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WATER-DILUTING EPOXIDE TELOMER BASED ON DIBUTYL ETHER OF ADIPINIC ACID

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Abstract: *A water-diluting epoxidetelomer was synthesized on the basis of allylglycidyl ether and dibutyl ether of adipinic acid under the effect of free radicals being generated during thermal decay of ditretbutyl peroxide. The reaction proceeds in one stage, the process is wasteless and fire-safe while the unreacted allylglycidyl ether returns to the reaction. The synthesized epoxytelomer is a low-viscous resin of light-yellow color, soluble in water, chloroform, acetone, M.w.=380-400 g.mol^{-1}, epoxide number –18-19%. The composition and structure of the obtained telomer were established due to physical and chemical investigations. The composition materials of hot and cold curing were developed on the basis of the obtained telomer. The curing process was studied by a method of differential-thermal analysis to show that the obtained materials were characterized by high heat-resistance and thermal stability. It revealed that the epoxide telomer has surface-active properties.*

Keywords: *allylglycidyl ether, dibutyl ether of adipinic acid, hardener, epoxide group, composition, surface tension, epoxide number*
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Introduction

The epoxide telomeres (ET) and paint-lacquer coatings thereon are widely used in various industries due to their high adhesion, strength and protective properties [1,2]. However, the paint-lacquer coatings widely used now contain up to 80% of volatile organic solvents. In this connection, the modern technologies of the creation of paint-lacquer coatings are developing toward reduction of solvents and creation of film-forming systems on water basis which considerably decreases the volume of harmful emissions into the atmosphere. At the same time, these technologies are rather economical due to the absence of organic solvents irretrievably lost during the formation of coatings in their composition [3,4].

When adjusted for the fact that one of the main tendencies of the development of the modern paint-lacquer industry is the desire to decrease or completely exclude the use of flammable and toxic organic solvents, the new progressive materials have been created and produced. These include water-soluble paints, i.e. paint-lacquer systems polymerized directly on the protected surface [5].

At the same time, the coatings based on ET are notable for high hygiene and easiness of purification; they are irreplaceable for dressing of placements at enterprises of pharmaceutical and food branches of industries. The carboxylic acids, substituted carboxylic acids and their functional derivatives (anhydrides, esters, etc.) can be used as epoxyoligomers in creating water-soluble film-forming agents (FFA) [6,7].

The study into these classes of compounds by the radical telomerization has been attributable, on the one hand, to variety of functional groups and as a rule, to wider accessibility of low (C_1-C_4) representatives of each series of the compounds, on the other hand, by practical interest in long-chain compounds, linear and branched structures consisting of oxygen-containing functional groups, the synthesis of which is strongly complicated by traditional methods. A radical telomerization makes it possible to carry out technologically simple transition from the

simplest compounds to the highest representatives of this class with various structures and lengths of the hydrocarbon chain.

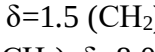
For practical purposes, the carboxylic acids are of the greatest interest as telogens, and for scientific purposes – esters of these acids

Many diacids have gained great importance in technology, esters of adipinic acid are plasticizers of polymers. In addition, it should be noted that the adipinic acid is produced in large quantities as an intermediate product in the production of synthetic polyamide fibers [8-10].

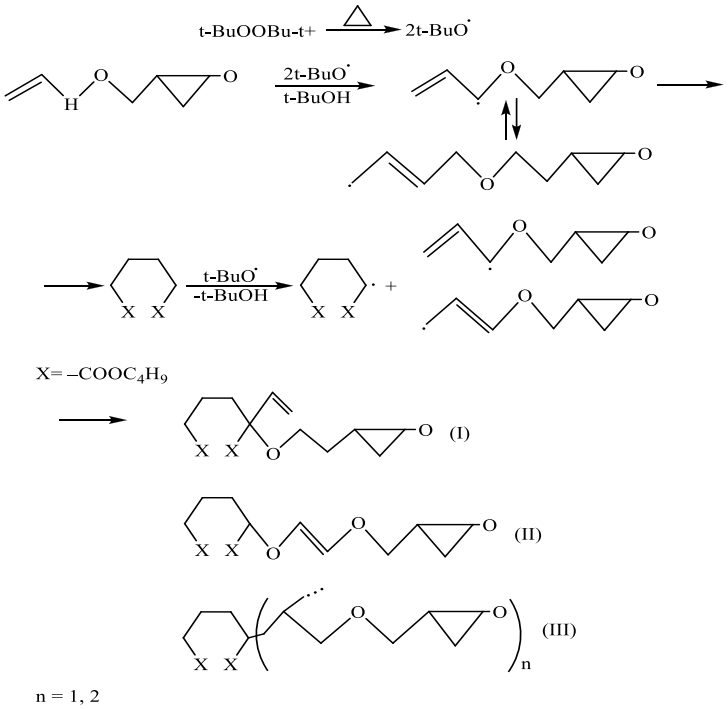
Allowing for the above-mentioned, and continuing the investigations in this direction [11] the synthesis of epoxide telomer with epoxide and ester group in its structure was of interest.

