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INFLUENCE OF CARBONISED RICE HUSK FILLER ON CHANGES IN DEFORMATION AND STRENGTH PROPERTIES OF POLYETHYLENE DURING THERMAL AGEING

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The influence of a new filler of natural origin on the thermal oxidation process of high-pressure polyethylene has been studied. The studied filler is carbonized rice husk, a waste product of agricultural production. It has been established that CSF exhibits some thermostabilising effect, preventing the decrease of deformation and strength characteristics of the polymer after its exposure for 3 hours at 170ºC. The introduction of CSF allows to keep the yield strength at the level of 77% (10% wt. CSF) and 46% (5% wt. CSF), while for unfilled aged LDPE this index does not exceed 3% of the initial sample. The breaking stress of the filled samples remains at the level of the unoxidized ones. A synergetic effect was revealed when the investigated filler and standard antioxidant Irganox 1010 were used. At the introduction of 10% wt. of CSF and 0,2% wt. of phenolic stabilizer, there is no decrease in destructive stress after the thermal aging of the material.

Keywords: polyethylene, filler, carbonized rice husk, thermo-oxidation, strain-strength characteristics.

КӨМІРТЕКТІ КҮРІШ ҚАБЫҒЫНЫҢ ТОЛТЫРҒЫШЫНЫҢ ТЕРМИЯЛЫҚ ҚАРТАЮ КЕЗІНДЕ ПОЛИЭТИЛЕННІҢ ДЕФОРМАЦИЯЛЫҚ БЕРІКТІК ҚАСИЕТТЕРІНІҢ ӨЗГЕРУІНЕ ӘСЕРІ

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Жаңа табиғи толтырғыштың жоғары қысымды полиэтиленнің термототығу процесіне әсері зерттелді. Зерттелген толтырғыш – бұл ауылшаруашылық өндірісінің қалдықтары болып табылатын көміртекті күріш қабығы. ККТ 170ºС температурада 3 сағат бойы экспозициядан кейін полимердің деформациялық-беріктік сипаттамаларының төмендеуіне жол бермейтін кейбір термостабилизациялық әсер ететіні анықталды. ККТ енгізу аққыштық шегін 77% (ККТ 10% масс.) және 46% (5% масс. ККТ) деңгейінде сақтауға мүмкіндік береді, бұл ретте толтырылмаған ескірген ЖҚПЭ үшін бұл көрсеткіш бастапқы үлгі көрсеткіштерінің 3%-дан аспайды. Толтырылған үлгілердің деструктивті кернеуі тотықпаған деңгейде сақталады. Зерттелген толтырғыш пен стандартты антиоксидант Ирганокс 1010-мен бірге пайдалануда синергетикалық әсер анықталды. 10% масс. ККТ және 0,2% масс. фенолды тұрақтандырғыш енгізгенде материалдың термиялық қартаюынан кейін деструктивті кернеудің төмендеуі байқалмайды.

Түйін сөздер: полиэтилен, толтырғыш, карбонизацияланған күріш қабығы, термототығу, деформация және беріктік сипаттамалары.

ВЛИЯНИЕ НАПОЛНИТЕЛЯ ИЗ КАРБОНИЗОВАННОЙ РИСОВОЙ ШЕЛУХИ НА ИЗМЕНЕНИЕ ДЕФОРМАЦИОННО-ПРОЧНОСТНЫХ СВОЙСТВ ПОЛИЭТИЛЕНА ПРИ ТЕРМИЧЕСКОМ СТАРЕНИИ

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Изучено влияние нового наполнителя природного происхождения на процесс термоокисления полиэтилена высокого давления. Исследованный наполнителя представляет собой карбонизированную рисовую шелуху, являющуюся отходом сельскохозяйственного производства. Установлено, что УКН проявляет некоторое термостабилизирующее действие, препятствуя снижению деформационно-прочностных характеристик полимера после его экспозиции в течении 3-х часов при 170ºС. Введение УКН позволяет сохранить предел текучести на уровне 77% (10% масс. УКН) и 46% (5% масс. УКН), в то время для ненаполненного состаренного ПЭВД этот показатель не превышает 3% от показателей исходного образца. Разрушающее напряжение наполненных образцов сохраняется на уровне неокисленных. При совместном использовании исследованного наполнителя и стандартного антиоксиданта Ирганокс 1010 выявлен синергетический эффект. При введении 10% масс. УКН и 0,2% масс. фенольного стабилизатора не наблюдается снижения разрушающего напряжения после термического старения материала.

