RESEARCH OF OLIGOMERS FOR COLORING POLYMERS.

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Abstract. *Epoxy polymers stand out among other polymer materials in a number of properties, playing an important role in aerospace, automotive, shipbuilding and other industries. The purpose of the study is to synthesize epoxy resins based on epichlorohydrin with diphenylolpropane and obtain oligomeric dyes based on them. Their widespread use in technology is associated, firstly, with the high manufacturability of epoxy resins, and secondly, with a unique combination of performance characteristics of their curing products. The optimal conditions for the synthesis of epoxy oligomers have been determined. The structure of the obtained epoxy oligomers was determined by IR spectroscopy and the contents of epoxy and hydroxyl groups in the oligomer were calculated. Dyes containing carboxyl and N-arylsulfonylamide groups capable of quantitatively reacting with the epoxy groups of oligomers were selected.*

Keywords: *polymer, oligomer, epoxide, IR spectrum, glisten, epilchlorohydrin*

Introduction. Epoxy oligomers have found wide application in various fields of technology, in particular, as a component of binders for various composite materials with high physicochemical characteristics, adhesion to various substrates, good dielectric and other valuable properties [1].

Epoxy polymers stand out among other polymer materials in a number of properties, playing an important role in aerospace, automotive, shipbuilding and other industries. Their widespread use in technology is associated, firstly, with the high manufacturability of epoxy resins, and secondly, with a unique combination of performance characteristics of their curing products [2].

The high reactivity of the epoxy group and the thermodynamic compatibility of epoxy oligomers with many substances make it possible to use a variety of hardeners and carry out curing reactions under various technological conditions. Of no small importance are such features of the synthesis processes as the absence of volatile products and low shrinkage [3,4].

Epoxy polymers have high static values and impact strength, hardness and wear resistance. They are characterized by significant temperature and heat resistance. New epoxy oligoaryloxyphosphazenes based on a mixture of chlorophosphazene were synthesized and identified by NMR (nuclear magnetic resonance) spectroscopy, and the epoxy number was measured [5].

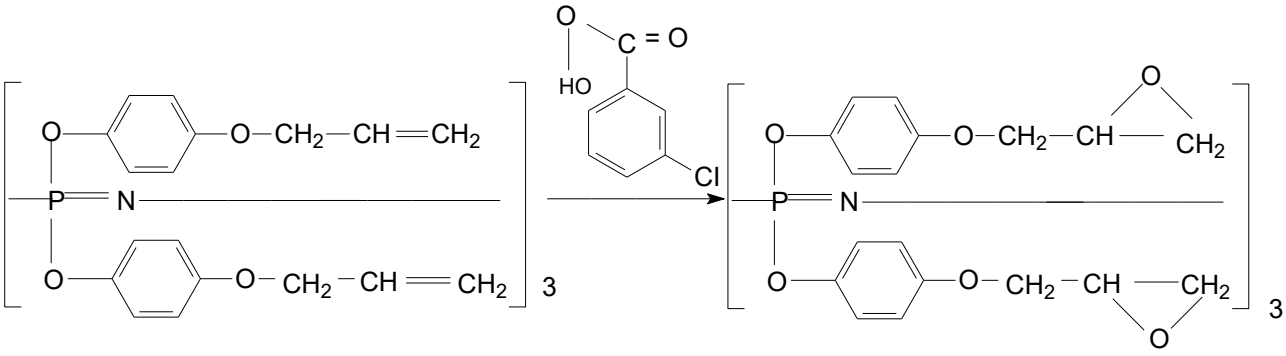
The main objective of this work was to improve the manufacturability of the synthesis of phosphazene-containing epoxy resins. In most studies, the most accessible phosphazene, hexachlorocyclotriphosphazene (HCF) [6], is used as a phosphazene base. However, it remains

the most expensive component, therefore, in order to reduce the cost of the final product, a mixture of oligomeric cyclophosphazenes, previously synthesized according to the following scheme, was used

$$PCl_5 + NH_4Cl_{(изб)} \xrightarrow{ZnCl_2} (NPCl_2)_n + HCl$$

Zinc chloride in an amount of 3 mol. % of PCl_5 is PCl_5 both a catalyst, reducing the reaction time from 50 to 2 hours, and also promotes the formation of cyclic products [7]. The reaction is carried out in boiling chlorobenzene. Under these conditions, a mixture of only cyclic chlorophosphazenes with n = 3:8 is formed. The composition of the mixture was confirmed by ^{31}P NMR spectra (Figure 1.a), according to which the mixture composition includes 49% GPC, 24% octachlorotetraphosphazene[8], 3, 12 and 12% cyclic polymers with a ring size from n=5 to 7: 8 respectively. During this reaction, no by-products are formed, and excess ammonium chloride and the catalyst are easily removed by filtration. The resulting mixture of chicleic products is light brown crystals, highly soluble in non-polar organic solvents. The mixture was used as a phosphazene base for further transformations without additional purification of hexachlorocyclotriphosphazene, and the process was significantly simplified [9].

