UDC 665.93+666.3.022.66
DOI: 10.15587/1729-4061.2019.185728

DETERMINING THE EFFECT OF THE COMPOSITION OF AN ALUMINOSILICATE BINDER ON THE RHEOTECHNOLOGICAL PROPERTIES OF ADHESIVES FOR WOOD

S. Guzii
PhD, Senior Researcher*
E-mail: sguziy2@gmail.com
P. Kryvenko
Doctor of Technical Sciences, Professor*
E-mail: pavlo.kryvenko@gmail.com
O. Guzii
Technician**
E-mail: gusii.elena777@gmail.com
S. Yushkevych
Department of Chemical Technology of Ceramics and Glass
National Technical University of Ukraine
«Igor Sikorsky Kyiv Polytechnic Institute»
Peremohy ave., 37, Kyiv, Ukraine, 03056
E-mail: mars970909@gmail.com
*V. D. Glukhovsky Scientific Research Institute
of Binders and Materials**
**Kyiv National University of
Construction and Architecture
Povitroflotsky ave., 31, Kyiv, Ukraine, 03037

Досліджено основні реотехнологічні властивості алюмосилікатних адгезивів для склеювання масивів деревини. Відзначено, що для адгезивів на основі лужного алюмосилікатного зв'язуючого складу $Na_2O\cdot Al_2O_3\cdot 4{,}5SiO_2\cdot 17{,}5H_2O$ динамічна в'язкість в діапазоні швидкостей від 0 до 200 RPM змінюється від 6933 сП до 368,4 сП, а середня пластична в'язкість становить величину 86,27 сП. При однаковому значенні поверхневого натягу і роботи когезії, найменшим кутом змочування ($\cos\Theta=0{,}7973$) і найбільшими коефіцієнтами змочування ($s=0{,}8986$) і млинності ($f=-6{,}5$ мН/м), а також роботами сил адгезії ($Wa=58{,}23$ мН/м), змочування ($Ww=25{,}83$ мН/м) характеризується підкладка бука, надалі – вільхи, ясеню, сосни, берези і дубу.

Для адгезивів на основі лужного алюмосилікатного зв'язуючого складу $Na_2O\cdot Al_2O_3\cdot 6SiO_2\cdot 20H_2O$ динамічна в'язкість в діапазоні швидкостей від 0 до 200 RPM змінюється від 5340 сП до 374,4 сП, а середня пластична в'язкість становить величину 85,72 сП. При однаковому значенні поверхневого натягу і роботи когезії, найменшим кутом змочування ($\cos\Theta=0{,}5876$) і найбільшими коефіцієнтами змочування ($s=0{,}7938$) і розтічності ($f=-19{,}34$ мН/м), а також роботами сил адгезії ($Wa=74{,}46$ мН/м), змочування ($Ww=27{,}56$ мН/м) характеризується підкладка вільхи, надалі – сосни, дубу, берези, бука і ясеню.

Для адгезиву складу $Na_2O\cdot Al_2O_3\cdot 4{,}5SiO_2\cdot 17{,}5H_2O$ при малих значеннях швидкості зсуву від 0,0378 до 1,05 1/сек зусилля зсуву збільшується від 26,21 dyne/cm^2 до 48,64 dyne/cm^2. Отримані дані значно перевищують ці ж показники рідинного скла при великих швидкостях зсуву від 14 до 39 1/сек.Для адгезиву складу $Na_2O\cdot Al_2O_3\cdot 6SiO_2\cdot 20H_2O$ на малих швидкостях зсуву спостерігається різкий сплеск зусилля зсуву від 40 до 110 dyne cm^2. Це пов'язано з процесами диспергації кремнеземистої складової. При збільшенні значень швидкості зсуву від 5 до 42 1/сек зусилля зсуву збільшується від 110 до 158 dyne/cm^2. Це пов'язано зі стабілізацією значень в'язкості з утворенням однорідної структури адгезиву

Ключові слова: алюмосилікатний адгезив, динамічна і пластична в'язкість, поверхневий натяг, кут змочування, зусилля зсуву, дерев'яна підкладка

*Received date 21.10.2019
Accepted date 06.12.2019
Published date 24.12.2019*

1. Introduction

Glued wooden structures are widely used in construction, primarily due to their high strength characteristics, moisture resistance, and a relatively low cost of installation [1, 2]. Another advantage of glued structures is the utilization of substandard wood [3]. Wood gluing mainly involve organic adhesives based on polyvinyl acetate emulsions that has water resistance indicators of D2...D4 [4], as well as phenol-formaldehyde [5], acrylic [6], epoxy [7], polyurethane [8], and others.

The share of mineral adhesives is insignificant and they are mainly used for gluing cellulose-containing materials. It is promising in order to glue wood arrays to use mineral aluminosilicate-based adhesives [9]. They should ensure, at the level of organic ones, that the adhesive joint strength is not lower than strength of wood for chipping along the fibers and stretching across the fibers. They also should demonstrate the required weatherability and the capability to withstand sufficient loads.

Mineral adhesives represent heterogeneous physical-chemical systems (suspensions). They consist of three or more phases, separated by an interface. The liquid phase is a dispersed medium with the suspended solids (dispersed phases) distributed in it, whose sizes vary from 0.5 to 100 μm. Phases may differ from each other in composition and properties, component content, thermodynamic character and in the degrees freedom. Typically, solid components in a dispersed environment are bound by a phase rule [10].

For the case where a dispersed medium is an alkaline aluminosilicate binder, highly-filled with functional additives, it manifests its heterogeneity and predisposition to sedimentation with a change in the dynamic viscosity over time.

Therefore, it is a relevant task in terms of colloidal chemistry to regulate aggregate stability and processes of structure formation in alkaline aluminosilicate suspensions that serve as a base for mineral adhesives from a technological point of view.

To control the processes of structure formation and the rheological properties of aluminosilicate adhesives, thinning and stabilizing chemical additives are used. These additives make it possible to purposefully change both their electric-surface and rheological characteristics aimed at modifying the phase interface «solid body – solution».

2. Literature review and problem statement

We did not find any papers reporting studies into the rheotechnological properties of adhesives for wood arrays. Given the fact that an aluminosilicate adhesive contains in its composition metakaolin, micro silica, and liquid glass, it is advisable to analyze scientific works on the rheology of the components specified above.

Paper [11] reports results of the gelation of a composite colloidal-silica system. It is shown that it occurs due to the hydroxylation of silica particles with the formation of primary aggregates that are chemically bonded by a gel-like siliceous phase. The influence of Cl^-, NH^{4+}, OH^- ions from a liquid phase on the formation of a silica skeleton has remained unclarified from the rheokinetic point of view.

In [12], a rotary viscosimetry method was applied to study the dynamics of the destruction of dispersed structures in aerosil A-175 in water and aqueous solutions of non-iogenic polyethylene oxide. It was found that the presence of gas (air) inclusions causes the structural and hydrodynamic instability of dispersions. The aerosil dispersions, modified by polyethylene oxide, belong to the thixotropically structured systems. Increasing the concentration of polyethylene oxide leads to a substantial increase in the structure arrangement of the system and changes the rheological behavior of the dispersion. At the concentrations of polyethylene oxide $SPEO<1.25\cdot10^{-4}$ mol/l, dispersions demonstrate the quasi-Newtonian current character. At $SPEO>2.5\cdot10^{-3}$ mol/l, the dispersion current demonstrates attributes typical of highly structured solid-state (Rebinder) systems.

