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INFLUENCE OF 2,5-DIHYDROXY-2,5-DIMETHYLHEXYNE-3 ON THE THERMO-OXIDATING PROPERTIES OF LOW DENSITY POLYETHYLENE AND ITS COMPOSITE MATERIALS

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Abstract: *The paper presents results of the study into the effect of 2,5-dihydroxy-2,5-dimethylhexyne on basic physicomechanical characteristics of compositions based on polyolefins and synthetic rubbers. As polyolefins there was used low density polyethylene, polypropylene, and as synthetic rubbers - nitrile-butadiene rubber, styrene-butadiene rubber, butyl rubber. It found that during the processing of LDPE and DDH compositions on rollers, a physicochemical and partially chemical interaction occurs between DDH and LDPE molecules which leds to an improvement in the physicomechanical, thermophysical parameters, as well as the rheological properties of the obtained materials. It revealed that the introduction of 2,5-dihydroxy-2,5-dimethylhexyne helped to increase the thermo-oxidative stability of composite materials. It I shown that in the presence of synthetic rubber, the compositions were more susceptible to thermo-oxidative aging.*

Keywords: *ultimate tensile strength, elongation at break, thermo-oxidation, viscous-flow state, thermal ageing.*
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Introduction

With the development and improvement of engineering and mechanical engineering, aviation, military, automotive, space technology, etc. more and more attention of scientists and specialists began to attract research works aimed at developing new types of polymer materials that sometimes had unexpected and useful properties. The latter circumstance became possible as a result of mixing different in nature polymers produced in the polymer industry [1-5]. In this case, it seemed possible to significantly affect the change in the micro- and macrostructure of the obtained composite materials, and respectively their properties. However, the mixing of polymers in an extruder or on rollers does not mean that it is possible to obtain polymer compositions with improved properties with any combination.

Polymeric composite materials combine beneficial properties of mixture components as a result it is possible to vary their physical and physic-mechanical characteristics by varying the ratio of mixture components and modifiers in a fairly wide range. However, this approach does not always allow achieving desired results, since the whole problem rests on the technological compatibility of the mixture components. This is due to many factors: the difference in molecular weight, effective viscosity and melting point of the original polymer components, polarity and ability to inter-diffuse heterogeneous macro-segments in the melt, resistance to thermo-oxidative degradation and structuring which are most manifested in the process of mixing and processing by methods of injection molding and extrusion [6, 7].

Structural-chemical modification of industrial polymers and composite materials based on them with low molecular, weight unsaturated functional compounds allows to obtain polymer materials with improved performance properties [1, 5]. In recent years, special attention has been paid to the modification of industrial thermoplastics using unsaturated compounds containing various functional groups [8, 9].

In this connection, the aim of this work was to study the development and modifiers can significantly improve the properties of composite materials based on polymer blends.

Experimental part

The work presents results of the preparation of compositions based on low density polyethylene (LDPE) grade 15803-020 of the Sumgayit production "Orgsintez", melt flow index (MFI) 4.5 g / 10 min.

Isotactic polypropylene **(PP)** with MFI = 6.48 g / 10min, density 907 kg / m^3, ultimate tensile strength 32.6 MPa, elongation at break 205 %, flex strength 27 MPa, heat resistance 151°C.

Nitrile butadiene rubber **(SKN-40)** is a synthetic polymer with 40% acrylic acid nitrile (NAA) content. This is the product of the radical copolymerization of butadiene with NAA in an aqueous emulsion.

Butyl rubber **(BR)** - a synthetic rubber obtained based on isobutylene. Usually under this name are implied copolymers of isobutylene with isoprene 2-5%.

Styrene-butadiene rubber **(SSR)** is one of the highest volume production the synthesis of which is carried out in emulsion by free radical mechanism. SSR ("styrene synthetic rubber") refers to non-crystallizable copolymers of irregular structure with statistical distribution of monomer units.

As the modifier, we used 2,5-dihydroxy-2,5-dimetilhexyne-3 **(DDH)** with T_{mp} = 368-370 K synthesized by us. This unsaturated diol of acetylene series of a symmetric structure was obtained and identified by the method described in [3].

