

OBTAINING TRANSPARENT COMPOSITES BASED ON HYBRID SILICATE HYDROGELS AS SPECIAL MATERIALS FOR INCREASING THE FIRE RESISTANCE OF GLASS STRUCTURES

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<https://doi.org/10.23939/chcht18.04.535>

Abstract. Developing a new generation of transparent hydrogel firefighting mineral-polymeric materials is an urgent task. These composites are used to produce refractory glass structures, particularly double-glazed windows. These double-glazed windows are multilayer structures made of silicate glass sheets, with gaps filled by a transparent material that turns opaque under flame exposure, reducing heat load and maintaining structural integrity for a specified duration. This article presents research on the synthesis and properties of transparent polysilicon hydrogels, used as a component in hybrid mineral-organic composites for manufacturing fire-resistant transparent glass structures. A method for producing polysilicate acid hydrogels in the presence of polyvalent metal ions has been developed. Full-factor experiment results established the sol-gel process time frame, influenced by many factors. The research demonstrates the feasibility of creating a transparent hybrid polymer-mineral hydrogel material containing polyvalent refractory salts and polysilicate acid, which can transform into a highly porous refractory material under high temperatures.

Keywords: hydrogel; polysilicic acid; composite; refractory glass.

1. Introduction

In recent decades, polymeric hydrogels, which include crosslinked systems of hydrophilic macromolecules capable of retaining significant amounts of water while maintaining the properties of solids, continue to attract great interest. The combination of solid and liquid properties leads to a wide range of applications, from technical industries to the food industry and

medicine. At the same time, the development of various technologies necessitates the development of new types of hydrogels for specific tasks. They usually have to combine a number of specific and seemingly mutually exclusive properties: gas permeability, increased mechanical strength, optical transparency, electrical conductivity, *etc.*¹⁻⁶ In particular, in the construction industry, hydrogels are used in slab joint sealing systems in underground tunnels, for waterproofing basement walls, and as a filling for window glass units to make them resistant to fire spread.^{7,8}

The task of developing new effective hydrogel compositions for use in such fire-resistant glass units involves combining a whole range of diverse but specified properties and is still relevant. Fires pose a great threat to human life, and also cause significant material damage in general.^{9,10} Fire in all types of premises spreads very quickly, and the multifunctionality and complexity of modern buildings significantly increase the fire hazard. Passive fire protection measures, such as fire barriers (wall partitions), can effectively delay the spread of flames and combustion products. However, openings in their design (windows and doorways, elevator shafts, stairwells) that provide natural light significantly reduce the fire resistance of buildings.¹¹⁻¹³ To create an obstacle to the penetration of fire and smoke into the premises adjacent to the fire zone, glass structures with fire-resistant properties are installed in wall openings in accordance with building standards.^{14,15}

One of the most important elements of these structures is a fire-resistant double-glazed unit, the inter-glass space of which consists of one or more transparent layers that ensure the functional properties of this product.¹⁶⁻¹⁸ Such double-glazed windows can be made with an inner layer of different nature: - from polymers resistant to fire and ignition, which are carbonized at high temperatures, forming an opaque thermal insulation layer;^{12,17} - polysilicic acid hydrogel (based on liquid glass), which foams when heated, providing thermal insulation properties; - special polymer hydrogel with a

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high content of water or salt solutions, which foams, releases water and becomes an opaque xerogel at high temperatures; this provides the necessary degree of thermal insulation and maintains integrity.^{14,16}

Most of the glass fire protection systems on the market today (including Pyronova® by Schott, Pyrobel® by AGC, and Contraflam® by Vetrotech) are based on silicate hydrogels. At the same time, their manufacturing technology is quite costly and time-consuming, and the thermal stability of the resulting insulating foam is in the range of 700-750°C, which requires an increase in the number of glass layers in a double-glazed unit and complicates production.

This prompts a constant search for new systems capable of performing fire protection functions. One of the options for a double-glazed window with fire-resistant properties is a design, in which the layers between the glass sheets are filled with a transparent hydrogel based on organic polymers or a composite polymer-organic material. Excellent fire-resistant and thermal insulation characteristics in the case of hydrogel filling are achieved due to the primary evaporation of free and bound water (in such compositions it can be up to 80%), which occurs with increasing temperature. At the same time the polymer-inorganic residue foams, ultimately turns into a fire-resistant xerogel and acts as a reliable barrier to the spread of thermal radiation, as well as fire and smoke, ensuring the integrity of the insulating glass unit.^{19,20} Such systems provide a higher degree of protection compared to monolithic refractory glass, which can maintain its integrity at significant temperature changes but does not prevent the spread of thermal radiation that can be dangerous to people in adjacent spaces and initiate a fire in nearby objects. Unfortunately, the use of hydrogels of this type for the manufacture of fire-resistant insulating glass units in the industry is somewhat limited by their multicomponent nature, which imposes certain risks. These risks are associated with the need to ensure stable and reproducible properties of the product not only immediately after manufacture but also throughout the entire period of operation under the influence of environmental factors, such as ultraviolet radiation and temperature changes, which can degrade the optical characteristics of these materials over time.^{21,22}

Therefore, there is an urgent need to develop hydrogels with improved properties that would be transparent during the operation period and at the same time possess the basic properties necessary to ensure fire resistance.

