Alkali resistant epoxy binders for pultrusion

A. I. Leshtaev[1*], *I. P.* Storozhuk[1], *M. A.* Orlov[1], I. A. Polikarpova[1], *R. R.* Ivan'kov[1], and *S. S.* Muzyka[1]

[1]Bauman Moscow Technical University, 105005, ul. Baumanskaya 2-ya, 5/1, Moscow, Russia

Abstract. Alkali-resistant hot-curing epoxy binders based on ED-20 and new amine hardeners "Amikrost" have been developed, intended for the production of glass-composite fittings for construction purposes. The rheological properties of epoxy compositions were determined, using differential scanning calorimetry and thermogravimetric analysis, the temperature dynamics of the curing process of epoxy compositions and the thermal-oxidative resistance of cured samples were studied. The alkali resistance of cured epoxy compositions and specimens of composite reinforcement in 40% alkali aqueous solution was evaluated. It is shown that the developed amine hardeners provide high alkali resistance of composite reinforcement in comparison with the currently used anhydride hardener iso-MTHPA, which is especially important for reinforcing buried and hydraulic concrete.

1 Introduction

The popularity of composite reinforcement obtained by pultrusion is increasing every year due to its advantages over traditional metal reinforcement such as light weight, high mechanical strength, good oxidative and acid corrosion resistance, and dielectric properties. [1-3] The lighter weight of building structures reduces the load on the foundation of the structure, which allows to extend its service life. [2-4] Composite reinforcement, unlike its metal counterparts, better tolerates tensile loads, which makes it possible to use it to strengthen the most critical concrete structures. [1-9]

As a binder in the production of composite reinforcement by pultrusion from continuous glass or basalt fiber, hot curing epoxy resins are used, the properties of which largely depend on the chemical structure of the epoxy resin, hardener and reaction accelerator. [10-12] In particular, the curing modes, mechanical properties and chemical resistance of the binder strongly depend on the nature of the hardener. [7, 10-12] From a practical point of view, an important problem for epoxy binders in composite reinforcement operating in concrete is their alkali resistance. [2] This is especially true of reinforcement operating in water-saturated concrete of buried and hydraulic structures. [2, 4, 7]

2 Purpose of the study

* Corresponding author: storozhuk-ip@inbox.ru

The aim of the study was the development and study of alkali-resistant epoxy binders for the production of composite reinforcement for building purposes by high-temperature pultrusion.

3 Materials and research methods.

The following materials were used in the work: epoxy resin ED-20, anhydrous iso-MTHFA hardener, Amikrost-1 and Amikrost-2 amine hardeners, Agidol accelerator, which were mixed in various proportions.

As research methods in the development of epoxy alkali-resistant compositions, the following were involved: the rotational method for determining dynamic viscosity, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and the determination of physical and mechanical characteristics in tension of blades from cured compositions.

For rheological studies, a Brookfield DV-e rotational viscometer was used. To assess the thermal effects during the curing of epoxy compositions and determine the glass transition temperatures of cured materials, a DSC device "NETZH DSC 204 F1 Phoenix" was used, the temperature rise rate was 10°C per minute, argon was used as an inert atmosphere, the sample weight was 12-13 mg. The thermal and oxidative stability of the cured compositions when heated in air was evaluated using a TGA instrument "NETZH TG 209 F1 Libra" at a constant heating rate of 5 degrees per minute, the weight of materials was 7-10 mg.

4 The discussion of the results

The study of the curing process and determination of the gelation time is important for the development of compositions and technology for the preparation of epoxy binders, therefore, at the first stage of the work, the curing kinetics of a significant number of compositions was studied. To do this, we used a setup consisting of a heated magnetic stirrer, a silicone bath, and a Brookfield DV-e rotational viscometer. A glass container with preheated to 100°C and mixed components of the epoxy composition was loaded into a preheated silicone bath, the mixture was thermostated at a temperature of 100°C, the spindle was immersed, and the viscosity of the reaction mixture was measured until it thickened.

The most technologically advanced and reactive compositions presented in Table 1 were selected as objects for further research.

Table 1. Composition of epoxy binders.