Mixing of the polymer blends and DDH performed on the friction roll at a temperature 130-150°C, rolling time 15 minutes. Pressing plates for testing the physical-mechanical properties were carried out at a temperature of 160-170°C.

Ultimate tensile strength, elongation at break was determined on a tensile testing machine RM-500 in accordance with GOST 11262-80.

The melt flow index (MFI) was determined on a MELT FLOW TESTER, CEAST MF50 (INSTRON, Italy) brand rheometer at a temperature of 190°C and a load of 5 kg.

Thermal aging of the samples was carried out at 80°C in an oven. Periodically, every 50 hours of thermal aging, the samples in the form of blades were checked for property changes.

Results and discussion

It was interesting at the beginning to consider the effect of the concentration of DDH on the initial LDPE. Since one of the main indicators in the process of processing polymer materials is the change in melt flow, the MFI of the initial and modified samples of LDPE was determined first of all (Table 1). It can be seen from obtained results that the MFI values increase upon transition from initial LDPE to its modified DDH samples. At the same time, with an increase in the amount of modifier from 1.0 to 5.0, mass particles per 100 mass particles of LDPE, the MFI of the samples decreases from 7.4 to 4.8 g / 10 min. This means that the modifier in LDPE has two functions - it has a plasticizing effect and acts as a dynamically vulcanizing agent for increasing intermolecular physicochemical interaction. However, the chemical interaction of DDH with LDPE macromolecules is not ruled out, because DDH molecules have highly reactive hydroxyl groups and a triple bond.

Table 1. Some physico-mechanical properties of the initial and modified polyethylene.

№	Composition formulation		Ultimate tensile strength, MPa	Elongination at break, %	MFI, g/10min
	LDPE	DDH			
1	100	-	11.5	550	4.5
2	100	1.0	12.9	580	7.4
3	100	3.0	13.4	852	6.1
4	100	5.0	12.3	716	4.8

It was found that complete mixing of the components on the rollers is achieved within 10-15 minutes. A further increase in temperature and mixing time leads to partial destruction of LDPE. The results of studying the tensile strength of the samples indicate that with the loading of DDH into the composition of LDPE, the ultimate tensile strength (σ) increases. With an increase in the DDH content from 1.0 to 5.0 particles, the change in σ of the modified LDPE samples has an extreme dependence. A similar dependence is found between the relative elongation of the sample under tension (ε) and the content of DDH in the composition. The best results of σ and ε are achieved with the introduction of 3.0 phr of modifier per 100 phr of LDPE.

The results of studying the thermo-oxidative degradation of the initial and modified LDPE show that the loading of DDH into the composition of LDPE improves the thermo-oxidative stability of the polymer, i.e., the values of mass loss and the rate of destruction at the same temperatures are reduced (Fig. 1). Intensive destruction of the initial LDPE begins at 200°C, and for modified samples of LDPE at 235°C. On the DTA curves during thermo-oxidative degradation of modified LDPE samples in the range 107-112°C, a minimum is manifested associated with softening and the transition of the samples to a viscous flow state, i.e. the loading of small amounts of DDH into the composition of LDPE practically does not affect the temperature range of softening of the polymer. Noticeable processes occur starting from 150°C. However, intense heat is detected in the temperature range 215-327°C. These results are in good agreement with the results of TGA during thermo-oxidative degradation of modified LDPE samples.