Paper [13] investigated the electrokinetic and rheological properties of kaolin dispersions with a volumetric share of solid phase particles at $\varphi=0.20$ and $\varphi=0.47$ in the presence of a sodium silicate dispersant ($Xs=0.075$ mg dispersant/m^2 and $Xs=0.225$ mg dispersant/m^2). Dispersions with $Xs\leq0.075$ mg dispersant/m^2 demonstrated plastic behavior (when tested for shear) and the characteristics of a gel (at vibrational tests) due to the large aggregation of kaolinite particles. Dispersions with a dispersant in the amount $Xs\geq0.105$ mg/m^2 demonstrated rarefaction characteristics at shear and behaved as viscoelastic fluids at vibrational tests. Such a behavior is typical of dense dispersions with lamellar colloidal particles, which are well stabilized by electrostatic repulsion, which is characteristic of the stabilized highly concentrated dispersions.

Works [14, 15] report results from regulating the rheological properties of kaolin and kaolin-hydrolysaceous clay suspensions and ceramic slurries. It is shown that control becomes possible due to effective organo-mineral diluents. The effect of diluents is associated with a change in the electrokinetic potential of the system due to the parallel progress of two processes – cation exchange and physical adsorption of anions. The authors did not study the influence of diluents on the reokinetics of dispersions over time. It was noted in [16] that the nonaqueous layered silicate suspensions exhibit a complex rheology behavior due to the sensitivity of the structure to the flow. The nature of nonequilibrium and metastable structures, caused by the flow in the investigated layered silicate suspensions with their linear and non-linear viscous elastic properties, is based on a fractal scaling theory, whereby the space of percolation networks, consisting of clusters with a mass fractal dimensionality of DfÀ2, makes it possible to identify the formation of aggregates in the flow of a dispersed environment. It was noted that the suspension shear speed is associated with a reversible aggregation process. After stopping the flow, the authors observed the thixotropic properties in the suspension, associated with local restructuring at the nanolevel.

Since the main phases in the process of polycondensation of aluminosilicate structures are zeolite-like new formations [17, 18], work [19] carried out a research of the rheological characteristics of natural zeolite aqueous suspensions. It is shown that at pH7 at the concentration of particulate matter to 20 % the suspensions demonstrated a Newtonian behavior and withstood higher loads at shear. With a solid phase content exceeding 35 %, the suspensions showed hysteresis and had a limit of fluidity, which increased exponentially at an increase in solid substance. The emergence of the yield strength and its rapid growth at a relatively low concentration of solids, compared with other concentrations of particulate matter in suspensions, were explained by intra-particle interaction.

From a technological point of view, the dilution and increased fluidity of aluminosilicate suspensions is possible under conditions of cavitation treatment [20–23], following which the dynamic viscosity of the compositions was characterized by pseudoplasticity and homogeneity.

3. The aim and objectives of the study

The aim of this study is to determine the effect of the composition of an alkaline aluminosilicate binding agent on the rheotechnological properties of aluminosilicate adhesives for wood, which would make it possible, under industrial conditions, to control the time it takes for both causing and gluing the arrays of wood.

To achieve the set aim, the following tasks have been solved:

– to define the rheotechnological characteristics of sodium soluble glass as the dispersed phase of an aluminosilicate adhesive;

– to determine the rheotechnological characteristics of an aluminosilicate adhesive based on the alkaline aluminosilicate binding agent with a composition of $Na_2O\cdot Al_2O_3\cdot 4.5SiO_2\cdot 17.5H_2O$;

– to determine the rheotechnological characteristics of an aluminosilicate adhesive based on the alkaline aluminosilicate binding agent with a composition of $Na_2O\cdot Al_2O_3\cdot 6SiO_2\cdot 20H_2O$.

4. Materials for obtaining rheotechnological aluminosilicate adhesives and methods to study them

In order to obtain the alkaline aluminosilicate binding agent with a composition of $Na_2O\cdot Al_2O_3\cdot(4.5–6)SiO_2\cdot(17.5–20)H_2O$ to serve as a model system, we used metakaolin, micro silica, and sodium liquid glass. Calculation of the optimum ratio of oxides was carried out taking into consideration recommendations from [24–26]. We adjusted the composition of the binding agent for alkaline oxides by using their aqueous solutions.

According to work [9], it is expedient to use adhesives with a ratio of basic structure forming oxides SiO_2/Al_2O_3= =4.5 and SiO_2/H_2O=17.5 for gluing wood arrays. The adhesives at ratio SiO_2/Al_2O_3=6 and SiO_2/H_2O=20, representing a more elastic system [27–31], should be use to glue plywood and structural elements with an enhanced flame resistant of the adhesive joint.

To obtain an aluminosilicate adhesive for gluing wood arrays, a series of functional organo-mineral additives were expediently introduced into the composition [32]. The additives would contribute to the regulation of rheological characteristics – viscosity, spreadability, wetting angle, etc. The set of the organo-mineral additives is the «know-how» and is not disclosed in this work.

We prepared the alkaline aluminosilicate binder and the adhesive based on it at a laboratory dissolver.

Conditional viscosity of suspensions was determined using the viscometer VZ 246 with a hole diameter of 4–6 mm at a temperature of 20±2 °C.

The rheological characteristics were acquired using the Brookfield viscometer LV D2T in the speed range from 0 to 200 RPM applying the spindles LV-2C(66) and LV-3C(67).

We determined a surface tension coefficient for the aluminosilicate adhesives by a drop separation method [5, 33]:

$$\gamma = \frac{mg}{nD},\ \text{mN/m},$$

where: m is the mass of a suspension, g; g is the acceleration of gravity force, m/cm^2; n is the number of drops, n=25; D is the capillary diameter, mm (D=5 mm).

We determined the work of adhesion (*Wa*), cohesion (*Wk*), wetting (*Ww*) forces, as well as wetting (*S*) and spreadability (*f*) coefficients, according to data from paper [34].

Wetting angle was determined by digital photography followed by image processing using the software paint.net and COMPASS.

The wood backings used were alder, birch, pine, ash, oak, and beech wood. The samples of wood were characterized by an equilibrium humidity of 12 % and a surface roughness of 80 µm. The criteria that were chosen for estimating the rheotechnological characteristics of aluminosilicate adhesive suspensions included: dynamic viscosity, plastic viscosity, the cosine of the wetting angle, surface tension, and shear force.

The object selected for comparing the rheotechnological characteristics was sodium liquid glass with silicate module *Ms*=2.84 and density 1.383 g/cm^3.

5. Results from studying the rheotechnological properties of aluminosilicate adhesives

The main dispersive environment both for the alkaline aluminosilicate binder and the adhesive on its base is sodium liquid glass. Determining its rheotechnological characteristics is important to understand changes in the rheotechnological characteristics of aluminosilicate adhesives when they are used to wet the surface of wooden backings made from different types of wood in the process of coating and gluing.

Fig. 1–3 show results of change in the dynamic and plastic viscosity of sodium liquid glass, as well as adhesives obtained based on the binding agents with a composition of $Na_2O{\cdot}Al_2O_3{\cdot}4.5SiO_2{\cdot}17.5H_2O$ and $Na_2O{\cdot}Al_2O_3\times$ $\times6SiO_2{\cdot}20H_2O$, depending on spindle rotation velocity and the momentum; Fig. 4 – shear efforts on shear rate.

