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THERMO- AND LIGHT STABILIZING ACTIVITY OF VINYLOXYCLOPROPANE ADDUCTS WITH THIOLS IN THE COMPOSITIONS BASED ON PVC

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ТЕРМО- И СВЕТОСТАБИЛИЗИРУЮЩАЯ АКТИВНОСТЬ АДДУКТОВ ВИНИЛОКСИЦИКЛОПРОПАНОВ С ТИОЛАМИ В СОСТАВЕ КОМПОЗИЦИЙ НА ОСНОВЕ ПВХ

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ABSTRACT

During exploitation of PVC products, the negative impact of high temperatures and light, and also the destructive influence of various microorganisms, leads to the deterioration of physical-mechanical properties and change of products painting. For prevention of the dehydrochlorination process of PVC, it is necessary to use the effective complex stabilizers, including biostabilizers, differing with their high processability and simultaneously possessing biocidal properties.

In this work the results of investigations of influence of the synthesized sulphur-containing epoxycyclopropanes as stabilizing additives for prevention of the dehydrochlorination process of the compositions based on plasticized PVC have been presented. The influence of these compounds as co-stabilizers in the composition of complex stabilizers – stearates Ca ($CaSt_2$) and Zn ($ZnSt_2$) on thermo- and light stability of PVC-compositions and also on their physical-mechanical and exploitation indices has been studied. It has been established the synthesized epoxy- and cyclopropane-containing mono- and disulphides jointly with stearic acid salts form the synergic mixtures, which can improve the physical-mechanical properties of PVC compositions, their thermal and light stability.

АННОТАЦИЯ

При эксплуатации изделий из ПВХ негативное воздействие высоких температур и света, а также разрушительное влияние различных микроорганизмов приводит к ухудшению физико-механических свойств и изменению окраски изделий. Для предотвращения процесса дегидрохлорирования ПВХ необходимо применение эффективных комплексных стабилизаторов, в том числе биостабилизаторов, отличающихся своей высокой технологичностью и одновременно обладающих биоцидными свойствами.

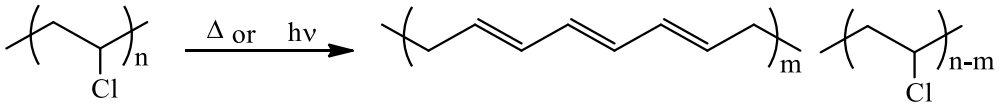
В представленной работе приведены результаты исследований влияния синтезированных серосодержащих эпоксициклопропанов в качестве стабилизирующих добавок для предотвращения процесса дегидрохлорирования композиций на основе пластифицированного ПВХ. Изучено влияние этих соединений как со-стабилизаторов в составе комплексных стабилизаторов – стеаратов Ca ($CaSt_2$) и Zn ($ZnSt_2$) на термо- и светостабильность ПВХ-композиций, а также на их физико-механические и эксплуатационные показатели. Установлено, что синтезированные эпокси- и циклопропансодержащие моно- и дисульфиды совместно с солями стеариновой кислоты образуют синергические смеси, способные улучшать физико-механические свойства ПВХ-композиций, их термо- и светостабильность.

Keywords: polyvinyl chloride, epoxycyclopropane, thiol, composition, thermal stability, color stability, biostabilizer.

Ключевые слова: поливинилхлорид, эпоксициклопропан, тиол, композиция, термостабильность, светостабильность, цветостойкость, биостабилизатор.

Introduction

It was known that the main lack of PVC is its low thermo- and light stability. The production of PVC products is carried out at higher temperatures, and during their exploitation, the negative impact of light leads to a change of the product painting. In addition, the chemical conversions – detachment of hydrogen chloride occurring in PVC macromolecules are accelerated in the presence of air oxygen. Moreover, the dehydrochlorination process is autocatalytic and the hydrogen chloride isolated in this case accelerates the reaction [1-3].



The dehydrochlorination reaction behavior leads to the formation of conjugated double bonds in the macromolecule chain, as a result of which the polymer acquires painting from yellowish to red-brown and even black color. The appearance of polyene units is accompanied by deterioration of the physical-mechanical properties of the polymer. Since the polyene blocks are inclined to oxidative destruction, the carbonyl, hydroxyl, ether, and other oxygen-containing groups are appeared in the processing in the presence of oxygen in the polymer macromolecule chain (according to IR spectroscopy data).

For prevention of the dehydrochlorination process of PVC usually two or more different types of stabilizers are used simultaneously, the mixture of which is selected so that it has a synergic effect, i.e. the stabilizing effect of the mixture was stronger than the effect of its individual components [4].

