Optimization approach to assessing the physical and mechanical properties of polymer composites

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Abstract. It has been shown that one of the most significant components of composite building materials (CCM) are fillers, which help improve their structural and operational characteristics. The stages of the processes of structure formation of CSM are given. The role of energy characteristics, dispersion of fillers and degree of filling in the formation of optimal structures is emphasized. Existing approaches for theoretical assessment of the properties of composites, based on solving the Lamé problem for a thick-walled sphere, are presented.This article is devoted to an experimental study of the properties of epoxy composites with fillers having different elastic-plastic and strength properties. Glass, ceramic, and chalk powders were considered as fillers; their elastic moduli were, respectively, greater, approximately equal, and less than those of pure polymer.The studies were carried out using mathematical methods of experiment planning. A full factorial experiment was carried out with the construction of a planning matrix and relative values of response functions. Explanatory graphical dependencies have been constructed.The research results can be used to predict the properties of CCM based on the properties of the initial components, as well as to clarify the extreme indicators of properties.

1 Introduction

In numerous works published both in our country and abroad, a large amount of experimental and theoretical research has been carried out on polymer composite materials. The processes of structure formation [1], hardening [2], physical and mechanical properties [3] and durability [4] of polymer composites composed on the basis of various binders, fillers and aggregates, and modifying additives have been identified [5, 6, 7].

One of the most essential components of polymer composites (plastics) - filler - serves to improve the performance characteristics of the material, give it various specific properties and reduce cost. Filled plastics are used mainly as structural materials, the mechanical strength of which is determined by the strength and deformation characteristics of the polymer base and filler [8, 9, 10, 11].The technological properties of plastics and possible methods of processing them into products also largely depend on the filler. The filler content in thermoplastics is, as a rule, 30%, in thermosets it is more than 50%, and in highly filled plastics it can exceed the presence of polymer by 3 or more times.

The inclusion of a filler in a polymer means replacing part of the intermolecular contacts of the polymer-polymer type with contacts of the polymer-filler type [12, 13, 14, 15].

The first act of interaction between a polymer and a filler is the adsorption of polymer molecules on the surface of the filler. The degree of adsorption binding of polymer molecules to the surface of the filler is determined by the chemical nature of its surface and the chemical structure of the polymer, which determines the possibility of the formation of intermolecular bonds on the surface of the fillers. As a result of the adsorption of polymer molecules on the surface of the filler, it binds and significantly limits mobility in the surface layer [5, 6, 16, 17].

In accordance with modern views, bonds of a chemical nature are divided into ionic, atomic and metallic. Ionic bonds are caused by the mutual electrostatic attraction of uniformly charged ions. The mechanism of ionic bonding can be simplistically represented as filling the electron shells of two bonded atoms to a "stable" state.The ionic bond energy can reach up to 350 kcal/mol. A chemical bond also arises between identical neutral atoms due to the interpenetration of electron atoms of adjacent atomic nuclei and the joint possession of electrons. Such a bond is called atomic (covalent or homopolar). The covalent bond energy is also high, up to 200 kcal/mol.Covalent bonds are most typical for organic compounds, which often have polarity. The metallic bond is characteristic of metals and can be considered as a hybrid of ionic and covalent bonds [3, 17, 18].

The uniqueness of the fillers in the mixture is expressed in the fact that its highly dispersed particles act as active adsorbents and structural components.

The appearance of these properties is determined by the crystallographic properties of the filler. The adsorption capacity of the filler can be controlled within certain limits by dispersion. Roughness and porosity also increase the sorption capacity of the filler. All mineral powders as adsorbents are divided into basic (positively charged) and acidic (negatively charged).

Based on energy capacity, the following can be distinguished [19]:

a) a group of mineral powders with a high positive potential and a large number of adsorption centers in the form of Ca + 2, Mg + 2 cations on the surface of particles - calcite, dolomite, limestone;

b) a group of mineral powders with a high negative charge potential and a significant number of adsorption centers on the surface of particles in the form of O2 oxygen ions - quartz, kaolinite, flint, granite, trachyte, etc.;

c) a group of mineral powders with a reduced potential of a negative sign due to the presence on the surface of particles that compensate for cations of different valences K+, Na+, Ca+2,

Mg+2, Fe+2, Fe+3, etc. – feldspars, muscovite and especially hornblende, augite, asbestos, gabbro, diabase, etc.;

d) a group of mineral powders with a predominantly neutral particle surface - talc, graphite, etc. Mineral powders can be polymineral, i.e. consisting of several minerals. In polymineral powders, within certain limits, the rule of efficiency of physical and mechanical properties applies, which is reflected in the general nature of the interaction of powders with the polymer.

