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MODIFICATION OF EPOXY RESINS BY POLYISOCYANATES

Epoxy resin compositions modified by compounds containing isocyanate fragments are recently of considerable scientific and practical interest. However, only some of them are widely used. Urethane fragments in the molecular structure of epoxy units of oligomeric molecules cause the improvement of the deformation-strength properties of polymer materials. The aim of this work is the development and study of film-forming composites with improved physical, mechanical and chemical properties by modifying the epoxy oligomers by the polyisocyanates.

Introduction. Epoxy and polyurethane materials have superior performance properties, so they are used for the production of high quality coatings [1]. Each of the mentioned types of polymers has its advantages and disadvantages: epoxies have low shrinkage during hardening, high chemical resistance, hardness, adhesion to polar surfaces and high dielectric performance, but they are inferior to polyurethane materials in resistance to aromatized fuel, abrasion resistance, adhesion to aluminum and nonferrous metals. On the other hand, polyurethanes have limited resistance to alkalis and acids and they are inferior to epoxy resin in strength and hardness.

There are different ways of mutual modification of both types of polymers, which are nowadays presented in numerous publications, mostly in the patents, the number of which is progressively increasing. Analyzing the available references on the subject, we can identify the following ways of obtaining epoxy-urethane coatings: coatings obtained with the use of epoxy-urethane oligomers; coatings produced by hydroxyl-containing epoxy oligomers, isocyanates and their adducts, coatings produced by oligoepoxides, polyisocyanates and other reactivity compounds, coatings produced without the use of isocyanates. In order to improve chemical resistance as well as the elasticity of epoxy resin composition blocked isocyanates were used on the basis of the epoxy resin ED-20 as a modifier [2]. As shown by the authors, the reaction of an epoxy resin with an isocyanate at a high temperature results in forming heat resistant polyoxazolidones. This gives hardness to the coating, improves its mechanical and electrical properties, and urethane linkage of the polymer coating, formed alongside with poly-oxazolidones, makes it elastic.

It is known that by varying the chemical structure of hydroxyl component and polyisocyanate, we can alter significantly the hardening process conditions (temperature, rate of drying) as well as performance characteristics of the coatings. Due to the diversity of the chemical structure of the raw materials, the properties of anticorrosion coatings of paints and lacquers can vary widely. In order to properties of the resulting composite film-forming systems on the basis of epoxides and polyisocyanates it is necessary to study the effect of the quantitative and qualitative structure of the film-forming epoxy-isocyanate compositions on the physical and mechanical properties of coatings.

Main part. This paper presents the results of complex study of performace characteristics of coatings on the basis of epoxy resin modified by aliphatic polyisocyanate promising to protect steel constructions from corrosion in a humid atmosphere. It is known that an intense destruction of the polymer coating and corrosion of protected metal occur during the use under various atmospheric conditions.

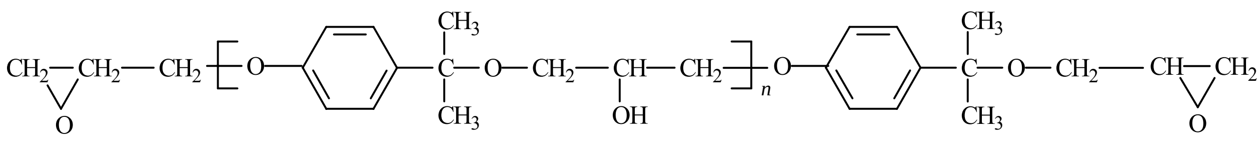
In this connection the evaluation of the coatings resistance under atmospheric conditions and the prediction of their service life is an important task.

Epoxy brand ED-20 was used as the object of study (Scheme 1), the characteristics of which are presented in Table 1.

Table 1

Properties of epoxy resin ED-20

Index	Value
The average molecular weight	390–430
Epoxy group content, %	19.9–22.0
Hydroxyl content, %, not more	1.7
Density at 20°C, kg/m^3	1,166
Viscosity at 20°C, Pa·s	13–28
Volatile substances content, %, not more	1.0



Scheme 1

It is known that aliphatic isocyanates are less prone to yellowing under UV light, that's why they are preferred in varnish compositions. In this context, commercially produced aliphatic polyisocyanate 2K 100 was chosen as a modifier. Polyethylene polyamine was used as a hardener (TU 6-02-594-85).

Film-forming composites were obtained by adding a modifier in the amount of 1–5% by weight of dry matter to epoxy ED-20 resin and hardener (PEPA), followed by stirring the mixture to obtain a homogeneous mass. Films on the metal (copper, steel) and glass substrates were cast from the obtained lacquer solutions. The coatings were made with the help of hydraulic spraying. Plates with formed coatings were stored for 7 days at a temperature of 20–26°C before testing.