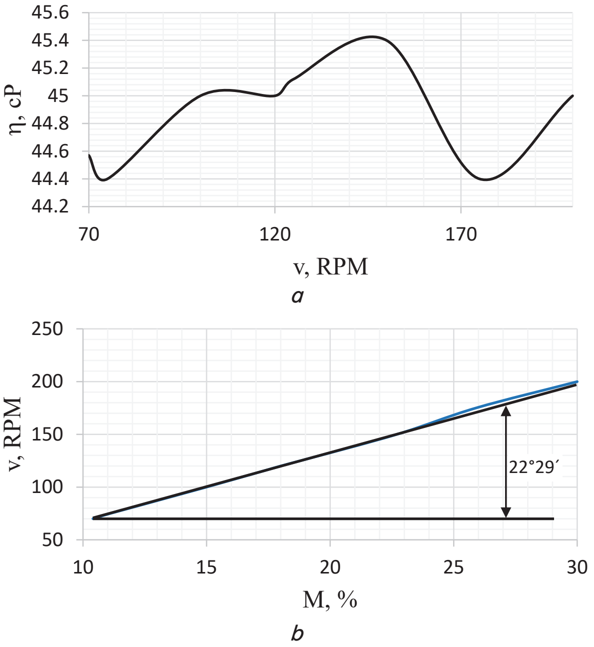


Fig. 1. Change in viscosity depending on spindle rotation velocity and the momentum: *a* – dynamic; *b* – plastic

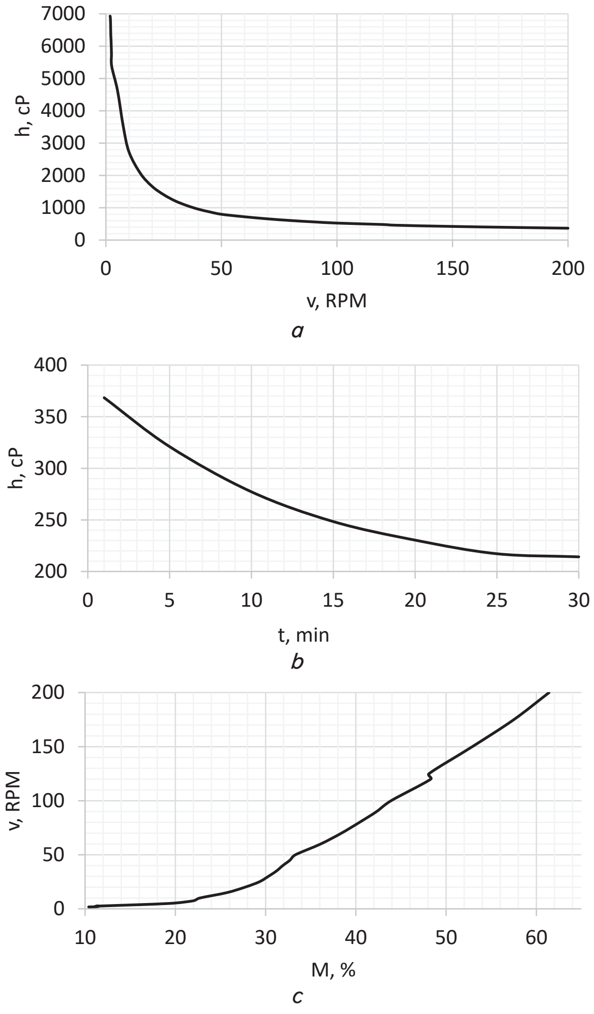
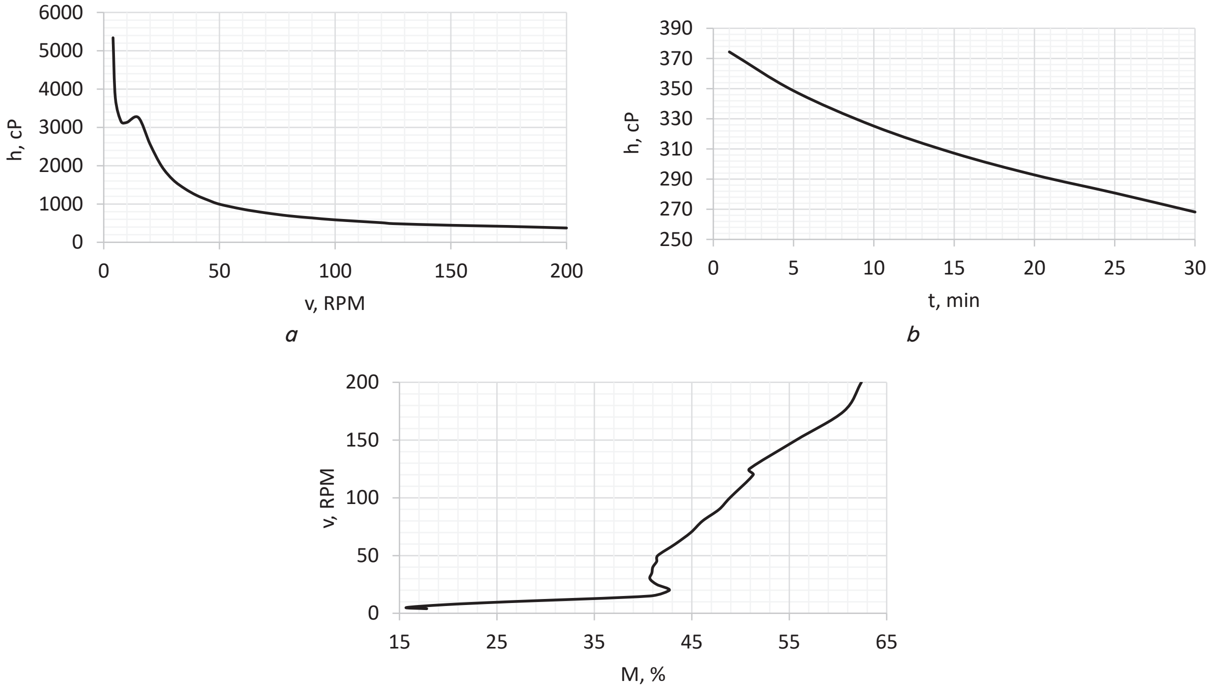


Fig. 2. Change of viscosity in the aluminosilicate binder with a composition of $Na_2O{\cdot}Al_2O_3{\cdot}4.5SiO_2{\cdot}17.5H_2O$ depending on spindle rotation velocity and time and the momentum: *a, b* – dynamic; *c* – plastic