Thus, the filler mainly performs the function of an adsorption mineral, with the help of which a significant part of the polymer passes into a film state. In addition, the filler increases the contact surface between grains and the density of the microstructure.

The filler in the microstructure, at certain ratios of polymer and filler, acts as a high-strength structure-forming component that fills most of the volume.

The dispersion and granulometric composition of fillers is extremely important. A significant increase in the surface of filler grains leads to an increase in the rigidity of polymer gels and the emergence of large internal stresses in the filled polymer [14, 18, 20].

Fillers used in polymer concrete are obtained from acidic rocks (quartz, andesite, diabase, granite) from ceramics (fireclay, acid-resistant ceramics, expanded clay) from carbon-containing materials (graphite, coal, coke, soot). From carbonates (dense limestones, dolomites), etc. The highest acid resistance of polymer concrete is obtained with fillers made of graphite and coke, average with andesite and ground ceramics, and lowest with ground quartz [2, 4, 21, 22].

The filler, unlike sand and especially crushed stone, has a highly developed surface. The specific surface area of the filler is thousands of times greater than that of crushed stone and many tens of times greater than the specific surface area of medium-grained sand. The filler is obtained, as a rule, by artificially grinding various types of rocks in mills, due to which a large total surface of the smallest particles and the corresponding free surface energy are created.At the first moment of the formation of fresh surfaces of rock fractures, they are free from the influence of another environment. Under the influence of free surface energy, foreign substances (gases, vapors, dust, etc.) from the environment are adsorbed on filler particles.Positive adsorption of molecules, atoms and ions occurs the more intensely, the more developed and less saturated with foreign substances the surface of powder particles; freshly prepared fillers are always more active in adsorption than fillers stored in a warehouse [2, 23].

As is known, optimal physical and technical characteristics of composites are achieved at certain concentrations of the dispersed phase filling the dispersed medium. When the content of filling components increases beyond the optimal amount, the strength of the composites decreases, which is due to the lack of binder to completely wet the filler particles.As a result, the solidity of the mixture is disrupted, the volume of voids in the composite increases and, as a consequence, its density and physicochemical resistance decrease.

Despite the significant volumes of work performed, at the same time, it should be noted that at the moment, the quantitative dependences of changes in the strength and elastic-plastic properties of materials depending on the ratio of the elastic moduli of the filler and polymer, both in theoretical and experimental aspects, have not been fully identified.

In connection with the development of computer technology, the role of mathematical modeling for studying the structure and properties of building composite materials has sharply increased [24, 25, 26, 27, 28, 29, 30, 31].For a static description of the state of the body, representative volumes with a minimum volume of material are considered, which contains a sufficient number of carriers of the considered process mechanisms.In this case, spherical models (effective and structural) are often used as a representative volume.At the same time, it should be noted that in the literature there is no clarity on how the mutual transition from the results obtained in one of these models to the results of another is carried out: from a simply connected model to a doubly connected one, and vice versa.

The intensive development of BCM (building composite materials) stimulates their theoretical research. At the same time, the theory of BCM is being developed and deepened, aimed at increasing the number of applied problems in the mechanics of composites [1, 24, 28, 29, 32].

Numerous works are devoted to theoretical studies of polymer composites [33 – 43].The study of the strength and elastic-plastic properties of two-phase building composites with granular filler based on the application of the Lamé problem for a calculation model in the form of a thick-walled sphere is given in [24, 25,26, 44, 45].An estimate of the upper and lower limits of the effective modulus values is given: “according to Christensen”; “according to Voigt”; “according to Reiss” [26, 27,46].

This work is devoted to experimental studies of the physical and mechanical properties of polymer composites with various fillers.

2 Purpose and objectives of the research

The purpose of the research was to establish quantitative dependences of changes in the strength and deformation properties of polymer composites on the density, strength and elastic modulus of fillers.

Research objectives:

1. Justify the choice of fillers to achieve the goal of establishing the effect of the filler on the strength and elastic modulus of epoxy composites.
2. Draw up an experimental plan to establish the dependence of changes in the elastic-strength properties of polymer composites on the ratio of deformative and other properties of the filler and polymer.
3. Obtain quantitative dependences of changes in the properties of composites on the characteristics of their constituent components, suitable for predicting the properties of materials.
4. Determine extreme indicators of the properties of BCM using global optimization methods and artificial neural networks.

