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Heat-Resistant Composition On The Basis Of New Epoxysulphoimide Resin of Branched Structure

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ABSTRACT: *With the aim of synthesis of new heat-resistant epoxy compounds, by the reaction of 2-hydroxypropyl-1,3-bis-esterosulphoimide of saccharin-6-carboxylic acid with esters of the same acid, triglyceride of saccharin-6-carboxylic acid has been obtained. In the second stage, by interaction of tripotassium salt of the synthesized triglyceride of saccharin-6-carboxylic acid with epichlorohydrin, triglyceride triglycidyl of saccharin-6-carboxylic acid has been obtained. The yield of purposeful product was 87.5%. The composition and structures of the obtained compounds have been determined by methods of elemental analysis and IR spectroscopy. On the basis of the synthesized triglyceride triglycidyl of saccharin-6-carboxylic acid and polyethylene polyamine the thermostable epoxy sulphoimide composition has been obtained. For comparative estimation of the thermal stability and physical-mechanical properties of the obtained composition, it has been also made the composition on the basis of industrial epoxy diane resin ED-20 and polyethylene polyamine. The hardening process of the compositions was studied by methods of thermogravimetry and differential-thermal analysis on derivatograph of "Paulik-Paulik-Erdey" system at temperature rise rate of 5℃/min in the air current and weighed sample of 200 mg. The study of physical-mechanical properties was carried out on a tearing machine. It has been experimentally established that the optimal quantity of hardener is 20 wt.h. per 100 wt.h. of resin. The degree of hardening of the epoxysulphoimide composition under the optimal hardening regime reached 93%. It has been found as a result of investigations that the synthesized epoxysulphoimide resin is technologically efficient during hardening, does not require an availability of hardening accelerator, and the composition material on the basis of the obtained resin is characterized by sufficiently high thermal and physical-mechanical indices in comparison with material on the basis of the industrial resin ED-20.*
KEYWORDS: *triglyceride of saccharin-6-carboxylic acid, thermostable epoxy sulphoimide composition*

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I. INTRODUCTION

The materials on the basis of epoxide oligomers have been widely used in industry due to the complex of valuable properties. The polymers on the basis of epoxide oligomers are currently one of the best types of binders for a large number of the polymer composition materials, widely used on industrial scales. This has been stipulated by availability of a number of important technological properties, such as good adhesion to many materials, the absence of formation of by-products (including volatile substances) during hardening, low shrinkage of epoxy polymer materials, high chemical resistance, good electrical isolation properties and durability [1]. Now, a complex of requirements is presented for epoxide resins for creation of the composition materials. The binder must have good processability and be resistant to exploitation factors, including higher temperature. In practice, in most cases, diane epoxide resins are used and by selection of hardeners, a required complex of technological and physical-chemical properties of the used epoxide compositions is provided. The lack of epoxide compositions on the basis of ED-20 resin is their not very high thermal and heat resistance [2]. It was known that the polymer composition materials made on the basis of compounds, a composition of which includes epoxy- and sulfoimide groups possess high physical-mechanical and thermal properties. Epoxyimide resins, in which glycidyl groups have been connected directly with imide cycle, after hardening with hardeners of both amine and anhydride types get a high thermal stability [3,4].

The purpose of this work is the synthesis of new epoxysulphoimide resin of the branched structure and creation of thermostable compositions on its basis.

II. EXPERIMENTAL PART

Synthesis of triglyceride on the basis of 2-hydroxypropyl-1,3-*bis*-ester-sulphoimide of saccharin-6-carboxylic acid. A mixture of 20 g (0.04 mol) of 2-hydroxypropyl-1,3-*bis*-esterosulphoimide of saccharin-6-carboxylic acid, 1 g (0.004 mol) of methyl ether of saccharin-6-carboxylic acid and 2 g of PbO in 200 ml of DMFA in mixing was heated to 124°C for 2 h. The reaction mass was filtered and washed with distilled water. The obtained powdered product of coffee-milk color was dried at room temperature and brought to a constant mass in a vacuum. *M.p.*=167°C.

Similarly, the above-mentioned compound has been synthesized on the basis of ethyl and isopropyl esters of saccharin-6-carboxylic acid.

The physical-chemical properties of glycerin and solvents were corresponded to literature data [5].

The infrared spectra were taken on IR-Fourier – spectrometer LUMOS (firm BRUKER, Germany) in the range of wave frequencies of 600-4000 cm^{-1}, with use of accessory of NPVO with ZnSe crystal. A crystal diameter – 1 cm. Number of the sample scans – 24, measurement duration – 30 sec [6, 7].

