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Investigation of Adhesive Strength and Thermomechanical Characteristics of Epoxy Coatings and Their Modified Forms

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ABSTRACT: The existing protective polymer coatings are analyzed. The results of a study of the dependence of the adhesive strength of epoxy resin on the amounts of urethane and silicon diurethane modifiers are highlighted. Increasing the ratio of hydroxylurethane:epoxy resin to 15:85, compared with the original sample, causes an increase in adhesive strength by 20%, which is associated with an increase in the proportion of urethane bonds. However, a further increase in the amount of modifying additive (30%) significantly reduces the strength, due to the lack of epoxy groups for the formation of a network structure during curing. The epoxy number of this hybrid oligomer is 6.84% and the epoxy equivalent value is 617.3 g/mol. Increasing the curing temperature from 120 to 150°C reduces the process time to 30 versus 90 minutes. The strength of samples based on silicon diurethane in all temperature ranges and duration of curing is practically the same as the first samples.

KEYWORDS: polymer coating, epoxy resin, hydroxylurethane, silicon diurethane, adhesive strength, epoxy number, epoxy equivalent.

I. INTRODUCTION

The destruction of metal and other structures as a result of interaction with the surrounding aggressive environment leads to significant economic costs. In recent years, numerous scientific and practical studies have been carried out aimed at creating protective coatings based on inorganic and organic substances and their compositions [1–4].

In construction practice, materials based on alkyd, perchlorovinyl resins, vinyl chloride copolymers, polyvinyl acetals, fluorine-containing polymers, epoxy resins, polyurethanes, furyl resins, petroleum polymer resins, chlorosulfonated polyethylene, chloroprene compounds, thiokols, etc. have found application [5].

The share of epoxy coatings is about 50% of the total world production of all types of resins [6]. Composites based on epoxy resins are widely used in the manufacture of protective structural, waterproofing and decorative coatings, laying floors, and plaster coatings [7]. Coatings based on epoxy resin have proven themselves to protect surfaces from the action of alcohol, wine, fruit juices.

Modification of the epoxy polymer is the only program for improving the adhesion, structure-forming and other characteristics of the protective coating. A widely used modifier is a polyurethane oligomer. In some cases, this oligomer is used to increase the impact strength of the resin [8]. As noted by the authors of [9], polyurethane macromolecules are mainly bound to the epoxy oligomer due to the interaction of a physical nature. At the same time, they do not exclude the presence of chemical bonds between these macromolecules, and it is these bonds that play a decisive role in improving the tensile strength, which is associated with the formation of a grafted network structure. A chemical bond is formed between the terminal isocyanate groups with the epoxy group. The formation of this chemical bond was also proved in [10] and the increase in the impact strength of the epoxy resin was explained.

Most of the work is aimed at improving the characteristics of polymer composite coatings, namely the glass transition temperature and other physical and mechanical characteristics. The improvement is related to the ratio of the

initial oligomers, and at epoxy/polyurethane = 1.5, the maximum increase in impact strength is observed [11]. In this work, the change in strength characteristics is associated with the formation of hydrogen bonds between hydroxyl and isocyanate groups, respectively, of epoxy and polyurethane polymers.

Epoxy-siloxane polymers are one of the overmodifications of epoxy resins; they are characterized by the properties of silicones and epoxides [12]. In this case, it is the epoxy that participates in the curing, and the siloxane groups are responsible for the highest thermal stability and anticorrosion characteristics. Sillarized resins are characterized by increased resistance to atmospheric and temperature influences. Some varieties of such resins maintain their original technological characteristics after heat treatment in the temperature range of 200-300°C. Such coatings are resistant to sunlight and retain their gloss and adhesive strength for several months.

The authors are conducting research on the creation of modified epoxy oligomers, characterized by increased adhesion and anti-corrosion characteristics. Early works covered data on the synthesis of hydroxylurethane (HUS) and silicon diurethane (SIL) based on non-toxic 1,2-propylene carbonate and 1,3-propylenediamine, which were successfully used to modify the commercial epoxy resin ED-20 [13].

II. SIGNIFICANCE OF THE SYSTEM

The article discusses the mechanical activation study of low-grade phosphorites of the Central Kyzylkum. The study of methodology is explained in section III, section IV covers the experimental results of the study, and section V discusses the future study and conclusion.