3 Materials and methods

The most preferable, from the point of view of obtaining strong and durable composites for construction purposes, as mentioned above, are materials with fillers of a certain nature, which, as a rule, are characterized by different strength and elastic-plastic properties. Optimization of the composition for the lowest possible polymer capacity of the composite while maintaining high strength characteristics is achieved through the use of fillers of different granulometric compositions.

When conducting studies of filled epoxy composites, we used crushed waste optical glass of the TF-10 grade, containing the ternary system K2O–PbO–SiO2, powders from broken ordinary clay bricks, and chalk as fillers.It is known that by combining fillers of different dispersion, it is possible to obtain composites with improved properties compared to materials based on single-fraction fillers. For this purpose, composites based on multifraction fillers were studied.Optimization of the compositions was carried out using methods of mathematical experimental planning. A full factorial experiment consisting of 4 experiments was considered. The type of fractions and the content of filler of a certain grain composition were taken as variable factors: X1 – 0.16-0.315 mm, X2 – less than 0.16 mm.In the manufacture of epoxy composites, ED-20 grade resin was used as a binder; the curing components were aminophenol hardener (AF-2) and polyethylene polyamine (PEPA).

The planning matrix indicating the coded and natural values of the factors is given in Table. 1.

Table 1. Planning Matrix and Operational Matrix for Powder Filled Formulationsfrom ground optical glass and ground bricks.

№	Codedfactorvalues		Natural values of factors (component content, %)	
	X1	X2	Fillerfraction, mm	
			0.16 – 0.315	lessthan 0.16
1	+1	-1	100	0
2	-1	+1	0	100
3	+1/3	+2/3	100/3	200/3
4	+2/3	+1/3	200/3	100/3
5	-1	-1	0	0

The compositions with all fillers were made equally mobile. In this case, the content of waste glass and broken brick was 300 parts by mass per 100 parts by mass of resin, and chalk was 100 parts by mass per the same amount of resin.In each case, the maximum filler content was taken to be 100%.

Statistical processing of the experimental results made it possible to identify dependencies characterizing the change in the compressive strength, as well as the elastic modulus of epoxy composites, on the type of filler used.In addition, using artificial neural networks in the MATLAB system, the experimental dependences of compressive strength and elastic modulus for various fillers were approximated.When modeling artificial neural networks, the following library functions of the MATLAB system were used: feedforwardnet, train, sim.

4 Experimental results and their analysis

The test results of filled composites are summarized in table. 2, where the controlled parameters of the composites under study were the compressive strength (Rcs) and the elastic modulus (E).

Table 2. Strength and deformation characteristics of filled composites.

	Filler					
	glass TF-10		brickfight		chalk	
No.	Rcs,MPa	E, 10^3MPa	Rcs,MPa	E, 10^3MPa	Rcs,MPa	E, 10^3MPa
1	82.0	6.5	116.0	9.7	93.25	2.44
2	91.0	8.1	115.2	9.8	91.09	1.84
3	77.0	6.2	105.2	9.0	92.09	4.08
4	83.0	8.3	121.3	9.4	97.41	2.36
5	89.3	1.47	89.3	1.47	89.3	1.47

The values in Table 2 can be related to the planning matrix in Table 1.

Here we consider the problem of determining the entire set of permissible coded values of factors at which the maximum of both strength and elasticity modulus of the studied composites will be observed.This is due to the fact that possible values of factors may practically not be realized, so the task arises of determining equivalent values of factors at which the maximum of specified indicators will be achieved. This problem is proposed to be solved using existing tools (library functions) of artificial neural networks, which are implemented in the MATLAB system (mentioned above).

A visual representation of the data in Table 2 is shown in Fig. 1–2.

