Optimization of conditions for the formation of functional coatings based on carboxymethylcellulose with chromium

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Abstract. The possibility of increasing the strength and improving the functional properties of coatings based on biopolymers by adding metal powders is considered. An approach has been proposed that makes it possible to form composites based on carboxymethylcellulose with specified mechanical properties. The procedure for adjusting the process of formation and increasing the strength of a protective coating based on carboxymethylcellulose with chromium powder is shown. For the numerical calculation of the composition and temperature conditions for the manufacture of composite materials, a software module developed in the Microsoft Visual Studio environment was used. The calculation makes it possible to determine the combination of components of the coating composition that provides the highest mechanical strength for a given value of the relative deformation of the biocomposite. An example of calculation is given for a protective coating based on carboxymethylcellulose with chromium powder. The calculation results were confirmed experimentally. Using the proposed approach makes it possible to increase the mechanical strength of coatings by 40% and improve the adhesive strength to 1 point.

1 Introduction

Composite materials based on cellulose and its derivatives are of great interest for practical applications. Renewable wood and herbaceous raw materials are an alternative to synthetic polymers, they are environmentally friendly and relatively low cost. Hybrid materials based on biopolymers with inorganic components make it possible to form composites with unique functional properties. Particularly widely used is a simple water-soluble cellulose ether – carboxymethyl cellulose. The demand for carboxymethyl cellulose is explained by its good stabilizing and film-forming properties. Films and coatings based on carboxymethyl cellulose attract researchers because they are characterized by good biodegradability, environmental friendliness and high barrier properties. Carboxymethylcellulose films and coatings are most widely used in the food, pharmaceutical, and textile industries. However, they are characterized by excessive fragility [1], which contributes to a decrease in mechanical properties. The key problem in the manufacture of carboxymethyl cellulose films and

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coatings is the unstable rheological properties of the initial polymer solutions. One of the most important characteristics is the viscosity of aqueous solutions of carboxymethyl cellulose.

The physico-chemical characteristics of carboxymethyl cellulose during the synthesis from cellulose are influenced by many factors: the type of plant raw material (herbaceous or woody), the geographical location of growth, and the characteristics of the chemical processing of cellulose. As a consequence, aqueous solutions of the polymer at equal concentrations of the polymer carboxymethyl cellulose often have significantly different viscosities. When forming films and coatings from such compositions, the mechanical and protective properties of the materials are unstable. The unstable strength properties of biopolymers force researchers to look for solutions that increase the mechanical and functional properties of films and coatings.

One of the ways to create materials with good mechanical and barrier properties is to modify and fill carboxymethyl cellulose polymer matrices with inorganic particles. The works [2], [3] present the results of modeling and testing films based on gelatin-carboxymethyl cellulose. Thus, the introduction of the carboxymethyl cellulose component into the composition of gelatin films in an amount of 15.83 (wt.%) improves the mechanical and barrier properties of the films [2]. Granular media made from natural materials, treated with process fluids containing carboxymethyl cellulose, significantly improve the quality of coatings for parts with complex surfaces [3, 4]. Filling the carboxymethyl cellulose matrix with graphene nanoplatelets leads to an increase in the tensile strain and hydrophobicity of the composite [5]. Chitosan-carboxymethylcellulose composites with the addition of reduced graphene oxide show good mechanical reinforcement of the matrices and an increase in the tensile strength of the matrices [6].

For films based on carboxymethylcellulose/polyacrylamide reinforced with lithium titanate nanoparticles, the tensile strength increased from 0.73 MPa to 1.14 MPa [7]. Protective coatings based on carboxymethyl cellulose exhibit good resistance to static aggressive environments – concentrated acids and alkalis [8]. The results of the above studies indicate the possibility of creating functional materials based on a detailed study of their properties. However, in the conditions of serial industrial production, the analysis of the structural features and chemical composition of the used carboxymethyl cellulose and composites based on it is a difficult task. Solving this problem is not always possible within the enterprise and requires considerable time. It should be noted that technologies for the formation of films and coatings based on carboxymethyl cellulose are commercial, mostly closed, and are published in fragments.