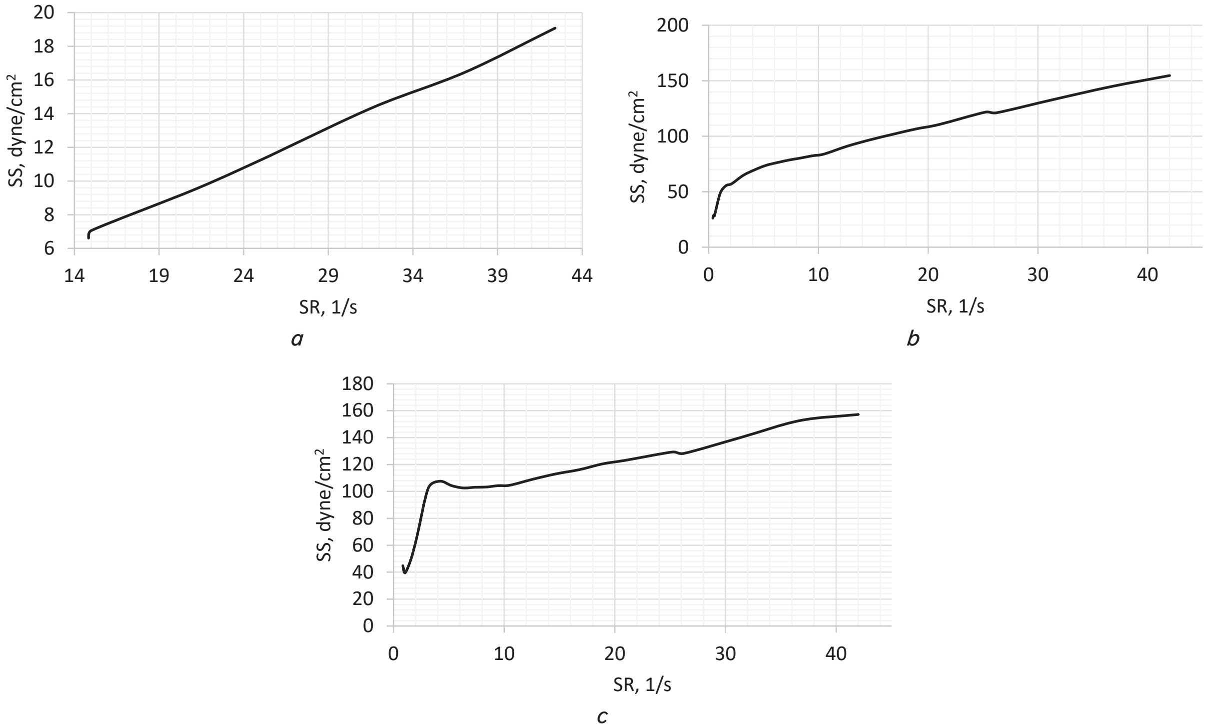


a

b

c

Fig. 3. Change of viscosity in the aluminosilicate binder with a composition of $Na_2O{\cdot}Al_2O_3{\cdot}6SiO_2{\cdot}20H_2O$ depending on spindle rotation velocity and time and the momentum: *a, b* — dynamic; *c* — plastic



a

b

c

Fig. 4. Dependence of shear efforts on the shear rate of adhesive suspensions, obtained based on: *a* — pure liquid glass; *b* — binder with a composition of $Na_2O{\cdot}Al_2O_3{\cdot}4.5SiO_2{\cdot}17.5H_2O$; *c* — binder with a composition of $Na_2O{\cdot}Al_2O_3{\cdot}6SiO_2{\cdot}20H_2O$

Fig. 5–7 show results from wetting the surface of backings made from wood of different breeds with sodium liquid glass and the adhesives that were obtained based on binders with a composition of $Na_2O{\cdot}Al_2O_3{\cdot}4.5SiO_2{\cdot}17.5H_2O$ and $Na_2O{\cdot}Al_2O_3{\cdot}6SiO_2{\cdot}20H_2O$.

The colloidal-chemical characteristics of sodium liquid glass and the suspension of adhesives based on the alkaline aluminosilicate binder with compositions $Na_2O{\cdot}Al_2O_3\times$ $\times4.5SiO_2{\cdot}17.5H_2O$ and $Na_2O{\cdot}Al_2O_3{\cdot}6SiO_2{\cdot}20H_2O$ are given in Tables 1–3.

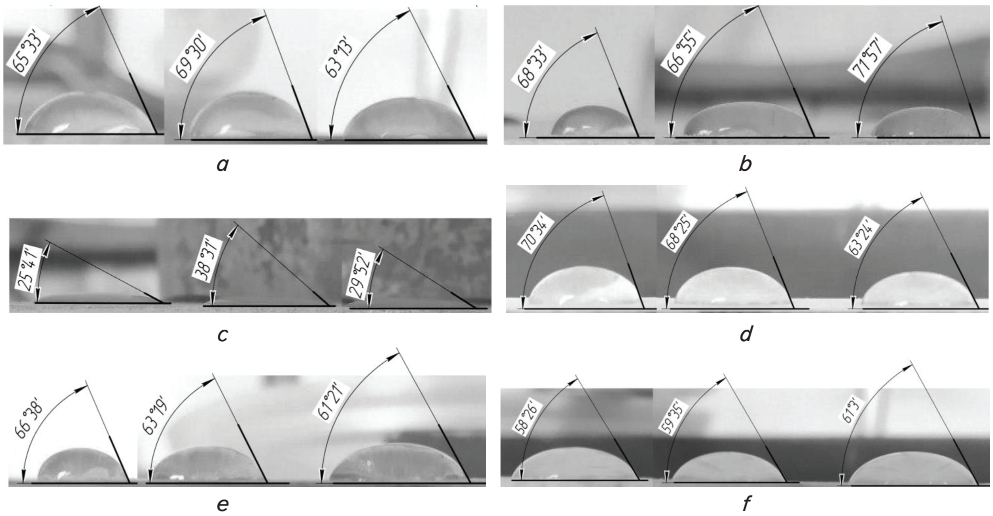


Fig. 5. Wetting angle of liquid glass on wooden backings: *a* – Alder, Θ_{av}=65°92′; *b* – Birch, Θ_{av}=68°82′; *c* – Pine, Θ_{av}=31°08′; *d* – Ash, Θ_{av}=67°28′; *e* – Oak, Θ_{av}=63°59′; *f* – Beech, Θ_{av}=59°64′

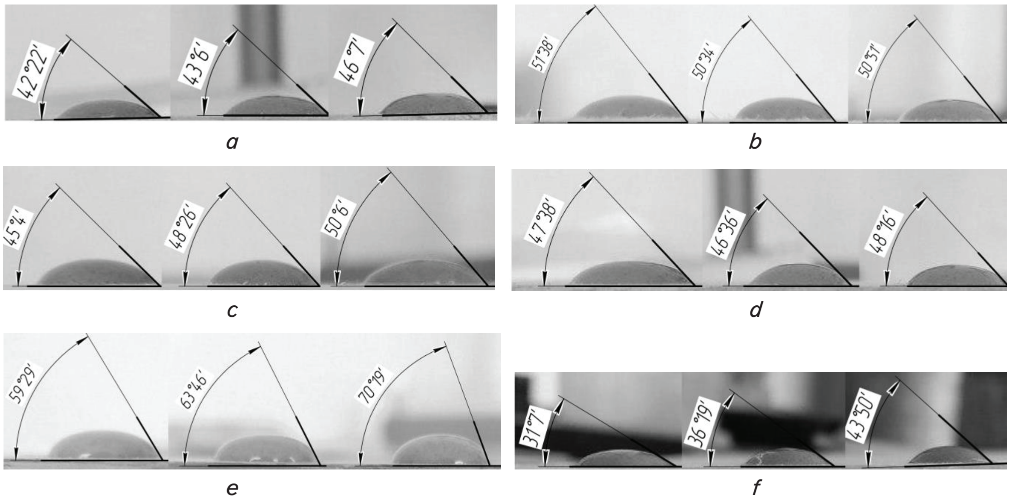


Fig. 6. Wetting angle of the adhesive suspension based on the alkaline aluminosilicate binder with a composition of $Na_2O{\cdot}Al_2O_3{\cdot}4.5SiO_2{\cdot}17.5H_2O$ on wooden backings: *a* – Alder, Θ_{av}=44°17′; *b* – Birch, Θ_{av}=50°74′; *c* – Pine, Θ_{av}=48°09′; *d* – Ash, Θ_{av}=47°3′; *e* – Oak, Θ_{av}=64°31′; *f* – Beech, Θ_{av}=37°13′

