Influence of coloring on the properties of epoxy binders and fiberglass rebar based on them

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Abstract. At present, polymer composite materials are widely used in the construction and automotive industries, products for which must meet not only operational, but also aesthetic requirements. Since color is one of the most important design elements, much attention is paid to the coloring of structural composites. There is a fairly wide range of different methods for coloring polymer composites, but each method has both advantages and disadvantages. This article discusses two methods for coloring a hot amine-cured epoxy composition, which is used for the manufacture of composite fiberglass reinforcement: by adding pigment and organic dyes to the epoxy composition. It has been found that organic dyes dissolve in all components of the epoxy composition, but become colorless upon heat treatment. When adding an insoluble dispersed pigment, the color remains unchanged even after the thermal curing of the epoxy matrix. The addition of up to 0.5 mass parts of iron oxide pigment ("red FEPREN TP-303") to the epoxy binder slightly reduces the mechanical strength of the composite and significantly increases its thermal stability.

1 Introduction

Reinforced polymer composite materials (PCM) have become widely known due to their outstanding characteristics of strength and elastic modulus per unit weight compared to traditional metal products [1–3]. Since reinforced composite materials are widely used in our daily life, for example, in automobiles, building facades and interiors, household appliances, etc., the aesthetic appearance of composite products becomes another important requirement for commercial composite products [4–6]. As you know, color is the main aesthetic element that can give unique features to traditional forms of products [7, 8]. However, in most cases, the colors of composite materials are achromatic, they are devoid of saturation and color tone, that is, they differ from each other only according to the "lighter-darker" principle, which is determined by the color of the reinforcing material and / or haze that occurs due to light scattering in the filled polymer matrix [9, 10].

Surface painting is still widely used for coloring reinforced composite products, since this is the easiest way to add color to exteriors and interiors [11, 12]. Despite the simplicity of this technology, there is always a concern that layers of paint can peel off from the

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composite due to mechanical stresses caused by temperature differences, weathering, or friction [13–15]. Treatment of the surfaces of reinforced composites with paint primer can improve the adhesion of paint to composite surfaces, but in the end, paint layers can be damaged and worn out, in addition, this additional technological operation leads to an increase in the cost of products made of reinforced composite materials [16, 17].

As an alternative to PCM surface coloring, it is proposed to color reinforcing fibrous materials, such as glass fiber or polymer fiber, with organic dyes [18, 19]. With this approach, dyes must have a strong bond with the surface of the fibers and good adhesion to the polymer matrix, since otherwise weak adhesion may occur at the interface between the reinforcing fibers and the polymer matrix, which will lead to fiber delamination from the matrix [20].

Another method of coloring PCM, for example, based on curable polymer matrices, is the use of special colored gelcoats, which already have pigment in their composition. Gelcoats are applied to the equipment before laying the main reinforcing layers and subsequent impregnation (infusion) with binders. After demolding, the surface of the composite product will have a color. However, this method is far from being suitable for all technologies for obtaining products from reinforced composite materials.

Another common method of dyeing is the addition of dyes or pigments to the binder (matrix), which, when stirred, either dissolve in the binder or create a suspension with a uniform distribution of particles over the volume [21, 22]. To implement this method, a significant range of dyes and pigments are available on the market. Moreover, experiments are constantly being carried out with the search and testing of new options for implementing this method of coloring PCM.

For example, there are reports on the preparation of black-colored nano-modified composites using multi-walled carbon nanotubes or graphene oxide as a black pigment in a polymer matrix [23–25].

Resistant paint and varnish compositions based on epoxy resins and iron oxide powders are known, which are successfully used for painting various surfaces [26]. Successful experiments with the coloring of epoxy resins and reinforced PCM stimulate the use of colorants based on organic dyes and dispersed insoluble pigments to impart aesthetic properties to composite products.

2 Purpose of the study

The aim of our work was to study the sedimentation resistance of a hot-cured colored epoxy composition used to obtain glass-composite reinforcement by pultrusion, as well as to study the effect of coloring a polymer matrix on its mechanical properties, thermal and chemical resistance.

3 Research results

3.1 Materials

The following organic dyes and pigments were used in the work: methylene blue, rhodamine C, pigment "red FEPREN TP-303", which were introduced into the epoxy composition based on ED-20 resin, Amikrost amine hardener and Agidol curing accelerator.

