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The choice of pigments for paints and varnishes on epoxy binder

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Abstract:

The object of research is decorative polymer composites. Epoxy resin ED-16, which was cured with polyethylenepolyamine, was used as a binder for polymer composites. Organic and inorganic pigments were used to color the compositions. The aim of the work is to experimentally substantiate the techniques and methods for obtaining effective anti-corrosion protective materials for decorative purposes based on epoxy binders. **Method.** The study of structural changes in paints and varnishes was carried out by IR spectroscopy, based on the absorption of individual functional groups in the IR region. Determination of tensile strength and relative elongation of epoxy composites were established using physical and mechanical methods. **Results.** Using infrared spectroscopy methods, it was found that the degree of polymerization of paint and varnish polymeric materials is significantly influenced by the nature of the pigment used. The dependences of the change in the tensile strength and relative elongation on the type of pigment and its content were experimentally established. re composite materials based on an epoxy binder with various pigments. The purpose of the research is to substantiate the proposed methodology for analyzing the color change of protective coatings and to evaluate the decorative properties of epoxy composites used in marine climate conditions.

1 Introduction

To increase the durability of building structures, it is necessary to take measures that reduce or exclude aggressive effects on them [1], [2]. One of such ways to extend the service life of structural elements is the use of various protective coatings based on polymeric and other binders [3], [4], [5]. Long-term and reliable operation under specific operating conditions can be ensured by coatings based on epoxy resins, which have increased adhesion to various surfaces, good electrical insulating properties, have increased strength, and are technological during application [6], [7], [8]. To date, various types of enamels, paints, mastics, polymer solutions and polymer concretes based on them are used in the practice of anticorrosion work, which are multicomponent systems in their composition [9], [10], [11], [12]. It should be noted that to date, the influence of the main constituent components on the structure, physical, mechanical, and operational properties of epoxy materials for decorative purposes has not been fully studied.

The main component of epoxy polymer coatings, which combines all elements into a single monolith, is a binder, which is used in the manufacture of compositions using epoxy resins. Epoxy resins include compounds containing more than one epoxy group, which are located at the ends or along the main chain of the molecule or in the alicycle ring [13].

Due to their high reactivity, epoxy groups interact with many polyfunctional compounds to form a three-dimensional polymer. A coating based on a material of optimal composition and with the correct curing technology is characterized by good adhesion, elasticity, low internal stress, impact resistance, and high protective properties [13], [14], [15]. An important issue in the technology of obtaining composites is the processes of structure formation, which occur mainly at the stages of production and use of mixtures for ready-to-use composites [16]. After being applied to the protected surface at the initial time, they form coatings with low physical and mechanical properties. In the future, epoxy resins undergo a change in molecular weight and structure during the curing process [17]. Such changes occur directly on the substrate, which are completed mainly after complete hardening. To some extent, it can continue during the operational period, although, for the latter, the processes of aging of composites are more characteristic [18]. The resulting coating is a high molecular weight spatial polymer.

Pigments and fillers are important components of composite building materials, which give composites high mechanical strength, rigidity, chemical resistance, decorative effect, etc. [19]. The choice of the type and number of pigments and fillers is an important task for obtaining a material with a set of necessary properties. The first requirement when choosing disperse additives is their physicochemical compatibility with the binder, which excludes the occurrence of undesirable reactions in the contact zone of the organic and mineral phases. It is important that pigments, fillers, and fillers are economical and available, and that they must correspond to the purpose and operating conditions.

Colored polymeric materials are colloidal systems in which the dispersion phase is distributed in the dispersion medium [20], [21], [22]. The structure formation of such systems is determined by the processes of adsorption interaction between the polymer and the surface of pigmented particles. The adsorption of a polymer on a pigment depends on the presence of reactive groups on the surface of the pigment, active groups of the polymer, and the nature of the bond that occurs during the formation of adsorption layers.

