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USE OF BIS-ADDUCTS OF ETHANEDITHIOL WITH ALKYL- AND CYCLOALKYL SUBSTITUTED METHYLENE DIOXOLANES IN THE COMPOSITION OF POLYVINYL CHLORIDE

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Abstract: By free radical addition of ethanedithiol to alkyl- and cycloalkyl-substituted methylene dioxolanes, the bis-adducts tested then as a plasticizer for PVC have been obtained. It has been established as a result of the carried out investigations that the introduction of the synthesized compounds into PVC composition improves the physical-mechanical properties, which has been connected with the availability of sulfur atoms, carbonyl groups and ether bond in the molecules of bis-adducts. The high operational indices from PVC-plastics indicate good plasticizing properties of the synthesized bis-adducts, and therefore they can be recommended for practical use.

Keywords: polyvinyl chloride, plasticizer, methylene dioxolane, ethanedithiol, bis-adduct

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Introduction

Owing to a complex of useful technical properties, polyvinyl chloride (PVC) is used for preparation of a wide range of materials for various purposes [1-3]. The uniqueness of PVC is as follows: depending on the method of preparation, formulation and processing technology, this polymer provides a wide assortment of the materials and products characterized by various physical-mechanical and operational properties. These include: high resistance to aggressive media and combustion, low water absorption, absence of unpleasant odor, etc. Besides this, PVC macromolecules are easily modified by introduction of various additives into them. However, at normal temperature, PVC is brittle and inelastic, which limits its area of application. The thermal aging of PVC can be observed already at 100°C with the intensive decomposition of the polymer in the process of its processing, begins at temperature higher 160°C. The decay of PVC proceeds by elimination of HCl, which, in turn, catalyzes the decay of PVC, as a result of which there occurs a rapid and sequential detachment of hydrogen chloride along the macromolecule

with the formation of polyene sequences with conjugated double bonds, which is accompanied by the appearance and deepening of undesirable polymer coloring [4].

Over all period of service life, the materials and products from PVC are subjected to the action of aggressive media of various origins. Therefore, the creation of competitive formulations of PVC-plastics meeting modern technological and operational requirements is of practical interest recently. In this regard, the problem of creation of the effective plasticizers is rather topical. The rigidity, brittleness and other operational characteristics of PVC can be adjusted in a wide range by the introduction of plasticizers [5-8].

Now, the main quantity of the produced plasticizers (up to 85%) is used for PVC plasticization. The introduction of plasticizers into the structure of compositions from PVC makes it possible to increase their impact viscosity during bending and increase specific elongation at break, and by selection of the type and quantity of plasticizer in the composition, one can also obtain materials with given

elasticity conserved in a wide temperature range [9-11]. The use of plasticizers facilitates the processing of the composition, decreases the material brittleness, considerably increases the frost resistance, fire resistance and improves many other operational properties of plastics [12-15]. However, in spite of the wide variety of chemical composition of compounds used as plasticizers, the search for substances

possessing plasticizing properties is an extremely important and actual task.

In this work, with the aim of expansion of the assortment of PVC plasticizers, it has been proposed to use the bis-adducts on the basis of alkyl- and cycloalkyl-substituted methylene dioxolanes with ethanedithiol (EDT) as plasticizers.

Experimental part

The synthesis of alkyl- and cycloalkyl substituted methylene dioxolanes was carried out in line with the methodology described in the work [16].

The bis-adducts of ethanedithiol with alkyl- and cycloalkyl-substituted methylene dioxolanes were obtained according to the methodology described in the work [17].

To create the compositions, the suspension PVC of C-70 mark was taken. The plasticizer dioctyl phthalate (DOPh) ($\rho(20^\circ\text{C})=0.985 \text{ g/cm}^3$, B.p.= 383°C , F.p.= 205°C , acid number – 0.07 mg KOH/g, saponification number – 286 mg KOH/g), barium and calcium stearates were used without purification.