To assess the effect of coloring the polymer matrix on its properties, standard blades were manufactured by casting an epoxy binder into silicone molds (Fig. 1).

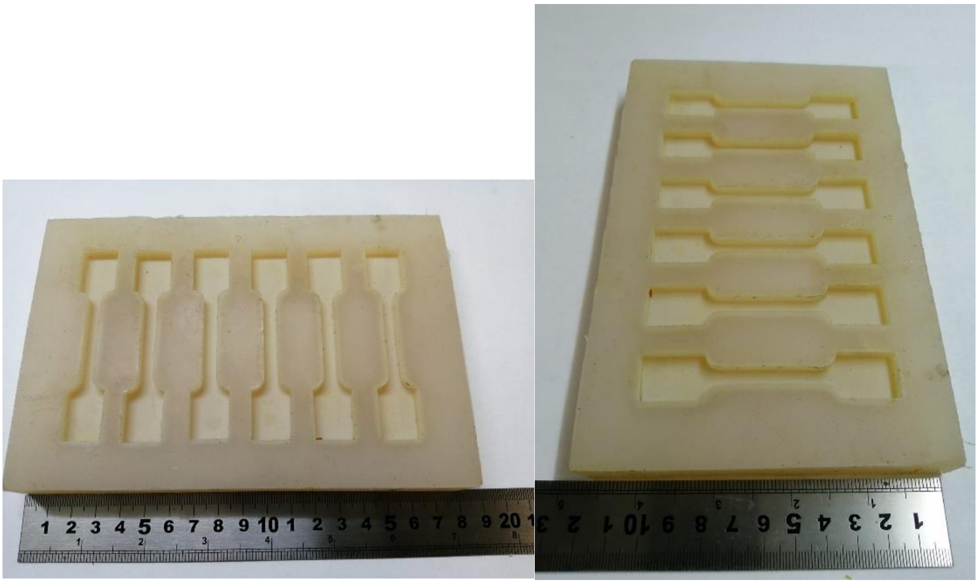


Fig. 1. Silicone molds for obtaining samples in the form of a "blade" for testing

4 The discussion of the results.

Selection of matching conditions

To evaluate the matching conditions, the solubility of dyes and the sedimentation resistance of the pigment over time, the following epoxy compositions were prepared, which were subsequently used for pouring into molds:

1. Epoxy binder based on ED-20, mixed with "methylene blue" in a ratio of 10/1 m.h.
2. Epoxy binder based on ED-20, mixed with "rhodamine C" in a ratio of 10/1 m.h.
3. Epoxy binder based on ED-20, mixed with the pigment "red FEPREN TP-303" in the ratio of 10/1 m.h.
4. Accelerator "Agidol", mixed with the pigment "red FEPREN TP-303" in the ratio of 2/1 m.h., and introduced into the epoxy binder.
5. Amine hardener "Amicrost", mixed with the pigment "red FEPREN TP-303" in the ratio of 2/1 m.h., and introduced into the epoxy binder.

According to the results of the batches, it was found that the organic dyes "methylene blue" and "rhodamine C" were well dissolved in all compositions while maintaining a stable color of the composition, the intensity of which did not change over time.

The pigment "red FEPREN TP-303" is best combined with the accelerator "Agidol" when mixed, in comparison with other components of the epoxy composition, without the formation of clots, and after three days of exposure at room temperature, no separation of the mixture was observed.

The resulting liquid colored compositions were placed in an oven for a day at a temperature of 600C in order to determine the sedimentation stability of the pigment and the thermochemical resistance of dyes, which simulated the process of preparing a binder during the impregnation of glass roving in the process of obtaining composite reinforcement by pultrusion. Compositions with organic dyes showed color fastness. The compositions with red pigment did not show sedimentation stability, except for the composition with the Agidol accelerator, which showed good stability when heated.

Thermochemical resistance of colored compounds

Epoxy compositions of compositions No. 1, 2 and 4 were selected for pouring into molds and obtaining "blades". The initial binder for the production of composite reinforcement has the composition: ED-20 // amine hardener "Amikrost" // accelerator "Agidol" with ratios of components in mass parts 100 // 21 // 2. Below are the compositions of colored compositions (OC):

1. Binder OK-1: ED-20 with "methylene blue" // amine hardener "Amikrost" // accelerator "Agidol" with a ratio of components 110 // 21 // 2 m.h.
2. Binder OK-2: ED-20 with "rhodamine C" // amine hardener "Amikrost" // accelerator "Agidol" with a ratio of components 110/21/2 m.h.
3. Binder OK-3 composition: ED-20 // amine hardener "Amikrost" // accelerator "Agidol" with pigment "red FEPREN TP-303" with a ratio of components 100 // 21 // 3 m.h.