The possibilities of modifying industrial epoxy oligomers with various organophosphazenes are considered. A new method has been proposed for creating a modifier for industrial epoxy oligomers of the EHD brand, using a mixture of amino derivatives of hexachlorocyclotriphosphazene and 4,4'-methyl-bis-(2-chloro-ani-line)



The purpose of the study is to synthesize epoxy resins based on epichlorohydrin with diphenylolpropane and obtain oligomeric dyes based on them.

Materials and methodology of the study.

Glycine - (aminoacetic acid, aminoethanoic acid, $C_2H_5NO_2$).

Glycine is a solid substance with a sweetish taste. Glycine is the simplest organic aliphatic amino acid belonging to the class of carboxylic acids. Formula: $C_2H_5NO_2$ molar mass: 75.07 g/mol, melting point 233 ^{0}C , density: 1.61 г/см^3.

Epichlorohydrin - (chloromethyloxirane, 2-chloromethyloxirane) C_3H_5ClO-an organic substance, a chlorine derivative of propylene oxide, with the formula $CH_2(O)CH\text{-}CH_2Cl$. Widely used in organic synthesis, used in the production of epoxy resins and glycerin. Highly toxic, colorless liquid with an irritating odor of chloroform. Molar mass 92.524 ± 0.005 g/mol, density 1.18066 g/cm³, melting point -48 °C, boiling point 117.9 °C.

Synthesis of epoxy oligomer from diphenylolpropane and epichlorohydrin

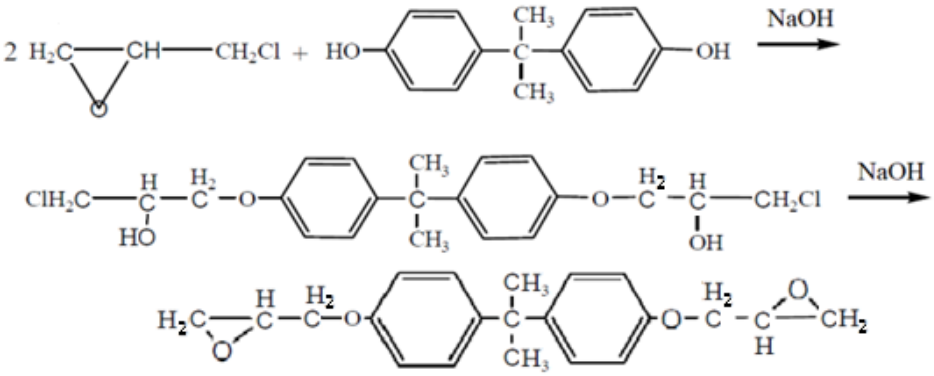
Starting substances (%)

Diphenylolpropane 46.4
Epichlorohydrin 37.3
Caustic sodium 16.3

A 15% sodium hydroxide solution (65% of the total amount) was placed in the flask, heated to 30 °C, and after adding diphenylolpropane, the mixture was heated to 50 °C, a mechanical stirrer was turned on and stirred until a suspension was formed, which was cooled to 30 °C. Then gradually add epichlorohydrin, making sure that the temperature of the reaction mass does not rise above 40 °C. After introducing the entire amount of epichlorohydrin, the mass was stirred for 30-40 minutes, the contents of the flask were heated to 60-65 °C and kept at this temperature for 1 hour. After this, add a second portion of 15% sodium hydroxide solution (22% of the total amount) and gradually increase the temperature to 70-75 °C. After 1 hour, introduce the remaining amount of alkali into the flask and continue the condensation process for another 45 minutes. Add water (100% of the mass of the starting substances) to the resulting oligomer, stir the mass heated to 60-70 °C for 15-20 minutes, then turn off the mixer and let the mixture settle. After separation into two layers, the aqueous layer was drained, and the oligomer was washed with water and the aqueous layer was separated again. Then toluene was added, the mass was stirred and transferred to a separating funnel, where it separated into two layers [11]. The water layer is drained, and the resin layer is transferred to a device for distillation under vacuum and the water-toluene mixture is distilled off at a residual pressure of 100-150 mm. After all the water has been distilled off, the solution is cooled to 30 °C, filtered on a Buchner funnel and again placed in a device for distillation under vacuum, where we distill off the toluene to obtain a 90% solution of the oligomer.