This work proposes an integrated approach that allows, without fundamental research under continuous production conditions, to adjust the production mode of functional films and coatings based on carboxymethyl cellulose with maximum mechanical strength. The possibility of producing composites with specified mechanical properties from carboxymethylcellulose of various qualities is demonstrated by the example of the formation of an anti-corrosion coating based on a carboxymethyl cellulose matrix with a plasticizer glycerin and a filler - chromium metal powder.

It is known that chromium has high corrosion resistance, and the biopolymer carboxymethyl cellulose has good barrier properties. To calculate the mechanical characteristics of the composite, a program developed by the authors was used in the Microsoft Visual Studio environment.

The purpose of this work is to identify the relationship between the mechanical properties of the coating and its composition and to determine the ratio of components in the coating that provide the highest mechanical strength and barrier properties of the composite.

2 Materials and methods

Coating samples were prepared by pouring, on fluoroplastic substrates, from aqueous suspensions of carboxymethylcellulose filled with reduced chromium powder ($d_{chrom} < 50$ μm) and plasticized with glycerin. Chromium powder and glycerin plasticizer were added to 100 g of an aqueous solution of carboxymethyl cellulose of the appropriate concentration. carboxymethyl cellulose was used with a degree of polymerization DP=400 and a degree of substitution DS=80. Mechanical tests were carried out on an RM-4 tensile testing machine. The coatings were removed from the fluoroplastic substrates and the relative deformation (ε) and tensile strength (σ) of the coatings during tensile testing of the sample were determined. The adhesion strength of the coatings to the steel substrate was assessed using the lattice notch method on a six-point scale (1 point - high strength, 6 points - unsatisfactory strength). The chemical resistance of the coatings was determined according to the method [9]: steel rods with coatings were immersed in aggressive environments (rod length 75 mm, diameter 11 mm).

The experiment used a second-order orthogonal design. The dependence of the strength and relative deformation of the coatings on the concentration of carboxymethyl cellulose, the content of glycerol and chromium, the size of chromium particles and the temperature of coating formation was revealed (x_1, x_2, x_3, x_4, x_5 - variables on a dimensionless scale). Sieving of chromium particles was carried out on an ELSA-2 electrostatic analyzer. The ranges of variation of the studied factors, determined in preliminary experiments, are given in Table 1. As a result of statistical analysis of the experimental data, two second-order polynomials were obtained, establishing the relationship between the mechanical strength and deformation of coatings from the studied factors. Next, a numerical calculation was carried out using the developed software module, which allows, using the relative deformation value specified in the program, to calculate the combinations of factors that provide the greatest strength of the coating for a fixed value of the composite deformation. The calculation time using the program does not exceed 1 second.

Table 1. Factors and ranges studied.

Factor	**Research range**
Carboxymethyl cellulose, %	1.5-3.5
Chromium, g	0.5-5.0
Glycerol, g	1.0-5.0
d chromium, μm	20-50
Temperature, ^{0}C	40.0-90.0

3 Results and discussion

After statistical processing of the experimental results, regression equations were obtained that establish the influence of the studied variables on the mechanical strength and relative deformation of coatings on a dimensionless scale:

$$\sigma=2{,}3 + 0{,}4 \cdot x_1 - 0{,}1 \cdot x_2 - 0{,}7 \cdot x_3 + 0{,}4 \cdot x_4 - 0{,}7 \cdot x_5 - 0{,}4 \cdot x_1 \cdot x_3 + 1{,}1 \cdot x_3 \cdot x_5 \quad (1)$$

$$\varepsilon=26{,}8 - 4{,}2 \cdot x_4 + 2{,}8 \cdot x_5 - 3{,}5 \cdot x_2 \cdot x_4 + 4{,}9 \cdot x_2 \cdot x_5 - 3{,}6 \cdot x_4 \cdot x_5 \quad (2)$$

The calculated and tabulated values of Fisher's criteria were 6.9 and 8.7 (for σ); 5.9 and 8.7 (for ε), respectively. To assess the significance of the coefficients, the Student's test was used, the significance level was 0.05. The mechanical strength of the coatings obtained in the experiments did not exceed 8 MPa. An assessment of the strength of the connection of coatings to a steel surface showed that the adhesive strength of coatings that do not contain chromium powder is 2-3 points; the coatings are brittle and prone to cracking, which is quite consistent with the information presented in [1]. When filling the polymer matrix with metal powder, it increases to 1 point due to the filling of the substrate unevenness with microparticles of chromium powder. Works [8, 10] show that agglomerates from the fine fraction of the filler powder are localized in microroughnesses of the metal surface relief. This helps to increase the adhesion strength of coatings to a steel surface due to the mechanical interactions of particles with the surface and the resulting van der Waals forces [10].