The solution to this problem may be the use of a composite hydrogel as an intermediate layer. A balanced composition of hydrogel contains mineral components, which at certain ratios can form a transparent inorganic hydrogel. The formed hydrogel provides the necessary

performance characteristics of the product – a transparent (at least 85% light transmission), form-resistant material in the inter-glass space of a double-glazed window. In this regard, hydrogels containing polysilicic acid as a component are of particular interest. Such systems belong to the class of mineral hydrogels and are used in sol-gel technologies for the production of refractory materials, carriers for catalysts, etc.²³⁻²⁷ However, there are only few studies describing the synthesis and properties of polysilicic acid hydrogels to obtain a material with a high light transmission coefficient and there are significant gaps in knowledge about the methods of their preparation, structure, functionality, and the possibility of creating compositions with organic polymers.²⁸⁻³² It is known that the presence of silicon oxide in the composition can lead to a decrease in thermal conductivity and contribute to the formation of an effective protective layer of mineral-carbon xerogel.³³⁻³⁵ However, there have been no reports of studies on transparent combined hydrogels that, in addition to a polymeric network, contain both nonflammable salts and silicates of polyvalent metals.

The aim of the research was to develop a synthesis method and to study the properties of hydrogels with polysilicic acid with the prospect of using them as components in the preparation of a transparent form-stable hybrid mineral-organic hydrogel. The combination of hydrogel ability to retain large amounts of water and the use of polysilicic acid, which is a well-known fire retardant and can serve as a cementing component for the formation of a mechanically strong and heat-resistant xerogel layer of refractory salts capable of withstanding temperatures up to 1100°C in one polymer-mineral hydrogel can be a prerequisite for the development of hydrogel materials for their use as fire retardants.

2. Experimental

2.1. Materials

2.1.1. Reagents. Sodium silicate, magnesium sulfate, aluminum sulfate, citric acid, 1-hydroxyethylidene-1,1-diphosphonic acid, and formic acid of PA grade were used without preliminary purification. Acrylamide, acrylic acid, N,N-methylene bisacrylamide, and formaldehyde were purchased from Aldrich and used without additional purification.

2.1.2. The synthesis of polyacrylamide and copolymers of acrylamide, acrylic acid, and N,N-methylene bisacrylamide was carried out according to the methods described earlier.³⁶

2.1.3. The synthesis of crosslinking agents based on them, namely poly-N-(hydroxymethyl)acrylamide and poly-N-(hydroxymethyl)acrylamide-acrylic acid-N,N-

methylene bisacrylamide, was carried out according to the methods described in our previous work.³⁷

2.1.4. The synthesis of the mineral hydrogel was carried out as follows: an aqueous solution of aluminum sulfate, magnesium sulfate, and monoacetic acid (or 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP) or formic acid) was prepared in a given range of their ratios and concentrations. Sodium metasilicate (disodium silicate pentahydrate) was dissolved in water at 60°C and, after cooling to 20°C, a certain amount of polyhydric alcohol (glycerin) was added to it to obtain a solution of a given concentration. Next, a solution of sodium metasilicate and glycerol was slowly added to the solution of mineral salts under very intense stirring at 1000 s⁻¹ on a homogenizer (Homogenizer HG-15A, DAIHAN Scientific, Korea). The composition was loaded into a glass unit, sealed, and heated at 80°C for a specified time or allowed to self-gell.

2.1.5. The synthesis of the hybrid hydrogel was carried out as follows: • mineral hydrogel composition was prepared according to the method described above; • a solution of polyacrylamide (25%) and a solution of poly-N-(hydroxymethyl)acrylamide (17%) were prepared, which were mixed in such a way as to achieve the ratio of polyacrylamide to poly-N-(hydroxymethyl)acrylamide within the specified limits from 1÷1 to 5÷1; • then the mineral composition (79%) was mixed with the polymer composition (21%). The mixture was thoroughly mixed, sealed, and heated at a temperature of 80°C for a given time.

2.2. Methods

Determination of the sample gelation moment: according to the procedure described in the article,³⁸ the mixture gelation moment was determined visually by tilting the vial with the sample by 30° relative to the vertical. The sample is considered to be gelled when the mixture surface is unbreakable and also tilts by 30°, but relative to the horizontal.