Results and discussion

The synthesis of epoxide telomer was carried out by interaction of allylglycidyl ether (AGE) with dibutyl ether of adipinic acid (DBEAA) under the effect of free radicals generated at thermal decay of ditretbutyl peroxide. The process of radical telomerization is a single-stage, wasteless, fire-safe while unreacted AGE after distillation and purification can be used again in the reaction. The obtained epoxytelomer is a low-viscous resin of light-yellow color, soluble in water, chloroform and acetone. The molecular weight determined by the cryoscopic method is in the range of 380-400 g·mol^{-1}; a quantity of epoxide groups is 18-19%, iodine number – 71.The composition and structure of the obtained telomer were confirmed by methods of elemental and spectral analyses, and purity – by thin layer chromatography.

In the IR spectra of telomerthe the absorption bands (taken on tablets ofKBr) typified by oxirane cycle  (1255, 850, 765 cm^{-1}) were detected. Also, the weak absorption bands with frequencies 1610, 1640 cm^{-1} indicate availability of internal C=C-bonds, 1740-1725 (ether groups) in the structures of telomers. In the PMR spectra the chemical shifts (ppm.): δ=1.5 (CH_2), δ=3.10 (), δ=3.10-3.20 (OCH_2), δ=8.05-8.25 (H-C) [12].

The totality of all obtained data allows to assume that the free-radical telomerization of AGE with DBEAA proceeds due to double bonds of AGE on scheme, in this case the epoxide group is kept.



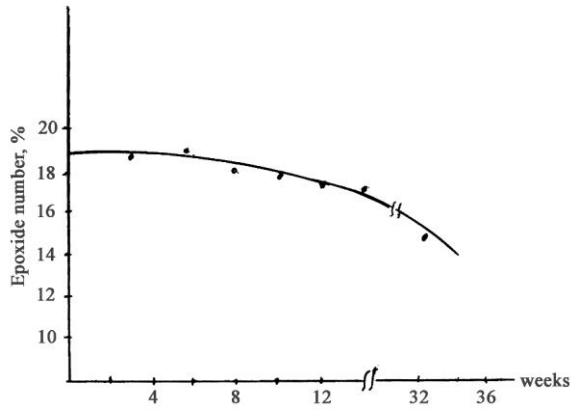


Fig. 1. Changes in epoxide number depending on time

It is well-known that important technological parameters in the course of epoxide resins processing are their viscosity. During long-term storage, the viscosity rises while the epoxide number is decreased which makes the epoxide resin unprocessable. Results of investigations showed that the synthesized telomere has a good stability. Changes in epoxide number depending on time are shown in Fig.1. As is evident from Fig.1, the epoxide group in the telomer is retained for a long time which is very important for epoxide resins processing.

It should be noted that the expansion of the use of water dispersions is often hindered by necessity of introduction of surface-active substances (SAS) for improvement of the wettability of coatings, which evaporating disturb the continuity of coating and favor the deterioration of their properties.

On the basis of the synthesized telomer, 12% aqueous materials were obtained. On the phase section of air-water, we have studied the surface-active properties of the synthesized epoxytelomer (Table 1).

It should be noted that this coating completely excludes the use of SAS.

We can observe from Table 1 that the addition of 0.5 wt % of epoxytelomer to the composition leads to decrease of surface tension of water from 72.53 to 40.1 erg/ cm^2 and no foam is formed which is very important for coating preparation.