The properties of compositions with pigments are determined by the following main indicators: the ability to create a strong bond between film-forming substances and particles of the pigment dispersed in it; the optimal content of the film-forming substance and pigments in the suspension; the degree of dispersion of the pigment; viscosity corresponding to the method of application; service life of the suspension; color and its stability in the coating film [23, 24]. Three cases of the influence of a pigment on the organization of the structure of a disperse system are typical for paintwork materials. Pigments with basic surface properties interact only with carboxyl groups of the polymer, pigments with acidic surface properties interact with amino groups, and pigments with amphoteric surface properties interact with amino and carboxyl groups of the polymer. The nature of the active groups of the polymer and the surface of the pigment determines the nature of the bond that arises between them - strong chemisorption or low-strength physical. In the case of epoxy polymers, the peculiarity of polymer-pigment interaction also lies in the fact that such materials are formed because of curing of low-molecular oligomers in the presence of pigment. The pigment affects the curing process of the oligomeric binder by entering chemical reactions, both with reactive groups of epoxy oligomers, and with hardeners, solvents, and plasticizers. It is known that some pigments accelerate the curing process, while others slow it down [25].

The strength and deformation characteristics of coatings, the nature of their change under the influence of various operational factors largely determine the durability of coatings. By purposefully changing the composition of compositions, it is possible to achieve a decrease in internal stresses and optimize the deformation-strength characteristics of coatings.

The aim of the work is to experimentally substantiate the techniques and methods for obtaining effective anti-corrosion protective materials for decorative purposes based on epoxy binders.

In this aspect, the research objectives are formulated as follows:

1. Establish the main patterns of structure formation of composites based on epoxy resins.

2. Obtain dependences of changes in the properties of decorative epoxy composites on the main structure-forming factors: the nature of pigments, the degree of interaction between the pigment and the binder.

3. Evaluate the effect of the pigment on the physical and mechanical properties of decorative epoxy composites.

2 Materials and Methods

During the research, epoxy resin of the ED-16 brand was used as a binder, polyethylene polyamine served as a hardener. Epoxy resin brand ED-16 has the following characteristics: molecular weight of 480-540; conditional viscosity on a ball viscometer no more than 10 sec.; curing at 100°C after 2 hours; the content of epoxy groups 16.0-18.0; gelatinization time with hardener not less than 3 hours; density at 50 °C 1155 kg/m^3.

Epoxy resin hardener is polyethylenepolyamine (PEPA), is a viscous liquid of light brown color, with a boiling point of at least 207 °C; density 950–1100 kg/m^3.

For coloring composites, pigments were chosen, which are widely used in the production of paints and varnishes of various colors. When conducting research, low-deficiency achromatic and chromatic, organic and inorganic pigments were used. The choice of pigments was determined by their properties: color, hiding power, degree of weather, acid, and alkali resistance. Of the achromatic pigments, aluminum powder was used; iron minium (red) was studied as chromatic pigments; cobalt violet dark; light ocher (yellow); iron blue (dark blue); iron oxide yellow; glauconite green; lead crown (yellow).

Minium iron is a natural inorganic pigment of red-brown color, consisting of iron oxide (at least 75-87%) with an admixture of clay minerals and quartz and obtained by fine grinding of iron ores. The hiding power of the pigment is 10-20 g/m^2. Minium iron is a durable pigment with high coloring power and anti-corrosion properties, light fastness, and chemical resistance.

Light ocher is a natural pigment consisting of clay minerals colored with hydrated iron oxides (11-18%) with an average hiding power of 65 to 115 g/m^2. Ocher is a common cheap pigment, light and alkali resistant.

Iron oxide yellow is a synthetic inorganic pigment, which is iron oxide monohydrate FeOOH. The content of iron compounds in terms of Fe_2O_3 is not less than 84-86%; pigment density - 4500-4700 kg/m^3; covering power –15-20 g/m^2; relative coloring – ability 95-100%. The pigment has high light resistance, weather resistance, high coloring power, good hiding power, resistant to alkalis, but soluble in acids, well dispersed in different media. The main disadvantage is low heat resistance.

Lead crown is a synthetic inorganic pigment of lemon color. The coloring power of the pigment is not less than 90%; covering power is not more than 45-60 g/m^2. It has high anti-corrosion properties.

Glauconite green is represented by the mineral glauconite (aqueous aluminosilicate of iron, calcium, potassium, and magnesium).

Iron blue is a blue synthetic inorganic pigment composed of iron and potassium ferrocyanide. Its coloring power is high and is at least 100%; covering power – 10-20 g/m^2; density 1850-1920 kg/m^3; specific surface – 3000 cm^2/g. Azure is not resistant to the action of alkalis; acid-resistant; has anti-corrosion properties.