Impact resistance of coating samples was evaluated using the device U1 according to the standard ISO 6272 and State Standard 4765-73. The method of determining the strength of films being hit is based on the instantaneous deformation of the metal plate with a varnished coating during the load free fall on the specimen.

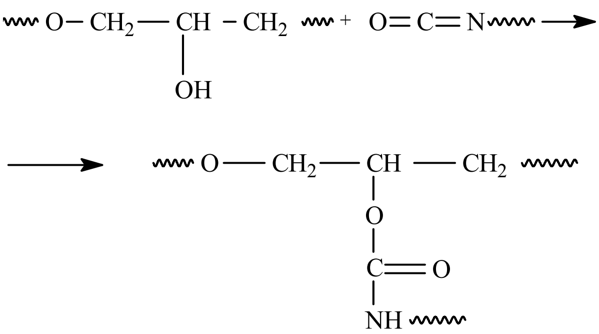
Hardness of a varnished coating was determined with the use of a pendulum device (ISO 1522). The essence of the method is to determine the decay time (the number of oscillations) of the pendulum in contact with its varnished coating.

Adhesive strength of the formed coating was determined in accordance with the standard method as well as ISO 2409 and State Standard 15140-78 using the cross-cut method. The essence of the method is to apply cross-cut of the finished coating, followed by a visual assessment of the state of the lattice coating.

Flexural strength of the coatings was determined using the device SHG1 (ISO 1519, State Standard 6806-73). To perform the determination a coated sample is bending slowly around the test cylinder, starting with a larger diameter at an angle of 180°. At one of the diameters of the cylinder a coating either cracks or breaks. In this case, we assume that the coating has an elasticity of the previous diameter of the test cylinder device in which it is not destroyed.

In epoxy-isocyanate catalyst systems without a catalyst, the main reaction at temperatures below 60°C is the reaction of urethane formation through the interaction of isocyanate and secondary hydroxyl groups of epoxy-oligomers (Scheme 2).

In cases when the coating formation occurs in vivo (without heat), the formation of cross-linked polymer is complicated by the fact that the reactivity system can go into the glassy state, so that the hardening reaction practically stops. Thus, low temperature hardening of epoxy composites does not enable us to produce coatings with high performance. Another significant drawback of such hardening is its duration. Therefore, the formation of coatings was performed not only under natural conditions, but also at elevated temperatures. To do this, we have chosen two heat settings: 7 days without heat (temperature I) and 2 h at 100°C (temperature II).



Scheme 2

To determine the optimal ratio of epoxy oligomer – modifier to perform a complex physical and mechanical tests of coatings with different contents of the modifier a number of physical and mechanical tests of coatings with different contents of the modifier was performed. The results are given in Table 2. As seen from Table 2, the bending strength reaches a maximum when the content of the modifier is 2–3%. Impact strength also increases with the increasing of the modifier content in the composition of the selected concentration range modifier. In this case, the hardness of the coating remained at an acceptable level for the operating conditions used in lacquer coatings.

Physical and mechanical properties of the coatings formed at different temperatures of hardening differ significantly. Increasing hardening temperature affects the concentration dependences of physical and mechanical characteristics of the coatings over the whole range of the investigated ratios of components. Thus, the coating containing the same amount of modifier and cured at an elevated temperature, have higher relative hardness, impact strength and elasticity of less than coatings formed without heat. Thus, the coatings containing the same amount of modifier and hardened at an elevated temperature, possess higher relative hardness, impact strength and less elasticity than those formed without heat. Such changes in the behavior of the physical and mechanical properties of the composites can be explained by a significant change in the level of molecular mobility and packing density in their transition to more "hard" conditions of hardening. However, increasing the hardening temperature does not change the general character of the modifying effect, but only determines its value.

Table 2

Physical and mechanical properties of the coatings, modified by polyisocyanate

Temperature range	Modifier content, %	Hardness, c. u.	Bending strength, mm	Impact strength, cm	Adhesion, score
I range	0.0	0.95	20	30	1
	1.0	0.74	12	30	1
	2.0	0.59	3	35	1
	3.0	0.49	1	45	1
	4.0	0.42	1	50	1
	5.0	0.37	1	50	1
II range	0.0	0.96	15	35	1
	1.0	0.89	3	45	1
	2.0	0.72	1	50	1
	3.0	0.60	1	50	1
	4.0	0.52	1	50	1
	5.0	0.48	1	50	1

According to the adsorption theory, the adhesive strength of the coatings is caused by the formation of physical and chemical bonds between the macromolecules and the active sites of the solid surface. The observed increase in the adhesive strength of the film-forming compositions developed by us, apparently is connected with the flexibility of the emerging polymer grid, which contributes to a more favorable arrangement of the polymer chains with respect to adhesion-active sites of the substrate. We should also note the contribution to the improvement of the adhesive strength of urethane groups capable of forming bonds of the coordination type with a metal surface.