Measurement of light transmittance of hydrogels: the light transmittance of hydrogels was determined using a spectrophotometer (UNICO 1201); the reference solution was distilled water, wavelength 550 nm, cuvette thickness 10 mm, ambient temperature 20°C. The percentage of the light beam that passed through the sample was measured (T , %).³⁹

Determination of the effective hydrodynamic radius and ζ -potential by the dynamic light scattering (DLS) method: the effective hydrodynamic radius of the polysilicic acid ash particles was determined using a DynaPro® Plate Reader III from Wyatt Technology.⁴⁰

3. Results and Discussion

The formation of a transparent shape-stable hybrid mineral-organic hydrogel can occur either via copolymerization of water-soluble monomers in the presence of bifunctional agents that form cross-links or via the condensation mechanism during polymerization due to the covalent interaction between functional groups in the chains of acrylamide copolymer and a polymer crosslinking agent obtained on its basis by polymer-analogous transformations.^{36,37} The scheme for obtaining a transparent shape-stable hybrid mineral-organic hydrogel via the condensation mechanism is shown in Fig. 1.

As a mineral component of the hybrid hydrogel, we used a polysilicic acid hydrosol formed by adding an aqueous solution of sodium metasilicate to a solution of salts of polyvalent metals (Mg²⁺ from magnesium sulfate and Al³⁺ from aluminum sulfate). Under certain conditions (described below), the silanol groups of sodium metasilicate react with cations of divalent and trivalent metals (magnesium and/or aluminum) to form silanol-metal bridges, which eventually (this process can take up to 40 days depending on the conditions) polymerize with the release of water to form inorganic silicate-metal polymers.⁴⁰

This effect (delayed process of gelation of the mineral component of the hybrid hydrogel) is a key advantage in the formation of a transparent, shape-stable hybrid mineral-organic hydrogel. In the spatial structure of a polymeric hydrogel, which is formed much faster (2-4 hours), due to the significant complication of diffusion processes, the formation of a mineral hydrogel slows down or even stops until critical conditions (high temperature in a fire) occur.

The formed hydrogel must have high light transmission, which is ensured by the mixture composition. Preliminary experiments have established that mixing aqueous solutions of aluminum (magnesium) sulfate with a solution of sodium metasilicate to obtain transparent compositions and hydrogels is possible only under certain conditions in the presence of organic acids and glycerin as stabilizers. It has been determined that to achieve the transparency effect in a wide range of component concentrations (up to 25% for magnesium and aluminum salts and up to 10% for sodium silicate), it is necessary to maintain the mixture pH not higher than 2 and the glycerin content not less than 10%. Among the organic acids, the expected results were obtained when using citric, 1-hydroxyethylidene-1,1-diphosphonic, or formic acids. Under such conditions, the resulting mixtures are cloud-free, stable at temperatures up to 100°C, and their gelation under normal conditions takes place over a sufficiently long time. Mixtures with the mentioned properties can be used to develop commercial

products with a known shelf life. It should be also noted that pH 2 is optimal for obtaining a polymer hydrogel using the method of prepolymer condensation. Glycerin in the final mixture and hydrogel obtained on its basis plays

the role of antifreeze, expanding the range of resistance to environments at negative temperatures. Table 1 shows the determined characteristics of gelation time and light transmission for polysilicic acid hydrogels.

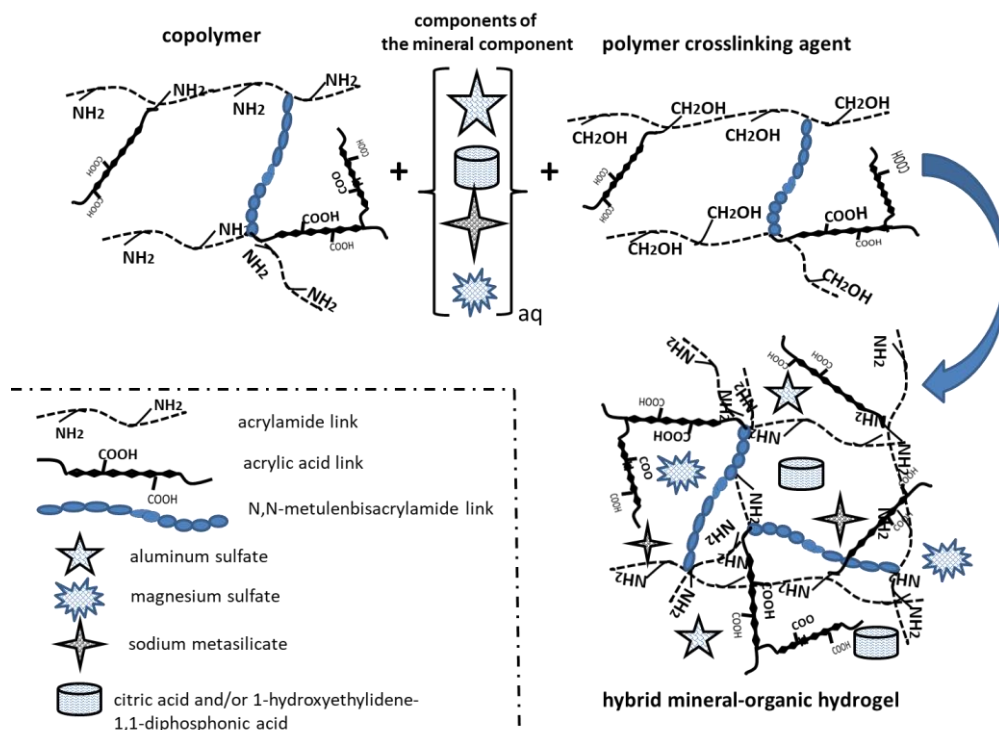


Fig. 1. Scheme for obtaining a transparent shape-stable hybrid mineral-organic hydrogel