After kneading, the colored epoxy compositions were poured into molds and cured at a temperature of 1400C for 4 hours, followed by slow cooling to 400C.

It was found that relative to the original unpainted blades (Fig. 2), the blades from the OK-1 and OK-2 compositions with organic dyes retained a slight staining, apparently due to insufficient thermal stability of the dyes or chemical reactions with their participation (Fig. 3 and 4).

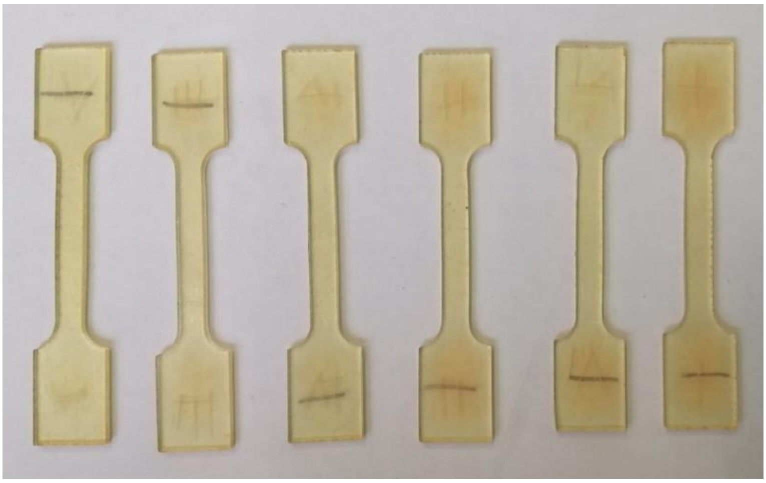


Fig. 2. Cured original blades without dyes and pigment

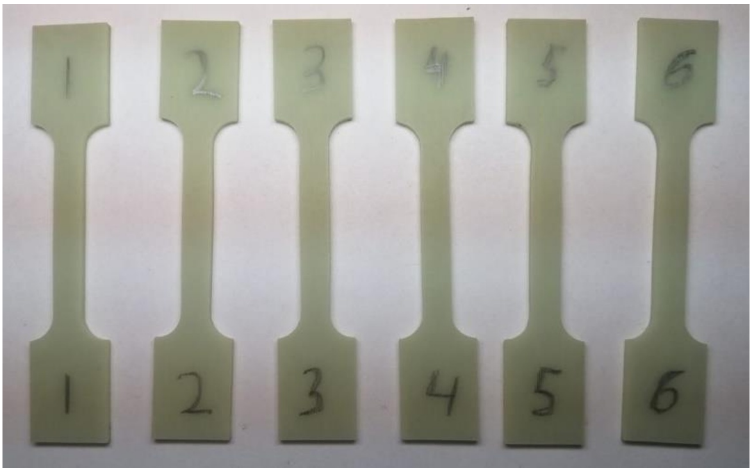


Fig. 3. Cured blades from OK-1 with methylene blue dye

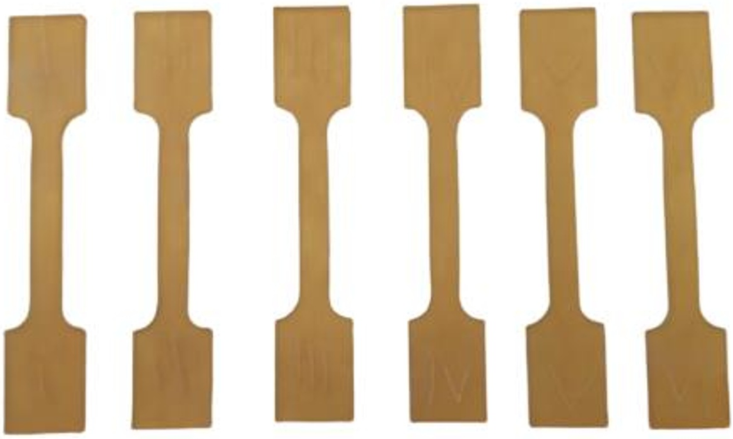


Fig. 4. Cured blades from OK-2 with the dye "rhodamine C"

The blades based on the epoxy composition OK-3 dyed with pigment “red FEPREN TP-303” showed good thermal stability of the color (Fig. 5).

