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USE OF GLYCIDYLOXYMETHYL SUBSTITUTED PHENYL (BENZYL) CYCLOPROPANES IN THE COMPOSITION OF EPOXIDE OLIGOMER ED-20 AS DILUENTS

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Abstract: By the interaction of phenyl (benzyl) substituted cyclopropylcarbinols with epichlorohydrin, the glycidylloxymethyl substituted phenyl(benzyl)cyclopropanes, used as active diluents of epoxide resin ED-20, were synthesized. It found that the addition of the obtained epoxy compounds to the epoxide resin decreases the viscosity of the resin and increases the lifetime of the compositions. The high degree of curing (96-98%) indicates the participation of the synthesized epoxy cyclopropanes in the cross-linking processes. Some physical-mechanical characteristics of compounds made with the participation of the synthesized epoxy cyclopropanes were established. The improvement of strength and heat-physical parameters of cured compositions in comparison with compositions made without diluents was revealed.

Keywords: glycidylloxymethyl substituted phenyl (benzyl) cyclopropanes, epoxide composition, modification, active diluents, curing.

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Introduction

The epoxide compositions are perspective materials widely used in such industries as construction, instrument-making, automobile industry, electrical engineering, etc. The epoxide resins are used in impregnating and filling compounds, for preparation of coatings meeting the corresponding operational requirements, etc [1-5]. The advantages of the epoxide resins are their mechanical and chemical resistance, high dielectric characteristics after curing, low shrinkage, excellent adhesion to metals, glass, wood and a number of other materials. The epoxide resins are easily combined with many polymers and oligomers, which are used to change some of their properties [6-8]. However, along with the positive properties, the epoxide resins of ED-20 type have a number of disadvantages, which include high viscosity, high exothermic effect

during their curing, as well as a short viability time. The epoxide compositions have a certain lifetime, after which they undergo the cross-linking, forming a net structure. The obtained materials with three-dimensional cross-linked structure are not dissolved and incapable of further processing. For elimination of these disadvantages, the modifiers – active or inactive diluents decreasing their viscosity and the temperature of the exothermic reaction, and also prolonging the viability of the composition are usually introduced into the composition of the epoxide resins [9-10]. Therefore, the development of methods for directional regulation of the properties of epoxide compositions by their modification with various additives plays a particular importance and actuality.

This work has been devoted to the investigation of modification of the properties of the epoxide resin ED-20 with the use of glycidyloxymethyl substituted

phenyl(benzyl)cyclopropanes as diluents and study into the properties of the cured compounds.

Experimental part

The synthesis of glycidyloxymethyl substituted phenyl (benzyl) cyclopropanes was carried out in keeping with the methodology described in work [11].

Modification of ED-20 with glycidyloxymethyl substituted phenyl(benzyl)cyclopropanes. 5-15 mass p. of glycidyloxymethyl substituted phenyl (benzyl) cyclopropane as a diluent and the calculated quantity of curing agent of polyethylene polyamine (PEPA) was added to 100 mass p. of epoxide resin of ED-20 type with stirring. Then the obtained mixture was stirred to a homogeneous mass for removal of air bubbles, the mixture was evacuated at 25-30 °C and the reaction mass was poured into specially prepared molds for curing.

Curing of compositions on the basis of ED-20 was carried out in the presence of PEPA,

the content of which was calculated according to the known formula based on epoxide number values. The following curing regime of the prepared compositions was selected by preliminary experiments: 16 h. – at room temperature; for 2 h – at 60°C, 2 h – at 80°C and 2 h – at 120°C.

The degree of cross-linking and the content of gel- and sol-fractions of the cured compositions were determined by extraction with acetone in Soxlet apparatus during the day, with the subsequent drying to a constant mass.

The conditional viscosity of the resin was determined using a ball viscometer ($d=2.37$ mm) at temperature 75°C.

