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EPOXY-CONTAINING ADDUCTS OF ROSIN ASLIGHT- AND THERMOSTABILIZERS FOR PVC

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***Abstract**: The thermo- and light-stabilizing activity of glycidyloxycarbonyl- and glycidyloxymethyl-substituted derivatives of the sulphur-containing rosin in the compositions on the basis of plasticized polyvinyl chloride were studied. It found that the proposed epoxy-derivative adducts of rosin possess thermal stability allowing them to withstand the processing temperature of polyvinyl chloride compositions. The developments showed that the proposed stabilizers can protect the polymer matrix against light radiation. It revealed that the film samples prepared with the help of the proposed stabilizers showed the high thermal stability, impact resistance, good frost resistance and mechanical strength.*

***Keywords**: rosin, polyvinyl chloride, epoxy-derivative, compositions, stabilizers, thermal stability, frost resistance*
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Introductıon

As it is known, the introduction of various additives such as plasticizers, stabilizers, antipyrenes, etc. into the composition materials is one of the main methods of adding specific properties thereto and improving physical-mechanical and technological parameters of materials [1-3]. Most synthetic polymers are noted for sufficient stability in temperature, light, atmospheric action, etc. However, this cannot be referred to PVC which is easily decomposed with HCl isolation in case of temperature and light influence [4].

The epoxide compounds are widely used as stabilizers for chlorine-containing polyolefins, in particular PVC. The use of epoxide compounds for PVC stabilization has a number of advantages in comparison with known stabilizers such as stearates, silicates, basic lead salts, phosphates, etc. The epoxide compounds as HCl acceptors cause no turbidity of the material, nor decrease electrical properties of the compositions. They are noted for good compatibility with PVC, so in this case the compositions do not sweat. Thus, the introduction of epoxy compounds into the composition of PVC-based compositions increases not only thermal, but also thermal-oxidative stability and improves the physical and mechanical properties of PVC products.

The purpose of this investigation was to prepare epoxy-derivatives of rosin and their testing as co-stabilizers in the PVC composition.

Experimental

The synthesis of the sulphur-containing rosin (compounds **1** and **2**) was presented in the work [5]. For preparation of the film materials, the suspension PVC of mark S-7059-M was used. Dioctyl phthalate (DOPh) was used as a plasticizer. The mixture of equal quantities of calcium and zinc stearate and complex barium-cadmium-zinc stabilizer (trademark Vigostat-BCC) was used as a stabilizer. Benazol-P was used as a light stabilizer.

The films samples on the basis of plasticized PVC containing stabilizers and bis-adducts **1** and **2**, suggested by us as co-

stabilizers were obtained by means of compositions rolling.

The PVC-based compositions with addition of synthesized bis-adducts were prepared by mixing components in the Brabender mixer. Then they were subjected to gelatinization and plasticization by keeping them in an oven at 90°C for 1.5-2.0 h. After that the rolling was produced at 150°C for 10 min., and then there was performed the pressing at the same temperature and pressure 5.0 MPa for 10 min. The cooling was carried out with water. The content of bis-adduct per 100 mass p. of PVC was 2 mass p. The composition mixtures were made both with the participation of calcium and barium stearates and without them.

The films of plasticized PVC containing the stabilizers synthesized by us were obtained on rollers. The stabilizers were preliminarily dissolved and added to PVC. The mixture swelling was carried out in an oven at 110°C for 1 h. The plasticization was realized at 160° C on the rollers till preparation of a homogeneous mass. The films were obtained on a four-roll laboratory calender at roll temperature 150-165ºC. The films thickness was 0.3±0.05 mm.

The thermo-gravimetric analysis of samples and initial products was carried out on Paulik-Paulik-Erdei derivatograph (heating rate – 5°C/min).