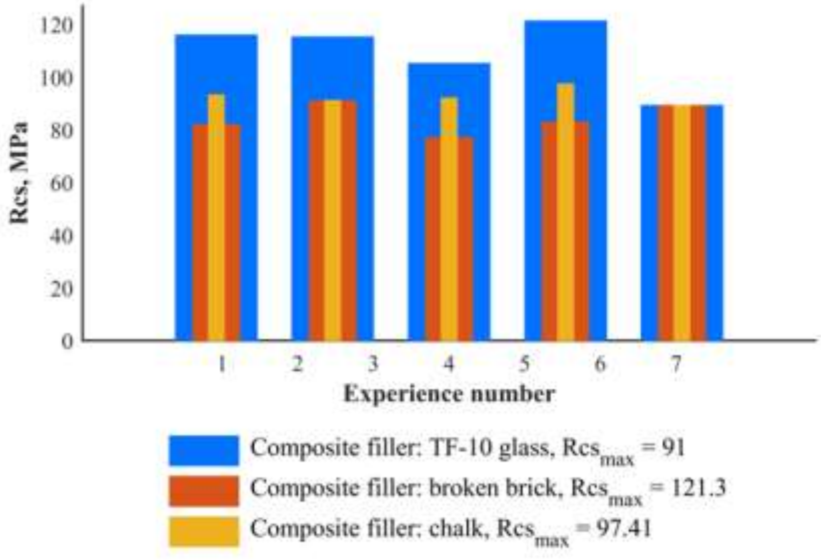

Fig.1. Dependence of ultimate compressive strength on the number of experiments.

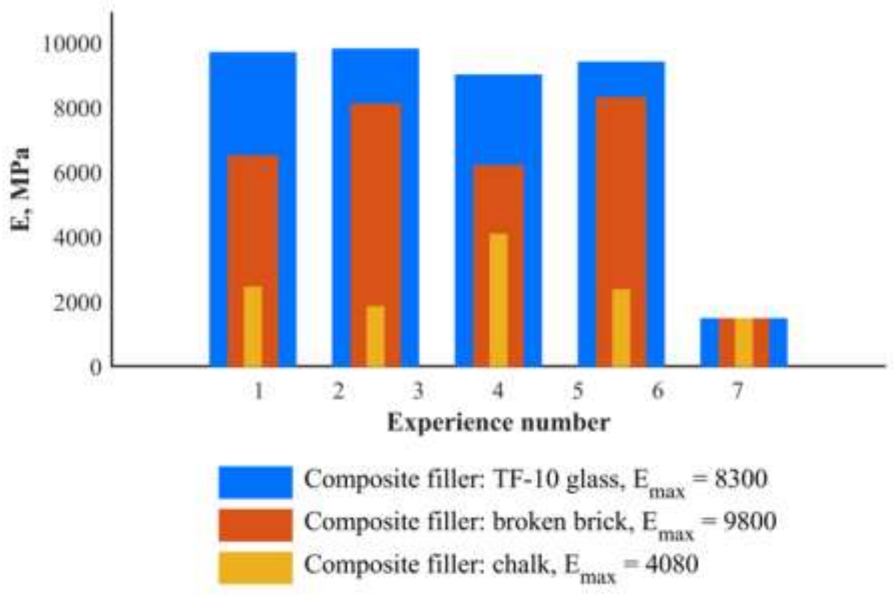

Fig. 2. Dependence of the elastic modulus on the number of experiments.

To determine the set of factors at which the maximum of both the compressive strength and the modulus of elasticity is achieved, first the neural network is trained (trained) using the library functions feedforwardnet, train, sim based on the data in Table 1 and Table 2, and then it is determined using the extended data array of approximation of new data.The term "data expansion" is the operation of uniformly padding data (coded factors) within acceptable limits, i.e., from –1 to +1.

Graphical results of the approximation are presented in Fig. 3–8.

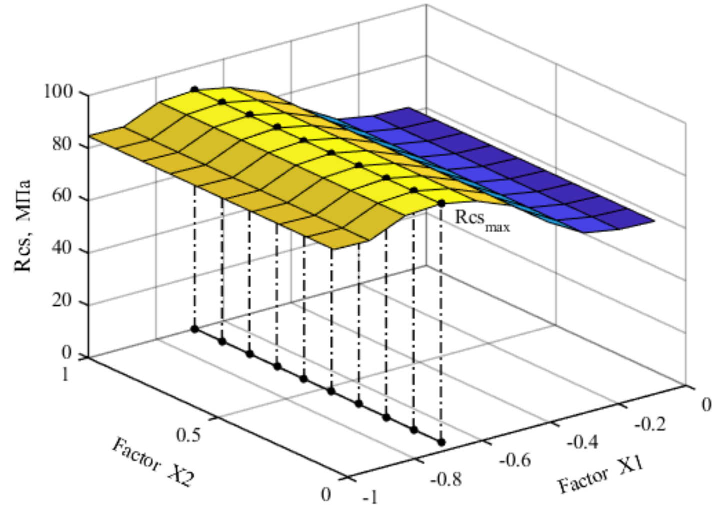

Fig. 3. Result of approximation of experimental data for the Rcы index with TF-10 glass filler.