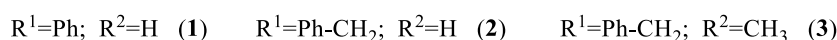
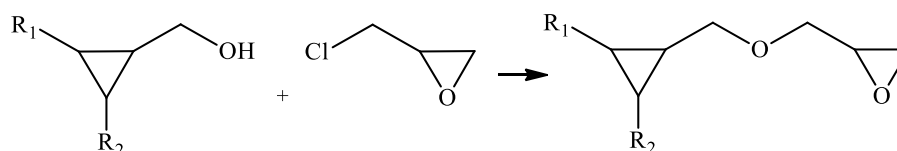
The adhesion strength of the glues during shear was determined in accordance with GOST 14759-69.

Results and discussion

With the aim of decreasing the viscosity and improving the recyclability of high-viscous epoxide resins, as well as the elongation of the lifetime of compositions based on them, the resins are usually subjected to dilution (modification) with low-viscous chemically active compounds containing epoxide groups. With that end in view, there were synthesized the glycidyloxymethyl substituted phenyl(benzyl)cyclopropanes **1-3**, which are used in the composition of epoxide resin ED-20

as active diluents. In our previous investigations, we have carried out a similar modification of the epoxide resin for decrease of its viscosity by means of glycidyloxycarbonyl substituted phenyl (benzyl) cyclopropanes obtained from phenyl (benzyl) substituted cyclopropanecarboxylic acids [12].

The compounds **1-3** were obtained by the interaction of phenyl (benzyl) substituted cyclopropylcarbinols with epichlorohydrin, according to the scheme below:



Some physical-chemical parameters of glycidyloxymethyl substituted

phenyl(benzyl)cyclopropanes are presented in Table 1.

As is known, the rheological properties of solutions depend on the type of intermolecular interaction. When it comes to the epoxide resin ED-20, the intermolecular interactions stipulate the formation of associates. When introducing active diluents into the composition of the

epoxide resin, these associates are destroyed. Therefore, it is necessary to find out firstly the optimal quantity of diluent in the composition, in which the less stable associates with low viscosity are formed.

Table 1. Some physical-chemical indices of glycidyloxymethyl substituted phenyl (benzyl) cyclopropanes.

Code of compounds	R ¹	R ²	MM	B.p., °C/mm.merc. c.	d_4^{20}	n_D^{20}	v, %	Content of epoxide groups* (found/calc.)
1	Ph-	H	204	112-118/4	1.1206	1.5210	86	27.82 / 27.94
2	PhCH ₂ -	H	218	119-122/4	1.1100	1.5180	83	25.96 / 26.15
3	PhCH ₂ -	CH ₃	232	126-129/4	1.1060	1.5090	78	24.24 / 24.57
ED-20	–	–	380	–	1.1680	1.5611	–	22.60

* – per the propylene oxide group (carried out according to GOST 12497-78, sec.3).

The compounds used by us as active diluents and simultaneously modifiers of some properties of the cured compounds are monoepoxide compounds. Since the epoxide groups participate primarily in the cross-linking process with appropriate curing agents, such monoepoxide compounds should be considered as agents breaking the chain, due to that a deterioration of the properties of the cured compositions occurs.

In the structure of the synthesized compounds, along with the epoxide functional groups, there are three-membered cycles and

other functional groups. As is known, the cyclopropane ring is a stressed cycle and in its opening, a large quantity of heat is isolated and the appearance of additional chemical bonds increasing the cross-linking density.

It revealed that the synthesized compounds **1-3** are well combined with epoxide resin and essentially reduce its viscosity. So, when introducing the compounds **1-3** into the structure of the composition in a quantity from 5 to 15 mass p. (per 100 mass p. of the epoxide resin), the conditional viscosity of the initial resin is dropped from 30 to 15 (Table 2).

Table 2. Influence of the content of compounds **1-3** on the viscosity and lifetime of compositions.