The elemental analysis was performed on method [8] based on pyrolytic combustion of the organic substance in an oxygen flow using the Pregle apparatus.

The curing process was studied by a method of differential-thermal analysis "Paulik-Paulik-Erdey" [9]. Sample hanging – 200 mg, channel sensitivity TG–200, DTA–250 μv, DTG–1 mv, temperature rise rate – 5°C/min in air current.

The study of physical-mechanical properties was carried out on the breaking machine WPM, VEB Thuringerindustriewerk, Rauenstein R-40, TUR-2092.

In this work, PEPA–polyethylene polyamine (PTC "Uralkhimplast", Russia) – a low-viscosity light liquid with the following characteristics: – dynamic viscosity (η) at 25ºC 90 mPa·s, amine number (A) 205 mg KOH/g was used as a hardener of the obtained epoxide resin.

The epoxide resin ED-20 – GOST 10587-84 (Mg = 390, content of epoxide groups 21.8 mass%) most widespread in the industry was used as epoxide resins.

The epoxide compositions were made by mixing. Polyamine hardener was introduced at temperature 20–25°C.

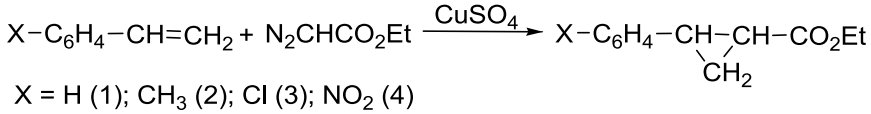
Preparation of tripotassium salt of triglyceride of saccharin-6-carboxylic acid. 2.24 g of (0.04 mol) KOH dissolved in 200 ml of distilled water on portions and with mixing added to 14.38 g (0.02 mol) of triglyceride of saccharin-6-carboxylic acid. After addition of all alkali solution, the reaction mass was evaporated on water bath to achievement of a constant mass and the crystals were filtered out. The end product was dried on air, then in a vacuum at 80-100ºC and then in a thermostat at120-140ºC to a constant mass. Yield – 89.4%.

Synthesis of triglyceride triglycidyl of saccharin-6-carboxylic acid. The mixture consisting of 20.83 g (0.025 mol) of tripotassium salt of triglyceride of saccharin-6-carboxylic acid, 230 ml of epichlorohydrin and 2.16 g of triethylbenzene ammonium chloride (TEBAC) was mixed at room temperature to obtain a suspension (25-30 min.). Then the reaction mass was heated to 40-50ºC and continued the mixing for another 1 h. Further, a calculated quantity of 20% alkali solution (~100ml) was gradually dropped from dropping funnel with mixing and continued the mixing for 30 min. At the end of condensation, the organic layer was separated from the water-salt layer and dried over $CaCl_2$. Then the unreacted epichlorohydrin was distilled and the resin was dried over P_2O_5.The obtained product is a light brown viscous substance, soluble in aprotic solvents, including acetone and dioxane. Yield – 15.52 g (87.5 %).

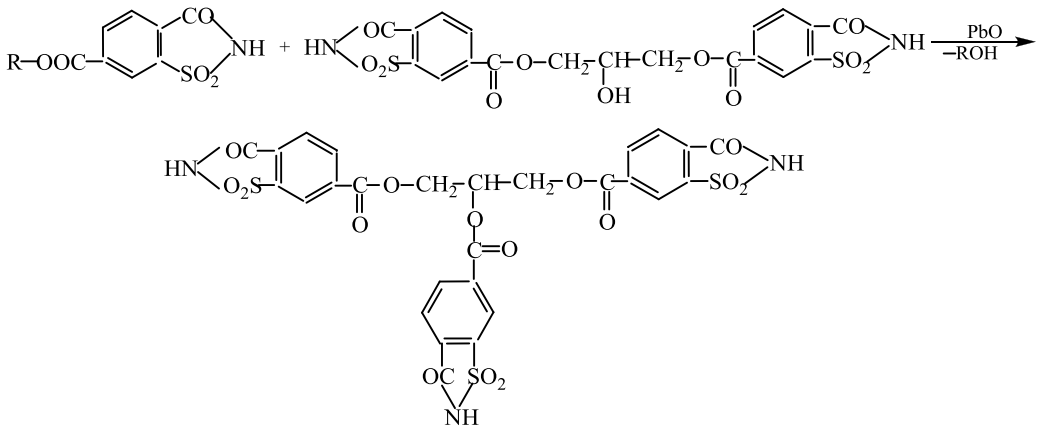
The content of epoxide groups has been found – 12.7%.