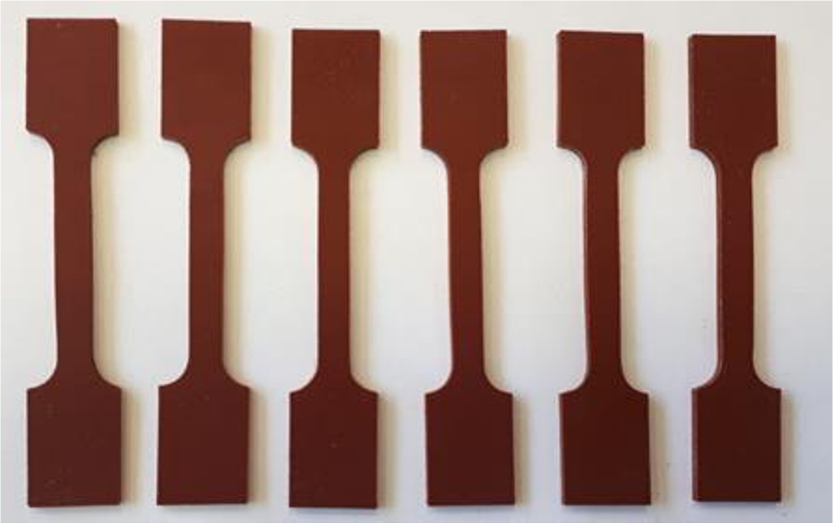
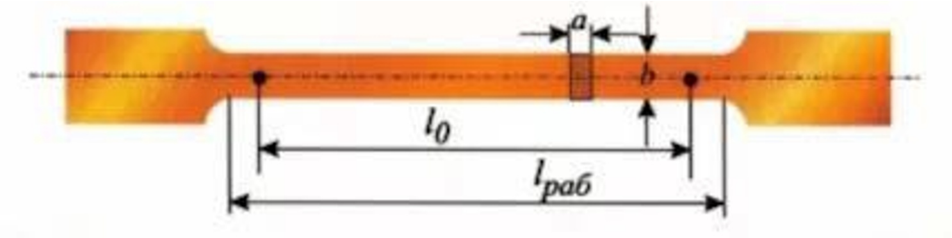


Fig. 5. Blades from OK-3 with the pigment "red FEPREN TP-303".

In order to clarify the effect of the pigment on the mechanical properties of the epoxy binder, tensile tests of the blades were carried out on a tensile testing machine to obtain the values of the tensile strength, modulus of elasticity and relative elongation of the samples according to GOST 11262-2017. We compared the mechanical properties of the blades from the epoxy composition without the addition of pigment and the blades from the colored composition OK-3. Both batches of samples included 6 blades.

The shape and geometric dimensions of polished samples of blades made of epoxy binders, obtained by free casting into silicone molds, are shown in (Fig. 6).



blade width b - 16mm, blade thickness h - 2mm and total length - 86mm.

Fig. 6. Blade sample according to GOST 11262-2017.

According to the results obtained during the tests (tables 2 and 3), it was shown that the pigment, made in an amount of up to 0.5 mass parts, has no or little adverse effect on the cured epoxy composition.

Table 2. Mechanical properties of blades based on unpainted epoxy composition

№ blade sample	σ_p, MPa	E, GPa	ε_p, %
1	83,47	3,29	1,53
2	83,22	3,36	2,00
3	83,07	3,30	1,86
4	81,98	3,30	1,40
5	81,97	3,36	1,70
6	80,66	3,38	1,39
Average value	82,39	3,33	1,65

Table 3. Mechanical properties of blades based on pigmented epoxy composition OK-3

№ blade sample	σ_p, MPa	E, GPa	ε_p, %
1	82,17	3,32	1,73
2	80,68	3,28	1,67
3	84,33	3,31	1,75
4	80,88	3,27	1,68
5	79,87	3,33	1,62
6	81,21	3,33	1,63
Average value	81,86	3,31	1,68

Thermal-oxidative resistance of cured compounds

To assess the effect of the pigment on the thermal and oxidative stability of the epoxy composition, a thermogravimetric analysis was carried out in air for unpainted and dyed samples, from the results of which it can be seen that the loss of 5% of the weight of the dyed composition occurred at 354.10C, while in the original composition such a weight loss is observed at 327.20C (Fig. 7).