Indices	ED-20	Composition of resin ED-20 with compounds (mass p.)								
		1			2			3		
		5	10	15	5	10	15	5	10	15
Conditional viscosity *, sec.	30	21	18	15	22	19	17	25	21	19
Lifetime** at 25°C, min.	40	68	72	77	76	79	82	79	84	88

* – determined on a ball viscometer (d=2.37 mm) at 75°C;

** – determined on the change of the epoxide number of the composition.

In Fig.1 the dependence of the relative viscosity (the ratio of the conditional viscosity of resin ED-20 with diluent for the conditional viscosity of pure resin) of resin ED-20 on the content of diluent – compounds **1-3** is shown.

The data presented in Fig. 1 show that an increase of the diluents content from 5 mass p. to 15 mass p. leads to the fact that the relative viscosity of the system is decreased in 1.2–2.7 times.

It is known that the composition of the epoxide resins primarily influences on their lifetime, and also on the compositions based on them. When using the compounds **1-3** in the structure of compositions, along with the decrease of the system, the increase of the lifetime of the composition was revealed. In Table 2 the influence of the active diluent content on the lifetime of the compositions is shown.

During the curing of the prepared compositions, the increase of the curing rate was observed, and the compositions with the

participation of the compound **1** was cured faster (within 25-30 min.) than those with the compounds **2** and **3** (30-45 min.).

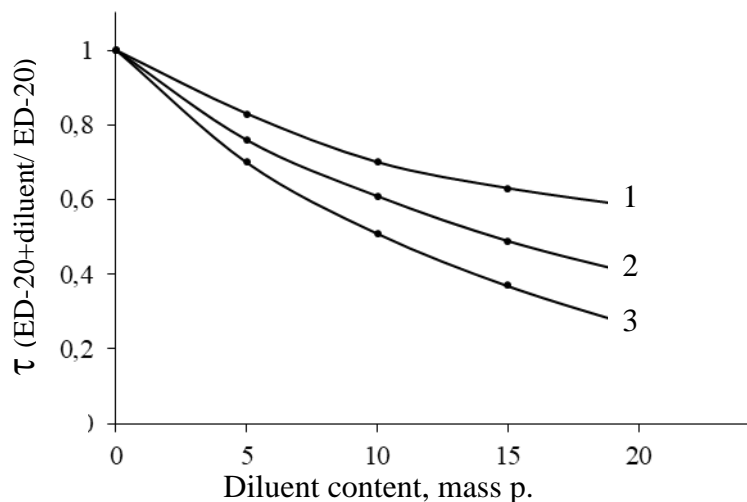


Fig.1. Dependence of the relative viscosity of the compositions "τ" on the diluent content: 1 – ED-20+compound **1**; 2 – ED-20+ compound **2**; 3 – ED-20+ compound **3**.

The degree of curing of the compositions was established by acetone extraction of the samples in a Soxhlet apparatus. The obtained results showed that the curing of these compounds reached 96-98%, which indicates the participation of the compounds **1-3** in the cross-linking processes. Moreover, the cross-

linking reactions proceed due to the opening of both epoxide groups and cyclopropane fragments, which was observed in the disappearance of the characteristic absorption bands of the cyclopropane group (at 1035 cm^{-1}) in the IR spectra of the cured compositions (Fig. 2).