№	Recipe code	The composition of the recipe	Mass fractions
1	EDA-5	ED-20/Amikrost-2/Agidol	100/22/2
2	EDA-6	ED-20/Amikrost-1/Amikrost-2/Agidol	100/16,5/5,5/2
3	EDA-10	ED-20/Amikrost-1/Agidol	100/21/2

Figures 1 and 2 show the dependences of the viscosity and reduced viscosity of epoxy mixtures on the curing reaction time, on the basis of which the time to reach the gel point is determined.

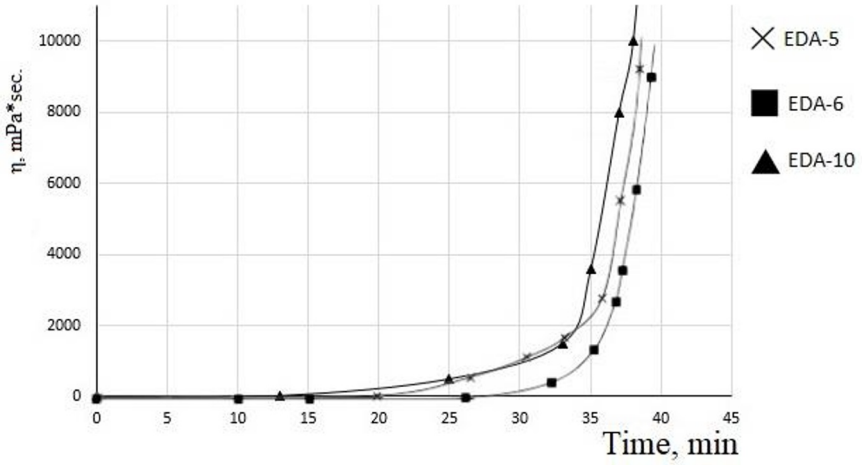

Fig. 1. The dependence of the increase in viscosity during curing of the developed epoxy binders at 100°C.

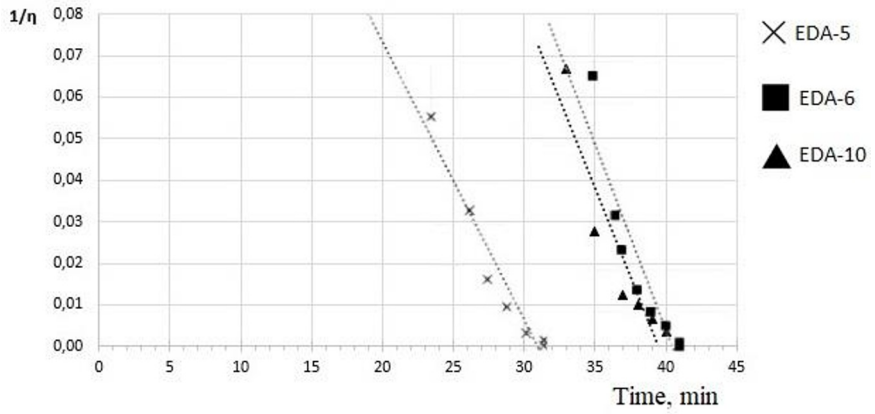

Fig. 2. Dependence of the reduced viscosity on the curing time of the developed epoxy binders at 100°C in the coordinates 1/η=f(t).

Table 2 presents the values of the time to reach the gel points of the developed binders obtained during the measurements of dynamic viscosity. From the presented graphs and Table 2, it can be seen that the beginning of the viscosity increase for the more active EDA-10 and EDA-5 compositions occurs 15 and 17 minutes after the start of the curing reaction, and for the less active EDA-6 composition, after 25 minutes. The shortest time to reach the gel point (31 minutes) is observed for the EDA-5 composition, apparently due to the greater reactivity of the Amikrost-2 hardener compared to Amikrost-1.

Table 2. Time to reach the gel point of the developed epoxy binders at 100°C.

№	Recipe code	Start time of viscosity increase, min.	Time to reach the gel point, min
1	EDA-5	17	31
2	EDA-6	25	41
3	EDA-10	15	40

The method of differential scanning calorimetry (DSC) was used to evaluate the temperature dynamics of the curing process of epoxy compositions, to select the optimal temperature for their curing, and to determine the glass transition temperatures of cured epoxy compositions.