The data shown in Table 1 demonstrate that, depending on the composition, samples of mineral hydrogel have a very wide range of light transmission that values from 15.4% to 95.1%. So, quite a lot of samples are characterized by a sufficiently high light transmission coefficient (over 80%). The first part of the research was devoted to the use of only citric acid as both a pH-lowering and a chelating agent. Aluminum sulfate plays a quite unambiguous role as an influencing factor on the mixture transparency. Samples where this salt is absent (samples 5, 8) have a rather high light transmission capacity (92.4-94.8%). A sample where the aluminum sulfate content is quite high is also very transparent (95.1%), but at the same time the concentrations of other components in the mixture is reduced. Replacing the acidulant with formic acid led to a decrease in spontaneous gelation time.

This dependence with a certain error can be considered proportional: the higher the concentration of formic acid, the less time it takes to gel the mixture. For example, sample 19 (17.00% formic acid) has spontaneously gelled after 4 days, when sample 10 (9.01% formic acid) - after 19 days. This is also observed

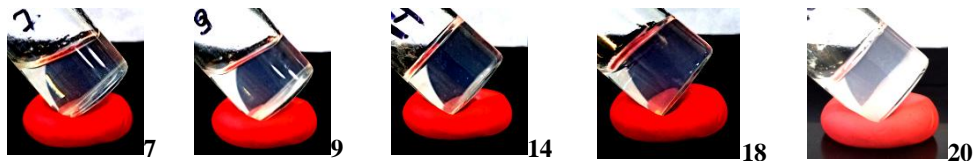
at high concentrations of citric acid in some cases. The use of HEDP (samples 20-22) resulted in results with a strong variation in self-gelling time, but with a light transmission value in a narrow range. It should be noted that rapid gelation can lead to a decrease in the light transmittance. The effect of some of the most influential components of the mixture on transparency will be investigated in a full-factor experiment.

Thus, gelation of experimental mixtures of this sample occurs in a wide time interval from 7 to 40 days. Fig. 2 shows photographs of hydrogel samples at the time of gelation containing polysilicic acid

The mixture can be used for a fire-resistant glass unit if its light transmission is at least 85%. For some samples, a decrease in light transmission was observed during the first 10 days, so measurements were made regardless of when gelation was recorded, on the 21st day after mixing the components. The light transmission coefficient of hydrogels decreases over time (the percentage decrease from the initial value is in the range from 1.5 to 15%). Therefore there is an interest in hydrogels, the transmission coefficient of which is at least 85% (which meets the requirements for transparent glass structures) on the 21st day of observation.

Table 1. Dependence of gelation time and light transmission on the composition of the reaction mixture during the preparation of polysilicic acid hydrogels in the presence of magnesium and/or aluminum salts

№	Composition, wt. %							Characteristics	
	MgSO ₄ ·7H ₂ O	citric acid	formic acid	HEDP	Al ₂ (SO ₄) ₃	Glycerin	Na ₂ SiO ₃ ·5H ₂ O	%T 550 nm	Self-gelation time, days
1	2	3	4	5	6	7	8	9	10
1	18.00	12.00	-	-	5.99	10.40	4.00	92.4	22
2	18.00	9.00	-	-	5.99	10.40	4.00	92.3	40
3	17.48	14.56	-	-	5.82	10.10	3.88	93.2	22
4	18.00	6.00	-	-	5.99	10.40	4.00	89.6	22
5	24.05	12.00	-	-	-	10.42	4.01	92.4	19
6	12.00	12.00	-	-	11.99	10.40	4.00	93.1	22
7	3.88	14.55	-	-	19.39	6.21	3.88	95.1	22
8	30.00	15.00	-	-	-	4.40	4.00	94.8	11
9	17.98	-	11.97	-	5.99	10.39	4.00	90.9	14
10	18.00	-	9.01	-	5.99	10.40	4.00	93.9	19
11	17.48	-	14.61	-	5.82	10.10	3.88	92.5	14
12	24.00	-	11.99	-	-	10.40	4.00	91.7	11
13	17.73	8.87	-	-	6.77	10.25	5.42	92.2	28
14	16.42	8.21	-	-	6.27	11.86	7.30	93.8	15
15	18.00	15.00	-	-	5.99	7.40	4.00	94.3	10
16	18.00	15.00	-	-	6.87	4.40	5.50	93.8	10
17	18.00	-	14.88	-	5.99	7.40	4.00	90.3	15
18	17.79	-	14.70	-	7.13	4.35	5.43	66.0	7
19	24.00	-	17.00	-	-	13.00	8.00	15.4	4
20	18.00	-	-	9.00	5.99	10.40	4.00	94.6	30
21	18.00	-	-	15.00	5.99	7.40	4.00	89.8	11
22	22.06	-	-	15.63	-	17.28	3.68	93.2	14

