Plasticized epoxy composites for manufacturing of composite reinforcement

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Abstract. Composite rebar is a promising building material due to its advantages over steel rebar. Polymer reinforcement consists of a hardened matrix reinforced with a continuous fiber. The main role of the matrix is to determine the performance properties of the composite and to distribute stresses in the reinforcing filler. Optimization of the polymer matrix composition in terms of strength and technical parameters makes it possible to obtain a composite with high performance properties. The aim of the research was to determine the effect of modifying additives on the properties of the matrix for the production of composites with high technical requirements. When performing research, we considered modifiers that interact differently with the components of the polymer matrix as plasticizers. The first type of additive is able to combine with reactive groups of epoxy resin to form a three-dimensional product. Urea resin was used as such a compound. The second group of samples contained a furfurolacetone monomer—a substance that does not contain reactive groups with the resin, but interacts with the hardener of the epoxy resin. And the third type of modifier is dioctyl phthalate, whose role is to change the intermolecular and intramolecular interaction of the spatial structure that it fills. Optimization of compositions to identify areas with high physical and mechanical values was carried out using mathematical methods of experiment planning. Based on the results of the research, it can be concluded that with the optimal content of plasticizers, in all cases, there is an increase in the compressive and tensile strength indicators compared to materials without additives. Further increase in the content of modifying additives (above the optimal amount) leads to a decrease in strength.

Keywords: composite reinforcement, polymer matrix, epoxy resin, hardener, plasticizer, dioctyl phthalate, furfural acetone monomer, urea resin, ultimate strength, modulus of elasticity.

1. Introduction

Currently, the problem of increasing the durability of building materials that can provide long-term and reliable operation of building structures and structures in aggressive environments is given the closest attention [1, 3, 5, 6, 7, 16, 17]. Reinforced concrete structures in many operating environments are more durable than metal and other structures. In reinforced concrete structures, metal reinforcement is protected from corrosion by concrete. Their service life is determined by the permeability of concrete when exposed to gaseous and liquid aggressive media. Concrete in aggressive environments gradually loses its protective properties. In this regard, the destruction of reinforced
concrete structures is often caused by corrosion of metal reinforcement. One way to solve this problem is to replace it with a composite one.

The literature contains numerous studies on the development of technology and the use of non-metallic reinforcement for reinforcing various building structures that are used in industrial, civil and transport construction [2, 4, 12].

In recent years, the use of composite (polymer) rebar in the construction industry has increased due to a number of advantages not inherent in steel rebar. Positive qualities determine the scope of application of composite reinforcement. First, it is immune to corrosion under the influence of salts, aggressive chemicals and moisture, which allows you to build concrete structures that are subject to permanent or temporary soaking, located in ground conditions, etc. Secondly, the low weight, which makes it possible to mount structures without massive lifting mechanisms. Third, composite fittings do not transmit electric current and are not susceptible to magnetic fields, which is the preferred option for objects under high voltage, in the nuclear, electrical and electronic industries, in medical institutions with magnetic resonance equipment. Fourth, durability, which compensates for the large initial investment in the construction of concrete structures with polymer reinforcement relative to reinforced concrete structures, increasing the service life and current costs associated with restoration and repair work.

Composite (polymer) reinforcement is a power rod made of thermosetting resin, continuous reinforcing and other fillers [19]. Glass, basalt, carbon or aramid fibers are used as reinforcing fillers. An important component in the composite is the matrix, which consists of a cured thermosetting resin that combines all the components into a single whole, which is responsible for the transmission and distribution of stresses in the reinforcing filler and affects the properties of the polymer composite, such as thermal, fire, moisture and chemical resistance.

The study of the behavior of materials for various types of use is one of the most important areas in the field of building materials science, since the strength and deformability of metal, concrete, wood, etc. data is used to develop methods for calculating the strength, endurance, durability, and stability of building products and structures [23, 24, 25, 26]. At the same time, the main research is the behavior of materials in the field of elastic and plastic deformations. Research and selection of the properties of the initial components used in the manufacture of composite reinforcement allows you to control its characteristics.

The following thermosetting polymer binders are widely used as binders for non-metallic reinforcement: epoxy, polyester, organosilicon resins and their compositions [8, 9, 20, 21]. In Russia, epoxy resin is widely used for these purposes. When cured, it has high strength, resistance to aggressive media, water resistance, and good adhesion to various materials [10, 13, 14, 15]. In addition to the positive performance characteristics, a significant disadvantage is identified (the fragility of the composite), which is not acceptable in composite fittings. To increase the plasticity of the epoxy matrix, plasticizers are introduced into the compositions at the preparation stage, which also reduce the viscosity of the composition. However, the addition of a large amount of plasticizing component can reduce the adhesion and strength properties of the cured composite. In this regard, optimization of the quantitative content of components in the polymer matrix is an important stage in the creation of composite fittings with high physical, mechanical, technical and operational characteristics.