In practice, the metal oxides, salts of organic acid, sulfur- or phosphoorganic compounds, phenols and their derivatives, and also the compounds containing epoxide groups are used as the stabilizers [5,6]. The most widespread PVC stabilizers are stearates Ca/Zn (or Ba/Zn). These stabilizers have a number of advantages over toxic cadmium stearate, although the latter on efficiency of stabilizing effect is higher. It should also be noted that these stabilizers traditionally used in the PVC compositions (stearates Ca, Zn and Ba) are less toxic compounds and increase the viscosity of the system. During stabilization of PVC, along with metal-carboxylate stabilizers, the organic co-stabilizers are often used in recent years [7].

Aging of PVC connected with dehydrochlorination under the influence of heat and light is also accelerated by the action of various microorganisms. For prevention of this phenomenon, it

is necessary to use the effective complex stabilizers, including biostabilizers [8,9]. However, many of these compounds are very toxic and are poorly combined with other components of the composition, which often limits their use. Now, the strict requirements are made to biocide stabilizers used in the compositions: these are efficiency in relation to a wide spectrum of microorganisms, high activity at low doses, low toxicity, action duration (in accordance with the product's service life), economy and accessibility. They must also possess stability during storage, processability in introduction into the composition, stability during processing, compatibility with the polymer matrix, low volatility, absence of unpleasant smell, etc. [10]. In the literature, however, there are limited data on multifunctional additives differing by their high processability, preventing biodestruction and acting as a biostabilizer, and also having the ability to exhibit biocidal properties. Among them, there are known the epoxide compounds stabilizing PVC due to the reaction of epoxide groups with hydrogen chloride isolated during detachment process [11-13]. For example, the epoxide compound – di-(isodecyl))-4,5-epoxytetrahydrophthalate has been used as a biocidal additive for preparation of a fungal-resistant coating in work [14].

The epoxide compounds are usually used as co-stabilizers and play a role of synergist for PVC stabilization jointly with stearates Ca and Zn [2,11]. However, the mechanism of synergic action, unfortunately, is not yet known. It has been also found that during thermal treatment, only 0.2-3.0% of the used epoxide compound is sewn to PVC macromolecule, i.e. the stabilizing effect of the epoxide compounds or the thermal destruction of PVC have not been connected with the cross-linking reaction [7,12]. Almost all the initial quantity of the epoxide compound at temperature 175°C is consumed for 30 minutes. About 35% of the initial substance is converted into isomeric chlorohydrins, the remaining 62-65% are converted into low-molecular compounds, the structure of which is not established.

Experimental

For carrying out of the investigation it was used: PVC suspension mark Petvinil-S-39/71; ester plasticizer dioctylphthalate (DOPh) (LG Chemical, Republic of Korea); thermostabilizers –Ca-stearate ($CaSt_2$) – ACSABCA-3 and Zn-stearate ($ZnSt_2$) – ACSABZN-53 (Akdeniz Kimyasal Ürünler, Turkey); epoxy-containing compounds **1–4** have been synthesized on methodology shown in [15], sulphur-containing mono- and bis-adducts of epoxycyclopropanes have been synthesized on analogous methodologies shown in [16].

Composition: PVC–100 mass p., DOPh –65 mass p., mixture of stabilizers – 4.0 mass p. (optimal quantity of stearates Ca and Zn in the system – 2.0 mass p. per 100 mass p. PVC, synthesized compounds as co-stabilizers – 2.0 mass p. per 100 mass p. PVC).

The compositions were obtained by mixing of the components in Brabender mixer at rate of 120 rev/min for 30 min. with the subsequent rolling on laboratory rollers. The samples for determination of physical-mechanical characteristics of PVC compositions were made by pressing.

The gelatinization was carried out in oven for 15 min at 170ºC.

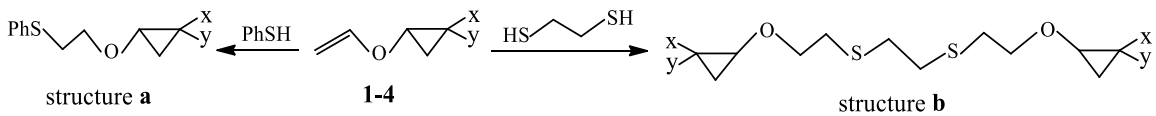
The strength characteristics (modulus of elasticity, strength, deformation at rupture) were carried out on INSTRON breaking machine on GOST 11262-80. The fungal resistance of the compositions was determined on GOST 9.049-91 [9].

The thermal tests were carried out on the films made from homogeneous mixture of stabilizer with PVC: the stabilizer was introduced into concentrated solution of PVC as a suspension in the presence of DOPh. For achievement of a uniform homogeneous distribution of the stabilizer, DOPh was added to the mixture. After evaporation of the solvent, the film was obtained.