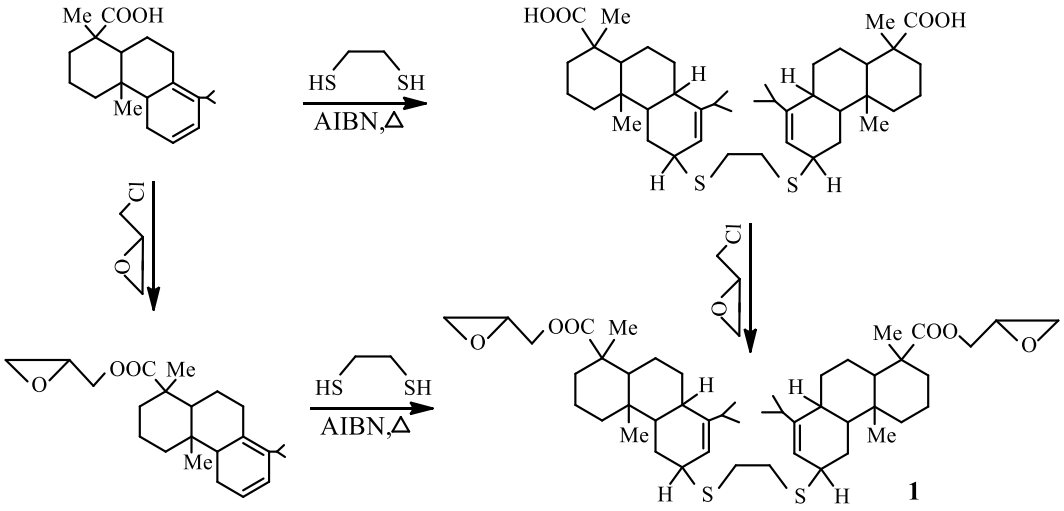
The light-warm aging of samples was carried out at temperature 70°C under lamp DPT-375 for 72 h (according to GOST 8979-75) [6]. The physical-mechanical parameters were determined on a tensile testing machine PM-30-1.

Results and discussion

In search of effective stabilizers, we worked out sulphur-containing epoxide compounds on the basis of accessible alternative raw material – rosin. The synthesis of intended adducts (compounds **1** and **2**) was carried out by two methods [5]:

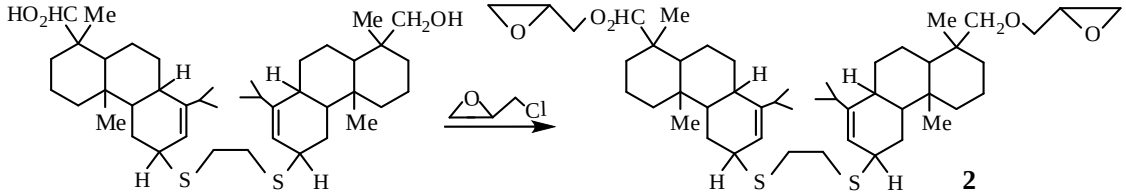
– preparation of glycidyl esters of rosin and its hydroxymethyl derivative with the subsequent addition of ethanedithiol thereto under conditions of the radical initiation;

– radical addition of ethanedithiol to rosin or its hydroxymethyl derivative with preparation of carboxyl- and hydroxyl-containing bis-adducts, then the synthesis of adducts of the appropriate glycidyl esters on their basis.



The glycidyl ester of rosin (as levopimaric acid) was obtained by means of the reaction of sodium salt of acid with epichlorohydrin. The reaction of glycidyl ester of levopimaric acid with ethanedithiol was carried out in the presence of AIBN at temperature 70°C for 60-120 min. AIBN was taken in a quantity of 0.5 mass%, and the ratio of glycidyl ester of levopimaric acid to ethanedithiol was 2:1. The bis-adducts (compounds 1 and 2) were obtained with almost quantitative yields. According to a similar scheme, the bis-adduct (compound 2) –

glycidyloxymethyl derivative rosin was obtained from hydroxymethyl derivative of rosin.



Using GPC analysis method, it found that the obtained adducts **1** and **2** are the individual compounds with MW=807 (calculated 810) and 778 (calculated 782), respectively. These compounds were low-viscous products that were easily dissolved in many organic solvents.

The epoxide compounds 1 and 2, containing tricyclic rosin fragments in a molecule, developed by us, are compatible with PVC, and as will be shown below, possess stabilizing properties.

The tests showed that the epoxide compounds worked out by us have higher thermal stability. Due to good compatibility with PVC, these compounds do not migrate to the surface of products made.