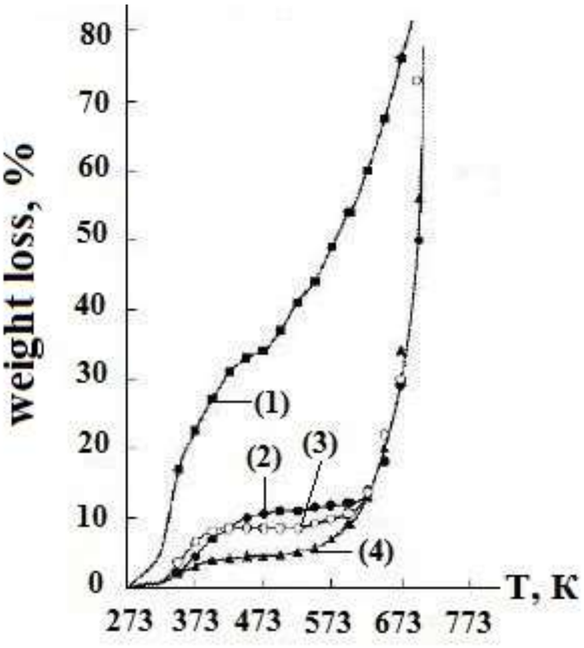

Fig. 1. TGA curves during thermo-oxidative degradation of the initial LDPE and its modified samples. 1 - initial LDPE, modifier content 1.0 phr (2), 3.0 phr (3), 5.0 phr (4).

Apparently, this is due to the fact that DDH in the composition of the compositions exhibits an antioxidant effect on the processes of thermooxidative degradation. There is reason to believe that, as a result of the thermomechanical action, the DDH molecules interact with the macromolecules of polyethylene during the processing of the compositions. As a result of the physicochemical and partially chemical interaction, the DDH functions as a dynamically vulcanizing component [10, 11]. In addition, functional groups - hydroxyl groups and a triple bond of the modifier actively interact with intermediate radicals and hydroperoxide groups arising from LDPE thermo-oxidative processes.

As a result of combined actions of these factors, the radical-chain processes of thermo-oxidative destruction of LDPE are inhibited, and the rate of destruction decreased, and the initial temperature of intense destruction shifted toward higher temperatures.

The resistance of polymeric materials to high temperatures is the main indicator that determines their operational properties. In this regard, the thermal aging of the initial and modified samples of LDPE was studied. Thermal aging of these samples was studied at 80°C for 10; 50; 100 and 150 hours.

Physical-mechanical properties of the samples after thermal aging at different durations of temperature exposure are given in Table-2. According to the data, modified samples exhibit relatively greater resistance to thermal aging than the initial LDPE. For example, after 50 hours of exposure to the temperature (80 ° C), the values of σ and ε of the initial and modified 3.0 and 5.0 phr DDH of polyethylene are respectively - (initial) 8.0 MPa and 50%; 11.5 MPa and 600%; 10.0 MPa and 500%.

Table 2. Some physical-mechanical properties of modified LDPE before and after thermal aging at 353 K.

Composition formulation	Before thermal aging		Duration of thermal exposure, hour							
			10		50		100		150	
	σ, MPa	ε, %	σ, MPa	ε, %	σ, MPa	ε, %	σ, MPa	ε, %	σ, MPa	ε, %
100LDPE+ 3DDH	13.4	890	12.5	795	11.5	580	10.0	490	9.5	375
100LDPE+ 5DDH	12.3	715	11.5	680	10.0	485	9.0	385	8	280
Initial LDPE	11.5	550	10.9	100	8.0	50	-	-	-	-

The obtained data indicate that DDH exhibited simultaneously the properties of a plasticizer which, as you know, contributes not only to the increase of thermo-oxidative stability of the compositions but also favorably affects the improvement of their processability. The DDH molecules distributed in the inter-spherolite space block macro-chains in the amorphous region from thermo-oxidative degradation. This circumstance allows us to interpret the fact of the stability of the modified composites as thermal aging.

It was interesting to study the effect of DDG on thermo-oxidative stability of composite materials based on a mixture of polymers: LDPE + PP + SKN, LDPE + PP + SSR, LDPE + PP + BR. It was important to find out how significant the role of each of components of the mixture in changing the thermo-oxidative stability. Table 3 shows the results of experimental studies of the thermal aging process of the above composite materials. Analyzing the data presented in this Table, it can be noted that at 80°C the presented composite materials ambiguously respond to an increase in the thermal aging time.