Graphs of the dependences of mechanical strength and relative deformation of coatings on the studied factors on a natural scale are shown in Figures 1-5. The values of fixed variables in natural scale for these dependencies are indicated in Tables 2-6.

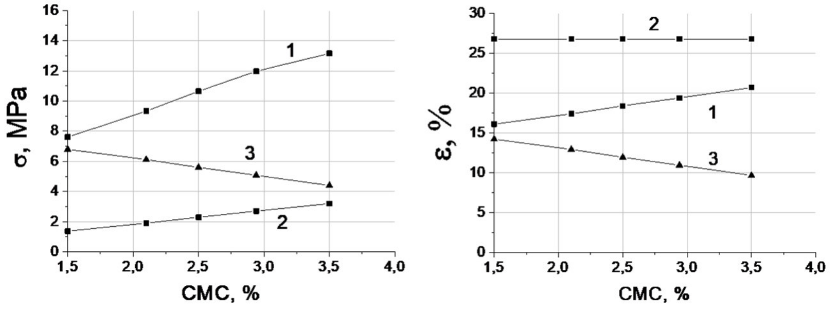

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Fig. 1. Effect of carboxymethyl cellulose concentration on mechanical strength - (a) and relative deformation - (b) of coatings.

Table 2. Values of fixed variables on a natural scale to identify the effect of carboxymethyl cellulose concentration on the mechanical strength and deformation of coatings.

Curve	Chromium, g	Glycerol, г	d chromium, µm	T, ° C
1	0.50	1.00	<20	40.0
2	2.75	3.00	<35	65.0
3	5.00	5.00	<50	90.0

The mechanical strength of coatings with increasing concentration of carboxymethyl cellulose increases when other factors are fixed in the center of the studied range and at its lower boundaries from 1.4 MPa to 13.7 MPa (Fig. 1 a, curves 1, 2). At maximum values of the factors, it decreases slightly from 6.8 MPa to 4.3 MPa (Fig. 1 a, curve 3). The deformation varies within the range of 26.8% - 9.7% (Fig. 1 b), increasing at the lower limits of the range (Fig. 1 b, curve 1), and decreasing when factors are fixed at the upper boundaries (Fig. 1 b, curve 3).

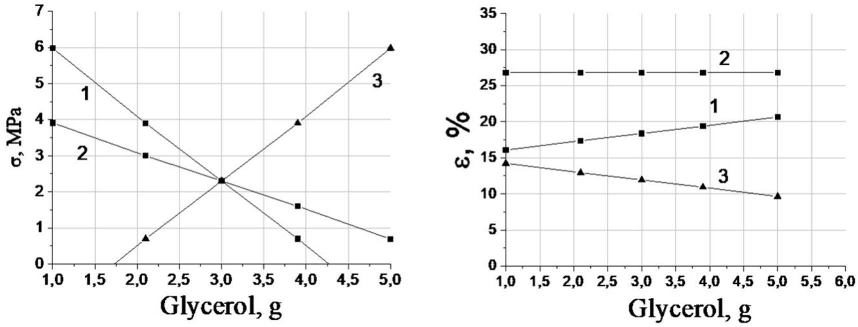

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Fig. 2. The influence of glycerol content on the mechanical strength - (a) and relative deformation - (b) of coatings.

Table 3. Values of fixed variables on a natural scale to identify the effect of glycerol content on the mechanical strength and deformation of coatings.

Curve	Chromium, g	Glycerol, г	d chromium, μm	T, ° C
1	1.5	0.50	<20	40.0
2	2.5	2.75	<35	65.0
3	3.5	5.00	<50	90.0

The plasticizer glycerin in the coating composition has an ambiguous effect on mechanical strength: it leads to a decrease in strength at minimum values of factors and values corresponding to the centers of the ranges, the relative deformation in this case quite naturally increases (Fig. 2 a-b, curves 1 and 2). When the factors are fixed at the upper limits of the ranges, the strength increases and the deformation decreases (Fig. 2 a-b, curve 3). In general, when the glycerol content changes, the mechanical strength does not exceed 6 MPa, the relative deformation is 26.8%. Curves that have no physical meaning (at the boundaries of the ranges) are not shown on the graphs.