The compositions were produced as follows: PVC of C-70 mark (100 g), pre-dried in a vacuum furnace at 50°C , was mixed for 30 min. at room temperature in a Brabender plastiograph with adducts (10-50 g), barium

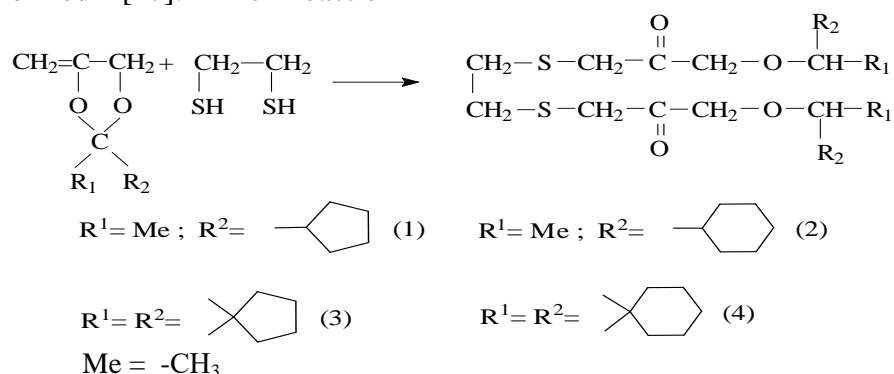
stearate (1.5 g) and calcium stearate. Similarly, the composition was prepared with the participation of the well-known plasticizer DOPh. The prepared mixtures were thoroughly mixed and gelatinized by keeping them in a drying box at 90°C for 100-120 min. After that, the obtained compositions were rolled at 150°C for 10 min. The plates with thickness of 2.0 mm from the obtained masses were then pressed at temperature 150°C and press pressure 5.0 MPa for 10 min, with subsequent water cooling to 40°C [18]. After conditioning of the plates at 20°C , the samples in the form of blades were cut out during the day.

The mechanical tests were carried out on the Instron breaking machine at tensile rate 20 mm/min. The evaluation of the plasticizer migration from the composition was carried out by immersion of the obtained plates in various liquids for time periods at selected temperature.

Results and discussion

The analysis of the reaction products using spectral methods showed that as a result of the addition reaction, mainly the bis-adducts of linear structure containing ketoester fragments are formed [17]. The reaction

proceeds with the opening of both the methylene groups and the dioxolane ring with the formation of compounds of the structure given below:



The obtained bis-adducts were tested as PVC plasticizers. For evaluation of the efficiency of the synthesized adducts as PVC plasticizers, the congelation temperature, thermal stability of adducts at 180°C and their hydrolytic stability (by mixing equal quantities

of adducts and water in an ampoule) at 100°C for 240 h were established.

Synthesized adducts are loosely colored viscous liquids, some of their characteristics are shown in Table 1.

Table 1. Physical-chemical properties of sulfur-containing ketoesters

Indices	Sulfur-containing ketoesters on the basis of monomers				DOPh
	1	2	3	4	
Color	Straw	Straw-pale	Straw	Straw	Colorless
Flash temperature, °C	204	209	212	216	205
Congelation temperature, °C	-61	-63	-62	-64	-50
Quantity of volatile substances in 6 h at 100°C	0.09	0.07	0.06	0.04	0.1

The sulfur-containing adducts of compounds 1-4 used by us as plasticizers showed good compatibility with PVC.

The evaluation of the plasticizer migration from the compositions (results of these tests are presented in Table 2) was carried out by immersion of the obtained plates in various liquids, particularly, into a mixture (75:25 on

volume) of isooctane and toluene (for 7 days at room temperature), water (for 7 days at 70°C) and 1% aqueous solution of sulfanol (for 24 h at 60°C). At the expiration of this time, the mass loss was determined. The mass losses in the circulating air media with temperature 100°C were identified as well.

Table 2. Results of tests for migration of plasticizer from PVC-compositions

Plasticizer on the basis of monomer	Mass loss, %			
	Isooctane+toluene	Water	1% sulfanol solution	Circulating air
1	16.2	1.2	2.2	3.8
2	16.7	0.8	2.3	3.6
3	16.5	0.8	2.4	3.4
4	17.2	0.9	2.2	3.3
DOPh	19.7	1.0	2.5	3.2

The tests of mixtures of equal amounts of these adducts with water, in an ampoule at 100°C for 240 hours, showed that they exhibit sufficient hydrolytic stability.

For samples of PVC plastics with sulfur-containing adduct, some physical-mechanical properties were established: tensile strength, specific elongation at break and tensile modulus of elasticity. Four parallel tests were carried out for each sample and the index average value

was found [19]. The results of physical-mechanical experiments of the tested samples of plastics are presented in Table 3.