Figures 3-5 show DSC curves for epoxy binders EDA-5, EDA-6, EDA-10 and DSC curves for determining the glass transition temperatures of cured compositions. As can be seen, the curves reflecting the thermal effects during the curing reaction of the epoxy resin ED-20 have two maxima, the temperatures of which for all compositions are given in Table 3.

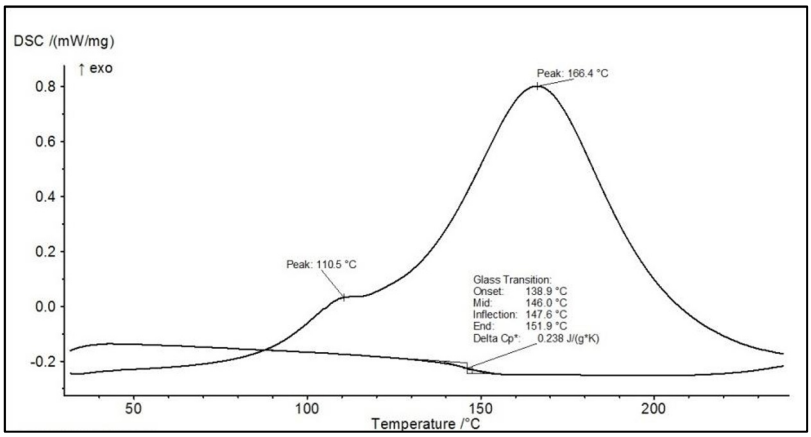

Fig. 3. DSC curve of the curing process and DSC curve for the cured epoxy binder EDA-5.

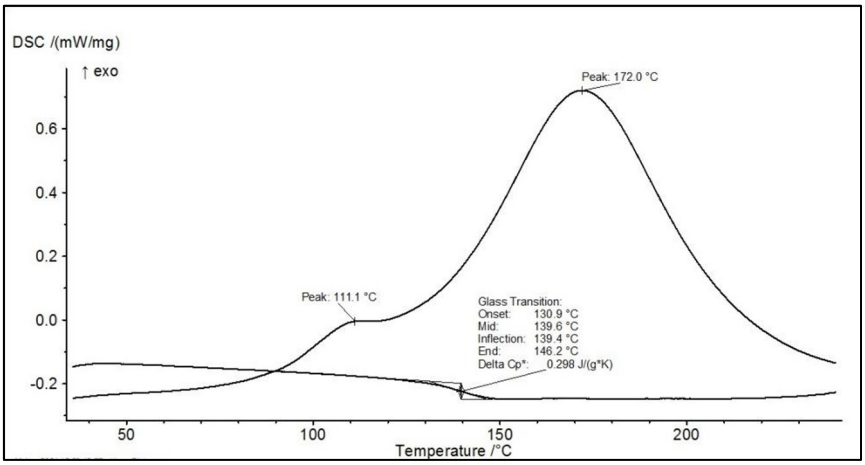

Fig. 4. DSC curve of the curing process and DSC curve for the cured epoxy binder EDA-6

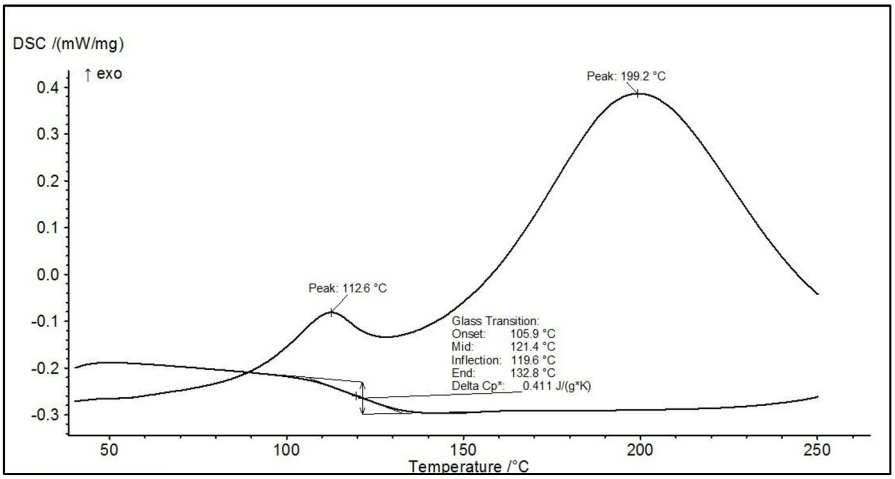

Fig. 5. DSC curve of the curing process and DSC curve for the cured epoxy binder EDA-10

Table 3. Temperatures of peaks of thermal effects during curing of epoxy compositions and glass transition temperatures of cured compositions.

