Antioxidants Based on Gossypol and Epichlorohydrin and Their Application Polyethylene

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Abstract. In this paper, the study of a new antioxidant based on gossypol with epichlorohydrin (ECH) was carried out in two ways: in the presence of 1% phosphoric acid and 0.5% alkali solution in a molar ratio of gossypol: alkali=1:2. Obtained in the presence of phosphoric acid, has the following characteristics: it is a homogeneous brown powder, average molecular weight 2300-3500, non-volatile, main component content 99.6% and in an alkaline environment, has the following characteristics: uniform brown powder, average molecular weight 2500-3800, non-volatile, main component content 99.7%. The technological regime of the optimal conditions for the synthesis of gossypol with epichlorohydrin is carried out at a molar ratio of 1:1 in the temperature range of 313–353 K in an alcohol solution. The structure of this compound was confirmed by IR, ^{1}H NMR, spectral and elemental analysis. For comparison, IR spectra of gossypol and its oligomeric derivatives GECH were taken. This obtained oligomer was applied to polyethylene as an antioxidant and improved its mechanical and thermal properties.

Keywords: gossypol, epichlorohydrin, antioxidant, elemental analysis, IR-analysis, ^{1}H NMR- analysis.

Abbreviations and notation: epichlorohydrin (ECH), gossypol and epichlorohydrin (GECH), gossypol and allyl halides (GAG), gossypol with allylthiourea (GATM), polyethylene (PE), low density polyethylene (LDPE).

Introduction.

Currently, there is an intensive growth in the production and use of polymer materials based on polyolefins and elastomers. At the same time, although they have valuable physicochemical properties, they have a significant drawback: polymer materials based on polyolefins and elastomers are subject to various types of aging under the influence of heat, light, oxygen, etc., and their properties are not always

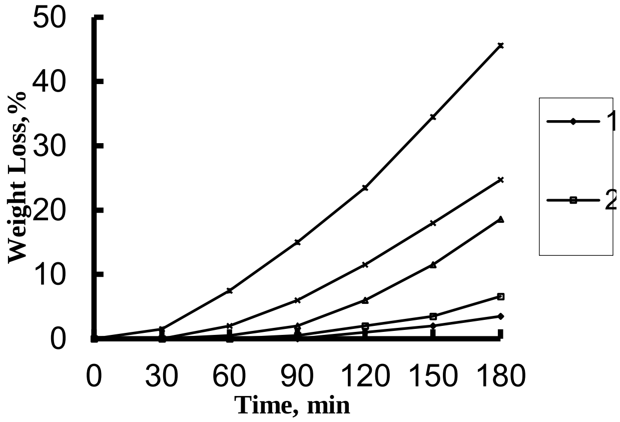
sufficiently stable. Therefore, one of the ways to increase the resistance of polymer materials to heat and oxygen is to introduce antioxidant stabilizers into them.
[1,2]. In recent years, foreign studies have also observed trends in replacing synthetic products with products of natural origin, the raw materials for the production of which are renewable resources [3,4], biological and chemical processes [5], the source of raw materials for the synthesis of which is waste from the wood processing industry (wood and bark of coniferous and deciduous trees) [6,7]. The introduction of a terpene substituent into the aromatic ring of phenols is possible through the interaction of phenols with terpene hydrocarbons, alcohols or halogen derivatives in the presence of acidic catalysts[8-10].

assessment of the effectiveness of antioxidants based on oligomeric derivatives of gossypol polyethylene.

As noted above, the addition of oligomeric antioxidants to polymers has important technical advantages - it ensures the non-volatility and non-leaching of antioxidants, and increases their compatibility with the polymer.

As with other polymers, the effect of oxygen alone on PE at ordinary temperatures is negligible. The addition of small amounts of antioxidants unlimitedly increases its service life. However, in sunlight, aging occurs quickly, i.e. Many antioxidants currently used are extremely ineffective. The greatest success in increasing the heat and light resistance of PE is achieved by introducing into it pigments such as carbon black, iron oxide and natural stabilizers, which isolate the entire mass of the polymer from light, with the exception of the surface layers.

In this regard, the thermostabilizing properties of the synthesized oligomeric antioxidants were studied. The effectiveness of the compounds GECH, GAB, and GATM was assessed in comparison with that of the well-known thermal stabilizer «Irganox-1010».(tetraester of β-(3,5-di-tert-butyl-4-hydroxyphenyl) propionic acid and pentaerythritol).
Analysis of the data obtained (Fig. 1) showed that during the thermal oxidation of stabilized LDPE, a significant induction period is observed. At the end of this period, the slope of the kinetic curves and anamorphoses for stabilized samples becomes the same as in the case of an unstabilized sample, which indicates the termination of the effect of the stabilizer. For an unstabilized LDPE sample, the mass initially increases slightly, apparently due to the absorption of oxygen, and after a few minutes decreases due to the destruction of the polymer.