Cobalt Violet Dark– is anhydrous cobalt phosphate $Co_3(PO_4)_2$. The pigment has high light, weather, and heat resistance.

Aluminum pigment powder - finely ground lamellar particles of primary aluminum, is a light powder of a brilliant light silvery color with a covering power of 2-3.3 g/m^2. Aluminum powder has anti-corrosion properties. The interaction reaction of the polymer binder with pigments is important.

To establish structural transformations in the epoxy polymer-pigment system, the IR spectroscopy method was used, based on the absorption of individual functional groups in the IR region.

Registration of the IR spectra of the material was carried out on the device "UR-20". Wavelengths of 1580–1600 cm^{-1}, the absorption band of the benzene rings of the epoxy resin and the absorption maximum in the region of 1230–1280 cm^{-1}, the absorption band of the epoxy bridge of the resin, were chosen as standard regions for the analysis of the spectra. The absorption region of the epoxy ring 1230-1280 cm^{-1} is the most suitable for quantitative analytical measurements since the absorption of the benzene rings of the epoxy resin is not superimposed on it. The degree of curing of the compositions was judged by the change in the absorption maximum of the epoxy bridge. For a more accurate determination of the extinction coefficient of these bond absorption bands, the "internal standard method" was used, which was the absorption band of vibrations of aromatic rings in epoxy resins. The ratio of absorption band heights at 1230–1280 cm^{-1} to 1580–1600 cm^{-1} served as a characteristic of the relative degree of curing.

In preparation for testing, solid samples were mixed with vaseline oil with a pestle in a dry porcelain mortar for 1–2 min. Then, the resulting suspension was applied to a polished KBr plate with a spatula and pressed from above with a second similar plate, slightly turning it, causing the suspension to spread into a thin uniform film. The plates clamped in the cell holder were placed in the main channel of the spectrophotometer.

The mechanical properties of the composites were determined on samples in the form of eights. Samples of the following sizes were used: length 50 mm, width 10 mm with a length of the working part 30 mm. The compositions were prepared manually. The amount of binder, pigment and hardener was made on electronic scales with an accuracy of 0.01 g. Samples were made in metal molds, which were covered with paraffin before laying the mixture. After laying, the samples hardened under normal conditions for 1 day, and then in a heating cabinet for 6 hours at a temperature of +80°C.

The tensile strength and elongation were determined on an IR 5057-50 tensile testing machine according to the Russian state standard GOST 18299-72 "Paint-and-lacquer materials. Method for determining the tensile strength, elongation at break, and modulus of elasticity." The spreading speed of the clamps of the machine corresponded to 10 mm/m. Each sample was marked, measured and labeled before testing. The properties of polymer composites were determined from the results of testing at least 3 parallel samples.

3 Results and Discussion

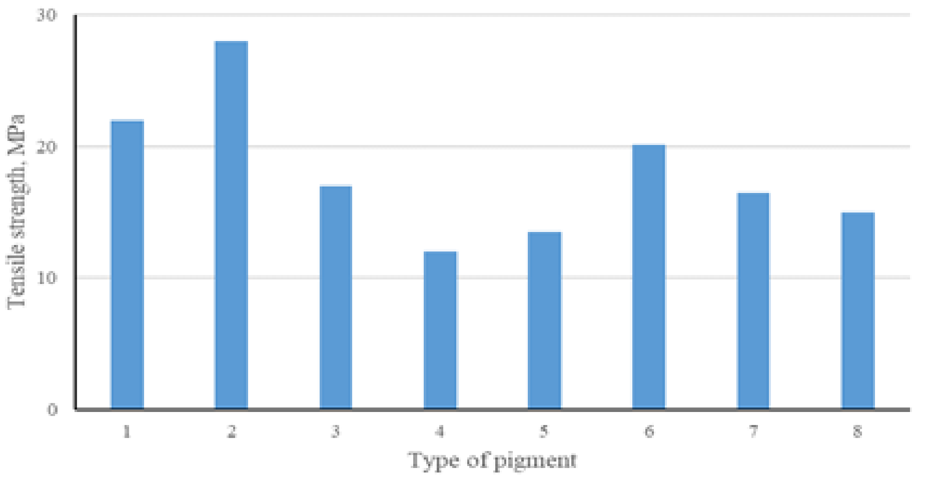
The study of structural changes in paints and varnishes was carried out by IR spectroscopy, based on the absorption of individual functional groups in the IR region. A comparison of the IR spectra of films of non-pigmented epoxy composite and compositions with various pigments shows that the degree of polymerization is greatly influenced by the type of pigment used. The calculated degree of curing of decorative compositions is given in Table 1.