III. METHODOLOGY

Epoxy resin (ED-20) and its modified forms were chosen as anticorrosive coatings for research [13]. Epoxyurethane and silicone epoxyurethane compounds were obtained on the basis of hydroxylurethane (HUS) and silicon diurethane (CUS), which were conventionally designated as EUS and SiEUS. Steel C35E was chosen as a metal substrate, on which a mixture of modified ED-20 and a hardener was applied. The hardener isophoronediamine was chosen for the study, which is a cycloaliphatic amine compound with a light color and low odor. This product is characterized by low viscosity values (dynamic viscosity approx. 18 ± 0.5 mPa*s at 20°C). The coating was obtained by applying a layer of material to the surface of the plate with a brush. The deposition was carried out at least 2 times, while the thickness of the coatings was about 20 μm . The working surface of steel is 10 cm^2 . To do this, the steel surface first went through a preparatory stage in the form of surface degreasing, drying of the steel material, polishing with sandpaper and acetone treatment. The coatings were then cured at 150°C for 15-30 minutes. Determination of the adhesive shear strength of coatings was carried out (GOST 14759-69) using an OR-type adhesion meter. The thermomechanical characteristics of the coatings were determined on a Geppler consistometer. For this, coatings in the form of tablets were used, which were prepared at a load of 1 kgf/cm^2 . Tests were carried out at room and higher temperatures, and cured coatings were used for testing at temperatures from 0 to 150°C. According to the thermomechanical properties of polymers and their T_c , it is possible to evaluate the kinetic flexibility of the chain by the so-called kinetic segment of the chain - to determine its molecular weight (M_s , g/mol) and the density of the structural network (N_c , mol/ cm^3),

$$M_c = \gamma \frac{3\rho RT}{E_B} \quad (1)$$

to calculate the modulus of high elasticity (E_v , MPa)

$$E_B = \frac{F\varepsilon_0}{S\Delta\varepsilon} \quad (2)$$

Molecular weight (g/mol) of the kinetic segment of the chain: (one) The modulus of high elasticity (E_v , MPa) was calculated: (2) where: S is the cross-sectional area of the sample, cm^2 ; ε_0 is the initial sample height, mm; ρ is the density of the test sample, g/ cm^3 ; F is the load on the sample, kgf ; $\Delta\varepsilon$ – highly elastic deformation, mm; T is the initial temperature of the highly elastic state, K; R is the gas constant, equal to 84.8 $\text{kgf}\cdot\text{cm}/\text{mol}\cdot\text{K}$; $\gamma = 1$; The crosslink density (N_c) was calculated using the formula:

$$N_c = \frac{\rho}{M_c} \quad (3)$$

The determination of the % content of the epoxy group was carried out according to GOST 12497-78. Epoxy equivalent values were calculated based on the epoxy number.

IV. EXPERIMENTAL RESULTS

The main task in creating composite anticorrosion coatings is to optimize their composition by adjusting the amount of additives introduced, which stabilizes the necessary performance characteristics of the coatings. Anticorrosion coatings, being in themselves composite materials containing oligomers, fillers, pigments, hardeners, etc., show a variety of technological characteristics. The amounts of additives introduced vary widely, as does their nature. So far, numerous additives are known, and their influence on the characteristics of finished materials has been studied. However, the results of numerous studies have also shown the impossibility of predicting their characteristics, which depends not only on the amounts of introduced components, but also on the method of their introduction, their dispersion, and on the characteristics of the surface of the introduced additives. Research has been conducted to establish optimal ED-20/HUS ratios; ED-20/KUS, as well as compositions of hardeners on the adhesive strength of coating films. Data on the composition of the modified epoxy resin are given in table. one.

Table 1.
The composition of the modified epoxy resin, wt%

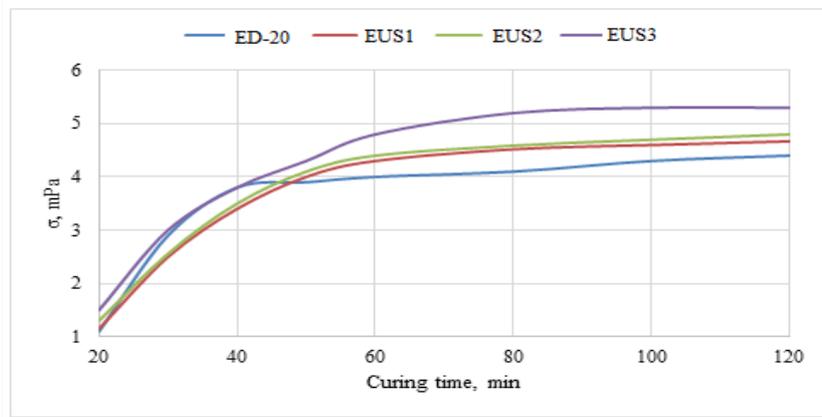
Name of the modified ES	ED-20	GUS	KUS
EUS1	95	5	
EUS2	90	10	
EUS3	85	15	
SiEUS1	95		5
SiEUS2	90		10
SiEUS3	85		15

To establish the amount of hardener, the amount of the epoxy group in the composition of the modified ED-20 (epoxy number/42) was determined, which are given in table. 2.