Table 1. Surface-active properties of epoxytelomer at the border of air-water

Concentration in water, wt.%	Surface tension δ, erg/cm^2, at t°,C		Wetting angle, cos Q	Foam-formation
	20°	40°		
0.5	40.1	36.50	0.7110	Foam is not formed.
0.25	42.3	39.40	0.6920	
0.125	45.4	41.60	0.6730	
0.0625	53.0	48.10	0.6510	
water	72.53	69.57	0.6316	

The composition materials were also obtained on the basis of synthesized telomer, and the curing process was studied by means of thermal analysis.

The thermal stability of epoxide compositions was estimated on the basis of activation energy of decomposition calculated by double method of logarithm. The data obtained on thermal stability of the investigated materials are presented in Table 2. T_{10}, T_{20}, T_{50}– temperature at which the composition loses 10, 20, 50% of weight, respectively. As is seen from Table 2, the obtained epoxide compositions have good thermal indices in relation to the industrial resin ED-20.

Table 2. Thermal indices of composition.

Composition (telomer:hardener)	T_{10}	T_{20}	T_{50}	E_{act}. kJ/mol	TGI,°C
Telomer : PEPA (100:20)	315	360	410	133.40	139
ED-20: PEPA (100:12)	310	350	395	130.5	120
Telomere+iso-MTHFA (100:85)	310	375	405	140.50	144
ED-20+iso- MTHFA **(**standard)	250	320	360	120.50	110
Telomer (self-cured)	270	320	365	150.30	–

An important index is the resistance of the coating against aggressive media (telomer: PEPA=100:12 mass p., thermal treatment of coatings– 80°C/2 h+120°C/2 h)

The chemical resistance of coatings was estimated by measurement of material swelling in water and aggressive media.The data obtained are presented in Table 3.

Table 3. Chemical stability of the composition on the basis of synthesized telomer

Medium	Mass of composition, g, in a day							
	0	1	2	3	4	5	6	180
Distilled water	0.9210	0.9300	0.9315	0.9430	0.9167	0.6225	–	–
3% NaCl	0.9820	1.0020	1.0612	1.0785	1.0430	1.0264	–	–
20%HCl	0.8990	0.8920	0.5840	0.4335	–	–	–	–
20%KOH	0.9550	0.9665	0.9635	0.9918	1.0218	1.0285	1.0344	1.1226

It is seen from Table 3 that the swelling increases in aggressive media, however, its value remains quite acceptable to recommend materials as alkali-resistant coatings.

Experimental

Methodology of preparation of epoxide telomer. The synthesis was carried out in a four-necked round-bottom flask equipped with a mechanical stirrer, reflux condenser, thermometer, and dropping funnel. The calculated quantity of DBEAA (1 mol) was loaded into the flask, heated to 143°C, and a mixture of AGE (1 mol) and DTBP (0.15 mol) was uniformly added dropwise for 1 h. The reaction mixture was stirred for 3 h at 143°C. The unreacted AGE was isolated by fractionation. The yield of telomer is 78%, epoxide number – 19%, iodine number – 71. The epoxide telomer is a low-viscous liquid of light-yellow color, soluble in water, chloroform, acetone and other polar solvents. The molecular weight determined by cryoscopic method made up 380-400 g $\cdot$mol^{-1}. The telomer viscosity is determined by Pinkevich viscometer to make 1720 sst.

The structure of the synthesized telomer was established by PMR and IR spectroscopy. The IR spectra were taken on spectrophotometer UR-20 in the field of 3400-300 cm^{-1}, the PMR spectra – on spectrometer“Bruker WM-250 MHz”in the solution of carbon tetrachloride with internal standard– hexachlorodisiloxane. The composition of telomer was determined by means of TLC and GLC. TLC was carried out on Silufol-254 plates with fixed layer of silicagel. The eluent was two-component system of ethyl acetate: benzene = 1: 3, with emerging in iodine vapor. GLC analysis was carried out on the device "Chrome 3" with flame-ionization detector and catarometer. CE-30 (5%), PEG-4000 (15%) were used as a liquid medium, the solid bearers were chromaton N-AW-DMS with particle sizes of 0.200-0.250 mm. The temperature interval of analyses – 30-500°C, gas bearer – helium, gas bearer – 40-60 ml$\cdot$min^{-1}.