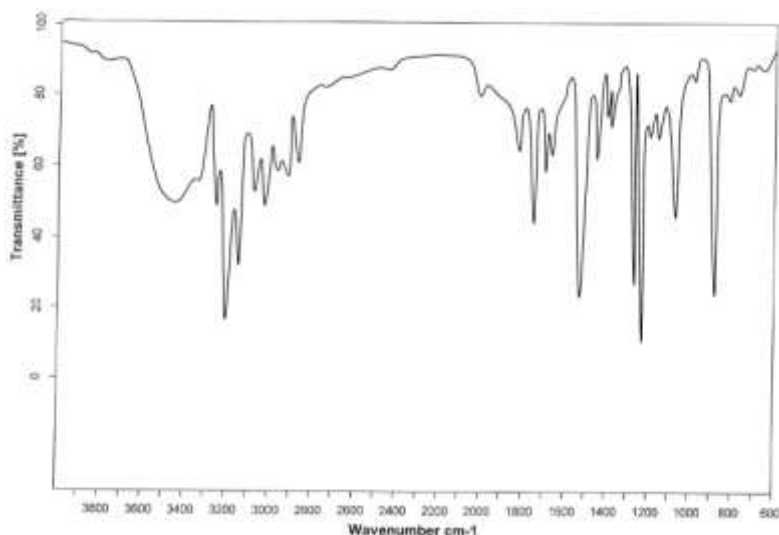


Fig. 2. IR spectrum of the cured composition on the basis of ED-20 and compound **1**.

The use of phenyl (benzyl) substituted epoxycyclopropanes in the composition of ED-20 leads to an increase in the net density and, in

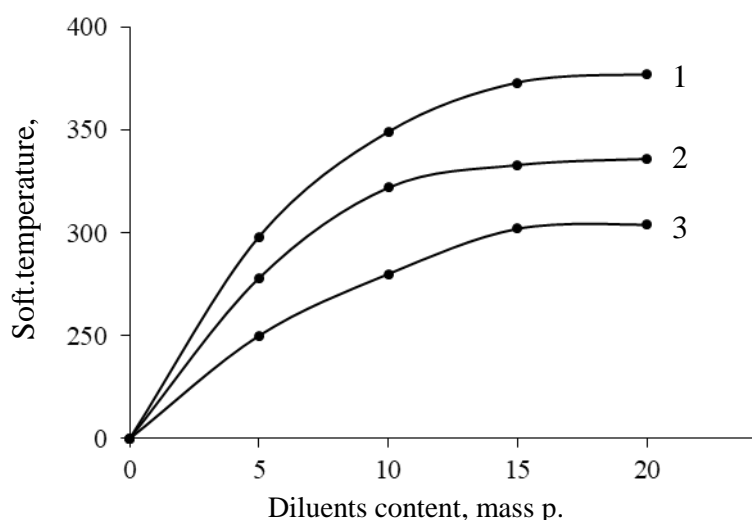
this connection, to an increase of the strength indices of the compounds, heat- and thermal stability and other characteristics (Table 3).

Table 3. Some physical-mechanical properties of the cured compositions on the basis of resin ED-20 with diluents 1-3 (curing agent – PEPA – 10 mass p. per 100 mass p. of resin)

Indices	ED-20	Composition of resin ED-20 with compounds (mass p.)								
		1			2			3		
		5	10	15	5	10	15	5	10	15
Destructive tensile stress, MPa	40.1	77.8	79.2	80.7	75.0	76.3	77.6	69.1	70.6	71.8
Adhesion strength, MPa	8.2	9.5	9.6	9.8	9.4	9.4	9.5	8.8	8.9	8.9
Continuation of Table 3.										
Brinell hardness, MPa	13.3	12.4	12.8	12.9	12.9	13.3	13.5	13.2	13.8	14.6
Vicat heat-resistance, °C	98	137	139	143	138	139	142	138	138	140
Softening temperature, °C	127	298	349	373	278	322	333	250	280	302
Water absorption, %	1.2	1.1	1.1	1.0	1.1	0.9	0.9	0.8	0.8	0.6

There is also observed an increase in the heat resistance values. With an increase of the content of the active diluent, the softening temperatures of the compounds are increased as well. Moreover, such increase becomes quite

noticeable at low (up to 10 mass p.) diluent concentrations, at diluent content 15÷20 mass p. the softening temperatures are not essentially changed (Fig. 3).

**Fig. 3.** Dependence of softening temperature of the cured compositions on diluent content in the composition of resin ED-20: 1 – compound 1; 2 – compound 2; 3 – compound 3.