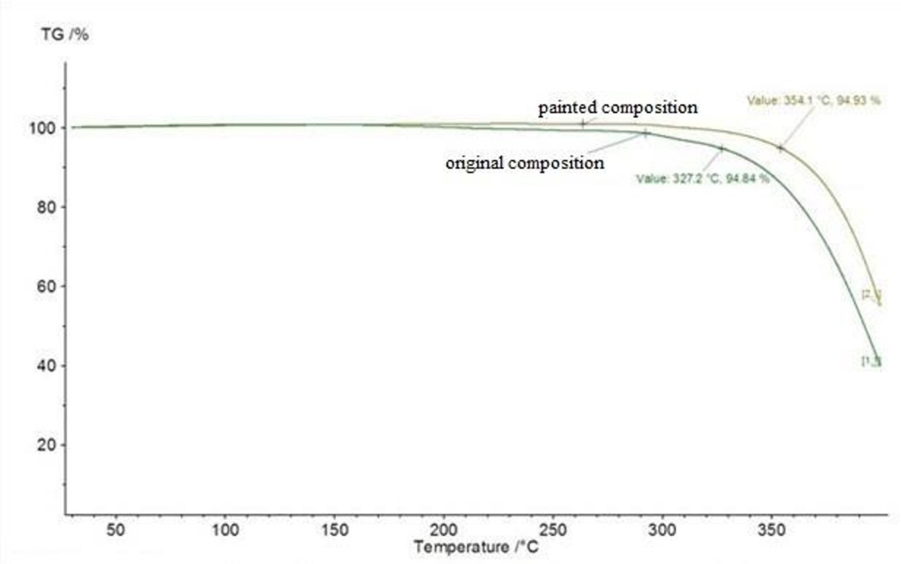


Fig. 7. Thermogravimetric curves for cured painted and unpainted epoxy compositions

From a practical point of view, this advantage in terms of the thermal and oxidative resistance of the painted samples is important, since during the pultrusion process, the polymerizers through which the rod of the future composite reinforcement passes are heated to high temperatures (300 °C), and in the event of an abnormal stop of the line, overheating of the composite is possible.

Alkali resistance of painted composites.

The study of the effect of red pigment on the alkali resistance of cured epoxy materials was continued on glass-composite reinforcing bars with a diameter of 10 mm obtained by pultrusion (Fig. 8). Painted and unpainted reinforcing bars were kept in a 40% aqueous solution of alkali (NaOH) at 60°C for 30 days, and then their mechanical tensile properties were determined. The test results are shown in tables 4 and 5, which show that the painted composite rods, compared to unpainted rods, have slightly, by 3.5-4%, higher tensile strength and tensile modulus. Obviously, this is due to the strengthening role of the finely dispersed iron oxide pigment.

Fig. 8. Samples of glass-composite reinforcing bars obtained on the basis of colored and uncolored epoxy binder

Table 4. Mechanical properties of unpainted reinforcing bars

Sample number	Nominal diameter, mm	Nominal cross-sectional area, mm^2	Working part length, mm	Tensile strength, MPa	Tensile modulus, GPa	Relative extension, %
1	9,44	69,99	380	1251,50	58,51	4,4
2	9,44	69,99	375	1204,50	58,13	4,6

3	9,44	69,99	377	1234,49	58,27	4,4
4	9,44	69,99	377	1212,70	58,17	4,5
5	9,44	69,99	375	1312,51	59,01	4,2
6	9,44	69,99	380	1257,58	58,61	4,3
Average value:				1245,55	58,46	4,4

Table 5. Mechanical properties of painted reinforcing bars

Sample number	Nominal diameter, mm	Nominal area, mm^2	Working part length, mm	Tensile strength, MPa	Tensile modulus, GPa	Relative extension %
1	9,44	69,99	380	1324,52	60,95	4,3
2	9,44	69,99	375	1312,85	60,83	4,1
3	9,44	69,99	377	1266,15	60,48	4,3
4	9,44	69,99	377	1254,01	60,39	4,7
5	9,44	69,99	375	1359,55	60,98	4,2
6	9,44	69,99	380	1287,97	60,52	4,2
Average value:				1300,86	60,60	4,3

The obtained results indicate that the developed method of painting is promising for the production of painted reinforcing bars intended for design or domestic purposes, as well as for marking branded building composite reinforcement, the color of which will indicate an increased alkali resistance of the reinforcement.