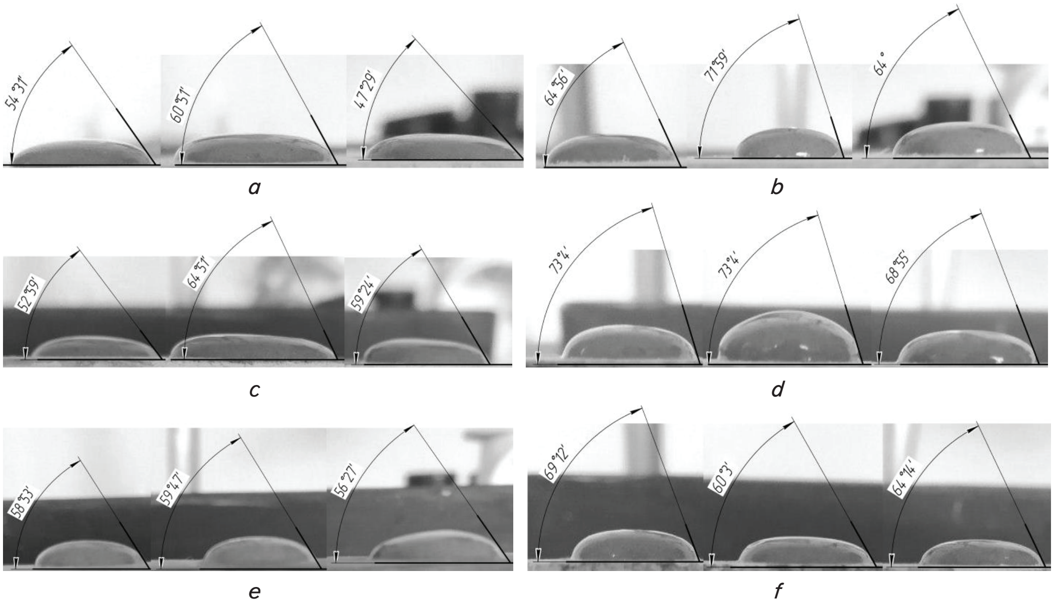


Fig. 7. Wetting angle of the adhesive suspension based on the alkaline aluminosilicate binder with a composition of $Na_2O{\cdot}Al_2O_3{\cdot}6SiO_2{\cdot}20H_2O$ on wooden backings: *a* – Alder, Θ_{av}=54°01′; *b* – Birch, Θ_{av}=66°72′; *c* – Pine, Θ_{av}=58°78′; *d* – Ash, Θ_{av}=71°78′; *e* – Oak, Θ_{av}=58°09′; *f* – Beech, Θ_{av}=64°52′

Table 1

Colloidal-chemical properties of liquid glass

Indicators	UM	Backing from wood breeds					
		alder	birch	pine	ash	oak	beech
Ms=2.84, density 1.383 g/cm^3, surface tension γ=54.3 mN/m, conditional viscosity v=14 s							
cosΘ	–	0.408	0.3613	0.8564	0.3862	0.4448	0.5054
Wa	mN/m	76.46	73.92	100.81	75.27	78.45	81.74
Wk	mN/m	108.6	108.6	108.6	108.6	108.6	108.6
Ww	mN/m	22.15	19.62	46.5	20.97	24.15	27.44
s	–	0.7041	0.6807	0.9283	0.69.31	0.7228	0.7527
f	mN/m	–32.14	–34.68	–7.79	–33.33	–30.15	–26.86

Table 2

Colloidal-chemical properties of aluminosilicate binder with a composition of $Na_2O{\cdot}Al_2O_3{\cdot}4.5SiO_2{\cdot}17.5H_2O$

Indicators	UM	Backing from wood breeds					
		alder	birch	pine	ash	oak	beech
density 1.427 g/cm^3, surface tension γ=32.4 mN/m, conditional viscosity v=65 s							
cosΘ	–	0.7173	0.6328	0.66796	0.6782	0.4335	0.7973
Wa	mN/m	55.64	52.9	54.04	54.37	46.45	58.23
Wk	mN/m	64.8	64.8	64.8	64.8	64.8	64.8
Ww	mN/m	23.24	20.5	21.64	21.97	14.05	25.83
s	–	0.8586	0.8164	0.834	0.839	0.717	0.8986
f	mN/m	–9.16	–11.9	–10.76	–10.43	–19.35	–6.5

Table 3

Colloidal-chemical properties of aluminosilicate binder with a composition of $Na_2O{\cdot}Al_2O_3{\cdot}6SiO_2{\cdot}20H_2O$

Indicators	UM	Backing from wood breeds					
		alder	birch	pine	ash	oak	beech
density 1.463 g/cm^3, surface tension γ=46.9 mN/m, conditional viscosity v=32 s							
cosΘ	–	0.5876	0.3952	0.5183	0.3127	0.5286	0.4302
Wa	mN/m	74.46	65.43	71.21	61.56	71.69	67.08
Wk	mN/m	93.8	93.8	93.8	93.8	93.8	93.8
Ww	mN/m	27.56	18.53	24.31	14.67	24.79	20.18
s	–	0.7938	0.6975	0.7592	0.6563	0.7643	0.7151
f	mN/m	–19.34	–28.37	–22.59	–32.34	–22.11	–26.72

6. Discussing the experimental results from studying the rheotechnological properties of aluminosilicate adhesives

Fig. 1, *a* shows that in the speed range from 70 to 200 RPM the dynamic viscosity of sodium liquid glass varies nonlinearly at a magnitude of 45±0.4 Pa·s.

The plastic viscosity of the liquid glass, which is determined from the cotangent of the inclination angle of the straight line in the dependence $v=f(M)$, amounts to the magnitude of 84.43 sP in the velocity range from 70 to 200 RPM. Difference in the values for dynamic and plastic viscosity can be explained by the structure arrangement of the structural components of glass, namely colloidal particles of ortho-, di- and trisilicates of sodium in the dispersed environment [35].

One can see from Fig. 2, *a* that in the speed range from 0 to 200 RPM the dynamic viscosity of the adhesive suspension based on the alkaline aluminosilicate binder with a composition of $Na_2O{\cdot}Al_2O_3{\cdot}4.5SiO_2{\cdot}17.5H_2O$ changes in line with an exponential dependence characterizing the pseudoplastic type of a liquid. The same dependence is observed for a change in the values of dynamic viscosity (v=200 RPM=const) d depending on the time of spindle rotation (Fig. 2, *b*).

Plastic viscosity of the adhesive with a composition of $Na_2O{\cdot}Al_2O_3{\cdot}4.5SiO_2{\cdot}17.5H_2O$ was determined based on the cotangent of the inclination angle of the straight line in the dependence $v=f(M)$. In the speed range from 0 to 200 RPM, its magnitude is 86.27 sP (Fig. 2, *c*). The increase in the values for plastic viscosity, in comparison with the same indicator for the liquid glass, is explained by the larger filling of the dispersed environment with the dispersive phase, as evidenced by the increase in spindle torque.

