additives on the heat resistance of polyethylene was investigated (Fig. 3).

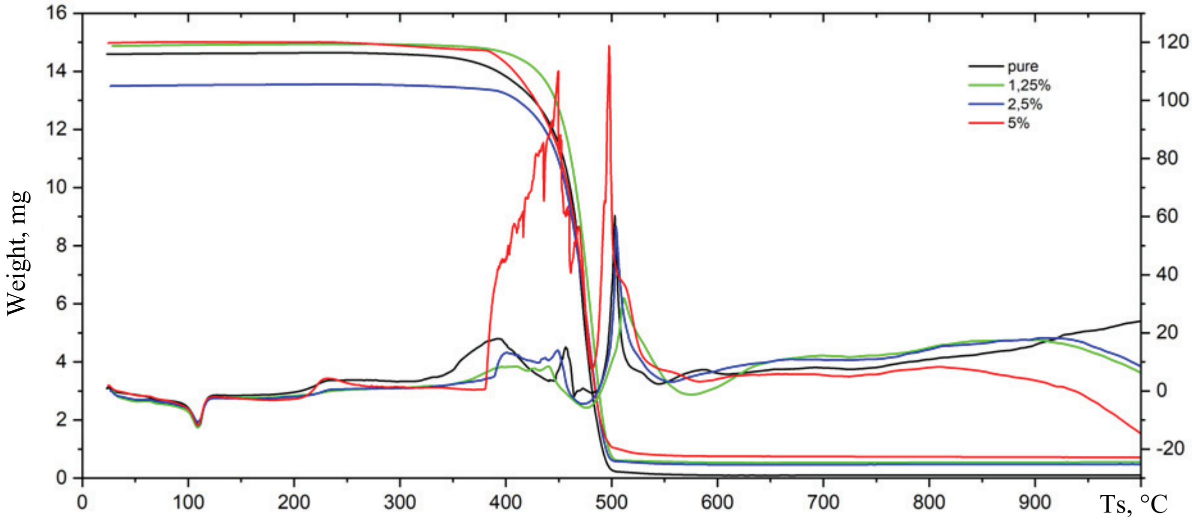


Fig. 3. TGA/DSC curves initial LDPE and LDPE filled with heat-treated microspheres Fe_2O_3

The comparison of mass loss and DSC curves of the investigated samples with the curve of the original LDPE is shown in Fig. 3. The onset temperatures of degradation of microsphere-filled composites, both according to the data of thermal effects and heat fluxes do not differ much from the pure polymer. The main degradation stages occur at temperatures (more than 350 °C), which are much higher than the processing temperature (180–210 °C). Thus, it can be concluded that there is no significant degradation during processing.

The study of DSC curves indicated that the destruction of the composite includes 2 stages: active combustion at temperatures of 330–480 °C, during which about 92–95 % of the mass of samples is lost and some amount of coke residue is formed, which is destroyed at the second stage at 480–550 °C (Figs. 3 and 4*a*). Increasing the content of microspheres leads to an increase in the proportion of coke residue even without considering the mass fraction of filler (Fig. 4*b*). Probably, microspheres play the role of substrate for carbon settling during degradation, and the higher the proportion of coke structures settled on microspheres, the earlier on the temperature scale the degradation process starts (Fig. 4*a*) and the higher the heat flux (Fig. 4*b*).

Composites with different content of heat-treated and initial microspheres were placed in a climatic chamber where they were subjected to cyclic exposure to UV irradiation, elevated temperature and humidity. After this testing for 168 hr. the samples were examined by FTIR spectroscopy (Fig. 5).