Table 2.
Main characteristics of hybrid resins

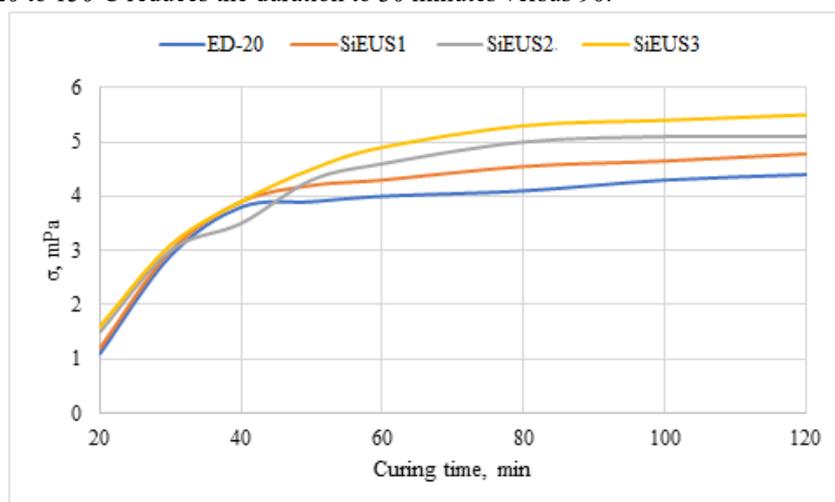
Sample	Epoxy number, %	Epoxy equivalent, g/mol	Amount of hardener *, g/100 gr resin
EUS1	17,80	235,9	36,0
EUS 2	15,61	269,0	31,6
EUS 3	13,42	313,0	26,5
Si EUS 1	18,97	221,4	38,4
Si EUS 2	17,89	234,7	36,2
Si EUS 3	16,77	250,5	33,9

According to the method, the values of the epoxy number and epoxy equivalent were determined. As the data in the table show, with an increase in the modifiers of the epoxy oligomer, the epoxy number (e.ch.) of the hybrid material decreases. Reduction of e.h. occurs due to the transformation of the oxirane ring into hydroxyl groups due to the reaction with the NH₂ group in the composition of the modifier. Based on the data obtained, the required amount of hardener was calculated. In practice, however, the required quantities of hardener are always greater than the calculated values. Adhesion strength was studied on daily aged coatings. To do this, the samples were applied to the surface of a steel sample, cured at a temperature of 110-150°C for 30-120 min, then at room temperature for 24 hours. The effects of temperature and curing time on the adhesive strength of hybrid coatings were studied.



Rice. 1. Dependence of the adhesive strength of coatings (EUS) on the duration of curing at a temperature of 120°C.

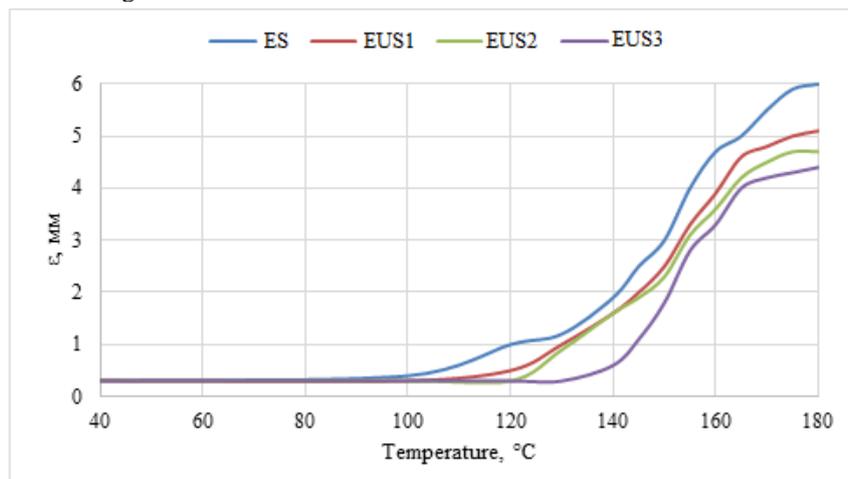
As the curves of the diagram show, with the content of HUS in the composition of the epoxy oligomer, a decrease in adhesive strength is observed at the initial moment of curing. Probably, at such concentrations of urethane bonds in the composition of the hybrid coating, sufficient amounts of chemical bonds are not formed to form an additional network structure. Increasing the ratio of KUS:ED-20 to 15:85 causes an increase in adhesive strength by 20%. The results obtained suggest that with an increase in the proportion of urethane bonds, the adhesive strength of the epoxy matrix increases. However, increasing the amount of modifying additive HUS to 30% significantly reduces the strength, which is associated with the insufficiency of epoxy groups for the formation of a network structure during curing. The epoxy number of this hybrid oligomer is 6.84% and the epoxy equivalent value is 617.3 g/mol. At the same time, the required calculated amount of hardener is reduced to 13.7 g/100 g. The system of this hybrid resin hardens for a rather long time (more than 2 hours) and the adhesive strength decreases by more than 2 times compared to the EUS3 sample and has lower values than the original ED-20. Probably, the decrease in adhesive strength is mainly associated with a decrease in the molecular weight of the cured coating, since other factors, such as the number of OH groups in the composition of the hybrid composite, are higher compared to the EUS3 sample. The study of the effect of curing temperature on the adhesive strength of coatings showed that an increase in temperature accelerates the curing process. Increasing the temperature from 120 to 150°C reduces the duration to 30 minutes versus 90.