№	Recipe code	T, °C first maximum	T, °C second maximum	T_c, °C
1	EDA-5	110,5	166,4	146,0
2	EDA-6	111,1	172,0	139,6
3	EDA-10	112,6	199,2	121,4

As can be seen from fig. 3-5 and Table 3, the first maxima on the DSC curves for the curable compositions are observed at almost the same temperature ≈111°C and have approximately the same area, which indicates that the thermal effect corresponding to these maxima is associated with the ED-20 reaction with "Agidol", which acts not only as a curing accelerator, but also as a hardener. This explanation is confirmed by the same content (2 parts) in all the epoxy compositions under consideration (Table 1).

The temperatures of the second maxima on the DSC curves are higher than the first ones and depend on the nature and composition of the hardeners. It is obvious that the hardener "Amikrost-1" in the composition of EDA-10 is less active compared to "Amikrost-2", the reaction with its participation is less exothermic (the intensity and area of this maximum is less than that of EDA-5 and EDA-6). The spatial network of the cured composition EDA-10 is less rigid, therefore, the glass transition temperature of this material is 121.4°C, which is 24.6 and 18.2°C lower compared to EDA-5 and EDA-6.

Hardener "Amikrost-2" in EDA-5 is more active, compared to "Amikrost-2", not only according to rheological tests (Table 2), but also according to DSC data: the second maximum for EDA-5 occurs earlier than others and observed at 166.4°C. In addition, this hardener forms a more rigid and heat-resistant crosslinked ED-20 structure with a glass transition temperature of 146.0°C.

For the epoxy composition EDA-6, an intermediate indicator is observed for the position of the second maximum (172.0 ° C), which is consistent with the composition of the mixed hardener, in which "Amikrost-1" / "Amikrost-2" as 16.5 / 5.5 m.h. (Table 1). This applies equally to the glass transition temperature of the cured EDA-6 composition with Tc=139.6°C.

Based on the results obtained using the DSC method, the optimal temperature was chosen for the industrial curing of the developed epoxy binders in a pultrusion plant for the production of fiberglass composite reinforcement. It is 140-150°C, which corresponds to the beginning of the second maximum of the exothermic effect. The choice of such a temperature range (and not higher) is associated with fears of overheating of the epoxy binder in the polymerization oven due to a powerful exothermic effect, which can lead to decomposition of the epoxy matrix with the formation of gaseous products of thermal-oxidative degradation, pore formation in the composite and, as a result, to a decrease in strength characteristics of composite reinforcement.

Due to the technological features of the pultrusion line and the possibility of abnormal overheating in the polymerization furnace, we have studied the thermal and oxidative stability of the developed epoxy binder formulations at an extreme temperature of 300°C. Tests of powders of cured epoxy compositions were carried out using the method of isothermal thermogravimetric analysis in an air atmosphere. The heating rate was 25°C/min, and the sample was heated from 30 to 300°C in 10.8 min. The resulting TGA curves are shown in Figure 6.

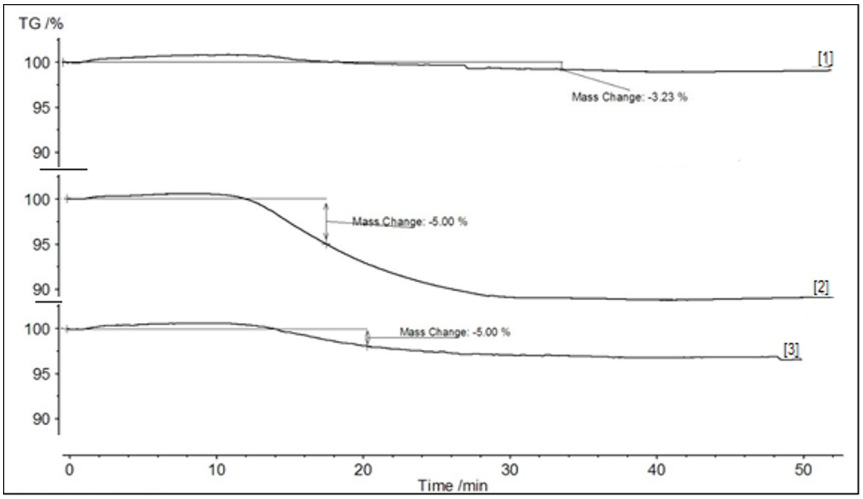

Fig. 6. Weight loss curves of cured epoxy binders: [1] - EDA-5, [2] - EDA-6, [3] - EDA-10 in isothermal mode at 300°C in air.