**Fig. 2.** Photos of polysilicic acid hydrogel samples (sample numbers correspond to those in Table 1)

Most of the samples are visually transparent, despite the presence of the colloidal phase of nanoparticles. This is demonstrated by DLS studies conducted over a certain time after mixing the components. Fig. 3 shows the DLS curves for some samples, where the presence of particles of different sizes

from 1 nm to 10000 nm is observed. The stable transparency values can be obtained in the absence of particles much larger than the wavelength of visible light. With a relatively high number of “large” particles, there is a significant probability of coalescence, sedimentation, and turbidity effects, which obviously cannot be positive.

To establish the relationship between transparency and particle content, a full-factorial experiment was conducted, the orthogonal plan of which is shown in Table 2. The constant parameters were the concentration of citric acid and aluminum sulfate, and the variables were the concentration of magnesium sulfate, sodium metasilicate, and glycerin. It has been previously investigated that the concentrations of magnesium sulfate, sodium silicate, and glycerin have the greatest influence on the transparency of the obtained mixtures.

The standard processing of the orthogonal plan allowed us to describe the dependence of the content of the 1-600 nm fraction particles on the reagents concentration at the plan scale by the following equation (1):

$$W_{<600} = 37 + 10x_1 + 10x_2 + 5x_1x_3 - 4x_2x_3 - 8x_1x_2x_3 \quad (1)$$

where x_1 - magnesium sulfate concentration %; x_2 - sodium silicate concentration %; x_3 - glycerin concentration %.

The variance of reproducibility s_v^2 is 3.11 versus the variance of adequacy s_a^2 of 3.86. The empirical value of the Fisher's criterion is 1.24. At the 95% confidence level with these degrees of freedom, the critical value of the Fisher's criterion is 19.2. Since the empirical value of the criterion is less than the critical value, the resulting equation should be considered adequate and there is no need to implement a composite plan to refine it. Equation (1), written in the plan coordinates, makes it relatively easy to navigate the importance of the factors, but for a more detailed analysis it is advisable to convert it into natural units:

$$W_{<600} = 442 - 26C_{MgSO_4} - 121C_{Na_2SiO_3} - 34C_{glycerin} + 2C_{MgSO_4}C_{glycerin} +$$

$$+ 9C_{Na_2SiO_3}C_{glycerin} + 8C_{MgSO_4}C_{Na_2SiO_3} - 0,5C_{MgSO_4}C_{Na_2SiO_3}C_{glycerin} \quad (2)$$

where C_{MgSO_4} - magnesium sulfate concentration %; $C_{Na_2SiO_3}$ - sodium silicate concentration, %; $C_{glycerin}$ - glycerin concentration, %.

The obtained equation (2) satisfactorily predicts the dependence of the content of the 1-600 nm fraction particles in the range of magnesium sulfate concentrations of 15–19%, sodium silicate 1.4–6%, and glycerin 9–15%. The graph in Fig. 4 shows the comparison of the values of the real responses with the predicted ones.

Fig. 5a shows the surface of the particles content dependence on the value of factors x_1 (magnesium sulfate concentration) and x_2 (sodium silicate concentration) at three constant values of factor x_3 (glycerin concentration), constructed according to Eq. (1). At the same time, Fig. 5b shows an isolinear model of the dependence. This surface allows us to visually analyze the influence of the factors. According to its nature, it can be predicted that a decrease in the concentration of magnesium sulfate increases the content of particles. This can be explained by the phenomenon of particle agglomeration at higher concentrations of components in the system.

Fig. 6a shows the surface of the particles content dependence on the value of factors x_1 (magnesium sulfate concentration) and x_3 (glycerin concentration) at three constant values of factor x_2 (sodium silicate concentration), constructed according to Eq. (2). An isoline model of dependence is depicted in Fig. 6b. Based on the nature of this surface, it can be predicted that with an increase in the glycerin content, the content of the 1-600 nm fraction particles decreases. This is obvious, because then the content of the aqueous phase, in which mineral particles can dissolve, decreases.