1 - GATM; 2 — GECH, 3 — GAG; 4 — Irganox-1010;
5-unstabilized PE. Antioxidant content - 0.2%
Fig.1. Kinetic curves of thermal oxidative destruction of PE at 598 K.

The compounds GECH, GAG and GATM are quite effective thermal stabilizers, superior to the currently widely used industrial thermal stabilizer Irganox-1010.

The high stabilizing properties of oligomeric stabilizers are due to the presence of a large number of hydroxyl groups in the gossypol molecule, their interaction with the products of thermal decomposition of hydrocarbons when exposed to high temperatures.

The physical and mechanical properties of stabilized LDPE samples were determined by various methods. The influence of stabilizers on the melt flow index (MFI) of LDPE, molecular weight distribution (MWD) and density was studied. The research results are presented in tables 3.1 and 3.2.

With the introduction of stabilizers GECH, GATM and GAG, a slight increase in the MFI of polyethylene is observed.

Increasing the fluidity of LDPE does not affect its other properties, such as melting point and processing temperature. From the data in Tables 3.1 and 3.2, we can conclude that the MWD also decreases slightly compared to the original LDPE, and this difference is significant.

Table 3.1.

Results of testing the physical and mechanical properties of original and stabilized polyethylene

Indicators	PE without additive	PE c 0,2% «Irganox-1010»	PE with 0.2% «GECH»	PE with 0.2% «GAG»	PE with 0,2% «GAG»
Properties of the original and stabilized samples before aging					
Density, g/cm3	0,9220	0,9198	0,9197	0,9197	0,9212

MFR, g/10 min	0,55	0,80	0,83	0,81	0,82
Tensile strength, MPa	26,05	27,75	27,84	27,92	28,12
Mol. wt. distribution.	1,56	1,39	1,30	1,31	1,31
Tin.pl., ºC	110	113	115	114	112
Relative content of carbonyl groups, %	0	0	0	0	0
Elongation at break, %	860	870	880	875	875

Table 3.2

Properties of the original and stabilized polyethylene samples after aging (24 hours at 250 °C)

Indicators	PE without additive	PE with 0.2% «Irgonox 1010»	PE with 0.2% «GECH»	PE with 0,2% «GAG»	PE with 0,2% «"GATM"»
Density, g/cm^3	0,9240	0,9570	0,9250	0,9263	0,9272
MTR, g/10min	0,23	0,56	0,58	0,52	0,51
Tensile strength, MPa	17,35	20,42	23,13	24,71	22,64
Mol. wt. distribution.	1,24	1,11	1,15	1,09	1,08
Tin.pl., ºC	125	129	135	132	131
Relative content of carbonyl groups, %	29,76	16,52	14,98	12,65	13,57
Elongation at break, %	351	390	405	410	400

Table 3.3 shows the dependence of the induction period and weight loss of PE on the content of stabilizers at 473 K for 8 hours of heating in vacuum and in air.

The data in Table 3.3 shows that stabilized samples exhibit a decrease in the amount of volatile destruction products and an increase in the induction period compared to the original PE. In this case, the greatest stabilizing effect both in vacuum and in air is observed in the presence of the oligomeric stabilizer GATM. For the stabilized sample, after 8 hours of heating in a vacuum, no release of volatile destruction products is observed; when heated in air, the induction period is 230 min, which is 3 times longer compared to the original PE. Under similar conditions, the original PE loses 6.8% of its mass in a vacuum and 9.42% of its mass in air, and the GATM-stabilized PE loses 1.5% of its mass in a vacuum and 6.3% of its mass in air. Thus, the experimental data obtained show that the stabilizing effect of the tested compounds in vacuum is significantly higher than in air. This difference appears to be due to the influence of oxygen on the stabilizing effect of the tested compounds [11].

Table 3.3.

Dependence of the induction period and weight loss of PE on the content of stabilizers for 8 hours of heating at 473 K

Samples studied	*Induction period, min*	*Weight loss, %*
In a vacuum		
PE	140	6,8
PE+1.0% GATM	440	1,5
PE+1.0% GECH	430	1,7
PE+1.0% GAG	415	2,8
On air		
PE	80	9,4
PE+1.0% GATM	230	6,3
PE+1.0% GECH	220	6,5
PE+1.0% GAG	190	7,7

A study of the influence of temperature on the stabilizing effect of the compounds used shows that the oligomeric stabilizer GATM at all studied temperatures leads to a decrease in the amount of released volatile destruction products and an increase in the induction period compared to the original PE.

Conclusion

(i). The kinetics of oxygen absorption by the original and stabilized LDPE was studied at different molecular oxygen pressures. It has been established that, along with reactions of inhibition of the polymer oxidation process, the oligomeric antioxidant leads to inhibition of the process of destruction of the polymer composition.

(ii). According to the obtained results, the amount of antioxidant based on gossypol and epichlorhydrin showed the highest thermal and mechanical strength when the amount was 0.2%.

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