Research results. Their widespread use in technology is associated, firstly, with the high manufacturability of epoxy resins, and secondly, with a unique combination of performance characteristics of their curing products [11].

We have synthesized epoxy resins based on epichlorohydrin (ECH) with diphenylolpropane (DPP) according to the following scheme:



The characteristics of the synthesized oligomers were determined (Table 1). 3.

Table 3.

Properties of synthesized (1) and industrial (2) oligomers based on ECH and DPP

State of aggregation	Content, mass		Viscosity at 25 °C
	Hydroxyl group	Epoxy group	
Viscous liquid	1,5	19,0	24 Па·с
Viscous liquid	0,8-2,5	22,0-14,5	16-28 Па·с

As can be seen from the table, the properties of the synthesized epoxy oligomers are close to those of industrial oligomers.

The influence of the nature of the solvent on the yield of the oligomeric product at a temperature of 200 ^{0}C was studied. Reaction duration is 20 hours[12].

Substance ratio EHG:DFP	Solvent	Product output %
1:2	Benzene	56,0
2:1	Benzene	70,0
1:1	Benzene	62,0
2:1	Alcohol	72,0
1:2	Alcohol	63,0
1:1	Alcohol	55,0
1:2	Water	66,4
2:1	Water	83,6
1:1	Water	56,7

As can be seen from the table, the oligomer yield is greater in an aqueous environment.

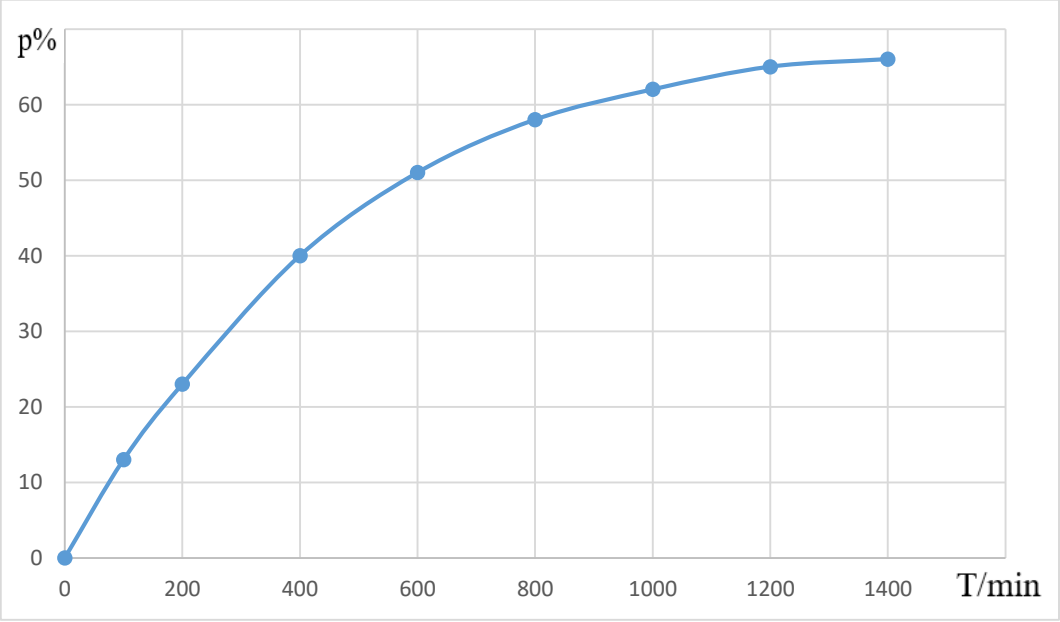


Fig.1. Effect of reaction time on the oligomeric product obtained from epichlorohydrin and bisphenol (A) 2:1, T=100^{0}C-200^{0}C, solvent – ethyl alcohol