The effect of chromium powder on mechanical properties must be considered in its entirety, taking into account changes in the size of chromium particles. As follows from the graphs, the content of chromium powder has a lesser influence, while the particle size has a greater influence (Fig. 3-4).

When a polymer solution with a concentration of 1.5% is filled with a fine fraction of chromium powder (< 20 μm) and a minimum glycerol content, a strength of ~8 MPa is realized, the relative deformation decreases from 16.1% to 1.3% (Fig. 3). As the concentration of CARBOXYMETHYL CELLULOSE, plasticizer content and chromium particle size increase, the mechanical strength of the coatings varies from 5 to 2 MPa, ε increases to 26.8%. An increase in the size of powder particles leads to an increase in mechanical strength, reaching 9.5 MPa with a minimal contribution of other factors, however, the deformation in this case is 70%, and for a fine powder fraction and fixation of factors at the upper limits of the ranges it reaches 100% (Fig. 4).

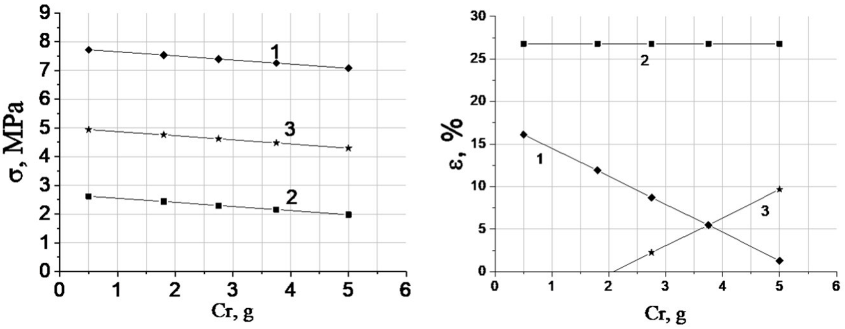

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Fig. 3. The influence of chromium content on the mechanical strength - (a) and relative deformation - (b) of coatings.

Table 4. Values of fixed variables on a natural scale to identify the effect of chromium content on the mechanical strength and deformation of coatings.

Curve	Chromium, g	Glycerol, г	d chromium, μm	T, ° C
1	1.5	1.00	<20	40.0
2	2.5	3.00	<35	65.0
3	3.5	5.00	<50	90.0

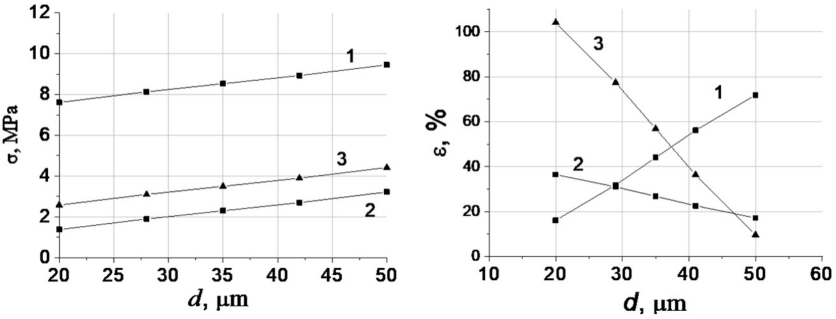

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Fig. 4. Effect of chromium particle size on mechanical strength - (a) and relative deformation - (b) of coatings.

Table 5. Values of fixed variables on a natural scale to identify the effect of chromium particle size on the mechanical strength and deformation of coatings.

Curve	Chromium, g	Glycerol, г	d chromium, μm	T, ° C
1	1.5	1.00	0.50	40.0
2	2.5	3.00	2.75	65.0
3	3.5	5.00	5.00	90.0

Coatings with a strength of 7.6 MPa are formed at T = 40 °C for a composition containing 0.5 g of chromium with a particle size of < 20 microns, 1.00 g of glycerol and a carboxymethyl cellulose concentration of 1.5%. The deformation of the coatings in this case is 16% (Fig. 5, curve 1). At higher temperatures (T = 90 °C), mechanical strength is in the range of 3.8 -0.8 MPa, deformation is 16.1% -20.4% (Fig. 5, curves 2 and 3).