The thermal treatment of the films was realized both in nitrogen atmosphere and in air. The dehydrochlorination rate, stabilization period before beginning of HCl isolation and dehydrochlorination rate constant after stabilization period, and also time to darkening of the composition at 180ºC were determined.

Results and discussion

As it was known, the epoxide groups react easily and quantitatively with HCl. The adducts, however, synthesized by us contain epoxide and cyclopropane groups being acceptors of HCl. Therefore we have used them as stabilizing additives for prevention of the dehydrochlorination process of the compositions based on plasticized PVC. In this work, the results of the investigations of influence of the synthesized sulphur-containing epoxycyclopropanes as co-stabilizers in the composition of complex stabilizers (Ca and Zn steareates) on thermo stability and color stability of PVC-compositions and also on their physical-mechanical and exploitation indices have been presented. For preparation of epoxy- and cyclopropane-containing mono- and disulphides we have carried out the radical addition reaction of thiphenol (structure **a**) and ethanediol (structure **b**) to epoxy-substituted vinylcyclopropyl ethers (compounds **1–4**) on scheme:



x=CO_2Gly, y=H (1); x=CH_2OGly, y=H (2); x=y=CO_2Gly (3); x=y=CH_2OGly (4)

The synthesized adducts have been then used in various quantities as co-stabilizers in the mixtures with Ca/Zn-stearates for improvement of the physical-mechanical, heat-physical and rheological (stabilization of viscosity of the system) properties of the polymer compositions. With the aim of elucidation of the stabilizing action of the epoxycyclopropane adducts synthesized by us with thiophenol and ethanedithiol, the color- and thermal stability of the compositions has been investigated. In this case, the effective stabilizing activity of adducts of the epoxide compounds (in a quantity of 2,0 mass %) was determined on their influence on beginning temperature of decomposition of the compositions (at a certain heating rate), on induction period duration and on HCl isolation rate (in mg per 1,0 g of the composition) for 3 h at temperature 175°C. The stabilizing capacity was studied by determination of a quantity of isolating HCl as a result of influence of high temperature on composition (Table 1).

Table 1

Influence of adducts 1–4 on change of induction period at various temperatures and destruction rate in the compositions based on plasticized PVC

PVC compositions with addition of epoxycyclopropanes			Induction period, min (before the beginning of HCl isolation)			T_{decom}, °C (heating rate 5°C/min)	Loss temperature 5 % mass, ºC
Number of composition	Epoxide number	Sulphur content in adduct	150°	175°	190°		
PVC	–	–	20	6	–	168	172
1a	14.52	10.82	91	72	37	171	175
2a	15.30	11.41	94	76	41	173	179
3a	21.71	8.04	110	89	45	187	193
4a	23.18	8.58	119	98	50	196	202
1b	18.55	13.79	97	75	39	179	186
2b	19.80	14.72	99	78	43	182	191
3b	25.95	9.63	128	106	51	204	211
4b	28.29	10.52	136	115	56	212	223

It follows from data of Table 1 that with increase of content of epoxide groups in the synthesized compounds, their stabilizing activity is increased. The low value of stabilizing ability of the compound **1a** has been connected with less content of epoxide groups (E.N.=14.52) in comparison with the compound **4 b** (E.N.=28.29). It also follows from data of Table that the thermal stability increases in transition from compound **1a (1b)** to compound **4a (4b)**. The obtained results show that an introduction of 2,0% sulphur-containing epoxycyclopropanes on the basis of PVC into composition leads to the increase of their thermal stability and decomposition temperature rise and also to the decrease of dehydrochlorination process rate. Thus, in the presence of stabilizers, a slight quantity of HCl is detached from PVC macromolecule, which may be connected with the inhibition of the dehydrochlorination reaction or interaction of the stabilizer with the polymer chain. In use of co-stabilizers, the probability of the dehydrochlorination reaction is considerably decreased. A difference in the distribution of polyene fragments in the chain of PVC macromolecule is also observed. In the absence of co-stabilizers, the induction period for plasticized PVC at 175°C corresponds to 6 min. In introduction of stabilizers Ca/Zn-stearates and 2.0 mass % of adduct of epoxy compound **4b** into composition, the induction period is increased from 6 min. to 115 min.

The change of PVC-compositions painting with use of epoxycyclopropane adducts at various duration of thermal influence has been also studied (Table 2).

Table 2

Change of painting of plasticized PVC samples stabilized with epoxycyclopropane sulphur-containing adducts 1 and 3 depending on the heating duration at 180°C.