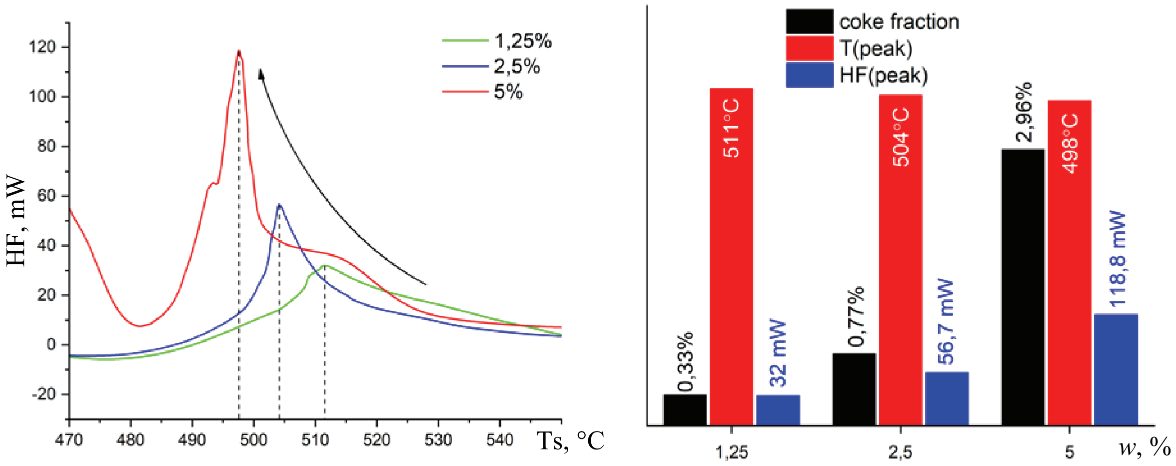


Fig. 4. TGA/DSC curves of LDPE filled with heat-treated microspheres Fe_2O_3

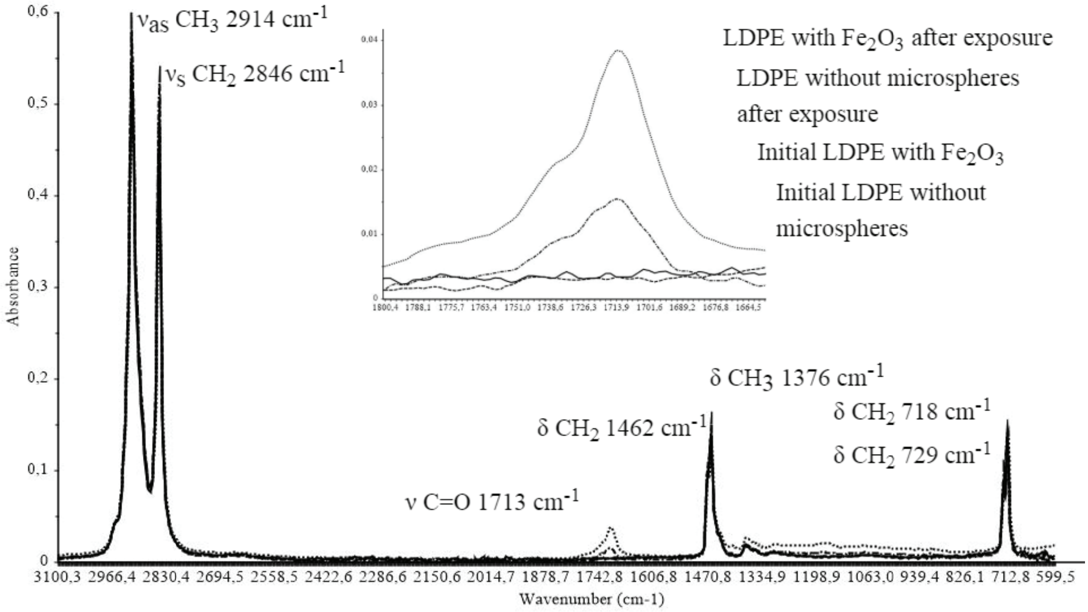


Fig. 5. FTIR spectra of initial LDPE and LDPE composite containing heat-treated Fe_2O_3 microspheres in the range 3100–600 cm^{-1}

The IR absorption peaks on the spectra of PE compositions containing heat-treated and initial microspheres correspond to the typical polyethylene functional groups present in the obtained compositions:

– 2914 cm^{-1} – asymmetric stretching vibrations of CH_2 groups [17];

– 2846 cm^{-1} – symmetric stretching vibrations of CH_2 groups [17];

– 1462 cm^{-1} – bending vibrations of CH_2 groups [18];

– 1376 cm^{-1} – bending vibrations of CH_2 groups [19];

– 729, 718 cm^{-1} – wagging bending vibrations of CH_3 groups.