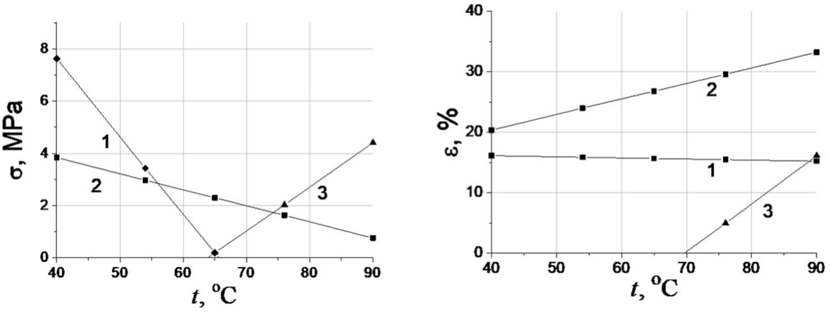

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Fig. 5. Influence of formation temperature on mechanical strength - (a) and relative deformation - (b) of coatings.

Table 6. Values of fixed variables on a natural scale to identify the influence of formation temperature on the mechanical strength and deformation of coatings.

Curve	Chromium, g	Glycerol, г	d chromium, μm	T, ° C
1	1.5	1.00	0.50	<20
2	2.5	3.00	2.75	<35
3	3.5	5.00	5.00	<50

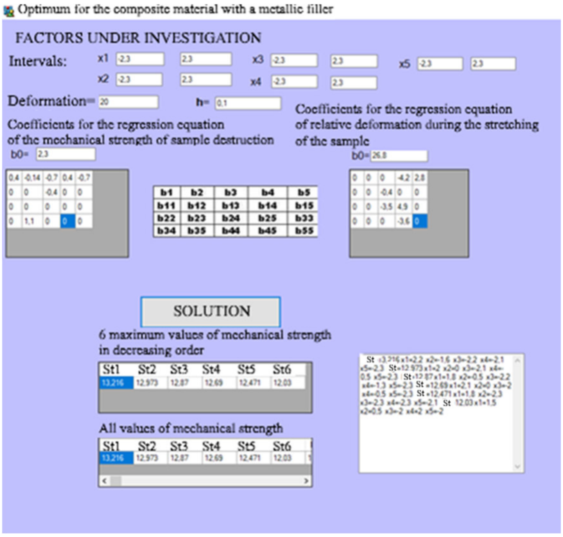
As noted, the obtained polynomial dependencies make it possible to formally evaluate the influence of the factors under study on the mechanical characteristics of coatings. A complete analysis of the equations in mass production conditions is impractical, since it is associated with time costs, and ultimately does not provide effective solutions. Therefore, to obtain the required combination of facts, a program previously developed by the authors in the Microsoft Visual Studio environment was used. The program allows, based on a given relative deformation of the composite that meets operational requirements, to calculate the maximum possible strength for the coating being formed. An array of studied factors was calculated on a dimensionless scale for which the required value of ε is realized. The resulting combinations of variables were substituted into the regression equation for mechanical strength.

Table 7. Optimal composition and mode of coating formation.

carboxymethyl cellulose, %	carboxymethyl cellulose (aqueous solution) + chromium + glycerin, wt. shares	d chromium, μm	T, ° C
1.5	100+3.24+1.26	<50 μm	43

The ratios of factors providing the highest strength value, after experimental confirmation of the recipe, were considered final. Figure 6 shows the results of numerical calculations obtained using the software module. Here the coefficients b_0 are the free terms of the regression equations, b_j are linear effects, b_{uj} are the effects of pairwise interactions, bjj are quadratic effects. The calculation was made for the value ε=20%, sufficient for industrial use of the coating. Table 7 shows the ratios of the composition components that provide the required deformation and optimal strength of the coating (12.0 MPa). The main consideration in favor of the given combination of factors was the possibility of obtaining a fraction of chromium powder (particles smaller than 50 μm) using sieve sieving and the relatively low curing temperature of the coating (~40 ° C).