The main physical and mechanical parameters required for non-metallic reinforcement when used in polymer concrete structures are the limits of tensile strength, compressive strength, cross-section strength, adhesion strength to concrete, and modulus of elasticity.

The aim of the research is to establish the influence of plasticizing additives on the physical and mechanical properties of the epoxy matrix.

2. Materials and method
When performing research, we considered modifiers that interact differently with the components of the polymer matrix as plasticizers. The first type of additive is able to combine with reactive groups of
epoxy resin to form a three-dimensional product. Urea resin was used as such a compound. The second group of samples contained a furfural acetone monomer—a substance that does not contain reactive groups with the resin, but interacts with the hardener of the epoxy resin. And the third type of modifier is dioctyl phthalate, whose role is to change the intermolecular and intramolecular interaction of the spatial structure that it fills.

Epoxy-Diane resin of the ED-20 brand (GOST 10587—84), which is a liquid reactive oligomer product based on diphenylolpropane diglycidyl ether, was considered as a binder. The main technical characteristics of epoxy-Diane resin are shown in table 1.

| Characteristic                        | Normative value                              |
|--------------------------------------|----------------------------------------------|
| External appearance                  | Highly viscous transparent liquid without visible mechanical inclusions and traces of water |
| Color on the iron-cobalt scale, max  | 4                                            |
| Mass fraction of epoxy groups, %     | 19.9 – 22.0                                   |
| Mass fraction of volatile substances, %, max | 0.5                                          |
| Mass fraction of hydroxyl groups, %, max | 1.7                                          |
| Dynamic viscosity, PA·s at 20°C      | 12-18                                        |
| The time of gelation with hardener, h, min | 5.0                                          |

Plasticizing additives in the experiment were urea resin of the PKP-52 brand (GOST 14231-88), furfuroacetone resin FAM and dioctyl phthalate (DOF). The main parameters for choosing plasticizers were compatibility with the binder, low volatility and effectiveness of the plasticizing action.

Urea resin of the PKP-52 brand is a product of polycondensation of urea and formaldehyde using urea-formaldehyde condensate and modifying additives. It is characterized by the following properties: conditional viscosity according to the viscometer VZ-246-10-60 seconds, gelatinization time at 100 °C - 55-85 seconds, mass fraction of non-volatile substances – not less than 67 %, mass fraction of free formaldehyde – no more than 0.25%.

Furfuraceous resin FAM (technical specifications 64.11.17-89)– homogeneous dark brown liquid with a viscosity of 25-40 seconds. according to VZ-4. Benzenesulfonic acid was used to cure FAM. Benzenesulfonic acid (BSC) is a dark gray crystalline product with a relative molecular weight of 158.18. This acid is well soluble in water, acetone, furfural and ethyl alcohol; it adsorbs moisture from the air. Technical BSC consists of monosulfonic acid of benzene - 98.4—98.6%; free \( \text{H}_2\text{SO}_4 \) - 1.2-1.4% and benzene – no more than 0.2%.

Dioctylphthalate (GOST 8728-88) – is a viscous, oily liquid having the following properties: chromaticity on the iron-cobalt scale of not more than 40, 982-986 density kg/m³ at 20°C; dynamic viscosity at 20°C (10-20)×10⁻³ PA·c; boiling point – 335°C; flash – not below 205°C; mass fraction of volatile substances is not more than 0.1 %.

To cure the epoxy resin, experiments used polyethylene polyamine (PEP) (technical specifications 6-02-594-75), which is obtained by esterification of phthalic anhydride with the addition of octanol with a powerful catalyst, for example, arylsulfonic acid at a temperature of 130 to 150 °C and tetraalkyltitanate, heated to 160-180 °C. Technical characteristics of polyethylene polyamine are given in table 2.

| Characteristic                        | Normative value                              |
|--------------------------------------|----------------------------------------------|
| External appearance                  | Viscous liquid from light yellow to dark brown color without mechanical inclusions |
| Boiling point, ° C, min.              | 207                                          |
Optimization of compositions to identify areas with high physical and mechanical values was carried out using mathematical methods of experiment planning. The following factors were taken as variable: X1 - the content of the hardener (polyethylene polyamine); x2 – the content of the plasticizer. The experiment planning matrix and the quantitative composition of the components are shown in tables 3 and 4.