It can be seen from the graphs that at the initial stage of heating, the samples add 2-3 wt% in weight, it is obvious that this is due to thermal-oxidative and hydrolytic reactions with oxygen and water vapor, which ultimately lead to the decomposition of the chemical structure of the epoxy material and weight reduction of the sample. Moreover, the thermal-oxidative resistance of cross-linked epoxy compositions significantly depends on the nature and composition of the hardeners, so the EDA-5 composition has the highest thermal-oxidative resistance, which loses 3.2% of the mass at about 27 minutes of isothermal heating and does not reduce its weight upon further heating, EDA-6 loses 5% of its mass at 18 minutes of heating and 10% at 30 minutes, EDA-10 occupies an intermediate position and loses 5% of its mass at 22 minutes of heating, and then its mass remains unchanged. In general, all three compositions showed good resistance to possible short-term overheating.

In order to confirm the increased alkali resistance of the developed amine-cured epoxy binders, blades 16 mm wide, 2 mm thick and 86 mm in total length were cast, cured and aged in a 40% NaOH alkaline solution at 90°C for 28 days, which were then tested on a tensile testing machine according to GOST 11262-2017 to obtain the values of ultimate strength, modulus of elasticity and relative elongation of samples at break. For comparison,

the same operations were performed with blades based on the EDI-75 epoxy binder (ED-20 with the anhydride hardener Iso-MTGFA), which is currently widely used in the production of composite fiberglass reinforcement.

Table 4 shows the deformation-strength properties of blades made of cured binders EDI-75, EDA-5, EDA-6 and EDA-10 before and after exposure to an alkaline solution. Figure 7 shows photographs of blades on an anhydride curing EDI-75 epoxy binder after exposure to an alkaline solution.

Table 4. Deformation-strength properties of cured epoxy binders before and after exposure to an alkaline solution.

№	Epoxy compound	E, GPa	**Δ** E, %	σ_P, MPa	**Δ** σ_P, %	ε, %	**Δ** ε, %
1	EDI-75 initial	3,30	-	75,61	-	2,63	-
2	EDI-75 after alkali	1,76	-47	51,41	-32	1,22	-54
3	EDA-5 initial	3,32	-	79,41	-	1,58	-
4	EDA-5 after alkali	3,37	+1,5	65,50	-17	1,51	-4
5	EDA-6 initial	3,29	-	80,62	-	1,59	-
6	EDA-6 after alkali	3,30	+0,3	84,85	+5,2	1,17	-26
7	EDA-10 initial	3,33	-	85,39	-	1,65	-
8	EDA-10 after alkali	3,34	0	79,51	-7	1,40	-15

Fig. 7. Samples made of cured binder EDI-75 after exposure for 28 days in 40% NaOH aqueous solution at 90°C.

As can be seen from Table 4, exposure of the blades from the binder hot anhydride curing EDI-75 leads to a significant decrease in tensile strength (-32%), elastic modulus (-47%) and elongation at break (-54%). After holding in an alkaline solution, the EDI-75 blades acquired an intense color (Fig. 7), shells appeared on the surface, and the geometric dimensions and weight of the samples decreased.

Unlike samples from EDI-75, samples from the developed epoxy compositions of hot amine curing after soaking in alkali practically did not change their color (Fig. 8), geometric dimensions and weight, and, most importantly, slightly reduced their deformation-strength properties (table 4). In particular, the modulus of elasticity showed especially high stability, which practically did not change, and even slightly increased,

compared with the original samples. The tensile strength and relative elongation of samples with amine hardeners after soaking in alkali decreased, but slightly, compared with EDI-75.

