

The synthesis of oligomeric derivatives of gossypol and the study of their antioxidative properties

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SUMMARY

A study was made of the synthesis of oligomeric derivatives of gossypol with epichlorohydrin and allyl halides. The structure of the oligomeric derivatives of gossypol was confirmed by IR spectroscopic and elemental analysis. The antioxidative capacity of the oligomeric derivatives of gossypol in the inhibition of low-density polyethylene (LDPE) was investigated. Study of the antioxidative properties of the synthesised oligomeric antioxidants by mass chromatography showed that comparison of the decomposition products of LDPE made it possible to conclude that the antioxidants affect the process of C–C bond rupture. The number of R–In bonds formed during the degradation of LDPE can serve as the main criterion of stability of stabilised specimens

known [2], it has hardly been used for the stabilisation of polymers. Meanwhile, this natural stabiliser can be used as a semiproduct for the synthesis of new antioxidants.

The inhibiting action of gossypol is due to the presence of four hydroxyl groups in positions 6,6' and 7,7'. Hydroxyl groups in position 1,1' are fairly inert. Aldehyde groups in the gossypol molecule reinforce the inhibition effect.

A special place among stabilisers is occupied by gossypol and its derivatives. In contrast to other antioxidants, these compounds are more effective and protect the polymer against thermo- and photodegradation. In view of this, we synthesised oligomeric antioxidants based on gossypol with epichlorohydrin (GECH) and gossypol with allyl halides (GAH).

INTRODUCTION

For cotton growing countries, and especially for Uzbekistan, the complex processing of the products of cotton farming, which forms the basis of agricultural production, is extremely important.

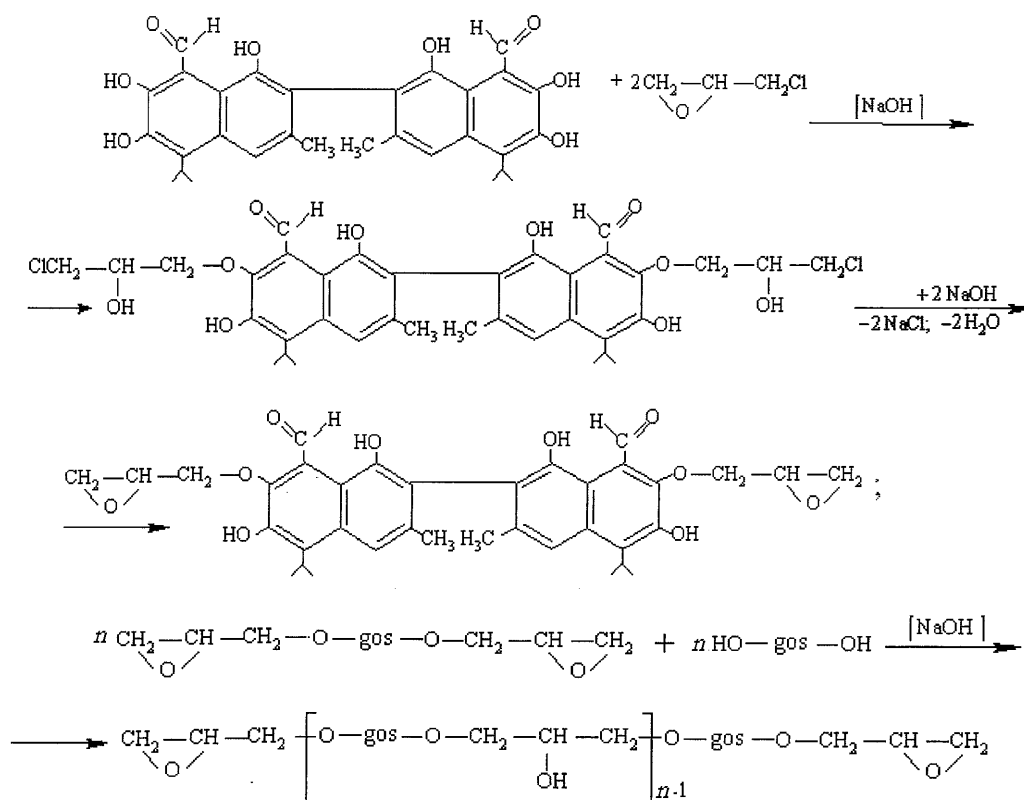
This paper sets out the results of investigations into the use of secondary products of oil and fat production – gossypol and its derivatives – as heat stabilisers for improving the heat resistance of polyethylene and other polymers.