Absorption peaks characteristic of the C=O bond were not observed on the spectrum of the original PE and the spectra of the composites before exposure.

After exposure in a climatic chamber for 168 hours, an increase in the intensity of the absorption band at 1713 cm^{-1}, corresponding to the C=O group, was observed in compositions with added microspheres. In the case of heat-treated microspheres, the observed effect was slightly higher from compositions with initial microspheres, which may be due to the higher catalytic activity of the heat-treated form.

The band at 1713 cm^{-1} belongs to stretching vibrations of C=O, the change in the intensity of which is traditionally associated with polymer degradation processes [20–22]. In particular, Pablos et al. [22] studied the effect of iron and calcium stearates on the degradation of PE under natural and artificial exposure using FTIR spectroscopy; it was found that PE containing stearates had a significant increase in the intensity of the carbonyl oxygen peak after photoaging. The increase in carbonyl group content leads to a decrease in the level of hydrophobicity of the material surface and promotes accessibility for further not only oxidative but also microbial degradation [21]. Zapata et al. [23] studied the effect of $CaCO_3$ nanoparticles on the photoaging of PENP. In the IR spectra of the photoaged LDPE / $CaCO_3$ composition, there is a strong peak at 1720 cm^{-1}, which is associated with the valence vibration of the C=O carbonyl group. The intensity of the carbonyl bands naturally increased with increasing exposure time of the composition [24, 25].

The study of samples before and after accelerated aging by the DSC method (Fig. 6)

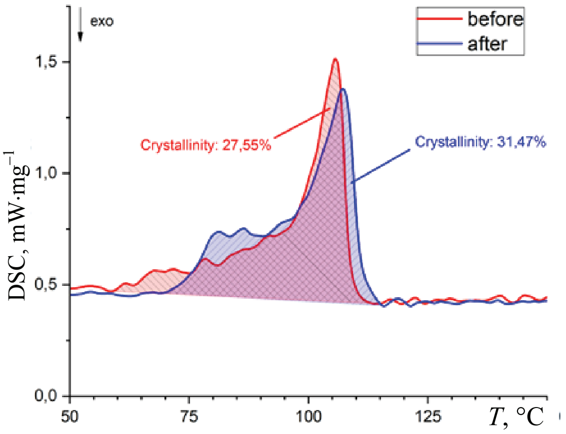
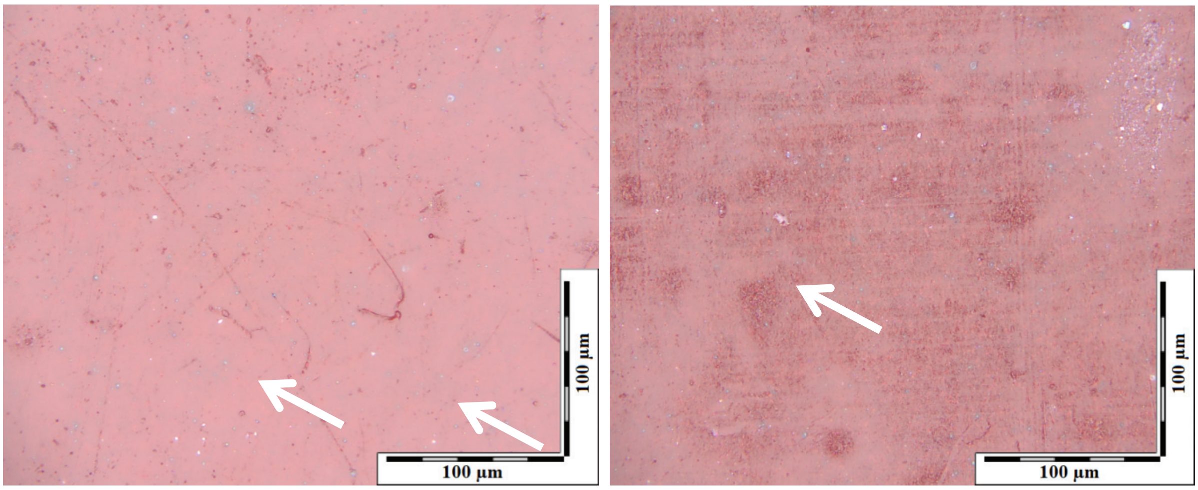


