DEPENDENCE OF THE ADHESIVE STRENGTH OF AN EPOXY COATING ON A STEEL SURFACE ON THE AMOUNTS OF A URETHANE MODIFIER

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Abstract. Protective polymer coatings are analyzed. The results of studying 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 size, 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%) is characterized by the presence of signs, 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%, the epoxy equivalent value is 617.3 g/mol. Increasing the curing temperature from 120 to 150ºC significant process duration up to 30 versus 90 minutes. The strength of samples based on silicon diurethane in all temperature ranges and duration of curing practically has the corresponding values with the first samples.

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

Introduction

The destruction of metal and other structures due to interaction with an aggressive environment leads to significant economic losses. In recent years, numerous scientific and practical studies have been conducted aimed at developing 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, furfuryl resins, petroleum polymer resins, chlorosulfonated polyethylene, chloroprene compounds, thiokols, and others have found application [5].

Epoxy coatings account for about 50% of the total global 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, floor laying, and plaster coatings [7]. Epoxy resin-based coatings have proven effective for protecting surfaces against alcohol, wine, and fruit juices.

Modification of the epoxy polymer is the only approach for improving the adhesive, structural-forming, and other characteristics of the protective coating. A widely used modifier is polyurethane oligomer. In some cases, this oligomer is used to increase the impact toughness of the resin [8]. As noted by the authors [9], the macromolecules of polyurethane with epoxy oligomer are mainly bonded through physical interactions. However, they do not rule out the presence of chemical bonds between these macromolecules, and it is these bonds that play a decisive role in improving tensile strength, which is associated with the formation of a grafted network structure. The chemical bond forms between terminal isocyanate groups

and the epoxy group. The formation of this chemical bond has also been proven in [10] and explains the increased impact strength of the epoxy resin.

Most studies focus on improving the properties of polymer composite coatings, particularly glass transition temperature and other physical and mechanical characteristics. These improvements are related to the ratio of the initial oligomers, with a maximum increase in impact toughness observed at an epoxy/polyurethane ratio of 1.5 [11]. In this study, changes in strength characteristics are attributed to the formation of hydrogen bonds between hydroxyl and isocyanate groups from the epoxy and polyurethane polymers, respectively.

Epoxysiloxane polymers represent a high level of modification of epoxy resins, combining the properties of both silicones and epoxies [12]. In these polymers, the epoxy component is responsible for curing, while the siloxane groups contribute to enhanced thermal stability and anticorrosion performance. Silylated resins are known for their increased resistance to environmental and temperature effects. Some types of these resins retain their original technological properties even after thermal treatment in the temperature range of 200–300ºC. These coatings are also resistant to sunlight exposure and maintain their gloss and adhesion over several months.

The authors are conducting research on the development of modified epoxy oligomers that exhibit enhanced adhesion and anticorrosion properties. Earlier studies presented data on the synthesis processes of hydroxyurethane (HUS) and siloxane diurethane (SUS), which were synthesized from non-toxic 1,2-propylene carbonate and 1,3-propylenediamine. These compounds were successfully used to modify the commercial epoxy resin ED-20 [13].

Experimental Section

For this study, epoxy resin ED-20 and its modified forms were selected as anticorrosion coatings [13]. Epoxyurethane and silicon-epoxyurethane compounds were synthesized based on hydroxyurethane (HUS) and siloxane diurethane (SUS), and were conditionally designated as EUS and SiEUS, respectively.

Steel grade C35E was chosen as the metal substrate, onto which a mixture of modified ED-20 and hardener was applied.

Isophoronediamine was selected as the curing agent; it is a cycloaliphatic amine compound with a light color and mild odor. This product is characterized by low viscosity values (dynamic viscosity of approximately 18 ± 0.5 mPa·s at 20°C).

The coating was applied to the surface of the metal plate using a brush. The application was performed at least twice, resulting in a coating thickness of about 20 μm. The working surface area of the steel was 10 cm^2. Prior to coating, the steel surface underwent a preparation process consisting of degreasing, drying, polishing with sandpaper, and treatment with acetone. The coatings were then cured at 150°C for 15–30 minutes.

Adhesion strength of the coatings under shear stress was determined according to GOST 14759-69 using an OP-type adhesion tester.

The epoxide group content (%) was determined in accordance with GOST 12497-78. The values of the epoxy equivalent were calculated based on the epoxy number.

Results and discussion

The main task in the development of composite anticorrosion coatings is to optimize their composition by adjusting the amount of additives introduced, thereby stabilizing the required performance characteristics of the coatings. Anticorrosion coatings, being composite

materials themselves, containing oligomers, fillers, pigments, hardeners, and other components, exhibit a wide range of technological properties. The quantity and nature of the additives introduced can vary greatly.