Gossypol and some of its derivatives are extremely active inhibitors of radical reactions (oxidation, polymerisation, and others) [1]. Here it is important to note that the effective concentrations of gossypol are significantly lower than its toxic level. In spite of the fact that the antioxidative action of gossypol has long been

EXPERIMENTAL

The new oligomeric antioxidants were synthesised on the basis of gossypol. Here, the additional reactants introduced, on their interaction, form higher-molecular-weight antioxidants than gossypol. On account of their high-molecular-weight nature, they are able to migrate, volatilise, and be extracted with solvents. This results in stability of the properties of the material and high effectiveness of the oligomeric stabilisers developed in this work.

The synthesis of an oligomeric antioxidant based on gossypol and ECH was carried out in an aqueous solution in the presence of an alkali. The reaction is accompanied with the interaction of the hydroxyl groups of gossypol in the 7,7' position with the epoxy groups of epichlorohydrin. The scheme of the reaction can be presented in the following way:



where gos denotes the gossypol residue.

From the given scheme it can be seen that diepoxide derivatives of gossypol and the same amount of gossypol can interact to form oligomers.

The oligomeric product of interaction of gossypol with ECH, obtained in an alkaline medium, has the following characteristics: homogeneous powder of brown colour, average molecular weight 2500–3800, non-volatile, content of main component 99.7% [3].

The structure of this compound was confirmed by IR spectral and elemental analysis. For comparison, IR spectra of gossypol and its oligomeric derivatives GECH were taken.

The IR spectrum of gossypol contains bands at 3540 and 3510 cm^{-1} corresponding to free phenol groups and bands at 3510–3400 cm^{-1} relating to stretching vibrations of the –OH group, and certain characteristic frequencies of the hydroxyl groups are closely related to the formation of an intramolecular hydrogen bond. Of most practical importance is the band of stretching vibrations of –OH in the 3200–3100 cm^{-1} region, while in the 1210–1260 cm^{-1} region there are bands relating to free deformation vibrations of the phenolic OH group, and also in the 1500 cm^{-1} region the narrow peak is shifted towards greater frequencies with reinforcement of the hydrogen bond. Bands relating to –CH– groups vibrate in the 3000 and 1429 cm^{-1} range. Stretching vibrations of the methyl group (–CH₃) are expressed in the 2960 cm^{-1} region, while those relating to deformation vibrations are expressed by narrow bands in the 1361 and 1316

cm^{-1} range. Weak bands relating to isopropyl groups of gossypol appear in the 1145 cm^{-1} region, with a shoulder at 1170 cm^{-1} . Bands in the 1620–1640 cm^{-1} region are due accordingly to stretching vibrations of the –C=O groups. Characteristic bands relating to aldehyde groups appear in the 1725 and 1000 cm^{-1} region.

In the investigation of IR spectra of the oligomeric antioxidant GECH, new bands were found, appearing in the form of a triplet in the range 2980, 2950, and 2875 cm^{-1} , an uncharacteristic position for aromatic ethers.

Characteristic bands for aromatic ethers, expressing asymmetric stretching vibrations of =C–O–C groups, can be seen in the 1440 and 1340 cm^{-1} region and in the 1240–1275 cm^{-1} range. The weak bands in the 1180 and 1150 cm^{-1} region express oscillating vibrations corresponding to aromatic ethers, and in view of this there are symmetrical stretching vibrations of =C–O–C groups in the 1020 and 1080 cm^{-1} range. In the spectrum of GECH, aldehyde groups of the aromatic ring can clearly be observed in the range 1725–1730 cm^{-1} , while in the spectrum of gossypol this peak is hidden by intramolecular hydrogen bonds. The disappearance of intramolecular hydrogen bonds in the spectra of GECH in the range 3100–3200 cm^{-1} in the form OH...O=C, which are expressed in the spectra of gossypol, and the appearance of new absorption bands in the 1440 and 1340 cm^{-1} region and in the 1240–1275 cm^{-1} range, corresponding to stretching vibrations of =C–O–C, demonstrate that in the gossypol molecule there are new bands relating to aromatic ethers of oligomeric antioxidant GECH.