Table 2. Orthogonal experimental plan and dependence of the content of the 1-600 nm fraction particles on the concentration of components in solution

Plan of the experiment						Content of particles of the 1-600 nm fraction, %.
Concentration, in natural values, %			Concentration, in plan coordinates			
Magnesium sulfate	Sodium silicate	Glycerin	Magnesium sulfate	Sodium silicate	Glycerin	
14.75	1.41	9.83	-1	-1	-1	25.46
19.80	1.47	10.27	1	-1	-1	20.05
15.18	4.34	10.12	-1	1	-1	37.94
20.40	4.53	10.58	1	1	-1	63.61
14.75	1.41	18.26	-1	-1	1	7.70
19.80	1.47	19.06	1	-1	1	56.62
15.18	4.34	18.79	-1	1	1	37.18
20.40	4.53	19.64	1	1	1	51.26
14.26	2.83	14.16	-1.3	0	0	87.74
20.87	3.00	14.98	1.3	0	0	27.42
17.15	1.02	14.29	0	-1.3	0	5.60
17.80	4.88	14.84	0	1.3	0	47.68
17.47	2.91	8.94	0	0	-1.3	39.38
17.47	2.91	20.18	0	0	1.3	29.06
17.47	2.91	14.56	0	0	0	39.25
17.47	2.91	14.56	0	0	0	35.77

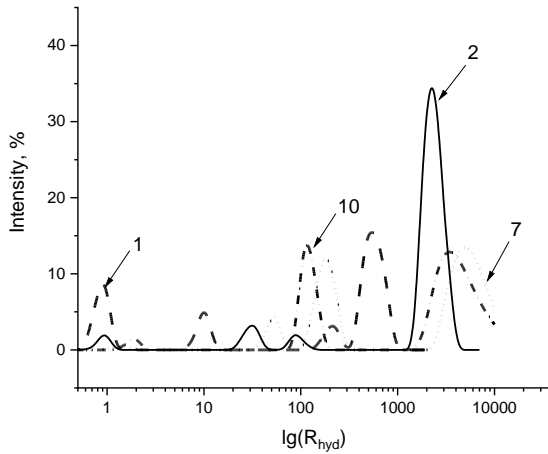


Fig. 3. DLS curves (by intensity) for samples 1, 2, 7, 10 according to Table 1

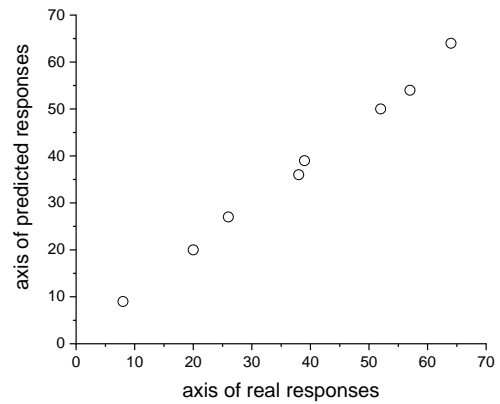
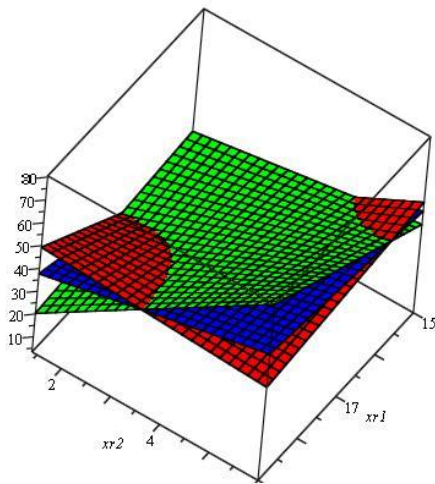
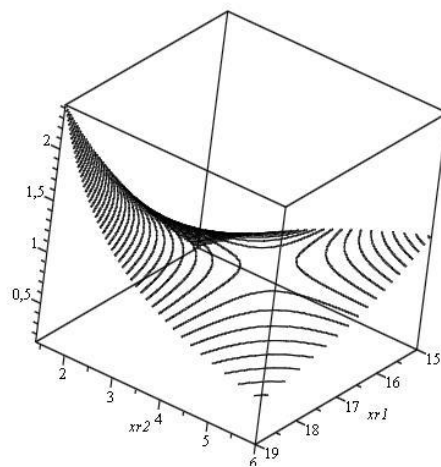


Fig. 4. Comparison of real feedback values with predicted ones

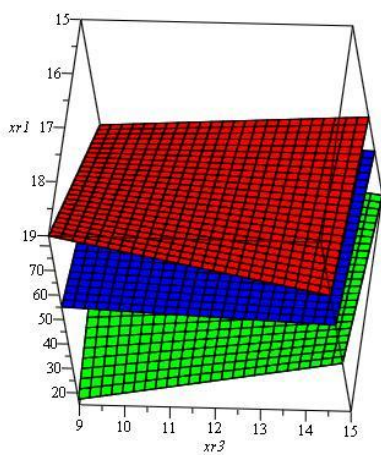


a)

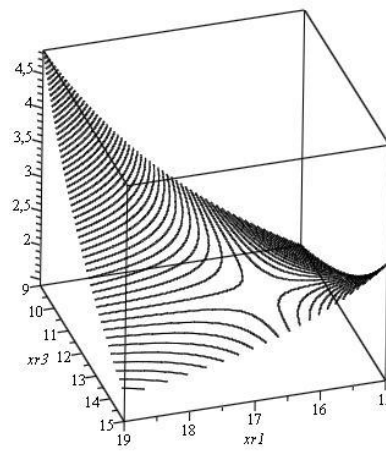


b)