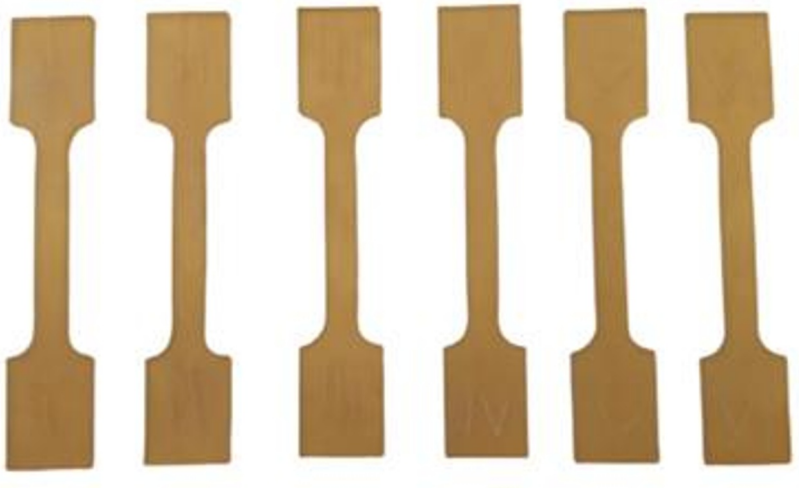

Fig. 10. Blades made of hardened ESA-10 binder after exposure for 28 days in 40% aqueous NaOH solution at 90°C.

For greater confidence in the suitability of the developed epoxy binders for the production of composite reinforcement for construction purposes, we produced pilot batches of composite reinforcement based on glass roving and EDA-6 and EDA-10 binders at the factory pultrusion plant of GALEN LLC (Cheboksary). It was found that the existing technological regimes for the production of reinforcement from EDI-75 are fully suitable for the use of the developed amine curing binders.

To compare the alkali resistance of composite reinforcement based on various binders, the reinforcement samples were kept in a 40% NaOH aqueous solution (imitation of wet concrete with pH=12.6-13.0) at a temperature of 60°C for 30 days. After that, reinforcing bars with a nominal diameter of 8.99 mm, a nominal area of 63.48 mm2 and a length of the working part of 380 mm were tested on a tensile testing machine. The test results are shown in table 5.

When comparing the test results given in tables 4 and 5, a good correlation of the reduction values (ΔE, ΔσP, Δε) of the strength and deformation properties of the cured epoxy binders and composite reinforcement based on these binders is visible, which indicates the important role of the epoxy alkali-resistant matrix in ensuring chemical resistance composite reinforcement. The results obtained open up new possibilities for the production of alkali-resistant composite reinforcement intended for operation in water-saturated buried and hydrotechnical concrete.

Table 5. Deformation-strength properties of composite fiberglass reinforcement before and after soaking in an alkaline solution.

№	Binder in rebar	E, GPa	Δ E, %	σ_P, MPa	Δ σ_P, %	ε, %	Δ ε, %
1	EDI-75 initial	59,5	-	1300	-	3,5	-
2	EDI-75 after alkali	24,6	-58	595	-54	2,5	-28
3	EDA-10 initial	60,6	-	1310	-	4,3	-
4	EDA-10 after alkali	57,5	-5	1198	-8	4,5	+4

5	EDA-6 initial	60,4	-	1250	-	4,4	-
6	EDA-6 after alkali	57,5	-5	1200	-4	4,5	-2

5 Conclusion

Based on the results of the study, it can be concluded that the developed epoxy compositions are suitable as binders in the production of alkali-resistant composite fiberglass reinforcement by the pultrusion method. Such reinforcement will be especially reliable for reinforcing concrete in the construction of buried and hydraulic structures.

6 Acknowledgement

This work was carried out within the framework of the program of state support for the centers of the National Technology Initiative (NTI) on the basis of educational institutions of higher education and scientific organizations (Center NTI "Digital Materials Science: New Materials and Substances" on the basis of the Bauman Moscow State Technical University).