One can see from Fig. 3, *a* that in the speed range from 0 to 200 RPM, the dynamic viscosity of the adhesive suspension based on the alkaline aluminosilicate binder with a composition of $Na_2O{\cdot}Al_2O_3{\cdot}6SiO_2{\cdot}20H_2O$ varies in line with an exponential dependence, which characterizes the pseudoplastic type of a liquid. The same dependence is observed for a change in the dynamic viscosity values (v=200 RPM=const) d depending on the time of spindle rotation (Fig. 3, *b*).

Plastic viscosity of the adhesive suspension based on the alkaline aluminosilicate binder with a composition of $Na_2O{\cdot}Al_2O_3{\cdot}4.5SiO_2{\cdot}17.5H_2O$, which was determined based on the cotangent of the inclination angle of the straight line in the dependence $v=f(M)$, amounts to a magnitude of 85.72 sP. Alder in the speed range from 0 to 200 RPM. The increase in the values of plastic viscosity, in comparison with the same indicator for the liquid glass, is explained by the larger filling of the dispersed environment with the dispersive phase, as evidenced by the increase in spindle torque.

Changes in the deformation characteristics of liquid glass and adhesion suspensions are shown in Fig. 4. It follows from the obtained experimental data that for liquid glass the shear effort is proportional to the shear rate and is linear in character (Fig. 4, *a*). For the adhesive of composition $Na_2O{\cdot}Al_2O_3{\cdot}4.5SiO_2{\cdot}17.5H_2O$ (Fig. 4, *b*) the character of change in dependence is similar to the liquid glass. There is an abnormal effect at small values of shear rate from 0.0378 to 1.05 1/s. The shear effort increases from 26.21 dyne/cm^2 to 48.64 dyne/cm^2, exceeding the same indicators for liquid glass at larger shear speeds from 14 to 39 1/s. For the adhesive of composition $Na_2O{\cdot}Al_2O_3{\cdot}6SiO_2{\cdot}20H_2O$ (Fig. 4, *c*), one observes at low shear speeds a sharp surge in shear effort from 40 to 110 dyne/cm^2. With an increase in the shear rate values from 5 to 42 1/s the shear effort increases from 110 to 158 dyne/cm^2.

The derived rheotechnological characteristics of the examined compositions contribute to understanding the changes in their colloidal-chemical characteristics when wetting a wood surface.

When applying liquid glass drops on wooden backings from different breeds, one can see that at the same parameters for surface roughness the wetting angle does differ; most likely it depends on the viscosity, surface charge, and density of the wood breed (Fig. 5).

The smallest value of wetting angle Θ_{av}=31°08′ is characteristic of pine, which is explained by the lower value of its density, porosity characteristics, etc.

For birch, the wetting angle value is the largest Θ_{av}=68°82′ and it is dense enough compared to other backings. The lowest value for wetting angle Θ_{av}=37°13′ is characteristic of beech wood, the largest, Θ_{av}=64°31′, of oak wood, which is explained by the lower value of its density, porosity characteristics, etc.

As seen from data in Table 1, at the same value of superficial tension and cohesive work, the smallest wetting angle (cosΘ=0.8564) and the largest coefficients of wetting (s=0.9283) and spreading (f=–7.79 mN/m), as well as the work of adhesion forces (Wa=100.81 mN/m), wetting forces (Ww=46.5 mN/m), for liquid glass are demonstrated by a pine backing.

When applying droplets of the adhesive based on the alkaline aluminosilicate binder with a composition of $Na_2O{\cdot}Al_2O_3{\cdot}4.5SiO_2{\cdot}17.5H_2O$ onto backings made from different types of wood, one can see that at the same parameters for surface roughness, the wetting angle does differ and, most likely, it depends on the surface charge and density of the wood breed (Fig. 6). The smallest wetting angle value Θ_{av}=54°01′ is characteristic for alder wood, the largest Θ_{av}=71°78′ for ash wood, due to the greater value of its density, the characteristics of porosity, etc.

It was noted that at the same value of surface tension and cohesive work (Table 2), the smallest wetting angle (cosΘ=0.7973) and the largest coefficients of wetting (s=0.8986) and spreading (f=–6.5 mN/m), as well as the work of adhesion forces (Wa=58.23 mN/m), wetting forces (Ww=25.83 mN/m), are demonstrated by backings made of beech, followed by alder, ash, pine, birch, and oak.

When applying droplets of the adhesive based on the alkaline aluminosilicate binder with a composition of $Na_2O{\cdot}Al_2O_3{\cdot}4.5SiO_2{\cdot}17.5H_2O$ onto backings made from different types of wood, one can see that at the same parameters for surface roughness the wetting angle does differ; most likely, it depends on the surface charge and density of the wood breed (Fig. 7). The smallest wetting angle value Θ_{av}=54°01′ is characteristic of alder wood, the largest Θ_{av}=71°78′ – of ash wood, due to the greater value of its density, the characteristics of porosity, etc.

It was shown that at the same value of surface tension and cohesive work (Table 3) the smallest wetting angle (cosΘ=0.5876) characterizes the alder backing, followed by pine, oak, birch, beech, and ash.

Such a behavior of suspensions clearly manifests thixotropy, it is consistent with data from papers [36, 37] and makes it possible to control the gluing of arrays of different types of wood with a certain time of survivability, which makes it possible to develop the mechanisms to feed aluminosilicate adhesives to gluing sites, to predict the conditions for thermal treatment of glued arrays, etc. Special features of this study relate, first, to that an aluminosilicate adhesive has a mineral nature and exhibits resistance to fire, and other factors; second, to that, by controlling its rheotechnological properties, it is possible to use it at automated lines for the production of wooden pallets.

Our studies in the future will be aimed at studying the yield strength of aluminosilicate adhesives by reducing the size of dispersed particles, providing for uniformity with the increased adhesive capacity under conditions of cavitation treatment of aluminosilicate suspensions.

6. Conclusions

1. It has been established that in the speed range from 70 to 200 RPM the dynamic and plastic viscosity of sodium liquid glass changes linearly and amounts to a magnitude of 45±0.4 sP and 84.43 sP, respectively. It was noted that at the same value of surface tension and cohesive work, the smallest wetting angle (cosQ=0.8564) characterizes the pine backing.

2. For the adhesive based on the alkaline aluminosilicate binder with a composition of $Na_2O{\cdot}Al_2O_3{\cdot}4.5SiO_2{\cdot}17.5H_2O$, the dynamic viscosity in the range of speeds from 0 to 200 RPM varies from 6,933 sP to 368.4 sP, and the mean plastic one amounts to a magnitude of 86.27 sP. At small values of shear rate from 0.0378 to 1.05 1/s, the shear effort increases from 26.21 dyne/cm^2 to 48.64 dyne/cm^2, exceeding the same indicators for liquid glass at large shear speeds from 14 to 39 1/s. It was noted that at the same value for surface tension and cohesive work, the smallest wetting angle (cosΘ=0.7973) is demonstrated by the beech backing, followed by alder, ash, pine, birch, and oak.