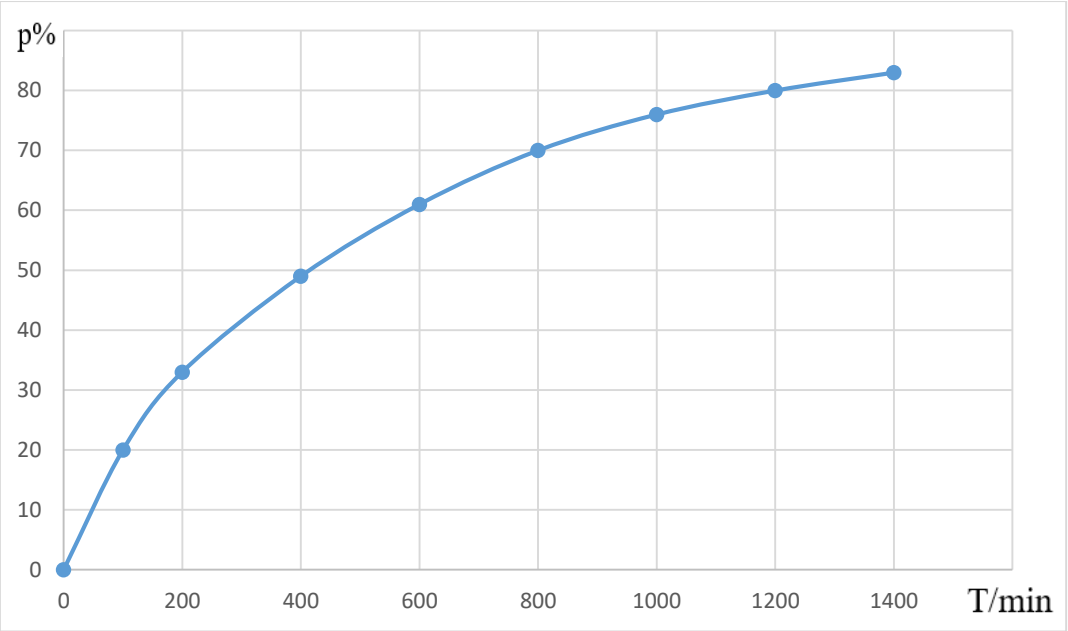


Fig.2. Effect of reaction time on the oligomeric product obtained from epichlorohydrin and bisphenol (A) 2:2, T^0 =100^{0}C-200^{0}C, water-solvent

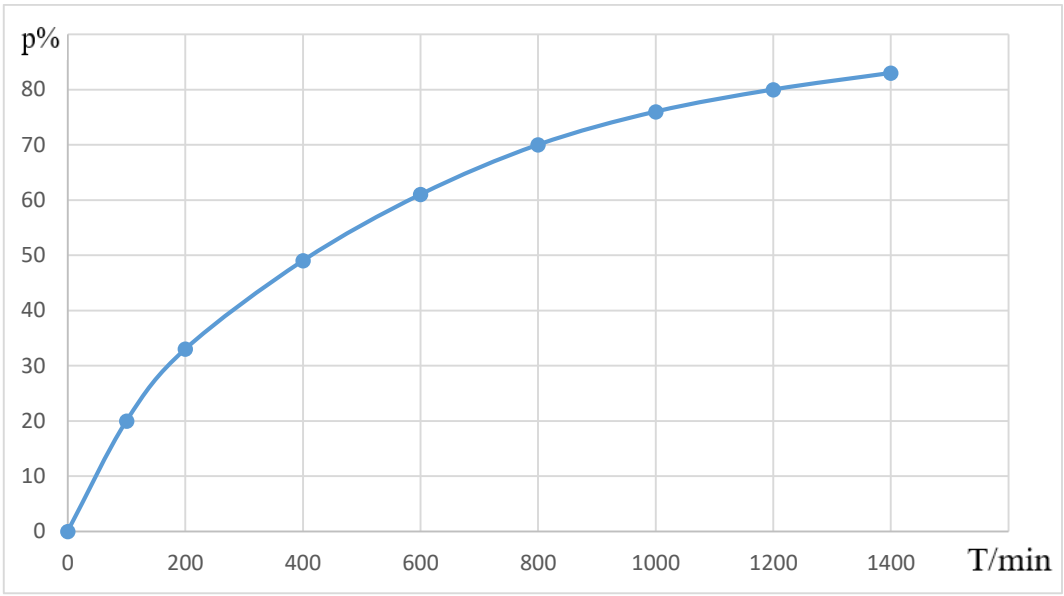


Fig.3. General graph of the effect of reaction time on the oligomeric product obtained from epichlorohydrin and bisphenol (A) in a ratio of 3 above and solubility in solvents.