5 Conclusions

Thus, the study showed that the coloring of hot-curing epoxy binders with a finely dispersed iron oxide red pigment leads to an increase by 7.5% in the thermal and oxidative stability of the material and a slight increase, by 3.5-4%, in the strength and tensile modulus of tensile strength of glass composite reinforcement based on the same binder.

6 Acknowledgement

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References

1. B. Zhang, L. Jia, M. Tian, N. Ning, L. Zhang, W. Wang, Surface and interface modification of aramid fiber and its reinforcement for polymer composites: A review, Eur. Polym. J., **147**, 110352 (2021)
2. N. Maruthi, F. Muhammad, R.. Narasimha, Conducting polymer based composites as efficient EMI shielding materials: A comprehensive review and future prospects, Synth. Met. **272**, 116664 (2021)

3. W. Zhou, X. L. Ji, S. Yang, J. Liu, L. H. Ma, Review on the performance improvements and non-destructive testing of patches repaired composites, Compos. Struct. 263, 113659 (2021)
4. M. Qu, Hou L. MaL, M. Yuan, J. He, M. Xue, Y. Zhou, X. Liu, J. He, Fabrication and color- gradient control of colorful superhydrophobic materials with mechanical durable, oil/water separation and recyclable properties, Appl. Surf. Sci. 466, 328–341 (2019)
5. C. Xu, C. Huang, H. Huang, Recent advances in structural color display of cellulose nanocrystal materials, Appl. Mater. Today, **22**, 100912 (2021)
6. P. Fei, F. Zeng, S. Zheng, Q. Chen, Y. Hu, J.. Cai, Acylation of blueberry anthocyanins with maleic acid: Improvement of the stability and its application potential in intelligent color indicator packing materials, Dyes Pigm, **184**, 108852 (2021)
7. S. Cochrane, The Munsell Color System: A scientific compromise from the world of art, Stud. Hist. Philos. Sci., **47**, 26–41 (2014)
8. G. Vitols, I. Arhipova, Y. Hirata, I. Ikarts, Colour extraction and analysis solution for design of cross-cultural websites, Procedia Comput. Sci., **77,** 215–220 (2015)
9. D. J. Kwon, Z. J. Wang, J. Y. Choi, P. S. Shin, K. L. DeVries, J. M. Park, Interfacial evaluation of carbon fiber/epoxy composites using electrical resistance measurements at room and a cryogenic temperature, Composites Part A, **72**, 160–166 (2015)
10. H. Zhang, W. Zeng, H. Du, Y. Ma, Z. Ji, Z. Deng, Q. Zhou, Comparison for color change between benzodifuranone and benzodipyrrolidone based epoxy coating, Dyes Pigm., **175**, 108171 (2020)
11. C. Soule, Pretreatment for the painting of plastics and composite materials, Met. Finish., **108**, 69–73 (2010)
12. C. Soule, Pretreatment for the painting of plastics and composite materials, Met. Finish., **98**, 90–92 (2000)
13. O. L. L. Cabrales, M. A. Vera, H. M. H. Garcia, R. M. Arroyo, A. I. M. Enriquez, J. L. A. Davila, M. A. L. H. Rodriguez, Effect of graphene oxide on wear resistance of polyester resin electrostatically deposited on steel sheets, Wear, 426–427, 296-301 (2019)
14. M. Cabrera, D. W. Vidal, M. J. A. Canada, Monitoring UV-accelerated alteration processes of paintings by means of hyperspectral micro-FTIR imaging and chemometrics, Spectrochim. Acta Part A, **253**, 119568 (2021)
15. Z. Kaszoska, M. Kot, D. B. Kostecka, A. F. Sajdak, Application of micro-indentation tests to assess the consolidation procedure of historic wall paintings, J. Cult. Heritage, **36**, 286–296 (2019)
16. M. Kardos, E. Korner, D. Penumadu, N. Modler, The influence of fiber volume fraction and fiber length on the evolution of pore content and the paintability of sheet molding compounds, Composites Part B, 185, 107760 (2020)
17. T. Mizutani, K. Arai, M. Miyamoto, Y. Kimura, Application of silica-containing nano-composite emulsion to wall paint: A new environmentally safe paint of high performance, Prog. Org. Coat., **55**, 276–283 (2006)
18. S. Sampath, G. S. Ramachandra, Effects of glass fibers on light transmittance and color of fiber-reinforced composite, Dent. Mater., **24**, 34–38 (2008)
19. J. Ma, J. Chen, B. Wang, W. S. Cai, The in-situ growth of BiVO 4 coatings on carbon fibers and their photocatalytic performance, Mater. Res. Bull., 77, 253–257 (2016)