3. For the adhesive based on the alkaline aluminosilicate binder with a composition of $Na_2O{\cdot}Al_2O_3{\cdot}6SiO_2{\cdot}20H_2O$ the dynamic viscosity in the speed range from 0 to 200 RPM varies from 5,340 sP to 374.4 sP, and the mean plastic one amounts to a magnitude of 85.72 sP. It was discovered that at low shear rates there is a sharp surge in shear effort from 40 to 110 dyne/cm^2, which is associated with the dispersing processes of silica component; and with an increase in the shear rate values from 5 to 42 1/s the shear effort increases from 110 to 158 dyne/cm^2, which is due to the stabilization of values for viscosity and the homogeneity of the adhesive structure. It was noted that at the same value for surface tension and cohesive work, the smallest angle of wetting (cosΘ=0.5876) characterizes the alder backing, followed by pine, oak, birch, beech. and ash.

Acknowledgements

Authors express their gratitude for the financial support of the work performed within the framework of budgetary financing No. 2DB-2017, as well as for the development of research topics in the Scientific cooperation program COSTActionCA15202 «Self-Healing Concrete: The path to sustainable Construction» in the framework program of the European Union HORIZON2020.

References

1. Hrulev, V. M. (Ed.) (1983). Derevyannye konstruktsii i detali. Moscow: Stroyizdat, 288.
2. Vernigorova, V. N., Sadenko, S. M. (2014). Klei i skleivanie. Penza: PGUAS, 120.
3. Tambi, A. A., Chubinsky, A. N., Chauzov, K. V., Kulikov, A. M. (2016). Research of adhesive bond of wood. Forestry bulletin, 2, 120–126.
4. Rindler, A., Hansmann, C., Konnerth, J. (2019). The effect of moisture on the mechanical response of wood, adhesive and their interphase by means of nanoindentation. Wood Science and Technology, 53 (4), 729–746. doi: https://doi.org/10.1007/s00226-019-01100-4
5. Ülker, O. (2016). Wood Adhesives and Bonding Theory. Adhesives – Applications and Properties. doi: https://doi.org/10.5772/65759

6. Pizzi, A. (1994). Advanced Wood Adhesives Technology. New York, 304.
7. Frihart, C. R. (2015). Introduction to Special Issue: Wood Adhesives: Past, Present, and Future. Forest Products Journal, 65 (1–2), 4–8. doi: https://doi.org/10.13073/65.1-2.4
8. Liu, X., Zhang, X., Long, K., Zhu, X., Yang, J., Wu, Y. et. al. (2012). PVA wood adhesive modified with sodium silicate cross-linked copolymer. Proceedings of 2012 International Conference on Biobase Material Science and Engineering. doi: https://doi.org/10.1109/bmse.2012.6466192
9. Krivenko, P., Petropavlovsky, O., Vozniuk, G. (2018). Alkaline Aluminosilicate Binder for Gluing Wood Board Materials. Key Engineering Materials, 761, 11–14. doi: https://doi.org/10.4028/www.scientific.net/kem.761.11
10. Sychev, M. M. (1986). Neorganicheskie klei. Leningrad: Himiya, 152.
11. Poddenezhniy, E. N., Boyko, A. A., Pahovchishin, S. V. (2003). Reologiya kompozitsionnyh kremnezemsoderzhashchih kolloidnyh sistem i modelirovanie protsessov ih destabilizatsii. Vestnik Gomel'skogo gosudarstvennogo tehnicheskogo universiteta im. P. O. Suhogo, 3, 20–27.
12. Zakordonskiy, V., Lazaruk, B. (2014). Processes of aggregation and rheology of aerosil A-175 dispersions, modified by polyethylene-oxide. Visnyk of the Lviv University. Series Chemistry, 55 (2), 472–485.
13. Amorós, J. L., Beltrán, V., Sanz, V., Jarque, J. C. (2010). Electrokinetic and rheological properties of highly concentrated kaolin dispersions: Influence of particle volume fraction and dispersant concentration. Applied Clay Science, 49 (1–2), 33–43. doi: https://doi.org/10.1016/j.clay.2010.03.020
14. Zdorenko, N. M. (2009). Reotehnologicheskie svoystva kaolinitovyh i kaolinit-gidroslyudistyh glinistyh mass s kompleksnoy organomineral'noy dobavkoy. Belgorod, 140.
15. Klimosh, Yu. A., Levitskiy, I. A. (2011). Reologicheskie svoystva shlikerov na osnove polimineral'nyh glin s dobavkoy elektrolitov. Steklo i keramika, 4, 19–22.
16. McIntyre, E. C., Filisko, F. E. (2009). Squeeze Flow Rheology of Zeolite Suspensions. Applied Rheology, 19 (4), 44322-1–44322-8. doi: https://doi.org/10.1515/arh-2009-0016
17. Provis, J. L, van Deventer, S. J. (2009). Geopolymers: Structures, Processing, Properties and Industrial Applications. Elsevier, 464. doi: https://doi.org/10.1533/9781845696382
18. Krivenko, P., Guzii, S. (2018). The effect of modifying additives on the modulus of elasticity and strength of adhesives based on an alkaline aluminosilicate binder. Proceed. of the 20. Ibausil. Internationale Baustofftagung. Weimar, 2-1213–2-1218.
19. Zacahua-Tlacuatl, G., Pérez-González, J., Javier Castro-Arellano, J., Balmori-Ramírez, H. (2010) Rheological Characterization and Extrusion of Suspensions of Natural Zeolites. Applied Rheology, 20 (3), 34037-1–34037-10. doi: http://doi.org/10.3933/ApplRheol-20-34037
20. Guzii, S., Hela, R., Kyrychok, V. (2013). Rehabilitation of Concrete Surfaces of Hydropower Engineering Structures Deteriorated by Soft Corrosion and Cavitation. Advanced Materials Research, 688, 107–112. doi: https://doi.org/10.4028/www.scientific.net/amr.688.107
21. Krivenko, P., Guziy, S., Abdullah Al Musa, J. (2015). The Influence of Cavitation Treatment on Amorphization of Kaolinite in the Dispersion of the «Kaolin–$Na_2O{\cdot}nSiO_2{\cdot}mH_2O$–NaOH–$H_2O$» Composition. Calcined Clays for Sustainable Concrete, 387–393. doi: https://doi.org/10.1007/978-94-017-9939-3_48
22. Krivenko, P. V., Guzii, S., Hela, R. (2017). The Influence of Cavitation Treatment on Nano Structuring of Alkali Aluminosilicate Binder for Intumescent Coatings. Materials Science Forum, 908, 63–70. doi: https://doi.org/10.4028/www.scientific.net/msf.908.63
23. Martyntsev, V., Guzii, S., Nazarenko, I., Glyva, V., Guzii, O. (2017). Investigation of rheo-mechanical properties of cement suspensions activated in a hydrodynamic cavitator. Technology Audit and Production Reserves, 6 (3 (38)), 18–25. doi: https://doi.org/10.15587/2312-8372.2017.119479
24. Kryvenko, P., Volodymyr, K., Guzii, S. (2016). Influence of the ratio of oxides and temperature on the structure formation of alkaline hydro-aluminosilicates. Eastern-European Journal of Enterprise Technologies, 5 (5 (83)), 40–48. doi: https://doi.org/10.15587/1729-4061.2016.79605
25. Barrer, R. (1982). Hydrothermal chemistry of zeolites. Academic Press, 360.
26. Mejía de Gutiérrez, R., Trochez, J. J., Rivera, J., Bernal, S. A. (2015). Synthesis of geopolymer from spent FCC: Effect of SiO_2/Al_2O_3 and Na_2O/SiO_2 molar ratios. Materiales de Construcción, 65 (317), e046. doi: https://doi.org/10.3989/mc.2015.00814
27. Kravchenko, A., Guzii, S. (2015). Determining the fire resistance properties of timber, protected by geocement-based coatings. Eastern-European Journal of Enterprise Technologies, 1 (5 (73)), 38–41. doi: https://doi.org/10.15587/1729-4061.2015.36843
28. Krivenko, P. V., Guzii, S. G., Bodnarova, L., Valek, J., Hela, R., Zach, J. (2016). Effect of thickness of the intumescent alkali aluminosilicate coating on temperature distribution in reinforced concrete. Journal of Building Engineering, 8, 14–19. doi: https://doi.org/10.1016/j.jobe.2016.09.003
29. Krivenko, P. V., Guzii, S. G., Bondarenko, O. P. (2019). Alkaline Aluminosilicate Binder-Based Adhesives with Increased Fire Resistance for Structural Timber Elements. Key Engineering Materials, 808, 172–176. doi: https://doi.org/10.4028/www.scientific.net/kem.808.172
30. Guzii, S. G., Krivenko, P. V., Bondarenko, O. P., Kopylova, T. (2019). Study on Physico-Mechanical Properties of the Modified Alkaline Aluminosilicate Adhesive-Bonded Timber Elements. Solid State Phenomena, 296, 112–117. doi: https://doi.org/10.4028/www.scientific.net/ssp.296.112
31. Krivenko, P. V., Guzii, S. G., Bodnarova, L., Valek, J., Hela, R., Zach, J. (2016). Effect of thickness of the intumescent alkali aluminosilicate coating on temperature distribution in reinforced concrete. Journal of Building Engineering, 8, 14–19. doi: https://doi.org/10.1016/j.jobe.2016.09.003
32. Ershov, Yu. A. (2013). Kolloidnaya himiya. Fizicheskaya himiya dispersnyh sistem. Moscow: GEOTAR-Media, 352.