Elemental analysis of the synthesised oligomer gave the following result: C 68.8%, H 5.12%, O 24.7%. The theoretically calculated elemental composition of GECH, on the basis of the structure given above, was as follows: C 68.1%, H 5.76%, O 25.1%.

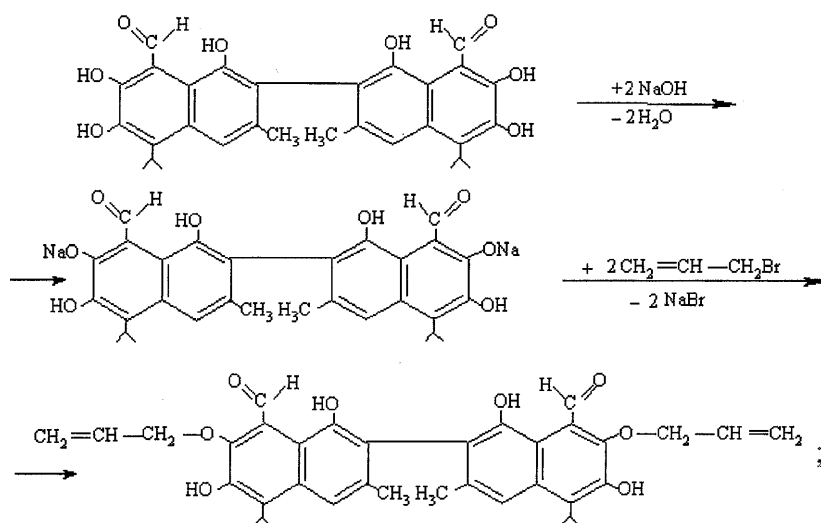
The interaction of gossypol with epichlorohydrin is characterised by complex development of the process, governed by the presence of different reactive functional groups.

The interaction of gossypol with epichlorohydrin was carried out with a molar ratio of 1:1 in the temperature range 313–353 K in an alcoholic solution. The kinetics of the process was followed from the change in the concentration of chlorine atoms in the reaction mass as the reaction proceeded.

The results show that, when gossypol interacts with epichlorohydrin in the presence of an alkali, as during the etherification of other polyhydric alcohols, initially the rapid interaction of the hydroxyl groups of gossypol with epoxy groups of the epichlorohydrin occurs, the rate of which does not depend on the change in temperature by 10–20°C, but then a relatively slower process of formation of ethers is observed in the following period.

Here, increase in temperature to 353 K leads to deepening of the oligomerisation reaction. The results of the investigations indicate that, with increase in temperature to 353 K, the rate of the reaction increases 1.13–1.32-fold. To produce oligomeric antioxidant GECH of higher molecular weight, it is evidently necessary to take an equimolar ratio of the reactants (Table 1).

The scheme of the reaction of gossypol and allyl halides (for the case of allyl bromide) can be presented in the following way:



The structure of the oligomeric antioxidants GAH synthesised on the basis of allyl halides was confirmed by IR spectral and elemental analysis. The IR spectrum of GAH indicates that, by comparison with gossypol, new bands appear in the form of a triplet in the regions 2990, 2950, and 2900 cm^{-1} , relating to stretching vibrations of the $=\text{C}-\text{O}-\text{C}$ groups of the aromatic ring. In the spectrum, strong absorption is noted only at 1450 cm^{-1} , with a shoulder at 1430 and 1420 cm^{-1} , relating to stretching vibrations of the $=\text{C}-\text{O}-\text{C}$ groups. The bands in the regions 1220, 1250, and 1300 cm^{-1} are due respectively to aromatic deformation vibrations of the $=\text{C}-\text{O}-\text{C}$ groups. The $-(\text{CH}_2)_3-\text{O}-$ groups characteristic of the oligomeric antioxidant GAH are expressed by oscillating vibrations at 750 cm^{-1} .

The experimentally determined/theoretically calculated elemental compositions of the synthesised GAH were as follows: C 70.2/70.9%, H 6.04/6.09%, O 22.3/22.9%, which corresponds to the empirical formula $\text{C}_{33}\text{H}_{34}\text{O}_8$. The satisfactory agreement of the experimentally determined and theoretically calculated elemental compositions on the basis of the given formula, combined with the results of physicochemical investigations, seems to indicate the correctness of the proposed structure of GAH.