By the interaction of phenyl (benzyl) substituted cyclopropyl carbinols with epichlorohydrin, the glycidylloxymethyl substituted phenyl (benzyl) cyclopropanes, used in the structure of epoxide compositions on the basis of ED-20 resin as reactive diluents were synthesized and characterized. The tests showed that their introduction into the composition of the resin ED-20 leads to a drop in the viscosity and an increase in the lifetime of the compositions.

The obtained results showed that some

characteristics of the cured compositions of PEPA with the use of phenyl (benzyl) substituted epoxycyclopropanes are improved. In particular, it is observed an increase of the tensile strength and an increase of the heat resistance of the compositions. Such increase of indices of the cured compounds was probably due to the fact that the used diluents, along with epoxide groups, also contain cyclopropane fragments in their molecules, which also participate in the cross-linking processes.

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**QLİSİDİLOKSİMETİL ƏVƏZLİ FENİL (BENZİL) TSİKLOPROPANLARIN
ED-20 EPOKSİD OLİQOMERİNİN TƏRKİBİNDƏ DURULAŞDIRICI KİMİ İSTİFADƏSİ**

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Xülasə: Fenil (benzil) əvəzli tsiklopropilkarbinolların epixlorhidrinlə qarşılıqlı təsirindən qlisidiloksimetil əvəzli fenil (benzil) tsiklopropanlar sintez edilərək ED-20 epoksid oliqomerinin tərkibində durulaşdırıcı kimi istifadə olunmuşdur. Müəyyən edilmişdir ki, sintez edilmiş epoksibirləşmələrin epoksid qətranına əlavə edilməsi ilə qətranın özlülüyü azalır, kompozisiyanın isə yaşama müddəti artır. Hazırlanmış kompozisiyaların bərkimə dərəcələri yüksək olduğu (96-98%) sintez edilmiş birləşmələrin tikilmə prosesində iştirakını göstərir. Alınmış kompaundların birsıra fiziki-mexaniki xarakteristikaları təyin edilmiş və müəyyən edilmişdir ki, durulaşdırıcının iştirakı ilə bərkidilmiş kompozisiyaların möhkəmlik xarakteristikaları və istiyə davamlılıqları müvafiq durulaşdırıcısız kompozisiyaların göstəricilərindən nəzərə çarpacaq dərəcədə üstündür.

Açar sözlər: qlisidiloksimetil əvəzli fenil(benzil)tsiklopropanlar, epoksid kompozisiyası, modifikasiya, aktiv əlavə, durulaşdırıcı, bərkidilmə.

ИСПОЛЬЗОВАНИЕ ГЛИЦИДИЛОКСИМЕТИЛЗАМЕЩЕННЫХ ФЕНИЛ(БЕНЗИЛ)ЦИКЛОПРОПАНОВ В СОСТАВЕ ЭПОКСИДНОГО ОЛИГОМЕРА ЭД-20 В КАЧЕСТВЕ РАЗБАВИТЕЛЕЙ

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Аннотация: Взаимодействием фенил(бензил)замещенных циклопропилкарбинолов с эпихлоргидрином синтезированы глицидилоксиметилзамещенные фенил(бензил) циклопропаны, которые были использованы в качестве активных разбавителей эпоксидной смолы ЭД-20. Установлено, что добавление полученных эпоксисоединений в эпоксидную смолу уменьшает вязкость смолы и увеличивает время жизни композиций. Высокая степень отверждения (96-98%) указывает на участие синтезированных эпоксициклопропанов в процессах сшивки. Определены некоторые физико-механические характеристики компаундов, изготовленных с участием синтезированных эпоксициклопропанов: выявлено улучшение прочностных и теплофизических показателей отвержденных композиций по сравнению с композициями, изготовленными без разбавителей.

Ключевые слова: глицидилоксиметилзамещенные фенил(бензил)циклопропаны, эпоксидная композиция, модификация, активный разбавитель, отверждение.