Table 1. Test results

Type of pigment	Relative degree of polymerization
–	1.00
Minium iron	0.93
Iron oxide yellow	1.09
Glauconite green	1.95
Cobalt violet dark	1.54
Aluminum powder	1.26
Iron blue	1.91
Lead crown	0.78
Light ocher	1.22

From the results of studies of paint and varnish compositions, the highest degree of curing corresponds to composites in which glauconite green was used as a pigment. High results correspond to composites with cobalt violet, iron blue, ocher, aluminum powder and iron oxide yellow. For the rest of the composites, the degree of cure was found to be lower than that of the unpigmented epoxy resin. For compositions with iron minium, by 7%, and for composites in which lead crown was used as pigments, by 28%. The highest degree of polymerization of compositions with glauconite green is probably because it forms stable carbon-oxygen-cobalt bonds, which leads to a high degree of polymerization. Lead crown is most likely a catalyst for slowing down the polymerization of epoxy resin. Such compounds are very unstable, they immediately destroy the epoxy ring, while forming ions that are not involved in further polymerization. The dependences of the change in tensile strength and relative elongation of paint-and-lacquer epoxy composites with various pigments are shown in Figure 1.

a)



b)

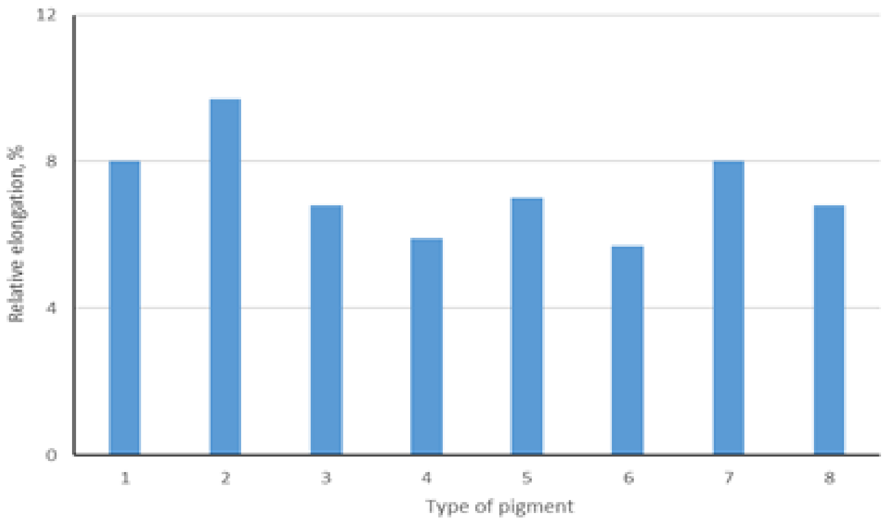


Fig. 1 - Dependence of change in tensile strength (a) and relative elongation (b) of paint-and-lacquer epoxy composites on the type of pigment: 1 - aluminum powder; 2 - lead crown; 3 – glauconite green; 4 - cobalt violet; 5 - light ocher; 6 - iron blue; 7 - iron minium; 8 - iron oxide yellow

The data of the conducted studies indicate that the use of one or another type of pigment, it is possible to regulate the deformation-strength properties of paints and varnishes in a wide range. Thus, the greatest tensile strength is achieved by introducing lead crown, aluminum powder and iron blue into the composition of paintwork materials. The relative elongation of materials increases in the case of the use of aluminum powder, lead crown and iron minium.

4 Conclusions

1. The processes of structure formation of epoxy composites with improved decorative properties have been studied. It has been established that the degree of polymerization of these materials is determined by the type of pigment used. The degree of curing increases with the use of pigments of glauconite green, iron blue, aluminum powder, iron oxide yellow, dark cobalt violet, ocher, and the introduction of iron minium and lead crown reduces it.

2. It is shown that due to the purposeful choice of pigment and filler, it is possible to regulate the deformation-strength properties of paintwork materials in a wide range. The compositions with aluminum powder and lead crown have the highest strength properties.

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