Fig. 6. DSC curves of LDPE composite containing heat-treated Fe_2O_3 before and after accelerated aging. The surface of the samples before and after aging was examined by optical microscopy (Fig. 7)



(a)

(b)

Fig. 7. Surface micrographs of samples with 5 % Fe_2O_3 crystalline spheres (a) before climate chamber, (b) after exposure in the climate chamber (arrows highlight numerous areas of surface erosion)

showed that the degree of crystallinity slightly increased after exposure in the climatic chamber as a result of prolonged treatment at elevated temperature. At the same time, the melting range shows a peak at lower temperatures (76–85 °C), which may be responsible for the melting of partially destructed fragments of branched macromolecules with a lower degree of order and reduced molecular weight. At the same time, the main peak shifted slightly to higher temperatures, which may be due to both measurement error and the possible formation of cross-linked structures that hinder primary melting.

The surface of the samples before and after aging was examined by optical microscopy (Fig. 7).

Microphotographs (Fig. 6) show significant surface erosion after exposure in the climatic chamber. This erosion is presumably related to the oxidation of the polyethylene surface and the occurrence of microcracks and spalling of the oxidized material as a result of cyclic heating and cooling.

Comparing the results with similar approaches, it should be noted that introduction of various additives into the composite composition affects mechanical properties. The aging of polypropylene (PP) composites reinforced with date palm nanofiber was studied by Basheer A. Alshammari and colleagues [26]. In this study [26] the authors showed similar results: strain at break decreased in the modified composites. The paper [27] analyzed the use of the most common metal stearates as additives initiating oxidative degradation of polyolefins. The study found that calcium stearate is most susceptible to oxidative degradation in contrast to zinc and magnesium stearates. The effect of accelerated weathering on poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) and PHBV-based nanocomposites with rutile titanium (IV) dioxide (PHBV/TiO_2) was investigated in paper [28]. In this case the addition of TiO_2 enhanced the mechanical properties of the nanocomposites, the nucleation effect retarded the degradation process under photo and moisture exposure, shifting the degradation process to longer periods of time. Thus, addition of various modifiers to polymer compositions is relevant, and the properties of the developed composites may differ depending on the sphere of application of such material.

4. Conclusion

The present study showed a promising possibility of using nanostructured iron oxide microspheres obtained by spray-pyrolysis of ultrasonic aerosols as an additive accelerating atmospheric aging of polyethylene.

After climatic tests of the original polyethylene and polyethylene modified with microspheres, a higher degree of surface oxidation was observed in the case of the modified material.

The study of the influence of the crystalline structure of iron oxide in the composition of the synthesized filler on the rate of atmospheric aging of polyethylene showed that the use of heat-treated (crystalline) microspheres slightly more effectively increased the intensity of the C=O bond peak on the IR spectra of the composite after aging in the climatic chamber, compared to the X-ray amorphous (initial) spheres.

Optical microscopy of the surface of polyethylene samples before and after aging showed strong surface erosion for polyethylene modified with microspheres, which may contribute to the active reproduction of microorganisms, provoking more intensive biodegradation compared to the original polymer.

The introduction of up to 5 wt. % of microspheres into PE did not lead to a significant change in the properties of the material, as shown by our studies, in connection with which it can be assumed that the developed material can find a wide application for the manufacture of packaging, agricultural and landscape films, which will decompose in natural conditions after the end of the service life.