It follows from the data in Table 3 that the introduction of the bis-adducts into the structure of the compositions from PVC results in an improvement of the physical-mechanical properties of the compositions on the following indices: tensile strength, specific elongation at break and elastic modulus at 100% deformation.

Table 3. Some physical-mechanical properties of compositions on the basis of PVC, plasticized with adducts of compounds 1-4

Indices	Type of plasticizer				
	DOPh	1	2	3	4
Tensile strength, MPa					
before aging	19.0	18.4	18.5	18.6	18.7
after aging	17.0	17.1	17.3	17.5	17.4
Specific elongation, %					
before aging	250	240	245	250	255
after aging	230	230	240	235	230
Frost resistance, °C	-45	-44	-42	-41	-43
Tensile modulus of elasticity, MPa	11.8	11.6	11.7	11.8	11.7
Critical dissolution temperature, °C	0.19	0.18	0.17	0.19	0.18
Water absorption in 24 h., %	0.21	0.19	0.20	0.18	0.21
Volatile substances, % (100°C, 1 h. under vacuum)	0.31	0.36	0.34	0.35	0.32
Decomposition temperature, °C	286	284	282	285	287

The samples made from PVC with use of adducts of the compounds 1-4 have values close to each other and with samples made with the participation of DOPh.

On the basis of experimental results it was revealed that the availability of sulfur atoms, carbonyl groups and ether bond in the composition of the obtained bis-adducts

provides these compounds with improved plasticizing ability. The good indices of physical-mechanical tests of the samples of PVC-plastics are indicative that the compounds introduced into the composition possess plasticizing properties and, consequently, can be recommended for practical use.

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ETANDİTİOLUN ALKİL- VƏ TSİKLOALKİL ƏVƏZLİ METİLENDİOKSOLANLARLA BİS-ADDUKTLARININ POLİVİNİLKLORİDİN TƏRKİBİNDƏ İSTİFADƏSİ

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Xülasə: Etanditiolun alkil və tsikloalkiləvəzli metilendioksolanlara sərbəst radikal birləşməsi ilə bis-adduktlar sintez edilərək PVX-ə plastifikator kimi sınaqdan keçirilmişdir. Aparılan tədqiqatlar nəticəsində müəyyən edilmişdir ki, PVX kompozisiyalarının tərkibinə həmin birləşmələrin daxil edilməsi kompozisiyaların fiziki-mexaniki xassələrini yaxşılaşdırır ki, bu da bis-adduktların molekulunda kükürd atomlarının, karbonil qruplarının və sadə efir rabitələrinin olması ilə əlaqədardır. PVX əsasında hazırlanan plastiklərin yüksək istismar göstəriciləri kompozisiyaların tərkibinə daxil olan birləşmələrin plastifikasiya xassələrinə malik olmalarını göstərir və onların praktikada istifadə olunmaları tövsiyə olunur.

Açar sözlər: sintez, polivinilxlorid, plastifikator, metilendioksolan, etanditiol, bis-addukt

ИСПОЛЬЗОВАНИЕ БИС-АДДУКТОВ ЭТАНДИТИОЛА С АЛКИЛ- И ЦИКЛОАЛКИЛЗАМЕЩЕННЫМИ МЕТИЛЕНДИОКСОЛАНАМИ В СОСТАВЕ ПОЛИВИНИЛХЛОРИДА

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Аннотация: Свободнорадикальным присоединением этандитиола к алкил- и циклоалкилзамещенным метилендиоксоланам были получены бис-аддукты, которые были испытаны в качестве пластификатора для ПВХ. В результате проведенных исследований установлено, что введение в состав ПВХ композиций синтезированных соединений улучшает физико-механические свойства, что связано с наличием в молекулах бис-аддуктов атомов серы, карбонильных групп и простой эфирной связи. Высокие эксплуатационные показатели пластиков из ПВХ свидетельствуют о хороших пластифицирующих свойствах синтезированных бис-аддуктов и поэтому они могут быть рекомендованы для практического применения.

Ключевые слова: поливинилхлорид, пластификатор, метилендиоксолан, этандитиол, бис-аддукт