Fig. 5. a - surface at a fixed glycerol content; b - isolinear model of dependence (x_1 - magnesium sulfate concentration %; x_2 - sodium silicate concentration %; x_3 - glycerin concentration %)



a)



b)

Fig. 6. a - surface at a fixed content of sodium silicate; b - isolinear model of dependence (x_1 - magnesium sulfate concentration %; x_2 - sodium silicate concentration %; x_3 - glycerin concentration %)

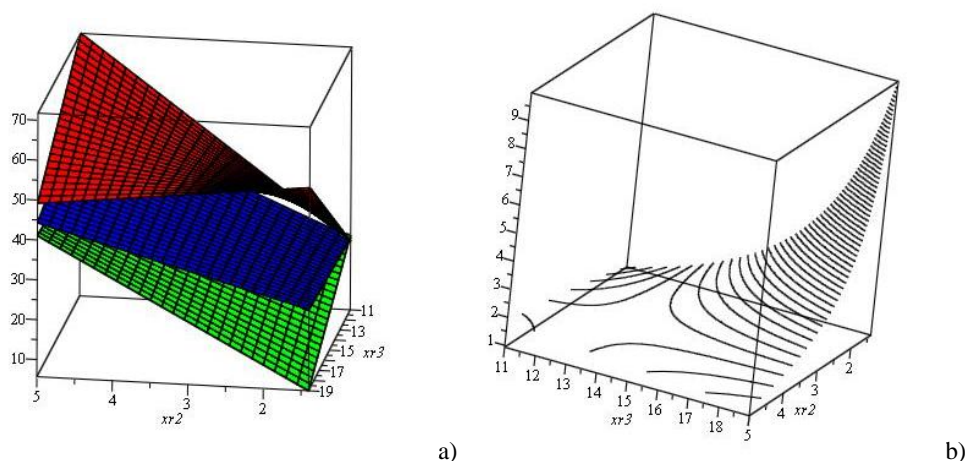


Fig. 7. a - surface at a fixed content of magnesium sulfate; b - isolinear model of dependence (x_1 - magnesium sulfate concentration %; x_2 - sodium silicate concentration %; x_3 - glycerin concentration %)

Fig. 7a shows the surface of the particles content dependence on the value of factors x_2 (sodium silicate concentration) and x_3 (glycerin concentration) at three constant values of factor x_1 (magnesium sulfate concentration), constructed according to Eq. (2). An isoline model of dependence is depicted in Fig. 7b.

Based on the nature of this surface, it can be concluded that a decrease in the concentration of sodium silicate in the system increases the content of the 1-600 nm fraction particles due to the dispersion of particles throughout the system without the formation of agglomerates.

Since this work aims to develop methods for obtaining stable colloidal solutions (polysilicic acid hydrogels), the content of particles of such a small diameter is desirable for several reasons. Firstly, a particle with a diameter commensurate with the wavelength of visible light creates minimal obstacles to the transmission of rays and is not visually noticeable, *i.e.*, the solution is transparent. It is the high transmittance of solutions and hydrogels based on them that is a prerequisite for the possibility of obtaining a liquid filling composition for a refractory glass unit. That is why the inorganic component, which will become the basis of a xerogel with refractory properties in a composite hydrogel, must have this property.

Nevertheless, although the mineral hydrogel shows signs of shape stability, its physical and mechanical characteristics are completely insufficient for use in the preparation of waterproof transparent glass products. Therefore, the next stage of research was to demonstrate that the introduction of a mineral component into the composition of a hybrid mineral-organic hydrogel can solve the problem.

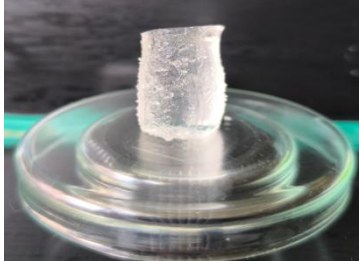

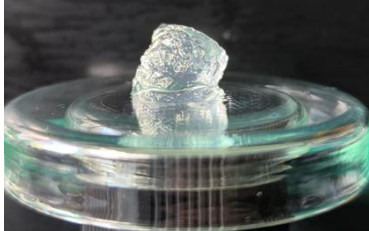

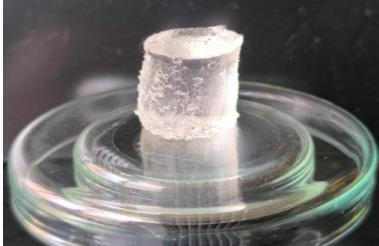

It is worth noting that in the process of hybrid hydrogels forming there are some nuances that are absent

in mineral hydrogels. The spontaneous gelation time of such a system will be much shorter due to the inevitable concentration of components responsible for the construction of polymer units (mineral and organic), which increases the likelihood of the formation of branched bonds. Determining the optimal acidity of the medium and its correlation between transparency and gelation rate requires further research