Internal strains occurring in the process of coatings formation and resulting in appearance of local connections between structural elements and adsorption interaction of a film-forming substrate with the service, affect the adhesion strength of the film to the metal. With the introduction of the modifier the flow of relaxation processes is facilitated in a grid formed by reducing the cross-linking density of the polymer due to its lateral flexible urethane branches.

The increased content of the modifier in the epoxy resin leads to higher impact resistance of coatings. This effect is probably associated with an increase in molecular mobility due to the introduction of flexible urethane units in the spatial structure of the polymer matrix, which contributes to the dissipation of mechanical energy input stroke [3].

It should be noted that the content of the modifier in the epoxy resin over 5 wt % led to a marked gas release in the mixture and, consequently, to the defectiveness of the produced film.

It was also determined that the increase in the polyisocyanate to 5 wt % causes significant deterioration of the protective characteristics of the coating due to their high water absorption, that can be explained by the increased porosity and lower density of the protective film, probably due to a significant plasticizing effect of the modifier. Due to the fact that the steel constructions and devices are used not only indoors, but also outdoors, in the water environment often aggressively affecting the surface of the metal, it seemed reasonable to evaluate the water absorption of protective layers of the formed coatings from the developed film-forming epoxy compositions.It was also determined that the increase in the polyisocyanate to 5 wt % causes significant deterioration of the protective characteristics of the coating due to their high water absorption, that can be explained by the increased porosity and lower density of the protective film, probably due to a significant plasticizing effect of the modifier. Due to the fact that the steel constructions and devices are used not only indoors, but also outdoors, in the water environment often aggressively affecting the surface of the metal, it seemed reasonable to evaluate the water absorption of protective layers of the formed coatings from the developed film-forming epoxy compositions.

Water absorption was determined by assessing the sorption capacity of varnish to water (see Fig.).

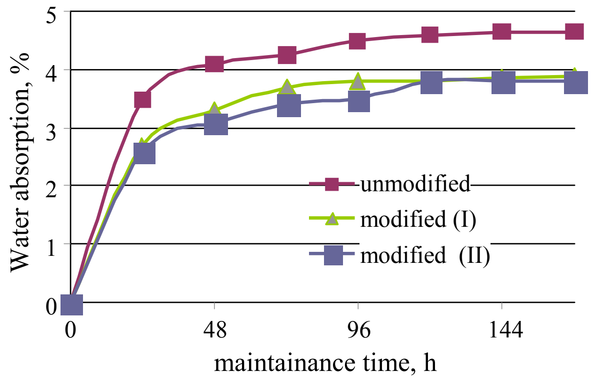


Fig. Water absorption of modified epoxy coatings

It is known that epoxy film formers possess high chemical resistance to concentrated acids and alkalis, and are widely used in chemical industry, for this reason it is useful to study the effect of the modifier on the chemical resistance of the coatings.

The effect of the modifier on the protective properties of the coatings formed at different temperatures has been studied. Relative evaluation of protective characteristics after exposure of samples in hostile environments for a month, performed with the use of the method [4], is shown in Table 3.

Table 3

The results of testing coatings exposed in various environments for a month

Modifier content, %	Relative value, %				
	H_2O	3% NaCl	10% NaOH	25% H_2SO_4	Petroleum solvent C2
0	60	40	50	20	100
3 (I drying mode)	80	70	70	50	100
3 (II drying mode)	80	70	70	50	100

As seen from Table 3, the obtained composites exhibit improved protective properties with respect to water, 3% NaCl, 10% NaOH, 25% H_2SO_4. These coatings can be recommended for use in the chemical industry to protect tanks, reactors, pipelines working in direct contact with aggressive environments from corrosion.

Quantitative testing of the modifier content of more than 5 wt % of isocyanate in epoxy compositions were not conducted, for the films are defective with a large number of pores due to gas release, however, a visual tendency of films to turbidity was seen, which may indicate a significant increase in water absorption with increasing modifier content in the film-forming composition.

Conclusion. New film-forming compositions on the basis of epoxy resin ED-20 and industrially-produced isocyanate were synthesized.

Protective coatings with improved adhesion, high impact resistance, moisture-and water-resistance, and high resistacet to other more aggressive environments were obtained on their basis.

Optimal modifier content at which lacquer composition possess the highest strain-strength and protective characteristics has been determined.

It has been determined that the polyisocyanate modifier catalyzes the hardening process of epoxy oligomers and increases their resistance to corrosion.

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