From the scheme given of the reaction between gossypol and allyl bromide (GAB) it can be seen that, to produce oligomeric antioxidant GAB of higher molecular weight, it is evidently necessary to take an equimolar ratio of the reactants (Table 2).

A study was made of the influence of different processing parameters on the process of interaction of gossypol with allyl halides: the ratio of the reacting components, the temperature, and the nature of the solvent. On the basis of the investigations, the optimum regime of the process was developed.

Our investigations of the dependence of the rate of the reaction, determined from the rate of consumption of allyl halides in reactions of migration oligomerisation,

Table 1. The influence of the molar ratio of reactants on the composition of the product during the production of oligomeric antioxidant GECH ($T = 338 \text{ K}$, $\tau = 2 \text{ h}$)

Gossypol:ECH molar ratio	Yield, %	Medium molecular weight (cryoscopic)	Elemental analysis, %			
			Carbon		Hydrogen	
			Calculated	Found	Calculated	Found
3:1	72.3	2380	69.1	68.1	5.7	4.8
2:1	87.7	3450	69.1	67.9	5.7	5.2
1:1	98.8	4860	69.1	68.8	5.7	5.1
1:2	85.6	3820	69.1	69.3	5.7	4.9
1:3	79.2	3340	69.1	69.2	5.7	4.5

Table 2. The influence of the molar ratio of reactants on the composition of the product during the production of oligomeric antioxidant GAB (T = 338 K, τ = 2 h)

Gossypol:AH molar ratio	Yield, %	Average molecular weight (cryoscopic)	Elemental analysis, %			
			Carbon		Hydrogen	
			Calculated	Found	Calculated	Found
3:1	77.3	2360	70.9	67.5	6.1	5.5
2:1	83.5	3430	70.9	69.6	6.1	5.6
1:1	94.6	4770	70.9	70.2	6.1	6.1
1:2	85.6	3740	70.9	68.7	6.1	5.9
1:3	79.2	2880	70.9	67.9	6.1	5.3

showed that the kinetic relationships of formation of the polymer product are characterised by an increase in the slope of the tangent on switching from iodine to a chlorine-containing compound, after which the slope of the tangent decreases little.

RESULTS AND DISCUSSION

Lengthening of the lifetime of polymer articles is an urgent not only chemical but also ecological problem. On the one hand, lengthening the service and storage time is equivalent to increasing the production of polymer articles and improving their quality. On the other hand, the accumulation of polymer waste brings to the fore questions of their recycling and environmental control.

The search for new methods for stabilising polymer articles with the aim of improving their service characteristics (primarily changing their surface properties) and synthesising antioxidants with a controllable lifetime remains urgent.

At present, questions of the ageing and stabilisation of polyethylene (PE), the search for ways to lengthen the service time, and the synthesis of the new antioxidants based on derivatives of gossypol, which is a local raw material, are being studied.

The activation energy of thermooxidative degradation of composite materials (E_a) was calculated by Reich's method [4].

Tables 3 and **4** give the corresponding data on the rates of thermooxidative and thermal degradation of initial and stabilised PE. Comparing the data in **Tables 3** and **4**, we see that they differ for all antioxidants (at the corresponding temperatures).

For example, the rate of thermooxidative degradation of initial PE at 613, 623, and 633 K is equal to 0.18, 0.22, and 0.26%/min respectively, and the rate of thermal degradation of the initial LDPE at 613, 623, and 633 K is equal to 0.16, 0.25, and 0.29%/min respectively. However, the activation energy of thermal degradation of the initial LDPE is higher than the

Table 3. The results of determining the rate of thermooxidative degradation of initial and stabilised LDPE

Temperature, K	Heating time, min	Amount of volatiles, %	Degradation rate, %/min	Activation energy, kJ/mol
Unstabilised LDPE				
613	360	63.8	0.177	110.1
623	360	77.3	0.214	110.1
633	360	92.5	0.257	110.1
Stabilised LDPE with GAH				
613	360	21.6	0.072	158.4
623	360	46.9	0.156	158.4
633	360	70.7	0.235	158.4
Stabilised LDPE with GECH				
613	360	20.7	0.069	152.7
623	360	51.3	0.171	152.7
633	360	71.8	0.239	152.7
Stabilised LDPE with Irganox-1010				
613	360	34.9	0.116	149.7
623	360	58.2	0.194	149.7
633	360	79.4	0.264	149.7