Number of epoxycyclopropane adduct	Medium	Change of painting on Gardner scale (from 1 to 18 un.)			
		Heating time, min			
		30	**60**	**90**	**120**
1a	Air	9	10	16	17
	Nitrogen	8	8	15	17
1b	Air	5	7	13	14
	Nitrogen	4	5	11	13
3a	Air	6	7	14	15
	Nitrogen	6	6	13	14
3b	Air	4	6	11	12
	Nitrogen	3	4	9	10
Unstabilized PVC	Air	14	16	17	18
	Nitrogen	12	15	16	18

So, during heating of the samples of compositions at 180°C for 30-120 min the additives improved essentially the stability of the polymer painting. In use of the mixture of stabilizers Ca/Zn-stearates with the synthesized adducts for 30 min influence of high temperature, a slight change of the samples (to 9 un. on Gardner 18-point scale) was observed. During further heating of the samples, the stabilizing action of epoxycyclopropane adducts was finished and the samples with stabilizer were strongly painted. The absence of painting in a case of addition of co-stabilizers to composition has been possibly connected either with catalytic action of epoxycyclopropane adducts on polyene structure or with catalytic oxidation of polyene structures in the PVC stabilization process. This is evidences by availability of the oxygen-containing fragments (–OH, –O–, –C=O etc.) in the IR spectra of PVC macromolecules. However, during heating of the samples in nitrogen medium these fragments are absent in the spectra.

The study of strength properties of the compositions made with the participation of epoxycyclopropane adducts **1-4**, containing ester group in their structure (**1a, 1b, 3a** and **3b)** showed that they possess higher impact resistance and good mechanical properties. In Table 3 a number of the physical-mechanical, thermal and other characteristics for compositions on the basis PVC, plasticized DOPh and stabilized by mixture consisting of Ca/Zn-stearates and sulphur-containing epoxycyclopropane adducts has been presented.

It follows form data presented in Table 3 that the strength indices of the compositions made with the participation of epoxycyclopropane adducts as technological additives are differed from indices of the compositions made in the absence of so-stabilizers. Moreover, the use of mixture of Ca/Zn-stearates jointly with epoxy compounds as co-stabilizers shows an improvement of the results on strength indices, which indicates to availability of synergic effect in the system.

The obtained data indicate also to the fact that the compositions made with epoxycyclopropane adducts along with the improved physical-mechanical and other indices acquire also the biocide properties, which allows their us in domestic sphere and medical practice.

Table 3

Properties of compositions on the basis of PVC with use of adducts 1 and 3.

Name of indices	PVC+ DOPh	PVC+ DOPh + CS*	Composition with epoxycyclopropane adducts			
			PVC+ DOPh+CS +**1a**	PVC+ DOPh+CS +**1b**	PVC+ DOPh+CS +**3a**	PVC+ DOPh+CS+**3b**
Tensile strength, MPa	19.0	19.5	21.4	21.8	21.7	22.2
Specific elongation at break, %	260	255	232	230	230	228
Tensile modulus of elasticity, МПа	11.8	11.7	12.2	11.8	12.0	12.4
Thermal stability (time before beginning of HCl isolation at175°C), min.	21	33	27	29	19	106
Time before beginning of painting change at 175°C, min.	14	42	55	60	67	69
Decomposition temperature, °C	168	171	177	186	194	210
Volatile (100°C, 1 h under vacuum), %	0.31	0.30	0.34	0.41	0.31	0.30
Fungal resistance, points	–	2	1	1	0	0

* – complex stabilizer $CaSt_2$ + $ZnSt_2$

Thus, the effective epoxide stabilizers for PVC possessing thermo- and color-stabilizing action have been obtained. It has been established that the synthesized epoxy- and cyclopropane-containing mono- and disulphides jointly with Ca and of Zn salts of stearic acids form the synergic mixtures able to improve the physical-mechanical properties of PVC-compositions, their thermo- and color stability.

The results of the investigations of color- and thermal stability of PVC-compositions with various content of the epoxide compounds showed that in all cases it is observed an availability of induction period (time to beginning of HCl isolation), which is increased with increase of content of epoxy compound in the composition and is decreased with temperature rise.

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МОНИТОРИНГ ОБЪЕКТОВ ОКРУЖАЮЩЕЙ СРЕДЫ С ИСПОЛЬЗОВАНИЕМ ЭКОЛОГИЧЕСКИ ЧИСТЫХ ЭЛЕКТРОДОВ

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MONITORING OF ENVIRONMENTAL OBJECTS USING ECOLOGICALLY CLEAN ELECTRODES

АННОТАЦИЯ

В обзорной статье представлены достижения инверсионной вольтамперометрии с модифицированными экологически чистыми углеродсодержащими электродами в экологическом мониторинге окружающей среды. Основной задачей исследований являлось полное исключение