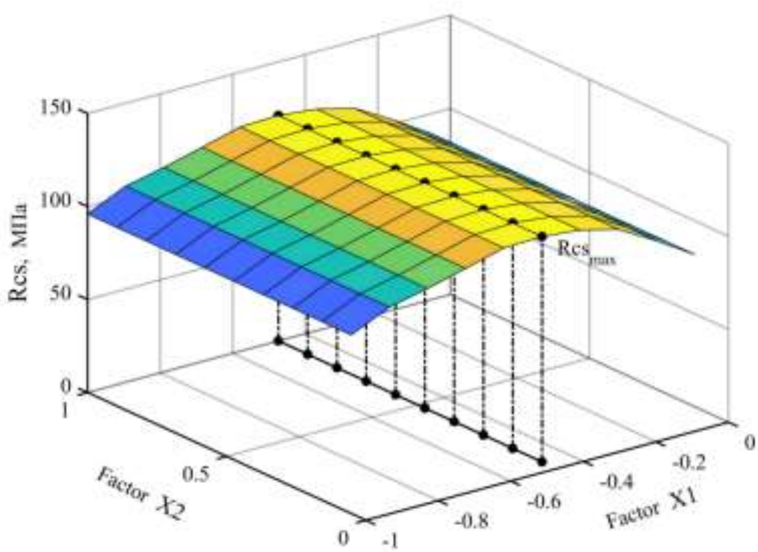

Fig. 4. Result of approximation of experimental data for the Rcы indicatorwith "brick brick" filler.

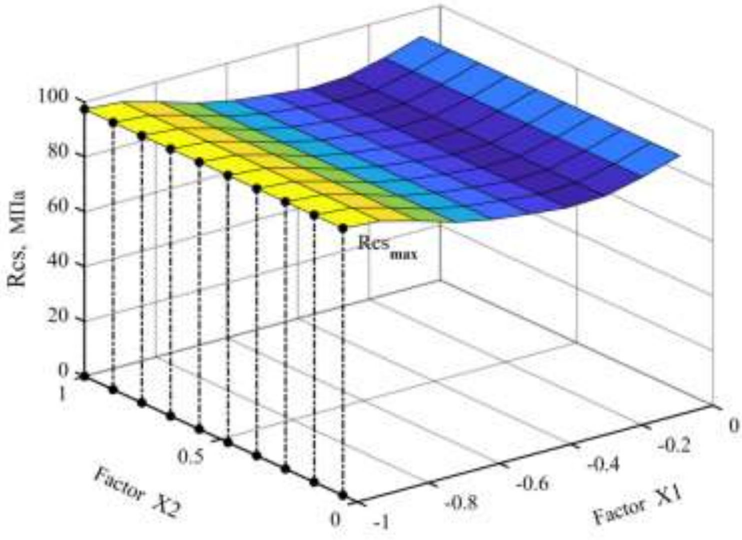

Fig. 5. Result of approximation of experimental data for the Rcs index with chalk filler.

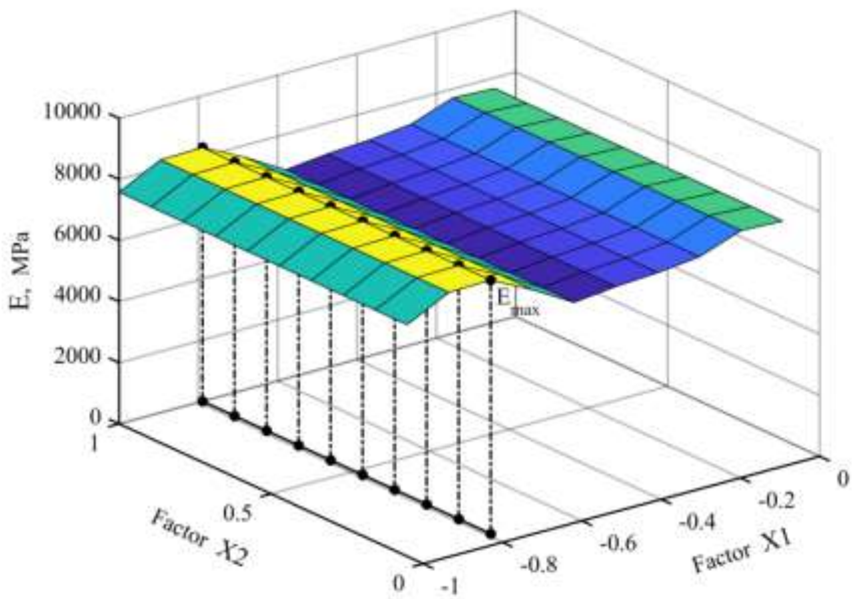

Fig. 6. Result of approximation of experimental data for the elastic modulus (E) with TF-10 glass filler.