Ключевые слова: полиэтилен, наполнитель, карбонизированная рисовая шелуха, термоокисление, деформационно-прочностные характеристики.

Introduction. Polymer composite materials due to the complex of their valuable qualities are widely used in many spheres of human activity. The use of fillers of various types (dispersed, fibrous, woven) allows not only to increase the strength characteristics of the material, but also to change its thermal, electrical, frictional, and other characteristics. The combination of thermoplastics, fillers of different natures and aggregate states, stabilizers, plasticizers, and other additives in the polymer composition allows to create materials with the widest range of properties and meeting the requirements of the most demanding areas of industry. However, during the processing of polymers into products and their further operation as a result of thermal-oxidative aging, the performance of the material deteriorates and its service life is reduced. Therefore, one of the important objects of research is the influence of various components of composite material, in particular fillers, on the resistance of polymers to various types of degradation.

A number of publications have been devoted to the study of thermal aging processes of filled polymers, including polyethylene [1-4]. However, they mainly consider the processes of aging and stabilization of polymers filled with mineral fillers.

At present, carbon-silica composite is proposed as a filler from natural renewable raw materials, which is carbonized rice stalk and husk waste in a pyrolysis furnace without access to oxygen at a temperature of 550-600°C [5]. According to [6], the composition of carbon-silicon filler (CSF) includes 47,26 % carbon, 50,38 % SiO_2, and 2,36 % impurities, mainly oxides of various metals.

Since a number of researchers [7-10] note the presence of a synergetic effect of rubber hardening at the joint use of carbon black and silicon dioxide, there is an increasing number of works on the study of the influence of complex filler CSF on the properties of various rubbers [11-15].

The aim of the study was to investigate the influence of carbon-silica filler obtained from natural raw materials on the thermal aging processes of high-pressure polyethylene.

Materials and methods. High-pressure polyethylene (LDPE) of 15313-003 grade (GOST 16337-77, changes 1-3) and carbon-silicon filler provided by «NeoCarbon» LLP (Republic of Kazakhstan) were used as objects of research. Characteristics of polyethylene are given in Table 1. The chemical composition of CSF filler is shown in Table 2. Irganox-1010 (pentaerythrol tetrakis(3-(3,5-di-tert-butyl4-hydroxyphenyl) propionate) produced by BASF was used as a stabilizer.

Table 1 – Characteristics of polymers

Polymer	Melt flow rate, g/10 min, T=190ºC	Melting point, ºC	Yield strength, MPa	Tensile breaking stress, MPa	Relative elongation at break, %
15313-003	0,35	106	10,8	14	450

Table 2- Chemical composition of carbon-silica filler

Chemical composition	Contents, %
Carbon	47,26
SiO2	50,38
Na2O	0,04
MgO	0,16
Al2O3	0,01
P2O5	0,11
K2O	1,72
CaO	0,28
TiO2	0,01
MnO	0,02
Fe2O3	0,01

Polymer compositions were prepared by mixing in melt in a Brabender mixer for 10 minutes after loading all components. The mixing temperature was 150°C. Rotor speed150 rpm.

Samples for physical and mechanical tests were obtained by pressing (GOST 12019-2021) at a temperature of 160°C. After pressing all samples were subjected to conditioning at room temperature for a day (GOST 12423-2013).

Aging of the samples was carried out at 170ºC for 1, 2, and 3 h.

Determination of deformation and strength properties of the samples was carried out on a tensile testing machine TestP 108 with automatic registration of results at a speed of 500 mm/min in accordance with GOST 11262-2017.

Results and discussion. Currently, there is a large amount of information on the successful modification of thermoplastics with mineral fillers to improve their performance. The study of the possibility of using inexpensive fillers of natural origin in polyethylene-based compositions is of undoubted interest for the development of new polymeric materials.

The investigations have shown that the introduction of the studied filler practically does not affect the strength of the material, only slightly reducing the breaking stress of the composition.