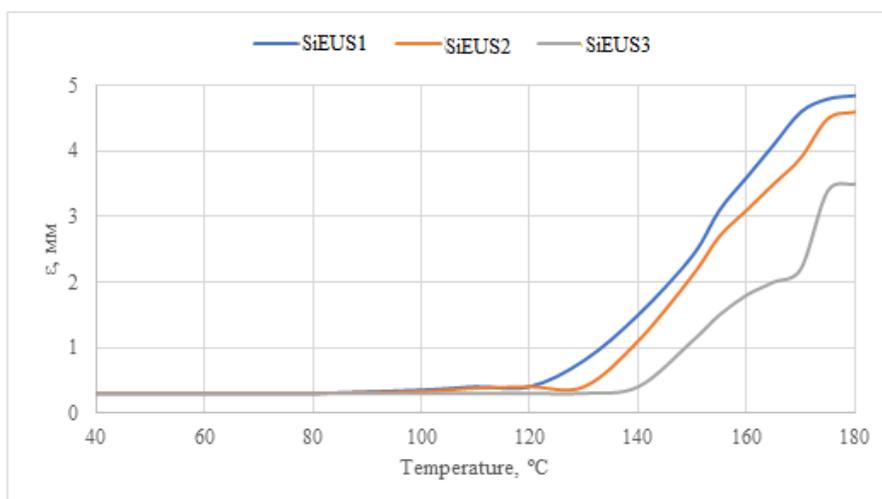
Rice. 2. Dependence of the adhesive strength of coatings (SiEUS) on the duration of curing at a temperature of 120°C.

The strength of SiEUS samples in all temperature ranges and duration of curing has almost the same values with EUS samples. However, an increase in the concentration of HUS in the reaction system to 30% does not cause a

significant decrease in adhesive strength, as is the case with HUS. It is likely that this is due to the participation of Si-O bonds in the formation of the network structure of the hybrid coating. However, these systems are characterized by an increase in tensile strength compared to EUS. It is likely that the Si-O bonds within the epoxy matrix exhibit the effect of the plasticizer, thereby causing an increase in tensile strength. The plasticizing action is usually associated with the formation of new chemical bonds and the formation of additional structures. Probably, in addition to an increase in the proportion of polar parts of the molecules, as a result of modification with the selected modifiers, it leads to an increase in hydrogen bonds, which contributes to the creation of a physical network, which, although to a lesser extent, serves to improve the deformation-strength characteristics, heat resistance and adhesion on various surfaces. It is known that the modification of epoxy oligomers with urethane bonds not only improves strength characteristics, but also increases heat resistance and a number of other functional characteristics. It is known that the modification of epoxy oligomers can increase the deformation heat resistance by 25–35% [14]. Thermomechanical characteristics can be determined from thermomechanical curves. The curves are the relationship between the deformation and the heating temperature of the coating samples, i.e. thermomechanical characteristics - this is a change in the mechanical characteristics of the samples under the influence of a load during heat treatment. The glass transition temperature was determined by the thermomechanical method, at a constant load of 2.5 N, with a cured coating thickness of 10 mm. The results of determining T_c are shown in fig. 3-4



Rice. Fig. 3. Dependence of highly elastic deformation on the heating temperature of EUS samples.