References

1. M. Orouji, E. Najaf, «Effect of GFRP rebars and polypropylene fibers on flexural strength in high-performance concrete beams with glass powder and microsilica», Case Studies in Construction Materials, **18** (2023) doi:10.1016/j.cscm.2022.e01769
2. A. R. Emparanza, R. Kampmann, F. De Caso, C. Morales, A. Nanni, «Durability assessment of GFRP rebars in marine environments», Construction and Building Materials», **329** (2022) doi:10.1016/j.conbuildmat.2022.127028
3. D. A. Hensher, «Fiber-reinforced-plastic (FRP) reinforcement for concrete structures: properties and applications», Elsevier, **42** (2016) doi:10.1016/c2009-0-09136-3
4. L. Ting, Z. Hong, S. Jiahui, K. Thomas, «Thermophysical and thermomechanical properties of basalt-phenolic FRP rebars under high temperature», Construction and Building Materials, **342(A)** (2022) DOI:10.1016/j.conbuildmat.2022.127983
5. L. Alaoud, Y. Al-Salloum, H. Abbas, «Experimental investigation for GFRP rebar couplers for reinforced concrete», Journal of King Saud University - Engineering Sciences, **33(2)**, 104-110 (2021)
6. L. Huang, J. Chen, J. Qu, Q. Dai, Modeling for bond-constitutive relationships of FRP rebars to concrete matrix, Construction and Building Materials, **263** (2020) DOI:10.1016/j.conbuildmat.2020.120654
7. M. Prashant Rawat, K. K. Singh, P. K. Singh, «Comparison of steel and fiber-reinforced polymer rebars for mining applications: A numerical approach», Materials Today: Proceedings, **33(8)** (2020) DOI:10.1016/j.matpr.2020.02.840
8. S. H. Alsayed, Y. A. Al-Salloum, T. H. Almusallam. Performance of glass fiber reinforced plastic bars as a reinforcing material for concrete structures, Composites Part B: Engineering, **31**, 6-7, 555-567 (2000)
9. B. Benmokrane, O. Chaallal, R. Masmoudi. Glass fibre reinforced plastic (GFRP) rebars for concrete structures. Construction and Building Materials, **9(6)**, 353-364 (1995)

10. A. G. Zagora, A. I. Tkachuk, I. V. Terekhov, Mukhametov R.R. Metody khimicheskoy modifikatsii epoksidnykh oligomerov (Obzor). Trudy VIAM, 2021, №7 (101), s. 73-85.
11. L.V. Chursova, N. N. Panina, T. A. Grebeneva, I. YU. Kutergina, Epoksidnyye smoly, otverditeli, modifikatory i svyazuyushchiye na ikh osnove, Sankt-Peterburg: TSOP "Professiya", 576 (2020)
12. Z. A. Kochnova, Ye. S. Zhavoronok, A. Ye. Chalykh, Epoksidnyye smoly i otverditeli: promyshlennyye produkty. Moscow, «Peynt-Media», 200 (2006)
13. N. G. Pavlukovich, A. I. Leshtaev, V. S. Buryakov, I. A. Polikarpova, M. A. Orlov, I. P. Storozhuk, V. A. Nelyub, A. S. Borodulin, Rheological Research of the Curing Processes of the Epoxy-Amine Compositions Based on ED-20 Resin. E3S Web of Conferences, **376**, 01016 (2023) DOI: 10.1051/e3sconf/202337601016
14. V. A. Nelyub, A study of the microstructure of dressed glass fibers. Polym. Sci. Ser. D., **9**, 96–100 (2016) https://doi.org/10.1134/S1995421216010147
15. V. A. Nelyub, A. S. Borodulin, Properties of Epoxy Materials Used for Production of Glass-Reinforced Plastics by the Winding Method. Polym. Sci. Ser. D, **11**, 147–153 (2018) https://doi.org/10.1134/S1995421218020132
16. V. A. Nelyub, Technologies of production of components of electric transmission line supports from epoxy binders by the winding method. Polym. Sci. Ser. D, **6**, 44–47 (2013) https://doi.org/10.1134/S1995421213010115
17. P. A. Belov, A. S. Borodulin, L. P. Kobets, et al., Kinetics of fiber impregnation by a binder. Gradient generalization of Navier–Stokes–Darcy equations. Polym. Sci. Ser. D, **9**, 205–208 (2016) https://doi.org/10.1134/S1995421216020039
18. P. A. Belov, L. P. Kobets, A. S. Borodulin, Impregnation kinetics of fibers with liquids: simulation within the generalization of Navier-Stokes equations. Inorg. Mater. Appl. Res., **5**, 403–406 (2014) https://doi.org/10.1134/S2075113314040182