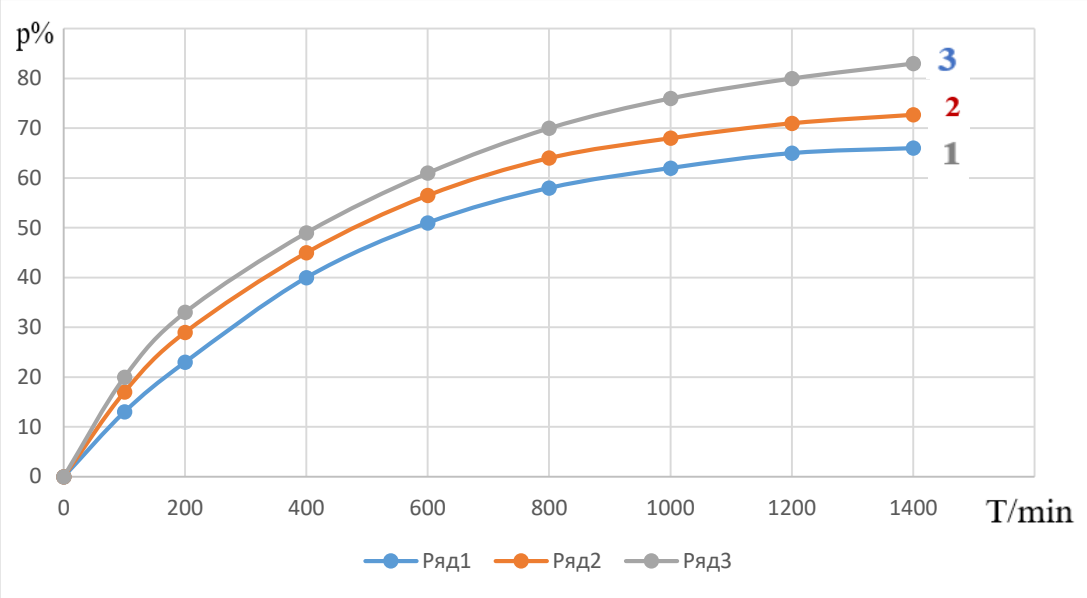


Fig.4. The influence of time on the reaction of bisphenol (A) and ECH in different proportions: 1- 1:1; 2-1:2; 3- 2:2. T^0=200^{0}C.

As can be seen from the above graph, at a temperature of 2000C, the effect of time on the reaction of bisphenol (A) and ECH in various proportions was studied [13]. According to the results obtained, the optimal conditions for this reaction are 2:2 at 18 hours with a product yield of 83%.

Let us consider the effect of reaction time on the oligomeric product obtained from epichlorohydrin and glycine in various solvents in the range T = 30m^{0}C.

Substance ratio ECH:G	Substance	T^0	Time/min	Product yield, %
1:1	1.4-dioxane	30	130	32,6
1:1	Benzene	30	130	57
2:1	Alcohol	30	130	66,7
1:2	Water	30	130	72,8

As can be seen from this general table, the reaction result is higher when water is used as a solvent [14].

Now let's look at these solvents one by one.

Effect of reaction time on the oligomeric product obtained from epichlorohydrin and glycine, 1:1, T^0 =30^{0}C-130^{0}C dioxane solvent.

Discussion. During the hydrochlorination of glycine, the formation of monochlorohydrin isomers occurs, where isomer-1 is subject to further hydrochlorination, where the final product is dichlorohydrins, and isomer-2 does not participate in subsequent compounds and represents a production waste.

Epichlorohydrin reacts readily with HCI at room temperature. As a result of the ongoing reaction, glycine 1,3-dichlorohydrin is formed: $ClCH_2CH(OH)\ CH_2CI$

In the composition of a concentrated solution of $CaCI_2$, the reaction with epichlorohydrin occurs quantitatively, which serves as the basis for the method for determining the epoxy group.

Under the condition of the interaction of alkalis (small doses) and epichlorohydrin, a connection with mobile H atoms is ensured with the further formation of chlorohydrins: $RCH_2CH(OH)\ CH_2CI$

- Reaction of epichlorohydrin with NH_3 or amines: RCH2CH(OH) CH2CI, where R=H, which is the organic residue resulting from the reaction

- Effect of C_3H_5CIO on the addition of inorganic acids in a dilute state $CH_2(OH)\ CH(OH)\ CH_2CI$, where R=H, is the final product formed

- The effect of epichlorohydrin on alcohols is manifested in the final formation of esters: $CICH_2CH(OH)\ CH_2OR$

Conclusions. Epoxy oligomers based on epichlorohydrin with diphenylolpropane and glycine were synthesized by polycondensation reaction. The optimal conditions for the synthesis of epoxy oligomers have been determined. The structure of the obtained epoxy oligomers was determined by IR spectroscopy and the contents of epoxy and hydroxyl groups in the oligomer were calculated. Dyes containing carboxyl and N-arylsulfonylamide groups capable of quantitatively reacting with the epoxy groups of oligomers were selected. Red and blue azo dyes were used as dyes. It has been shown that as a result of the binding of dyes to oligomeric fragments through a covalent bond, the oligomer consists of three homogeneous structural fragments of dyes: chromophore, oligomeric and modifying.

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