33. Glazacheva, E. N., Uspenskaya, M. V. (2015). Kolloidnaya himiya. Metodicheskie ukazaniya k vypolneniyu laboratornyh rabot. Sankt-Peterburg: Universitet ITMO, 62.
34. Guzii, S. (2017). Investigation of the influence of organomineral additives on the colloid-chemical properties of geocement dispersion. Technology Audit and Production Reserves, 3 (1 (35)), 38–43. doi: https://doi.org/10.15587/2312-8372.2017.105678
35. Figovskiy, O. L., Kudryavtsev, P. G. (2014). Liquid glass and aqueous solutions of silicates, as a promising basis for technological processes of new nanocomposite materials. Inzhenerniy vestnik Dona. Available at: https://cyberleninka.ru/article/n/zhidkoe-steklo-i-vodnye-rastvory-silikatov-kak-perspektivnaya-osnova-tehnologicheskih-protsessov-polucheniya-novyh
36. Panahov, G. M., Abbasov, E. M., Yuzbashiyeva, A. O., Rasulova, S. R., Guseynov, V. G. (2016). Rheological properties of structured disperse systems. Oil and Gas Business, 15 (2), 133–140.
37. Malkin, A. Ya., Isaev, A. I. (2007). Reologiya: kontseptsii, metody, prilozheniya. Sankt-Peterburg: Professiya, 560.

Показано, що значне зниження «вуглецевого сліду» у технології будівельного виробництва досягається за рахунок виготовлення клінкер-ефективних бетонів на основі портландцементів композиційних. Проведеними дослідженнями встановлено, що нерівномірний розподіл зернових фракцій суміші заповнювачів та їх підвищена загальна питома поверхня призводять до збільшення водопотреби, розшарування, водовідділення бетонної суміші та зниження міцності бетону. Для досягнення більш високої щільності упаковки зерен реалізовано підхід, який ґрунтується на оптимізації гранулометричного складу компонентів бетонної суміші. Встановлено, що підвищені показники ранньої міцності бетонів на основі низькоемісійних композиційних цементів досягаються за рахунок введення суперпластифікаторів на основі ефіру полікарбоксилату (PCE) та лужно-сульфатної активації. Для встановлення зв'язку між екологічними та технічними властивостями бетону визначено ефективність клінкеру в бетоні. При збільшенні міцності модифікованого бетону на основі портландцементу композиційного CEM II/B-M 32,5 R (клінкер-фактор 0,65) створюється можливість суттєвого зниження питомої витрати клінкеру на одиницю міцності до 4,5…3,0 кг/(м^3·МПа); відповідно CO_2-інтенсивність складає 3,9…2,6 кг CO_2/(м^3·МПа). Значна інтенсифікація процесів раннього структуроутворення наномодифікованих клінкер-ефективних бетонів забезпечується за рахунок комплексного підходу: оптимізації суміші компонентів, введення суперпластифікатора PCE та наномодифікаторів. З використанням методу лазерної дифракції доведено, що основний вклад у розвиток питомої поверхні наномодифікованої цементуючої матриці вносять ультратонкі частинки (K_{isa}=761,2 мкм$^{-1}$·vol. %) нано-SiO_2. Встановлено, що синергетичне поєднання мінеральних добавок в портландцементі композиційному та комплексного наномодифікатора «PCE+нано-SiO_2+C-S-H» забезпечує підвищені показники особливо ранньої міцності ($R_{c12год}$=6,4 МПа) та одержання бетонів класу C50/60 із швидким наростанням міцності (f_{cm2}/f_{cm28}=0,51). Таким чином, є підстави стверджувати про доцільність розроблення наномодифікованих клінкер-ефективних бетонів з метою забезпечення швидких темпів будівництва та вирішення проблем, пов'язаних з необхідністю реалізації стратегії низьковуглецевого розвитку

Ключові слова: клінкер-ефективний бетон, портландцемент композиційний, суперпластифікатор полікарбоксилатного типу, лужний активатор, наносиліка, рання міцність, показник емісії CO_2

UDC 666.9.035
DOI: 10.15587/1729-4061.2019.185111

DEVELOPMENT OF NANOMODIFIED RAPID HARDENING CLINKER-EFFICIENT CONCRETES BASED ON COMPOSITE PORTLAND CEMENTS

T. Kropyvnytska
PhD, Associate Professor*
E-mail: tkropyvnytska@ukr.net
M. Sanytsky
Doctor of Technical Sciences, Professor,
Head of Department*
E-mail: msanytsky@ukr.net
T. Rucinska
PhD, Associate Professor
Department of Building Physics
and Building Materials
West Pomeranian University
of Technology Szczecin
Piastow str., 50, Szczecin, Poland, 70-310
E-mail: teresa.rucinska@zut.edu.pl
O. Rykhlitska
Postgraduate Student*
E-mail: prohoniuchka@gmail.com
*Department of Building Production
Lviv Polytechnic National University
S. Bandery str., 12, Lviv, Ukraine, 79013

Received date 28.08.2019
Accepted date 20.11.2019
Published date 24.12.2019

1. Introduction

Concrete as a composite building material is widely used in construction due to its relatively low cost, variety of applications, high durability and environmental friendliness [1, 2]. It is the second most used material on the planet after water. Current trends lean towards increasing the cement content in concrete. Between 2004 and 2019 cement consumption