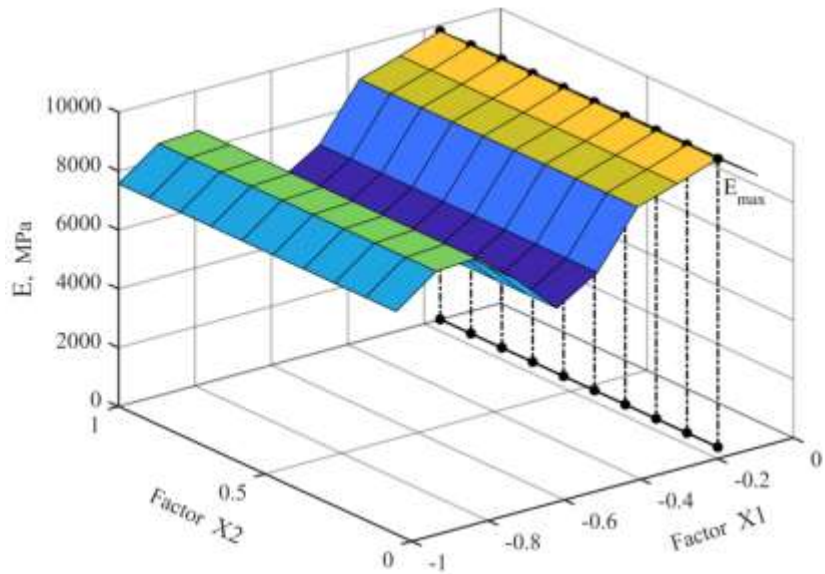

Fig. 7. The result of approximation of experimental data for the elastic modulus (E)with “brick” filler.

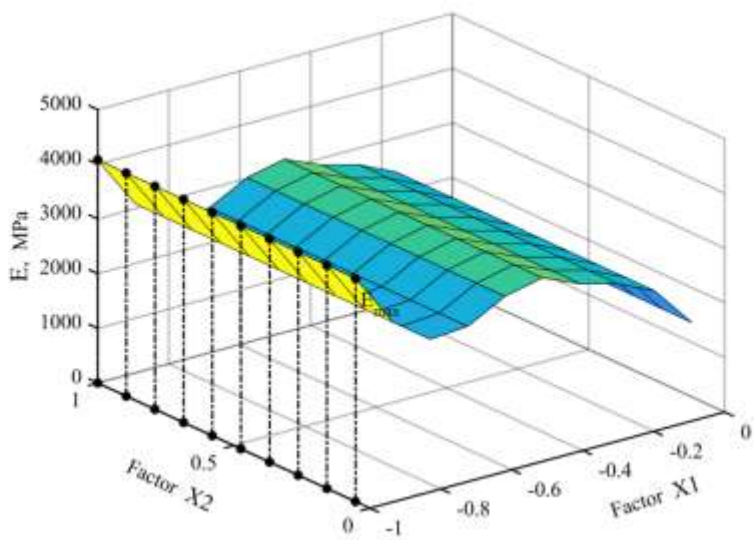

Fig. 8. The result of approximation of experimental data for the elastic modulus (E) with chalk filler.

The nature of the change in strength and elasticity modulus shows that factor X2 can have several values, at which the maximum of the corresponding indicator will remain maximum, i.e., unchanged.

Table 3 presents the results of determining the maximum strength values of composites with appropriate fillers.

Table 3. Results of determining the maximum permissible values of ultimate strength Rcs.

Typeofcompositefiller	EstimatedvalueRcs, MPa	Estimated values of factors (X1; X2)	Maximumtablevalue, MPa	Relativeerror, %
glass TF-10	91.0489	(-0.6842; 0.0526)	91	0.0538
brickfight	121.2181	(-0.4737; 0.0526)	121.3	0.0675
chalk	97.3510	(-1; 0.0526)	97.41	0.0606

The permissible sets of factor X2, at which the maximum tensile strength is observed, are given in Table 4.

Table 4. Set of acceptable values of factor X2.