The strength and deformation of the coating calculated were 12.0 MPa and 20.0%. In accordance with Table 2, coating samples were made and mechanical characteristics were determined. The following values were obtained in the experiment: σ=12.8 MPa, ε=18.1%, adhesive strength of the coating 1 point.



Intervals:
x1 -2.3 2.3
x2 -2.3 2.3
x3 -2.3 2.3
x4 -2.3 2.3
x5 -2.3 2.3

Deformation= 20
h= 0.1

Coefficients for the regression equation of the mechanical strength of sample destruction

b0= 2.3

0.4	-0.14	-0.7	0.4	-0.7
0	0	-0.4	0	0
0	0	0	0	0
0	1,1	0	0	0

b1	b2	b3	b4	b5
b11	b12	b13	b14	b15
b22	b23	b24	b25	b33
b34	b35	b44	b45	b55

Coefficients for the regression equation of relative deformation during the stretching of the sample

b0= 26.8

0	0	0	-4.2	2.8
0	0	-0.4	0	0
0	0	-3.5	4.9	0
0	0	0	-3.6	0

6 maximum values of mechanical strength in decreasing order

St1	St2	St3	St4	St5	St6
13,216	12,973	12,87	12,69	12,471	12,03

All values of mechanical strength

St1	St2	St3	St4	St5	St6
13,216	12,973	12,87	12,69	12,471	12,03

```
St =13,216 x1=2,2 x2=-1,6 x3=-2,2 x4=-2,1
x5=-2,3  St=12,973 x1=2 x2=0 x3=-2,1 x4=-
0,5 x5=-2,3  St=12,87 x1=1,8 x2=-0,5 x3=-2,2
x4=-1,3 x5=-2,3 St =12,69 x1=2,1 x2=0 x3=-2
x4=0,5 x5=-2,3 St =12,471 x1=1,8 x2=-2,3
x3=-2,3 x4=-2,3 x5=-2,1  St 12,03 x1=1,5
x2=0,5 x3=-2 x4=2 x5=-2
```

Fig. 6. Calculation results: view of the software module interface.

The chemical resistance of the coatings was visually assessed after testing in aggressive liquids for six months. Tests have shown that the coatings are resistant to organic solvents - styrene, 25% sulfuric acid solution, 25% and 40% alkali solution (NaOH).

4 Conclusion

Carboxymethyl cellulose-chrome biocomposite protective coatings of have been developed. It has been shown that the mechanical properties of coatings can be improved by combining the ratios of the composition components and coating curing modes. The composition and temperature of coating formation were calculated using a software module developed in the Microsoft Visual Studio environment. The resulting ratios make it possible to increase the mechanical strength of coatings by 40% and improve the adhesive strength to 1 point.

The calculation procedure proposed makes it possible to create functional coatings with specified mechanical properties based on biopolymers with various fillers.

References

1. M. Yildirim-Yalicin, F. Tornuk, O. S. Toker, Trends in Food Science & Technology **129,** 179-193 (2022)
2. M. Azarifar, B. Ghanbarzadeh, M. S. Khiabani, A. A. Basti, A. Abdulkhani, N. Noshirvani, M. Hosseini, Carbohydrate polymers **208**, 457-468 (2019)
3. E. Kolganova, A. Shishkina, G. Sanamyan, ICIE **2023** 739-748

4. V. Lebedev, Y. Kolganova, V. Shumyacher, D. Krivosheev, Journal of Physics: Conference Series, **2131** 042028 (2021)
5. S. Ebrahimzadeh, B. Ghanbarzadeh, H. Hamishehkar, International journal of biological macromolecules, **84,** 16-23 (2016)
6. P. Chen, F. Xie, F. Tang,T. McNally, International journal of biological macromolecules, **158,** 420-429 (2020)
7. M. Morsi, E. Abdelrazek, R. Ramadan, I. Elashmawi, A. Rajeh, Polymer Testing, **114,** 107705 (2022)
8. N. Antonova, Materials Today: Proceedings **38,** 1588-1591 (2021)
9. M.I. Karyakina, *Testing of paints and coatings* (M.: Khimiya, 1988)
10. N. Antonova, IOP Conference Series: Materials Science and Engineering **665** 012003 (2019)