To date, numerous additives have been identified and their effects on the properties of finished materials have been studied. However, the results of many studies have also shown the impossibility of fully predicting the performance characteristics of the coatings. This is not only due to the amount of added components, but also to the method of their incorporation, their particle size, and the surface properties of the additives used.

Studies were conducted to determine the optimal ratios of ED-20 to HUS, ED-20 to SUS, as well as the composition of hardeners with respect to the adhesion strength of the coating films. The data on the composition of the modified epoxy resin are presented in Table 1.

Table 1.

Composition of the modified epoxy resin, % by weight".

Modified resin designation ЭС	ЭД-20	ГУС	КУС
ЭУС1	95	5	
ЭУС2	90	10	
ЭУС3	85	15	
SiЭУС1	95		5
SiЭУС2	90		10
SiЭУС3	85		15

To determine the amounts of hardener, the content of epoxy groups in the modified ED-20 resin (epoxy number divided by 42) was measured, and the results are presented in **Table 2**.

Table 2.

Main characteristics of hybrid resins

Образец	Эпоксидное число, %	Эпоксидный эквивалент, г/моль	Количество отвердителя*, г/100 гр смолы
ЭУС1	17,80	235,9	36,0
ЭУС2	15,61	269,0	31,6
ЭУС3	13,42	313,0	26,5
SiЭУС1	18,97	221,4	38,4
SiЭУС2	17,89	234,7	36,2
SiЭУС3	16,77	250,5	33,9

**-изофорондиамин.*

According to the methodology, the values of the epoxy number and epoxy equivalent were determined. As shown by the data in the table, increasing the amount of epoxy oligomer modifiers leads to a decrease in the epoxy number (E.N.) of the hybrid material. The reduction in E.N. occurs due to the conversion of the oxirane ring into hydroxyl groups as a result of the reaction with the NH_2 group present in the modifier. Based on the obtained data, the required amounts of hardener were calculated. However, in practice, the necessary amounts of hardener are always higher than the calculated values.

Adhesion strength was studied on coatings after 24 hours of aging. For this purpose, samples were applied onto the surface of steel specimens and cured at temperatures between 110–150°C for 30–120 minutes, followed by curing at room temperature for 24 hours. The effects of curing temperature and duration on the adhesion strength of the hybrid coatings were investigated.

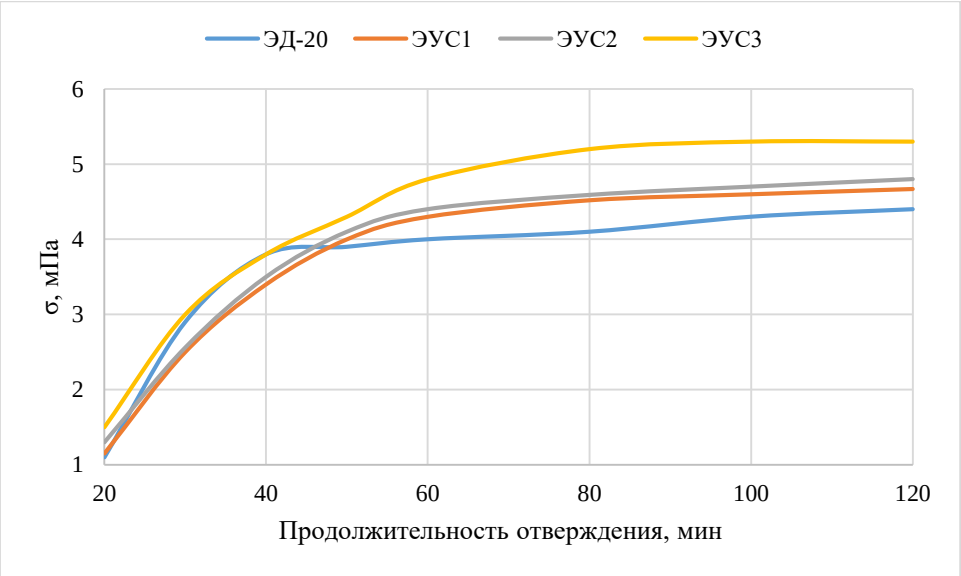

Fig. 1. Dependence of the adhesion strength of coatings (EUS) on curing time at 120ºC.