Type of composite filler	X1max	Acceptable values of factor X2
glass TF-10	-0.6842	0.0526; 0.1579; 0.2632; 0.3684; 0.4737; 0.5789; 0.6842; 0.7895; 0.8947; 1
brickfight	-0.4737	0.0526; 0.1579; 0.2632; 0.3684; 0.4737; 0.5789; 0.6842; 0.7895; 0.8947; 1
chalk	-1	0.0526; 0.1579; 0.2632; 0.3684; 0.4737; 0.5789; 0.6842; 0.7895; 0.8947; 1

Table 5 presents the results of determining the maximum values of the elastic modulus of composites with appropriate fillers.

Table 5. Results of determining the maximum permissible values of the elastic modulus (E)

Type of Composite filler	Estimated value E, MPa	Estimated values of factors (X1; X2)	Maximum table value, MPa	Relative error, %
glass TF-10	8303,9016	(-0,7895; 0,0526)	8300	0,0470
brickfight	9794,0394	(-0,4737; 0,0526)	9800	0,0608
chalk	4081,3541	(-1; 0,0526)	4080	0,0332

The permissible sets of factor X2, at which the maximum elastic modulus is observed, are given in Table 6.

Table 6. Set of acceptable values of factor X2

Type of composite filler	X1max	Acceptable values of factor X2
glass TF-10	-0.7895	0.0526; 0.1579; 0.2632; 0.3684; 0.4737; 0.5789; 0.6842; 0.7895; 0.8947; 1
brickfight	-0.4737	0.0526; 0.1579; 0.2632; 0.3684; 0.4737; 0.5789; 0.6842; 0.7895; 0.8947; 1
chalk	-1	0.0526; 0.1579; 0.2632; 0.3684; 0.4737; 0.5789; 0.6842; 0.7895; 0.8947; 1

The presented results can be used for cases when it is necessary to clarify a certain set of coded factors at which the maximum tensile strength and elastic modulus of composites are achieved, depending on the filler.

5 Conclusions

1. The patterns of structure formation of polymer composites with fillers of various natures are analyzed. The dependences of changes in the properties of polymer composites on surface characteristics, dispersion of fillers and degree of filling are shown.
2. Fillers were selected to establish dependencies to assess the influence of their elastic properties on the strength and deformability of polymer composites: glass (En>En); ceramics (En = En); chalk (En < Ep).
3. A full factorial experiment was implemented to obtain quantitative dependences of the change in strength and elastic modulus of epoxy composites on the type of filler.
4. Based on artificial neural networks of the MATLAB system, extreme (maximum) indicators of the properties of the studied composites with fillers were determined, which made it possible to find the coded values of the factors at which BCMs acquire extreme values of their properties.

References

1. A.N.Bobryshev, V.T.Erofeev, V.M. Kozomazov,*Physics and synergetics of dispersed disordered condensed composite syste*ms (The science, St. Petersburg,2012)
2. V.I. Solomatov et al.,*Reinforced polymer concrete in transport construction*(Transport, 1979)
3. V.I. Solomatov,A.N. Bobryshev, K.G. Himmler,*Polymer composite materials in construction* (Stroyizdat, 1988)
4. V.V. Paturoev,*Polymer concretes and structures based on them*(Stroyizdat, 1989)
5. P.-C.Ma, S.-Y.Mo, B. Z.Tang, J.-K. Kim, Carbon **48(6)**,1824-1834 (2010)
6. M.Rahmat, P. Hubert, Composites Science and Technology **72(1)**(2011)
7. J.Kathi, K. Y.Rhee, J. H. Lee, Composites.Part A. Applied Science and Manufacturing.**40(6)**, 800-809 (2009)
8. M.Rafiee, J.Rafiee, I.Srivastava et al., Small **6(2)**, 179-83 (2010)
9. L.Sun, R. F.Gibson, F.Gordaninejad, J.Suhr,Composites Science and Technology**69(14)**, 2392-2409 (2009)
10. L.-Ch.Tang, H.Zhang, J.Han et al.,Composites Science and Technology **72**, 7-13 (2011)
11. Y.Ni, L.Chen, K.Teng, J.Shi et al.,ACSAppliedMaterials&Interfaces **7(21)** (2015)
12. N.N. Barashkov,*Polymer composites: preparation, properties, application*(Science, 1984)
13. Ya.O. Bickerman, Advances in Chemistry**8**, 1431–1464(1972)
14. V.L. Vinarsky,*Epoxy resins in construction*(Budivelnik, Kyiv,1972)
15.R.Rahman, A.Haque, Engineering.Composites. Part B-engineering (2013)
16. Yu.S. Lipatov,*Interfacial phenomena in polymers*(Naukova Dumka, Kyiv,1980)
17. P.A. Rebinder,*Surface phenomena in disperse systems*(Nauka, 1979)
18. V.G. Khozin,*Strengthening epoxy polymers*(Publishing house PIK “House of Printing”, Kazan,2004)