5. Funding

This research received no external funding.

6. Conflict of interests

The authors declare no conflict of interests.

References

1. The Economist. *The Known Unknowns of Plastic Pollution*. Available from: https://www.economist.com/international/2018/03/03/the-known-unknowns-of-plastic-pollution [Accessed 4 March 2024]

2. Jakubowicz I. Evaluation of degradability of biodegradable polyethylene (PE). *Polymer Degradation and Stability*. 2003;80(1):39-43. DOI:10.1016/S0141-3910(02)00380-4

3. Chiellini E, Corti A, D’Antone S, Baciu R. Oxo-biodegradable carbon backbone polymers – Oxidative degradation of polyethylene under accelerated test conditions. *Polymer Degradation and Stability*. 2006;91(11):2739-2747. DOI:10.1016/j.polymdegradstab.2006.03.022

4. Ammala AJ, Bateman S, Dean KM, Petinakis E, et al. An overview of degradable and biodegradable

polyolefins. *Progress in Polymer Science*. 2011;36:1015-1049. DOI: 10.1016/j.progpolymsci.2010.12.002

5. Arráez FJ, María Luisa Arnal, Müller AJ. Thermal degradation of high-impact polystyrene with pro-oxidant additives. *Polymer Bulletin*. 2018;76(3):1489-1515. DOI:10.1007/s00289-018-2453-4

6. Cowie JMG, Arrighi V. *Polymers*. CRC Press; 2007. 520 p.

7. Contat-Rodrigo L. Thermal characterization of the oxo-degradation of polypropylene containing a pro-oxidant/pro-degradant additive. *Polymer Degradation and Stability*. 2013;98(11):2117-2124. DOI:10.1016/j.polymdegradstab.2013.09.011

8. Al-Salem SM, Al-Hazza'a A, Karam HJ, Al-Wadi MH, et al. Insights into the evaluation of the abiotic and biotic degradation rate of commercial pro-oxidant filled polyethylene (PE) thin films. *Journal of Environmental Management*. 2019;250:109475. DOI:10.1016/j.jenvman.2019.109475

9. Corti A, Muniyasamy S, Vitali M, Imam SH, Chiellini E. Oxidation and biodegradation of polyethylene films containing pro-oxidant additives: Synergistic effects of sunlight exposure, thermal aging and fungal biodegradation. *Polymer Degradation and Stability*. 2010;95(6):1106-1114. DOI:10.1016/j.polymdegradstab.2010.02.018

10. Kyrikou I, Briassoulis D, Hiskakis M, Babou E. Analysis of photo-chemical degradation behaviour of polyethylene mulching film with pro-oxidants. *Polymer Degradation and Stability*. 2011;96(12):2237-2252. DOI:10.1016/j.polymdegradstab.2011.09.001

11. Gusain R, Gupta K, Joshi P, Khatri OP. Adsorptive removal and photocatalytic degradation of organic pollutants using metal oxides and their composites: A comprehensive review. *Advances in Colloid and Interface Science*. 2019;272:102009. DOI:10.1016/j.cis.2019.102009

12. Arshady R. Microspheres for biomedical applications: preparation of reactive and labelled microspheres. *Biomaterials*. 1993;14(1):5-15. DOI:10.1016/0142-9612(93)90015-T

13. Paulose R, Mohan R, Parihar V. Nanostructured nickel oxide and its electrochemical behavior – A brief review. *Nano-Structures & Nano-Objects*. 2017;11:102-111. DOI:10.1016/j.nanoso.2017.07.003

14. Overcash JW, Suslick KS. High surface area iron oxide microspheres via ultrasonic spray pyrolysis of ferritin core analogues. *Chemistry of Materials*. 2015;27(10):3564-3567 DOI:. 10.1021/acs.chemmater.5b00766

15. Jakubowicz I, Yarahmadi N, Arthurson V. Kinetics of abiotic and biotic degradability of lowdensity polyethylene containing prodegradant additives and its efect on the growth of microbial communities. *Polymer Degradation and Stability*. 2011;96(5):919-928. DOI:10.1016/j.polymdegradstab.2011.01.031