Table 3 shows images of hydrogels of different natures, namely polymeric hydrogel based on acrylic monomers, mineral and hybrid hydrogels, as well as images of residues (xerogels) obtained after heating the hydrogels in a muffle furnace at a temperature of up to 700°C. It can be seen that the formation of a continuous layer of inorganic xerogel occurs only in the case of a hybrid mineral-organic hydrogel. The combination of the initial shape stability of a transparent hydrogel with the ability to form a mineral refractory residue as a highly porous material allows it to withstand long-term exposure to elevated temperatures and act as a fire retardant.

The photos show that the mineral hydrogel, which is unable to maintain its shape on its own, is shape-stable as part of the hybrid hydrogel. An even more striking difference is observed after exposure to high temperatures. If, as expected, the polymeric hydrogel charred to an almost imperceptible residue after water evaporation and the inorganic hydrogel dried to a dense heat-resistant material, the hybrid hydrogel under the same conditions and concentrations of components turned into a mineral-carbon composite of porous structure. Such material is obviously capable of withstanding high temperatures in the case of fire. Moreover, taking into account its initial ability to transmit at least 85% of light rays, it can be used to create fire-resistant double-glazed windows.

Table 3. Images of hydrogels of different natures (1-polymer, 2-mineral, 3-hybrid polymer-inorganic) and the residue (xerogel) formed while heating to 700°C

Hydrogel	Xerogel
1. polymer	
	
2. mineral	
	
3. hybrid mineral-organic	
	

4. Conclusions

Thus, the synthesis parameters were investigated and the optimal conditions for obtaining polysilicic acid hydrogels were established. These hydrogels can be used as a mineral component for the preparation of hybrid hydrogel composites in which the sol of metal silicate and silicic acid is stabilized by a hydrogel based on an organic polymer. Such a system can be used to produce a transparent, shape-stable hybrid mineral-organic hydrogel to fill the space between the glass panes of a double-glazed unit with special properties, namely, long-term preservation of the composite's transparency under natural conditions. In case of fire, under the influence of high temperature, water is removed from the composite that retards the rapid increase in temperature throughout the hydrogel layer. After the water is removed, due to the presence of a mineral component, a continuous layer of inorganic xerogel is formed on the surface close to the radiation source. The layer delays the spread of heat flux and preserves the integrity of the entire structure, preventing the spread of both fire and smoke.

Acknowledgements

The research results presented in this article were obtained with grant funding from the National Research Foundation of Ukraine under the competition «Science for the Reconstruction of Ukraine in the War and Postwar Periods» within the framework of the project 2022.01/0091 «Development of a hydrogel composition for fire-resistant double-glazed windows and its manufacturing technology».

Abbreviations

DLS - dynamic light scattering

HEDP - 1-hydroxyethylidene-1,1-diphosphonic

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Received: July 01, 2024 / Revised: August 06, 2024 / Accepted: September 11, 2024

ОТРИМАННЯ ПРОЗОРИХ КОМПЗИТИВ НА ОСНОВІ ГІБРИДНИХ СИЛІКАТНИХ ГІДРОГЕЛІВ ЯК СПЕЦІАЛЬНИХ МАТЕРІАЛІВ ДЛЯ ПІДВИЩЕННЯ ВОГНЕТІЙКОСТІ СКЛОКОНСТРУКЦІЙ

Анотація. Створення нового покоління прозорих гідрогелевих мінерально-полімерних протипожежних матеріалів є актуальним завданням. Ці матеріали застосовують для отримання на їхній основі вогнетривких скляних конструкцій, зокрема склопакетів. Склопакети є багатопшаровою конструкцією з листів силікатного скла, проміжки між якими заповнені прозорим матеріалом, який під дією полум'я перетворюється в непрозорий шар і зменшує теплове навантаження та забезпечує цілісність усієї конструкції на заданий час. Наведено результати досліджень синтезу та властивостей прозорих полікремнієвих гідрогелів, які використовують як компонент гібридних мінерально-органічних композитів для виготовлення прозорих конструкцій зі скла з покращеною полісилікатною кислотою в присутності іонів полівалентних металів. За результатами повнофакторного експерименту встановлено часові рамки золь-гель процесу залежно від складу, концентрації, рН розчину й оптимізовані умови отримання з високим коефіцієнтом світлопропускання. Показано принципову можливість отримання прозорого гібридного полімер-мінерального гідрогелевого матеріалу, що містить як складові тугоплавкі солі полівалентних металів і полісилікатну кислоту, який при дії високої температури здатний перетворюватись у високопористий непрозорий вогнетривкий матеріал.

Ключові слова: гідрогель, полісилікатна кислота, композит, вогнетривке скло.