**Table 3. Matrix of experiment planning**

| Factors of variation | Composition number |
|----------------------|--------------------|
|                      | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| The hardener (PEP)   | -1 | 0 | +1 | -1 | 0 | +1 | -1 | 0 | +1 |
| Plasticizer          | -1 | -1 | -1 | 0 | 0 | +1 | +1 | +1 |

**Table 4. Quantitative content of components per 100 wt. h. of resin, in wt. h.**

| Levels | PEP | DOF | PKP-52 | FAM + BSC * |
|--------|-----|-----|--------|-------------|
| -1     | 8   | 0   | 0      | 0           |
| 0      | 10  | 6   | 6      | 12          |
| +1     | 12  | 12  | 12     | 24          |

* - the curing agent benzoylacetate (BSC) was introduced in the amount of 20% of the FAM

The limits of tensile strength (Rₜ), flexural strength (Rₕ), compressive strength (Rₑ), and compressive modulus (E) were used as evaluation indicators

3. Results and discussion

In the course of physical and mechanical tests, numerical values of strength and modulus of elasticity were determined. After processing the results of the experiment, regression equations are obtained. The adequacy of the obtained regression equations was checked using Fischer's F-test in [22]. The F-test only checks that the adequacy variance does not differ significantly from the reproducibility variance, i.e. the model error and the error associated with the accuracy of the experiment on which the model is based are close to each other.

The calculated (tabular) value of Fischer's F-test is determined depending on the accepted confidence probability, in our case equal to 95%, and the number of degrees. As a result of research, it is established that the obtained regression equations are adequate (Fc < Ft) and they can be considered mathematical models of properties.

The obtained models are used to plot the dependence of the tensile, flexural, and compressive strength limits, as well as the dependence of the elastic modulus of epoxy composites on the quantitative content of hardener and plasticizing additives, which are shown in figures 1-3.

According to the obtained dependencies shown in figure 1, areas with large and small indicators are highlighted. The increase in compressive strength is detected at the introduction of no more than 6 wt. h. PKP-52 and 8-10 wt.h. PEP per 100 wt. h. ED-20. Adding more plasticizer significantly reduces
this indicator. The increase in bending strength relative to non-modified compositions is achieved with small amounts of urea resin (up to 4 wt. h. per 100 wt. h. binder), regardless of the amount of hardener in the range of factor $X_2$ variation from -1 to 0.

Figure 1. Graphs of changes in the physical and mechanical properties of the polymer matrix from the content of polyethylene polyamine and urea resin: compressive strength $R_c$ (a), flexural strength $R_f$ (b), tensile strength $R_s$ (c) and compressive modulus $E \cdot 10^3$ (g) in MPa (d)

With the introduction of urea resin in the amount of 6 wt. h. ($X_2 = 0$) and hardener $-12$ wt.h. ($X_1 = +1$), the composites show the maximum value of the tensile strength $R_R$, equal to 64 MPa. The content of more than 6 wt. h. PKP-52 per 100 wt. h. ED-20 in the compositions leads to a significant decrease in strength characteristics. The compression modulus of elasticity decreases when urea resin is introduced into composites.

When using furfurolacetone resin as a plasticizer, the maximum compressive strength of 115 MPa is observed in the region of $-1 < X_2 < 0$ with a hardener content of 12 wt. h. ($X_1 \approx +1$) per 100 wt.h. of resin. The tensile strength increases to 72 MPa (figure 2), while the optimal component content is 10-14 wt. h. FAM and 10 wt.h. PEP ($X_1 = 0$). The maximum value of the elastic modulus $E = 2.15*10^3$ MPa is found in the range of variable factors $0 < X_1 < +1$ and $-1 < X_2 < 0$. When the plasticizer is introduced in large quantities (when $X_2 > 0$), the modulus of elasticity decreases (figure 2).
Figure 2. Graphs of changes in the physical and mechanical properties of the polymer matrix from the content of polyethylene polyamine and furfural acetone resin: compressive strength $R_c$ (a), flexural strength $R_f$ (b), tensile strength $R_t$ (c) and compressive modulus $E \cdot 10^3$ (g) in MPa (d)

The graphs of the dependence of the strength properties of the polymer matrix on the quantitative content of the hardener and dioctyl phthalate show clear areas with optimal values of the indicators under consideration, all graphs have the shape of an ellipse. Thus, the compressive strength during the introduction of DOF increased to 118 MPa, while the optimal content of the plasticizer is from 4 to 8 wt. h. per 100 wt. h. of resin. In the area where $X_1$ and $X_2$ vary from 0 to +1, there is an increase in bending strength up to 80 MPa. The tensile strength also increases with the introduction of dioctyl phthalate. The maximum value ($R_t = 82$ MPa) is observed at zero levels of the factors under consideration. The elastic modulus of composites decreases when the plasticizer is introduced in quantities of more than 6 wt. h. per 100 wt. h. binder (figure 3 g).
4. Conclusion
Based on the results of the research, it can be concluded that the optimal content of plasticizing additives in terms of strength indicators is 6-7%, the amount of hardener for compositions modified with dioctyl phthalate and urea resin should be 10-11%, and for compositions with FAM – 12%. With the optimal content of plasticizers in all cases, there is an increase in the compressive strength (up to 116-118 MPa) and tensile strength (over 70 MPa) compared to materials without additives. Further increase in the content of modifying additives (above the optimal amount) leads to a decrease in strength.

The conducted research allows us to start further testing of the evaluation of optimization paths in the field of composite polymer reinforcement.

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