Thermal analyses were carried out on derivatograph MOM (Paulik-Paulik-Erdei) in the temperature range of 20-500°C, temperature rise rate – 5°/min, sample weighing – 200 mg, channel sensitivity – TG-200, DTG -1/m , λ - Al_2O_3 was used as a standard and the tests in the air atmosphere were carried out. It revealed that the epoxytelomer is cured with PEPA and iso-MTHFA in the soft temperature conditions, the curing reaction is completely over at 120° and 150°C, respectively. It should be noted that in the absence of hardeners the epoxytelomer is self-cured under the influence of temperature.

Conclusions

1. The water-diluted epoxide telomer has been obtained by means of free-radical telomerization of AGE with DBEAA with satisfactory yield. The process is one-stage, wasteless, ecologically pure, fire-safe.
2. It has been revealed that the epoxide telomer has surface-active properties and does not require the introduction of SAS in paint-lacquer compositions.The coatings and a number of composition materials characterized by high thermal and heat-physical properties have been obtained on the basis of the epoxytelomer.

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ADİPİN TURŞUSUNUN DİBUTİL EFİRİ ƏSASINDA SU İLƏ DURULAŞDIRILAN EPOKSİD TELOMERİ

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Ditretbutilperoksidin termiki parçalanması nəticəsində əmələ gələn sərbəst radikalların təsiri ilə allilqlisid efiri və adipin turşusunun dibutil efiri əsasında su ilə durulaşdırılan epoksid telomeri sintez olunmuşdur. Reaksiya birmərhələli olub tullantısızdır, yanğın təhlükəsi yoxdur. Reaksiyaya daxil olmayan allilqlisid efiri yenidən prosesə qaytarılır. Sintez olunmuş epoksitelomer aşağı özlülü olub açıq-sarı rənglidir, suda, xloroformda, asetonda həll olur. M.k.=380-400 q.mol^{-1}, epoksid ədədi 18-19%-dir. Alınmış telomerin tərkibi və quruluşu fiziki və kimyəvi üsullarla təyin olunmuşdur. Alınmış telomer əsasında isti və soyuq bərkimə ilə kompozisiya materialları alınmışdır. Bərkimə prosesi differensial-termiki analiz üsulu ilə öyrənilmiş və göstərilmişdir ki, alınmış materiallar yüksək istiliyə- və termo davamlılığa malikdirlər. Müəyyən edilmişdir ki, epoksid telomeri səthi-aktiv xassəyə malikdir.

Açar sözlər: allilqlisid efiri, adipin turşusunun dibutil efiri, bərkidici, epoksid qrupu, kompozisiya, səthi gərilmə, epoksid ədədi

ВОДОРАЗБАВЛЯЕМЫЙ ЭПОКСИДНЫЙ ТЕЛОМЕР НА ОСНОВЕ ДИБУТИЛОВОГО ЭФИРА АДИПИНОВОЙ КИСЛОТЫ

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На основе аллилглицидилового эфира и дибутилового эфира адипиновой кислоты под действием свободных радикалов, генерируемых при термическим распаде дитретбутилпероксида, синтезирован водоразбавляемый эпоксидный теломер. Реакция протекает в одну стадию, процесс безотходный, пожаробезопасный, не прореагировавщий аллилглицидиловый эфир возвращается в реакцию. Синтезированный эпоксителомер представляет собой низковязкую смолу светло-желтого цвета, растворимую в воде, хлороформе, ацетоне, М.в.=380 - 400 г.моль$^{-1}$, эпоксидное число–18-19 %. Состав и структура полученного теломера установлены физико-химическими методами анализа. На основе полученного теломера разработаны композиционные материалы горячего и холодного отверждения. Процесс отверждения изучен методом дифференциально-термического анализа и показано, что полученные материалы характеризуются высокой теплостойкостью и термостойкостью. Выявлено, что эпоксидный теломер обладает поверхностно-активными свойствами.

Ключевые слова: аллилглицидиловый эфир, дибутиловый эфир адипиновой кислоты, отвердитель, эпоксидная группа, композиция, поверхностное натяжение, эпоксидное число