Table 4. The results of determining the rate of thermal degradation of initial and stabilised PE

Temperature, K	Heating time, min	Amount of volatiles, %	Degradation rate, %/min	Activation energy, kJ/mol
Unstabilised LDPE				
613	360	55.7	0.157	138.5
623	360	73.4	0.254	138.5
633	360	88.2	0.285	138.5
Stabilised LDPE with GAH				
613	360	24.5	0.064	161.5
623	360	46.9	0.145	161.5
633	360	77.3	0.226	161.5
Stabilised LDPE with GECH				
613	360	17.5	0.062	172.6
623	360	37.3	0.123	172.6
633	360	59.4	0.208	172.6
Stabilised LDPE with Irganox-1010				
613	360	28.1	0.092	164.4
623	360	47.7	0.157	164.4
633	360	69.6	0.265	164.4

activation energy of thermooxidative degradation. Here, for stabilised specimens, the rate of thermooxidative and thermal degradation is slightly lower than for the initial specimen.

The obtained data make it possible to conclude that the oligomeric antioxidants employed possess a strong antioxidative effect.

A study was then made of thermal degradation in a vacuum instrument with a tungsten spring balance. The integral weight loss was determined in tests conducted on the spring balance in the temperature range 613–633 K. From these data it is possible to judge the stabilisation of the degradation process, setting in roughly at 30–80% weight loss of the initial polymer, when all the curves of the rates approach the abscissa, i.e. approach zero rate values.

Study of the antioxidative properties of the synthesised oligomeric antioxidants by mass chromatography showed that comparison of the decomposition products of LDPE made it possible to conclude that the antioxidants affect the process of rupture of the C–C bonds. The main criterion of stability of the latter may be the number of R–In bonds formed during the degradation of LDPE. The heat stability of the unstabilised specimen, as expected, proved to be lower than that of stabilised specimens. The presence of various bonds formed during extensive degradation of LDPE leads in this case to the formation of a large number of low-molecular-weight fragments, which is reflected in weight losses.

Analysis of the gaseous breakdown products of unstabilised LDPE showed that their composition does not differ from that of gaseous products of degradation

of stabilised LDPE. Carbon–carbon bond rupture in the temperature range 648–673 K proceeds with the formation of carbon monoxide and carbon dioxide in equal measure; further increase in temperature leads to an increase in the CO₂ content in the degradation products. Aliphatic fragments of PE decompose mainly with the release of CO₂ and the formation of phenyl-type radicals.

The kinetic curves of liberation of gaseous products of degradation of PE and stabilised PE with oligomeric antioxidants indicate that the decomposition of PE begins with the rupture of bonds between the methylene groups, as the predominant gaseous product in the first 5 min of degradation is CO₂. The effective activation energies of liberation of gaseous products from PE, calculated from kinetic curves, proved to be equal to 129.63 and 138.57 kJ/mol for CO₂ and CO respectively. Characteristic of PE stabilised with oligomeric antioxidant GECH is the liberation of a significantly smaller amount of CO₂ by comparison with other specimens and unstabilised LDPE. Such an effect may be due to the formation of stable R–In groups and low-molecular-weight fragments containing methyl groups, which vacate the hot zone without breaking down. On the other hand, as processes of thermal degradation of polyolefins in the region of high temperatures, by analogy with processes of degradation of PE, proceed by a radical chain mechanism, the different heat stability of the stabilised specimens may also be explained by the ability of the formed radicals to form crosslinked structures possessing increased heat stability by comparison with unstabilised linear specimens.

Thus, LDPE specimens stabilised with oligomeric derivatives of gossypol are superior in their properties both to an unstabilised specimen and to a specimen stabilised with industrial stabiliser Irganox-1010. The heat-stabilising effect of the stabiliser, ensuring an increase in the heat stability of the polymer, has been used as the basis for developing processes for the production and processing of composite materials based on LDPE.

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