The increase in the concentration of CSF expectedly leads to a constant monotonic deterioration of the elasticity of the material (Fig. 1). At the same time, the relative elongation at break for LDPE filled with less than 4 % wt of CSF remains at the same level as that observed in LDPE filled with a similar amount of other dispersed fillers.

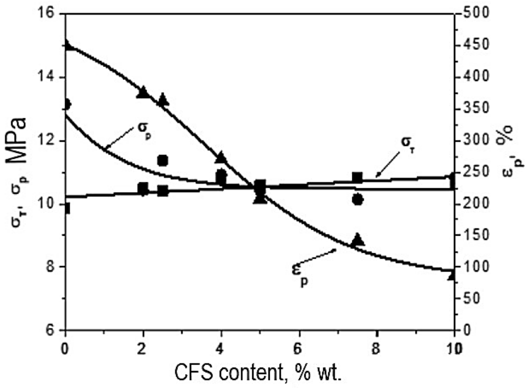

Fig. 1 – Influence of CSF concentration on deformation and strength characteristics of LDPE

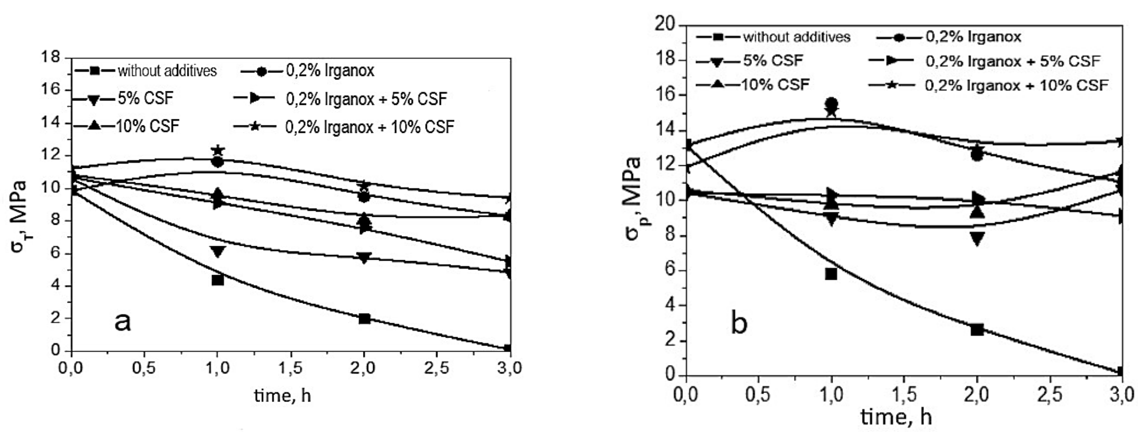

Fig. 2 – Change of yield strength (a) and breaking stress (b) of composites in the process of thermal aging

Since in addition to carbon black and silicon oxide, the CSF contains 2.36 % of impurities, which are oxides of various metals, it was of interest to evaluate the effect of this filler on the thermo-aging process of LDPE.

In the course of the research, it was found that the strength characteristics of LDPE filled with carbonized rice husk during aging decrease to a lesser extent than for unfilled polyethylene (Fig. 2, 3). This indicates the manifestation of some stabilizing properties by this filler. At the same time, the joint introduction of filler and CSF allows to keep the level of strength characteristics for a longer time (Fig. 3). Inhibition of the process of oxidation and destruction of polyethylene at the introduction of complex carbon-silicon filler is probably connected with the presence of metal oxides, which are able to interact with carboxyl groups formed at thermo-oxidation of polymer. The use of the antioxidant Irganox 1010 in the composition of polyolefin composition together with CSF preserves the strength properties of the aged material at the level of the initial unaged composite. That is probably connected to some synergetic action of the filler and antioxidant.