III. RESULTS AND DISCUSSION

The synthesis of epoxysulphoimide resin was carried out in two stages. In the first stage, it has been synthesized triglyceride of saccharin-6-carboxylic acid by interaction of 2-hydroxypropyl-1,3-*bis*-etherosulphoimide of saccharin-6-carboxylic acid previously obtained by us with esters of the same acid [10, 11]. The reaction proceeded as follows:



X = H (1); CH_3 (2); Cl (3); NO_2 (4)



R=-CH_3,-C_2H_5,-C_3H_7

A yield of purposeful product is 85%.

It has been found that the obtained product is a powder of light-coffee-milk color, soluble only in aprotic solvents, such as DMFA**,** DMAA**,** DMSO, etc.

The composition and structure of the obtained compound has been determined by elemental analysis and IR spectroscopy.

In the IR spectra of the obtained compounds (fig. 1) there are appeared the deformation absorption bands in the field of 1385, 1438, 1485 cm^{-1} of C-H-bond of CH_2 groups; the valence vibrations of C=O bond of amide (1643 cm^{-1}); the valence vibrations of C=O bond of ester (1719 cm^{-1}); the valence vibrations of C-O-bond of ester(1108, 1129, 1147, 1168 cm^{-1}); the valence (1252, 1277 cm^{-1}) vibrations of SO_2-group; the deformation (1553 cm^{-1}) and valence (3268, 3352 cm^{-1}) vibrations of N-H-bond; the deformation (674, 694, 713, 757, 788, 829, 867, 1607 cm^{-1}) vibrations of C-H-bond of substituted benzene ring.

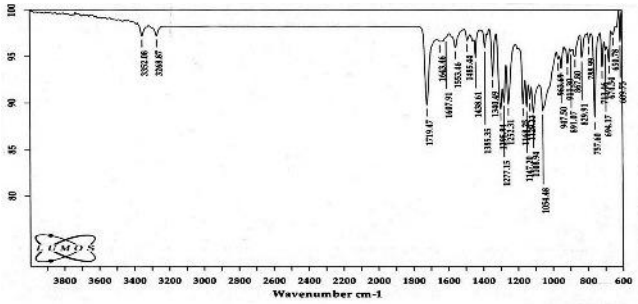
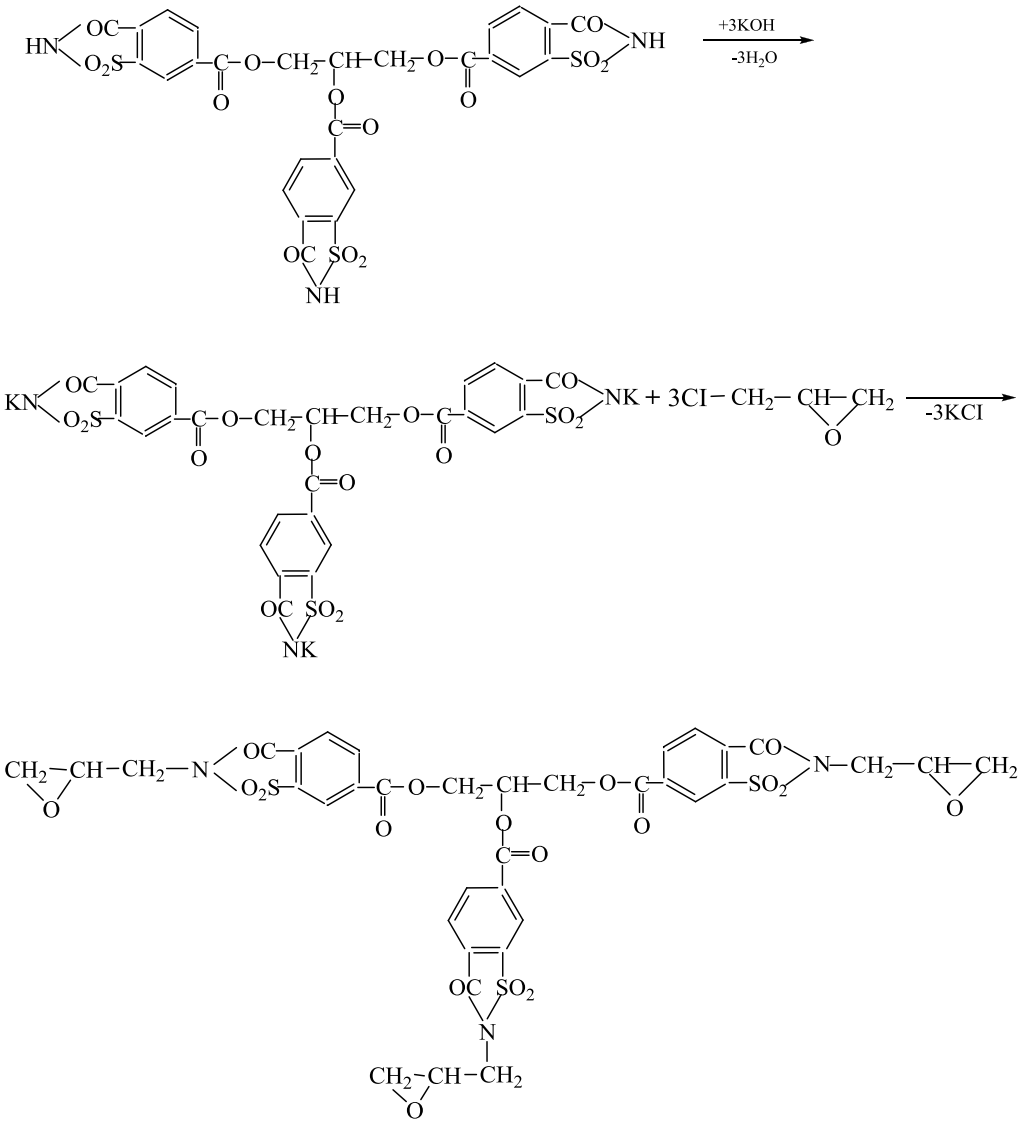