20. D. J. Kwon, P. S. Shin, J. H. Kim, H. S. Park, Y. M. Beak, K. L. DeVries, J. M. Park, Reinforcing effects of glass fiber/p-DCPD with fiber concentrations, types, lengths and surface treatment, Composites Part B, **123**, 74–80 (2017)
21. W. Zeng, Z. Deng, H. Wang, H. Zhang, Q. Zhou, Benzodifuranone based color-changing epoxy-polyamine coating, Dyes Pigm., **164**, 198–205 (2019)
22. K. Huang, Y. Zhang, M. Li, J. Lian, X. Yang, J. Xia, Preparation of a light color cardanol-based curing agent and epoxy resin composite: Cure-induced phase separation and its effect on properties, Prog. Org. Coat., **74**, 240–247 (2012)
23. C. M. White, R. Bank, I. Hamerton, J. F. Watts, Characterisation of commercially CVD grown multi walled carbon nanotubes for paint applications, Prog. Org. Coat., 90
24. J. A. Johnson, M. J. Barbato, S. R. Hopkins, M. J. O'Malley, Dispersion and film properties of carbon nanofiber pigmented conductive coatings, Prog. Org. Coat., **47**, 198–206 (2003)
25. A. Hosseinpour, M. R. Abadchi, M. Mirzaee, F. A. Tabar, B. Ramezanzadeh, Recent advances and future perspectives for carbon nanostructures reinforced organic coating for anti-corrosion application, Surf. Interfaces, **23**, 100994. (2021)
26. Y. Touazia, A. Abdia,*, A. Leshafc, K. Khimecheb, Influence of heat treatment of iron oxide on its effectiveness as anticorrosion pigment in epoxy based coatings.
27. 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
28. A. S. Borodulin, V. V. Maltsev, A. A. Bertaeva, S. Y. Fedorov, A. G. Tereshkov, V. A. Nelyub, G. V. Malysheva, A Method for Assessing the Adhesion Strength of an Elementary Fiber–Epoxy Matrix System. Polymer Science - Series D., **15(4)**, 517-522 (2022) DOI: 10.1134/S1995421222040049
29. O. V. Ovchinnikov, M. S. Smirnov, T. A. Chevychelova, A. I. Zvyagin, A. S. Selyukov, Nonlinear absorption enhancement of Methylene Blue in the presence of Au/SiO2 core/shell nanoparticles, Dyes and Pigments, **197**, 109829 (2022) https://doi.org/10.1016/j.dyepig.2021.109829
30. Y. A. Belousov, V. M. Korshunov, M. T. Metlin, D. A. Metlina, M. A. Kiskin, D. F. Aminev, N. P. Datskevich, A. A. Drozdov, Cl. Pettinari, F. Marchetti, I. V. Taydakov, Towards bright dysprosium emitters: Single and combined effects of environmental symmetry, deuteration, and gadolinium dilution, Dyes and Pigments, **199**, 110078 (2022) https://doi.org/10.1016/j.dyepig.2021.110078.
31. 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
32. 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
33. 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
34. V. A. Nelyub, Adhesive-Strength Evaluation via the Pull-Out Method in a Binder—Elementary-Filament System at Various Treatments of Filaments. Polym. Sci. Ser. D **11**, 263–266 (2018) https://doi.org/10.1134/S1995421218030127

35. A. S. Borodulin, Plasticizers for epoxy adhesives and binders. Polym. Sci. Ser. D, **6**, 59–62 (2013) https://doi.org/10.1134/S1995421213010036
36. 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
37. 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