For estimation of the beginning ($T_{begin.}$) and the final (T_{end}) temperatures of thermal decomposition of the samples and for calculation of the activation energy E_a of the thermal destruction process, we used TGA method (Table 1) [7]. To compare the obtained data with the data of industrial stabilizers, TGA-curves were taken for samples with the help of light stabilizers used: Benazol-P, thermostabilizer – calcium stearate and Vigostab-BCC.

Table 1. Thermal characteristics of sulphur-containing epoxy-derivatives of rosin and industrial catalysts

Compound	**Results of thermal analysis**		
	$T_{begin.}$, °C	**$T_{end.}$, °C**	**$E_{eff.}$, kJ/mol**
Compound **1**	243	306	40.9
Compound **2**	252	302	42.2
Vigostab-BCC	257	325	44.7

It follows from Table 1 that $T_{begin.}$ value of decomposition of the sulfur-containing epoxy derivatives of rosin (compounds **1** and **2**) and known stabilizers used in industry have similar values, while T_{end} value of decomposition of these samples strongly differed. Moreover, the samples proposed by us have considerably higher values. This is evidenced by the value of their $E_{ef.}$ termodestruction. All this has probably been connected with structural peculiarities (polycyclic structure) of the proposed stabilizers.

For estimation of the possibility of the use of the synthesized compounds as thermo- and light-stabilizers, the compositions on the basis of PVC with the use of DOPh plasticizer (40 mass % per 100 mass % of PVC) had been prepared. The films made from these compositions were then subjected to the thermogravimetric analysis (Table 2). The obtained data show that the values of both $T_{begin.}$and T_{end} increased when used as proposed additives. For estimation of the synthesized compounds as the light-stabilizers they were subjected to the accelerated light aging. Their efficiency was determined by values of stability coefficients on strength (K_σ) and relative elongation (K_ε). These parameters were identified as the percentage of retention of composition properties after light-warm aging [8].

Table 2. Some thermal and physical-mechanical characteristics of films made with the participation of proposed and known stabilizers (PVC – 100 mass p, DOPh – 40 mass p, stabilizer – 2 mass p, co-stabilizer – 2 mass p.).

Stabilizer	Results of thermal analysis			Light-warm aging	
	$T_{begin.}$, °C	$T_{end.}$, °C	$E_{eff.}$, kJ/mol	$К_{\sigma}$, %	$К_{\varepsilon}$, % *
Compound **1**	197	282	116.2	0.99	1.09
Compound **2**	202	296	113.6	1.04	1.02
Vigostab-BCC**	195	292	114.9	95.3	97.2

* – determined by [6];

** – data of works [8].

The test results showed that films made of PVC-compositions and stabilized by both the proposed compounds and standard stabilizers, after light-warm aging, in a case of using new additives, exceed the known ones. The stabilizing action of the used compounds has been studied by determination of HCl quantity, isolating as a result of effect of high temperature or light on composition (Table 3) [9].

Table 3. Stabilizing capacity of epoxy-containing derivatives of rosin (quantity of co-stabilizer – 2.0 mass p. per 100 mass p. of PVC).

Code of compo-unds	MW	Epoxide number, % found/calculated	Loss temperature of 5% mass,°C*	Time before beginning of HCl isolation at 175°C, min**
1	810	10.2 / 10.62	285	45
2	782	10.88 / 11.00	280	48

* – for compositions cured by PEPA [10];

** – for composition without addition – 20 min.

It follows from the data in Table 3 that as the content of epoxide groups increased, their stabilizing action increased as well. In this case, the efficiency of the stabilizing action of the proposed compounds is determined by the starting temperature of decomposition (at the defined heating rate) and the duration of induction period. The experiments showed that in all cases there is observed an availability of the induction period that is increased as the content of the epoxide groups increased and decreased with rise in temperature (Table 4).

Table 4. Influence of epoxy-containing derivatives of rosin on changes in the induction period and decomposition temperature of the PVC-based compositions at various temperatures.

Composition	Induction period (time before beginning of HCl isolation at temperature), min			Decomposition temperature, °C
	150°C	175°C	190°C	
PVC	18	6	–	168
PVC + comp.1	64	43	8	187
PVC + comp.2	69	48	9	193

It should be noted that the stabilizing activity of adducts 1 and 2 has been connected with availability of the sulfur atoms and epoxide group in the molecules of these compounds, easily reacting with HCl, isolated from PVC under action of temperature and light. Consequently, under the influence of the

epoxide additives, PVC dehydrochlorination rate falls sharply.