Figure 1: IR spectra of triglyceride of saccharin-6-carboxylic acid.

In the second stage, in interaction of the synthesized triglyceride of saccharin-6-carboxylic acid with KOH the tripotassium salt of this compound has been obtained. Further, in interaction of the obtained salt with an excess of epichlorohydrin, triglyceride triglycidyl (TGTG) of saccharin-6-carboxylic acid has been synthesized according to the following scheme:



Yield – 87.5 %. Epoxide number – 12.7% (found); 14.5% (calc.)

The structure of the obtained epoxyimide compound has been studied by a method of IR spectroscopy. In the IR spectra of the obtained compounds (fig. 2) there are appeared the absorption bands of the deformation vibrations of substituted benzene ring (1551, 1586 cm^{-1}); the valence vibrations of C–N-bond (1276 cm^{-1}) (overlapped with epoxide group); the deformation (1389 cm^{-1}) and valence (2880, 2933 cm^{-1}) vibrations of C–H-bond of CH_2 groups; the valence vibrations of C=O bond of ester (1711 cm^{-1}); the valence (1638 cm^{-1}) vibrations of C=O bond of imide cycle; the bands (1276, 922, 849 cm^{-1}); the valence (1175 cm^{-1}) vibrations of S=O bond in sulphoimides; the valence vibrations of N–H-bond (3250, 3348 cm^{-1}).

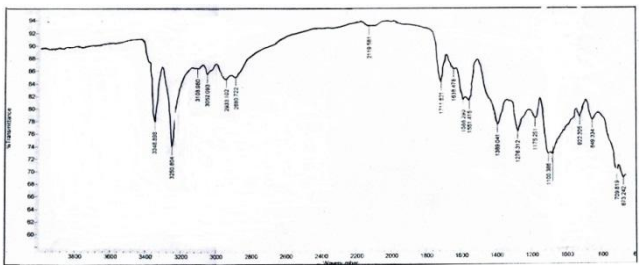


Figure 2: IR spectra of the obtained epoxyimide compound.

It was known that in order to obtain a high-quality epoxy material, it is necessary to create a composition characterizing by high physical-mechanical, heat and thermal parameters. These conditions are primarily achieved by correct selection of a quantity of hardener and hardening mode for epoxide compound. For this purpose, with use of synthesized TGTG of saccharin-6-carboxylic acid and polyethylene polyamine (PEPA) the composition of TGTG + PEPA has been obtained. For comparative estimation of thermal indices of epoxyimide oligomer the composition of structure epoxy diane resin (ED-20) + PEPA has been also made.

The optimal quantity of hardener has been chosen by methods of DTA and TGA [12]. The method has been based on the fact that in a case of an excess of hardener, the unreacted amine groups lead to a weight loss of the composition. The excess of unreacted epoxy groups acts similarly. Both phenomena deteriorate the thermal stability of the epoxide composition.