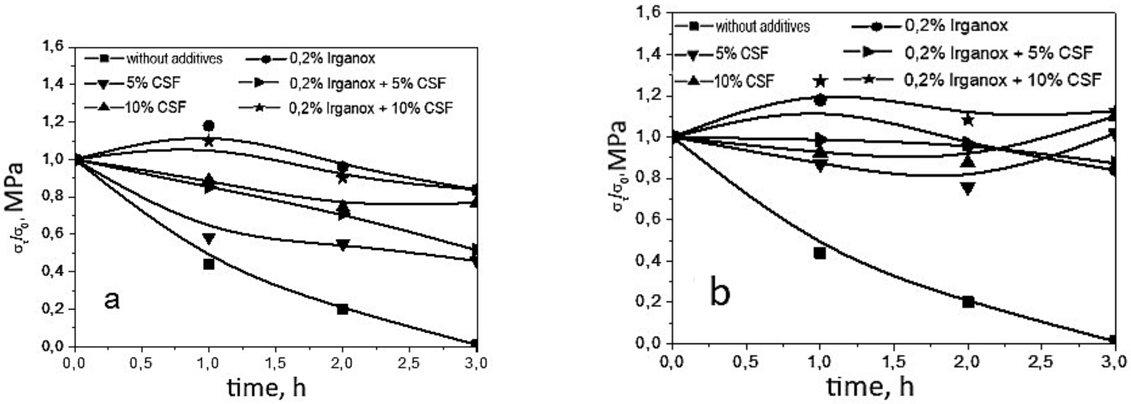

Fig. 3 – Rate of yield stress (a) and failure stress (b) of composites in the process of thermal aging

Polyethylene filled with CSF has significantly worse elasticity than the original one (Fig. 1), but in the process of its thermal aging the decrease in relative elongation at break is much slower (Fig. 4). Relative elongation of the samples aged for 3 hours at 170ºC, filled with 5 and 10% of CSF, is 65 and 40% of the values of samples not subjected to aging. The combination of UCS and the standard stabilizer of phenolic type Irganox1010 almost completely stops the reduction of elasticity of the aged material. However, it is necessary to take into account the lower value of elongation at break when filling polyethylene.

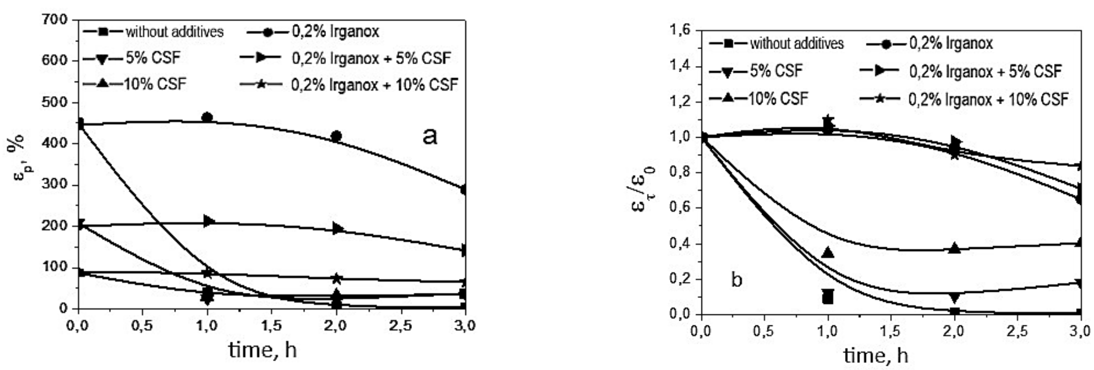

Fig. 4 – Change of yield strength (a) and breaking stress (b) of composites in the process of thermal aging

Conclusions. Thus, the studies that were conducted have shown that the use of CSF as a filler has a positive effect on the process of thermal oxidation of high-pressure polyethylene, reducing its intensity. The introduction of CSF into LDPE allows the yield strength after the exposition of samples for 3 hours at 170ºC at the level of 77% (10% wt. CSF) and 46% (5% wt. CSF), while the 6t of unfilled aged LDPE does not exceed 3% of the initial sample. The breaking stress of the filled samples remains at the level of the unoxidized ones. The use of this carbon-silicon filler in polyethylene compositions in combination with a standard stabilizer makes it possible to practically stop the thermal aging of the polymer, thus extending its service life. In spite of the fact that the introduction of 10% wt. of CSF into the polyethylene composition is more effective from the point of view of ensuring thermal stability, it seems reasonable to use smaller amounts of the filler. This is due to its negative effect on the elasticity of the material since the introduction of

10% wt. of CSF reduces the relative elongation of the composition by 4.5 times compared to unfilled LDPE. Nevertheless, the use of inexpensive filler from renewable plant raw materials is of undoubted interest, because, being a product of processing of agricultural waste, it allows to reduce the environmental load and reduce the cost of polymer compositions.

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