Compositions made on the basis of PVC with the use of epoxy-containing compounds **1** and **2**, having sulfur atoms as sulfide bond along with epoxide groups in their composition, have higher impact resistance, good frost resistance and mechanical properties (Table 5).

Table 5. Some properties of the PVC-based compositions with the use of epoxy-derivatives of bis-adduct of ethanedithiol with rosin

Name of index	Components included in the composition on the basis of PVC			
	DOPh(40)* Calcium and barium stearate (2)	DOPh (40) Comp.1(2)	DOPh (20) Comp.2 (20)	DOPh (40)
Tensile strength, MPa	19.6	19.8	19.6	19.0
Specific elongation at break, %	246	243	242	250
Tensile modulus of elasticity, MPa	11.8	11.7	11.6	11.8
Induction period at 170°C, min.	320	316	316	285
Frost resistance, °C	-51	-52	-52	-50
Volatile, % (at 100°C, 1 h under vacuum)	0.29	0.26	0.20	0.31
Decomposition temperature, °C	293	290	292	286

*-the content in mass p. is indicated in parentheses.

The values identified in the physical-mechanical and other properties of the prepared compositions showed that tensile strength, specific elongation at break and modulus of elasticity at 100% deformation are at the level of indices of compositions made only with the participation of widely used plasticizer DOPh and stabilizers – calcium and barium stearates [11].

Thus, it revealed that the synthesized epoxy-containing compounds in the composition of PVC-compositions show their stabilizing effect and can be used as stabilizers for PVC. It found that in this case the compositions made on the basis of PVC with the use of these compounds had relatively better indices in physical-mechanical properties as compared to indices of compositions made in the absence of these compounds.

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KANİFOLUN EPOKSİTƏRKİBLİ ADDUKTLARININ PVX ÜÇÜN İŞIQ VƏ TERMOSTABİLİZATORLAR KİMİ İSTİFADƏSİ

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Kükürd tərkibli qlisidoksikarbonil və qlisidoksimetil əvəzli kanifoldan istifadə etməklə plastifikasiya edilmiş PVX əsasında hazırlanmış kompozitlərin temperatura və işığa qarşı stabilliyi öyrənilmişdir. Müəyyən edilmişdir ki, kanifol əsasında hazırlanmış epoksid tərkibli adduktlar termiki davamlıdırlar və onlar PVX kompozisiyaların emal temperaturuna dözürlər. Göstərilmişdir ki, təklif olunan stabilizatorlar polimer matrisini işıq selindən qorumaq xüsusiyyətinə malikdirlər. Müəyyən edilmişdir ki, təklif olunan stabilizatorlardan istifadə etməklə hazırlanmış kompozisiya nümunələri yüksək temperatura, zərbəyə və şaxtaya davamlılıq və mexaniki möhkəmlik xüsusiyyətləri özündə əks etdirirlər.

Açar sözlər: *kanifol, polivinilxlopid, epoksid, stabilizator, temperatura davamlılıq, mexaniki möhkəmlik*

ЭПОКСИСОДЕРЖАЩИЕ АДДУКТЫ КАНИФОЛИ В КАЧЕСТВЕ СВЕТО- И ТЕРМОСТАБИЛИЗАТОРОВ ДЛЯ ПВХ

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Изучена термо- и светостабилизирующая активность глицидилоксикарбонил- и глицидилоксиметилзамещенных производных серосодержащей канифоли в композициях на основе пластифицированного поливинилхлорида. Показано, что предложенные эпоксипроизводные аддукты канифоли обладают термической устойчивостью, позволяющей им выдерживать температуру переработки поливинилхлоридных композиций. Разработки показали, что предложенные стабилизаторы способны защитить полимерную матрицу от светового излучения. Установлено, что изготовленные с участием предложенных стабилизаторов пленочные образцы проявляют высокую термическую устойчивость, ударопрочность, хорошую морозостойкость и механическую прочность.
Ключевые слова: *канифоль, поливинилхлорид, эпоксипроизводные, стабилизатор, термическая устойчивость, ударопрочность,*