As the curves on the graph show, at the initial moment of curing, a decrease in adhesion strength is observed when HUS is present in the epoxy oligomer composition. It is likely that at such concentrations of urethane bonds in the hybrid coating, there are not enough chemical bonds formed to create an additional cross-linked network structure. Increasing the ratio of SUS to ED-20 to 15:85 causes an increase in adhesion strength by 20%. The results suggest that increasing the proportion of urethane bonds improves the adhesion strength of the epoxy matrix. However, increasing the amount of the modifying additive HUS to 30% significantly reduces the strength, which is associated with an insufficient number of epoxy groups to form a cross-linked network during curing.

The epoxy number of such a hybrid oligomer is 6.84%, and the epoxy equivalent is 617.3 g/mol. At the same time, the required calculated amount of hardener decreases to 13.7 g per 100 g. This hybrid resin system cures quite slowly (more than 2 hours), and the adhesion strength decreases by more than two times compared to the EUS3 sample, with values lower than the original ED-20.

It is likely that the reduction in adhesion strength is mainly related to the decreased molecular weight of the cured coating, since other factors, such as the number of OH groups in the hybrid composite, are higher compared to the EUS3 sample.

The study of the effect of curing temperature on adhesion strength showed that increasing the temperature accelerates the curing process. Raising the temperature from 120ºC to 150ºC reduces the curing time from 90 minutes to 30 minutes.

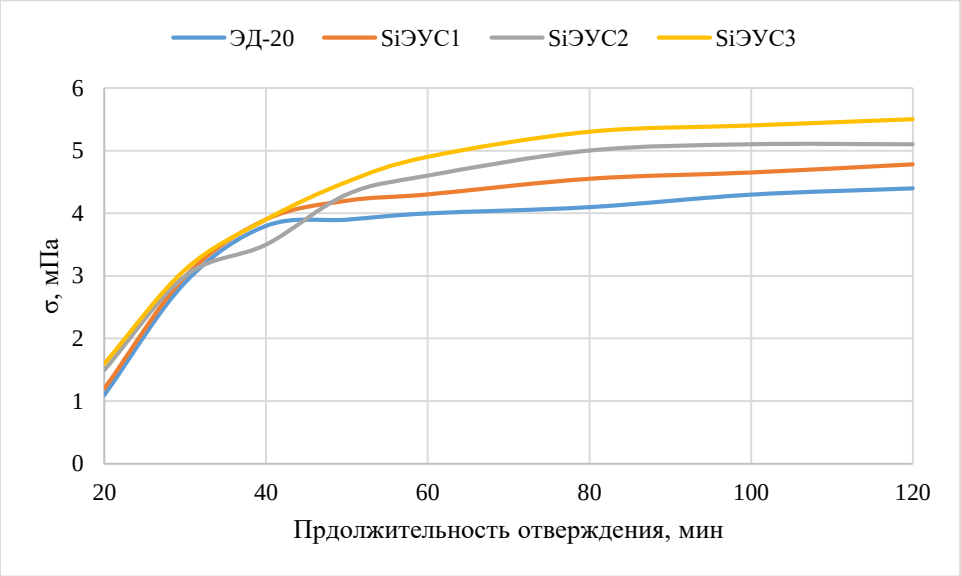

Fig. 2. Dependence of the adhesion strength of coatings (SiEUS) on curing time at 120ºC.

The strength of the SiEUS samples across all temperature ranges and curing durations is practically the same as that of the EUS samples. However, increasing the concentration of SUS in the reaction system to 30% does not cause a significant decrease in adhesion strength, unlike in the case of HUS. This is likely related to the involvement of Si–O bonds in the formation of the cross-linked structure of the hybrid coating.

Moreover, these systems demonstrate increased tensile strength compared to EUS. It is likely that the Si–O bonds within the epoxy matrix exhibit a plasticizing effect, thereby enhancing tensile strength. The plasticizing action is usually associated with the formation of new chemical bonds and the creation of additional structures.

Additionally, the increase in the proportion of polar molecular parts resulting from modification with the selected modifiers probably leads to an increase in hydrogen bonding. This contributes to the formation of a physical network which, although to a lesser extent, helps improve deformation-strength properties, thermal stability, and adhesion on various surfaces.

Conclusion

Thus, the study of the adhesion strength of coatings on a steel surface showed superior values for the modified epoxy oligomers. This is likely related to changes in the nature of intermolecular interactions. The strength of SiEUS samples across all temperature ranges and curing durations is practically identical to that of the EUS sample. However, increasing the concentration of SUS in the reaction system to 30% does not cause a significant decrease in adhesion strength, unlike in the case of HUS. This is probably due to the involvement of Si–O bonds in the formation of the cross-linked structure of the hybrid coating.

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