19. I.A. Rybyev,*Construction materials based on binders*(Higher School, 1969)
20. H.Li,K. Neville,*Reference Guide to Epoxy Resins*(Energy, 1973)
21. Yu.V. Maksimov,G.D. Lykov, E.I. Chekulaeva,Concrete and reinforced concrete**8**, 17–16(1974)
22. V.V. Paturoev, I.E. Putlyaev,*Mastics, polymer concretes and polymer silicates* (Stroyizdat, 1973)
23. R.Z. Rakhimov, A.K. Valiev, N.E. Murtazin,"The influence of the chemical and mineralogical composition of mineral fillers and fillers on the physical and chemical resistance of composite materials based on oligomers", in *Performance of composite building materials under the influence of various operational factors* (UPI, Kazan,1985)
24. O.Startsev, A.Makhonkov, V.Erofeev, S.Gudojnikov, WoodMaterial Science and Engineering**12(1)**, 55-62 (2017)
25. V.T.Erofeev, A.S.Tyuryakhin, T.P. Tyuryakhina, Construction materials and products **6**, 5–17 (2019)
26. V. T.Erofeev, A. S.Tyuryakhin, T. P.Tyuryakhina, A. B. Tingaev, Structural mechanics of engineering structures and structures**15(6)**, 407– 414 (2019)
27. V. Erofeev,ProcediaEngineering **165**, 1444-1447 (2016)
28. V.V. Vasiliev,V.D. Protasov, V.V. Bolotin et al.,*Composite materials*(Mashinostroenie, 1990)
29. B.V.Gusev, V.I.Kondrashenko, B.P.Maslov, A.S.Faisovich,*Formation of the structure of composite materials and their properties* (Scientific world, 2006)
30. V.T.Erofeev,A.S. Tyuryakhin, I.V. Erofeeva, Structural mechanics and calculation of structures**3**, 7–17 (2018)
31. R.Qiao, L. C. Brinson,*Composites Science and Technology*(2009)
32. M. R.Ayatollahi, S.Shadlou, M.Shokrieh, M.Chitsazzadeh, Polymer Testing **30(5)**, 548-556 (2011)
33. V.V. Bolotin,"Mechanics of composite materials and structures made from them", in *Structural mechanics: current state and development prospects* (1972)
34. B.M. Gladyshev,*Mechanical interaction of structural elements and strength of concrete*(Publishing house at Kharkov University, Kharkov,1987)
35. V.T. Erofeev, I.I. Merkulov, A.I. Merkulov,*Optimization of concrete compositions using numerical modeling*(Mordov Publishing House. University, Saransk,2006)
36. J.Manson, L. Sperling,"Polymer mixtures and composites", in *Chemistry*(1979)
37. V.A. Voznesensky, V.N. Vyrovoy, V.Ya. Kersh et al., *Modern methods of optimization of composite materials*(Budivelnik,Kyiv,1983)
38. V.V. Belov, V.T.Erofeev, D.A. Merkulov et al.,*Computer modeling and optimization of compositions of composite building materials: monograph*(ASV Publishing House, Moscow, 2015)
39. R.Christensen, *Introduction to the mechanics of composites: textbook*(Mir, Moscow, 1982)
40. B. E. Pobedrya,*Mechanics of composite materials: monograph*(Moscow University Publishing House, Moscow,1984)
41. L.Hamming, R.Qiao, P.Messersmith, L. C. Brinson, Composites Science and Technology **69(11-12)**, 1880-1886 (2009)
42. S.Yang, S.Yu, K.Woomin, H.Do-Suck, C.Maenghyo, Polymer**53(2)**, 623-633(2012)

43.M.Omidi, A. S.Milani, R.Seethaler, R.Arasteh, Carbon **48(11)**, 3218-3228 (2010)

44. V.D. Cherkasov,A.S. Tyuryakin,*Theory of doubly connected models of micromechanics of composites: monograph*(Mordov Publishing House. Univ., Saransk,2009)

45. V.I. Andreev,*Some problems, methods of mechanics of inhomogeneous bodies*(ASV, 2002)

46. A. S. Kravchuk,I. A. Tarasik,Apriori. Series: Natural and technical sciences**3**, 1–18(2014)