It has been experimentally established that the optimal quantity of hardener is 20 wt.p. per 100 wt.p. of resin. In this case, a ratio of the physical-mechanical and thermal properties of the obtained composition reaches its highest value.

The thermal stability of the epoxide compositions was estimated by values of half-decay period ($\tau/2$) of composition and activation energy of decay ($E_{act.}$).

It has been found by a method of thermogravimetry (TG), according to TG curve that the hardening process of TGTG + PEPA composition begins at 56ºC, passes through exo-peak of hardening at 89ºC, and at 122ºC the process is fully completed, then the thermal decay of the composition occurs.

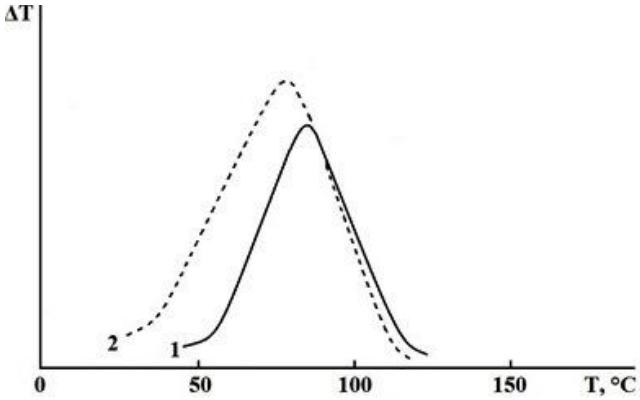


Figure 3: Differential hardening curves of epoxide compositions: 1 – TGTG+ PEPA; 2 – ED-20 + PEPA.

The optimal temperature and time mode of hardening have been found on a method [13], according to which a degree of hardening α is determined according to the difference between heat effect of the hardening reaction of an unhardened sample (Q_0) and heat effect of a partially hardened sample (Q).

A degree of hardening is calculated on formula:

$$\alpha = \frac{Q_0 - Q}{Q} \cdot 100$$

where: α - degree of hardening;
Q_0 - isolated heat at full hardening;
Q - isolated heat at partial hardening.

Thus, one can determine a degree of hardening (α) of the composition for given time (t) at T=const.

It has been determined that a degree of hardening of the composition TGTG + PEPA under optimal hardening condition reaches 93%. $E_{act.}$ of thermal-oxidative destruction calculated by a method of double logarithm [14, 15].

The obtained results are presented in **Table II**.

The synthesized epoxysulphoimide resin is technologically efficient during hardening, does not require an availability of hardening accelerator, and is also characterized by good physical- mechanical properties (**Table III**).

Summarizing above-stated one, one can conclude that the synthesized epoxysulphoimide resin is technologically efficient during hardening, does not require the use of hardening catalysts and as can be seen from the obtained data is profitably differed from industrial epoxide resins and can substitute them in the same areas, where heat-resistant epoxide compounds are necessary.

IV. CONCLUSIONS

The method of synthesis of epoxy sulphoimide resin of branched structure on the basis of triglyceride of saccharin-6-carboxylic acid has been developed.

On the basis of the synthesized resin and polyethylene polyamine a composition of the structure TGTG + PEPA has been made.

For comparative estimation of the thermal indices of the obtained composition, a composition of the structure epoxy diane resin ED-20 + PEPA has been also made.

It has been established that the thermal stability of compounds on the basis of epoxy sulphoimide, estimated on $E_{act.decom.}$ is considerably differed from composition materials on the basis on ED-20.

It has been found that the composition material on the basis of the synthesized epoxy sulphoimide resin is characterized by sufficiently high thermal and physical-mechanical properties in comparison with materials on the basis of the industrial resin ED-20.

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Table I. Physical constants of triglyceride of saccharin-6-carboxylic acid.

Compound	Brutto formula	Found / Calculated, %				M	M.p., °C	Yield, %
		C	H	N	S			
Triglyceride of saccharin-6-carboxylic acid	$C_{27}H_{17}O_{15}N_3S_3$	44.95 / 45.06	2.48 / 2.36	5.81 / 5.84	13.43 / 13.35	719	167	85

Table II. Thermal indices of epoxide compositions

Composition	$E_{act.decomp.}$ kJ/mol	Half-decay period τ/2, min	$T_{cur.}$, °C
TGTG + PEPA	258.50	75.22	89
ED-20+ PEPA	106.20	56.05	75

Table III. Some physical-mechanical properties of epoxide resins hardened by PEPA

Indices	**TGTG + PEPA**	**ED-20+ PEPA**
Tensile strength, MPa	58	55
Specific elongation, %	3.6	2.5
Degree of curing, %	93	98