Rice. Fig. 4. Dependence of highly elastic deformation on the heating temperature of SiEUS samples

Thermomechanical analysis has established that the EUS and SiEUS systems have underestimated strain values (ϵ) compared to the original ED-20. As can be seen from fig. 3, the introduction of HUS into the original epoxy resin in an amount of 5% increases the glass transition temperatures from 103 to 109°C, while the exact same amount of HUS increases the T_g values to 117°C. It is likely that the increase in T_c is primarily associated with a change in the structure of the cured oligomer due to a decrease in free volume. An increase in the concentration of HUS and KUS modifiers up to 15% contributes to the establishment of T_c values, respectively, equal to 134 and 145°C. In this case, the total number of deformation changes is less at the corresponding temperature intervals. The crosslink density calculated from the values of ϵ and T_c for the EUS1, EUS2 and EUS samples is 3.41*10⁻³; 4.13*10⁻³ and 4.25*10⁻³. The values of the crosslink density for the SiEUS samples are significantly higher compared to the EUS samples, which is probably due not only to an increase in the elastic modulus and a decrease in molecular weight, but also to an increase in the density of the cured samples due to a decrease in porosity. A decrease in the porosity of the samples leads to a decrease in their adsorption characteristics with respect to various adsorbates and an increase in stability, including corrosion resistance. The results of determining the values of the modulus of elasticity and the density of the crosslink are given in table. 3. Table 3 Changes in the thermomechanical properties of modified epoxy oligomers

Sample	T _c , °C	E _v , kgs/sm ²	N _c , mol/sm ³
ED-20	103	0,0352	1,96*10 ⁻³
EUS1	109	0,0371	3,41*10 ⁻³
EUS 2	122	0,0368	4,13*10 ⁻³
EUS 3	134	0,0408	4,25*10 ⁻³
Si EUS 1	117	0,0444	6,11*10 ⁻³
Si EUS 2	130	0,0469	8,96*10 ⁻³
Si EUS 3	145	0,0510	1,01**10 ⁻²

Based on the analysis of the experimental results, it can be assumed that the physico-mechanical characteristics of the epoxy oligomer improve when it is modified with a urethane bond and, especially, with the introduction of an organic silicon unit. Probably, in this case, the curing process and the nature of the hardener are also considered an important point. However, the data obtained show that the most common and effective hardener isophorondiamine, at its consumption of more than 20% than the required amount, practically does not change the experimental result. Therefore, the decisive factor for increasing the adhesive strength and physical and mechanical characteristics is the active groups in the matrix. The studied 3-compositions, in which the amount of the modifying additive is at least 15%, are of interest for the creation of hybrid coatings with improved operational properties in practice. Any polymer compound, regardless of the degree of order, tends to crystallize during curing. Crystallinity predetermines the thermal and mechanical characteristics of finished coatings. The degree of crystallinity of the coating depends on the existing intermolecular interaction in the system, due to which the predisposition of molecular particles to be integrated into the crystalline package increases. An increase in crystallinity is possible for polymers with a regular structure. Thus, the change in the crystallinity of the oligomer systems during curing indicates the degree of regularity of the networks formed. To establish the degree of crystallinity, X-ray phase analysis of the cast samples was carried out. The values of crystallinity calculated from the diffraction pattern of the samples are given in Table. 4.

**Table 4
Crystallinity of coatings, %**

Sample	ED-20	EUS1	EUS2	EUS3	SiEUS2	SiEUS2	SiEUS2
K, %	1,86	2,36	2,48	2,78	2,61	3,58	3,41

From the values of the degree of crystallinity, it can be concluded that the introduction of a silicon-containing fragment into the composition of ED-20 contributes to an increase in the regularity of the system. Probably, the formation of new bonds, networks that bind IV valence silicon, is also responsible for the increase in order in the system. As the data in Table. 4, all cured modified epoxies show relatively high crystallinity values. Consequently, in modified systems,



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a different nature of intermolecular interactions is observed, which affects the number and nature of intermolecular interactions.

V. CONCLUSION AND FUTURE WORK

Thus, the study of the adhesive strength of coatings on a steel surface showed more excellent values of this indicator for modified epoxy oligomers. It is likely that this is due to a change in the nature of intermolecular interaction. The strength of the SiEUS samples in all temperature ranges and curing duration is practically the same as the characteristics of the EUS sample. However, an increase in the concentration of HUS in the reaction system to 30% does not cause a significant decrease in adhesive strength, as is the case with HUS. It is likely that this is due to the participation of Si-O bonds in the formation of the network structure of the hybrid coating. The data obtained prove that the crystallinity of polymers depends on the concentration and nature of the introduced additives. Therefore, by changing the conditions for obtaining coatings based on the same matrix, one can obtain their various structures

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