16. Fontanella S, Bonhomme S, Brusson JM, Pitteri S, et al. Comparison of biodegradability of various polypropylene films containing pro-oxidant additives based on Mn, Mn/Fe or Co. *Polymer Degradation and Stability*. 2013;98(4):875-884. DOI:10.1016/j.polymdegradstab.2013.01.002

17. Gulmine JV, Janissek PR, Heise HM, Akcelrud L. Polyethylene characterization by FTIR. *Polymer Testing*. 2002;21(5):557-563. DOI:10.1016/S0142-9418(01)00124-6

18. Benítez A, Sánchez JJ, Arnal ML, Müller AJ, et al. Abiotic degradation of LDPE and LLDPE formulated with a pro-oxidant additive. *Polymer Degradation and Stability*. 2013;98(2):490-501. DOI:10.1016/j.polymdegradstab.2012.12.011

19. Amelia RPD, Gentile S, Nirode W, Huang L. Quantitative analysis of copolymers and blends of polyvinyl acetate (PVAc) using fourier transform infrared spectroscopy (FTIR) and elemental analysis (EA). *World Journal of Chemical Education*. 2016;4(2):25-31. DOI:10.12691/wjce-4-2-1

20. Minaeva VA, Minaev BF, Baryshnikov GV, Romeyko OM, Pittelkow M. The FTIR spectra of substituted tetraoxa[8]circulenes and their assignments based on DFT calculations. *Vibrational Spectroscopy*. 2013; 65:147-158. DOI:10.1016/j.vibspec.2013.01.001

21. Luo M, Olivier GK, Frechette J. Electrostatic interactions to modulate the reflective assembly of nanoparticles at the oil-water interface. *Soft Matter*. 2012;8(47):11923-11932. DOI:10.1039/C2SM26890F

22. Pablos JL, Abrusci C, Marín I, López-Marín J, et al. Photodegradation of polyethylenes: Comparative effect of Fe and Ca-stearates as pro-oxidant additives. *Polymer Degradation and Stability*. 2010;95(10):2057-2064. DOI:10.1016/j.polymdegradstab.2010.07.003

23. Zapata P, Palza H, Díaz B, Armijo A, et al. Effect of $CaCO_3$ Nanoparticles on the mechanical and photo-degradation properties of LDPE. *Molecules*. 2018;24(1):126. DOI:10.3390/molecules24010126

24. Miyazaki K, Arai T, Shibata K, Terano M, Nakatani H. Study on biodegradation mechanism of novel oxo-biodegradable polypropylenes in an aqueous medium. *Polymer Degradation and Stability*. 2012;97(11):2177-2184. DOI: 10.1016/j.polymdegradstab.2012.08.010

25. Li J, Yang R, Yu J, Liu Y. Natural photo-aging degradation of polypropylene nanocomposites. *Polymer Degradation and Stability*. 2008;93(1):84-89. DOI:10.1016/j.polymdegradstab.2007.10.022

26. Alshammari BA, Alothman OY, Alhamidi A, Jawaid M, Shaikh HM. Effect of accelerated weathering on the thermal, tensile, and morphological characteristics of polypropylene/date nanofiller composites. *Materials*. 2022;15(17):6053. DOI:10.3390/ma15176053

27. Ovchinnikov VA, Abushahmanova ZR, Mastalygina EE, Pantyuhov PV, et al. Kinetic features of oxidative degradation of polyethylene at addition of stearates of various transition metals. *Vse Materialy. Entsiklopedicheskiy Spravochnik = Polymer Science, Series D*. 2024;1:31-36. DOI:10.31044/1994-6260-2024-0-1-31-36 (In Russ.)

28. Antunes A, Popelka A, Aljarod O, Hassan MK, Kasak P, Luyt AS. Accelerated weathering effects on poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) and PHBV/TiO_2. *Nanocomposites. Polymers*. 2020; 12(8):1743. DOI:10.3390/polym12081743

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