Table 3. Effect of the thermal aging duration on ultimate tensile strength (σ) and elongation at break (ε) of polymer mixtures based on polyolefins and various elastomers at 90°C of modified DDH

Composition formulation, Phr	Before thermal aging		Duration of thermal exposure, hour							
			10		50		100		150	
	σ, MPa	ε, %	σ, MPa	ε, %	σ, MPa	ε, %	σ, MPa	ε, %	σ, MPA	ε, %

100LDPE+10PP+ 5SKN+3DDH	10.6	80	10.8	80	11.0	70	10.7	55	9.6	50
100LDPE+10PP+ 5SSR+3DDH	11.3	90	11.5	90	12.1	80	10.6	40	9.5	40
100LDPE+10PP+ 5BR+3DDH	11.9	110	12.2	100	11.2	90	10.3	75	9.8	65

With 50-hour aging, a certain increase in the ultimate tensile strength is observed, and a further increase in the aging time is accompanied by a decrease in the strength and elongation at break of the samples. A slight increase in the strength of samples of ternary mixtures can be interpreted as saying that “hardening” and compaction of the material occurs up to 50 hours of thermal exposure, as evidenced by the heat shrink of the material by 3.6%. In this case, the term “hardening” should be understood to mean a decrease in the defectiveness of the crystalline phase of ternary mixtures, which always favorably affects the increase in the strength of the samples [11. With an increase in exposure time of over 50 hours, polymer compositions gradually undergo thermo-oxidative aging which is expressed in the thermal destruction of macro-chains and their oxidation. In addition, one should take into account the fact that synthetic rubbers being composed of polymer mixtures are characterized by a significantly larger number of vulnerable double bonds which, in the process of thermal aging, are primarily subjected to rupture with simultaneous oxidation.

Conclusions

1. The LDPE was modified with a poly-functional organic compound 2,5-dihydroxy-2,5-dimethylhexyne-3. It found that the complete mixing of components on rollers occurrs at 403 K for 10-15 minutes and the optimal modifier content was 3.0 phr per 100 phr.
2. It revealed that in the course of processing of LDPE and DDH compositions there is a physicochemical and partially chemical interaction between DDH and LDPE molecules which leds to the improvement in physicomechanical, thermo-physical parameters, as well as in rheological properties of the obtained materials.

References

1. Berlin A.A., Volfson S.A., Oshman V.G. The principles of making composite materials. Moscow: Himiya Publ., 1990. 240 p. (In Russian).
2. Kahramanlyi Yu.N. Incompatible polymer mixtures and composite materials based on them. Baku: Elm Publ., 2013, 152 p. (In Azerbaijan).
3. Nguen Min Tuan, Chalaya N.M., Osipchik V.S. Structure and physicomechanical properties of mixtures of polypropylene and metallocene ethylene propylene elastomer. *Plasticheskie massyi- Plastics*, 2017, no. 9-10, pp. 12-16. (In Russian).
4. Simonov-Emelyanov I.D. The principles of creation and processing of dispersed structure composite materials. *Plasticheskie massyi- Plastics*, 2005, no. 1, pp. 11-16. (In Russian).
5. Kravchenko T.P., Ermakov S.N., Kerber M.L. and etc. Scientific-technical problems of obtaining composite materials based on structural thermoplastics. *Plasticheskie massyi- Plastics*, 2010, no. 10, pp. 32-37. (In Russian.)
6. Kakhramanov N.T., Gadzhiev R.Sh., Guliev A.M., Kahramanli Yu.N. The influence of various ingredients on the properties of polymer blends based on polyamide and polyurethane. *Plasticheskie massyi- Plastics*, 2013, no. 12, pp. 9-13. (In Russian).

7. Kazakov Yu.M., Volkov A.M., Ryizhikova I.G., Bauman N.A., Volfson S.I. Binary mixtures of ethylene-olefin elastomers to improve the balance of impact and deformation-strength characteristics of polypropylene compositions obtained in the reaction extrusion process. *Plasticheskie massyi- Plastics*, 2016, no. 9-10, pp. 3-6. (In Russian).
8. Kakhramanov N.T., Gusejnova Z.N., Gasanova A.A., Allahverdieva H.V., Mustafaeva F.A., Osipchik V.S. Reactive extrusion of dynamic elastoplastics on the basis of thermoplastic polyolefins and butyl rubber. *Chemical problems*, 2019, no. 2, pp. 267-274.
9. Kakhramanov N.T., Gasimova G.Sh., Pesetsriy S.S., Kakhramanly Y.N.,Gurbanova R.V. Physical and mechanical properties of nanocomposites based on block copolymer propylene with ethylene and graphite. *Chemical problems*, 2019, no. 1, pp. 72-80.
10. Panfilova O.A., Volfson S.I., Ohotina N.A., Minnegaliev R.R., Vahitov I.I., Karimova A.R. The effect of the composition of the vulcanizing group on the properties of dynamically vulcanized thermoplastic elastomers based on styrene butadiene rubbers and polyethylene. *Vestnik Kazanskogo tehnologicheskogo universiteta - Bulletin of Kazan Technological University*, 2016, vol. 19, no. 17, pp. 39-43. (In Russian).
11. Volfson S.I., Ohotina N.A., Panfilova O.A., Vahitov I.I. Methods for producing thermoplastic vulcanizates based on a mixture of rubbers and polypropylene. *Vestnik Kazanskogo tehnologicheskogo universiteta - Bulletin of Kazan Technological University*, 2015. vol. 18, no. 14, pp. 90-92. (In Russian).

2,5-DİHİDROKSİ-2,5-DİMETİLHEKSİN-3 –ÜN AŞAĞI SIXLIQLI POLİETİLEN VƏ ONUN KOMPOZİSİYA MATERİALARININ TERMOOKSİDLƏŞDİRİCİ XÜSUSİYYƏTLƏRİNƏ TƏSİRİ

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2,5-dihidroksi-2,5-dimetilheksinom-3-un (DDH) poliolefinlər və sintetik kauçuklar əsasında olan kompozisiyaların əsas fiziki-mexaniki xüsusiyyətlərinə təsiri tədqiqatlarının nəticələri təqdim olunmuşdur. Poliolefin olaraq aşağı sıxlıqlı polietilen (ASPE), polipropilendən, sintetik kauçuk olaraq isə butadien-nitril kauçuku, butadien-stirol kauçuku, butilkauçukdan istifadə olunmuşdur. ASPE və DDH vərdənələrdə emalı zamanı DDH və ASPE molekulları arasında fiziki-kimyəvi və qismən də kimyəvi qarşılıqlı təsir baş verdiyi müəyyən olmuşdur ki, bu alınmış materialların fiziki-mexaniki, istilikfiziki göstəricilərini və həmçinin reoloji xüsusiyyətlərini yaxşılaşdırır. 2,5-dihidroksi-2,5-dimetilheksinom-3-un daxil edilməsi kompozisiya materiallarının termooksidləşdirici davamlılığının yüksəlməsinə kömək etdiyi müəəyən olmuş, sintetik kauçuk iştirakı ilə kompozisiyaların daha çox termooksidləşdirici qocalmaya məruz qaldığı göstərirmişdir.

Açar sözlər: *dartılmada möhkəmlik həddi, nisbi uzanma, termooksidləşmə, özülüaxıcı hal, termiki qocalma.*

ВЛИЯНИЕ 2,5-ДИГИДРОКСИ-2,5-ДИМЕТИЛГЕКСИНА-3 НА ТЕРМООКИСЛИТЕЛЬНЫЕ СВОЙСТВА ПОЛИЭТИЛЕНА НИЗКОЙ ПЛОТНОСТИ И ЕГО КОМПОЗИЦИОННЫХ МАТЕРИАЛОВ

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В работе приводятся результаты исследования влияния 2,5- дигидрокси- 2,5-диметилгексина (ДДГ) на основные физико-механические характеристики композиций на основе полиолефинов и синтетических каучуков. В качестве полиолефинов были использованы полиэтилен низкой плотности (ПЭНП), полипропилен, а синтетических качуков - бутадиен-нитрильный каучук, бутадиен-стирольный каучук, бутилкаучук. Установлено, что при переработке композиций ПЭНП и ДДГ на вальцах происходит физико-химическое и частично химическое взаимодействие между молекулами ДДГ и ПЭНП, что приводит к улучшению физико-механических, теплофизических показателей, а также реологических свойств полученных материалов. Было установлено, что введение 2,5-дигидрокси-2,5-диметилгексина способствует повышению термоокислительной устойчивости композиционных материалов; показано, что в присутствии синтетических каучуков композиции более подвержены термоокислительному старению.

Ключевые слова: *разрушающее напряжение, относительное удлинение, термоокисление, вязкотекучее состояние, термостарение.*