Инженерно-строительный журнал, № 7, 2018

doi: 10.18720/MCE.83.13

Thermal-insulation boards from fibrous plant wastes and urea-formaldehyde binder

Теплоизоляционные плиты из волокнистых растительных отходов и карбамидоформальдегидного связующего

T.N. Vahnina,
I.V. Susoeva*,
A.A. Titunin,
Kostroma State University, Kostroma, Russia

Канд. техн. наук, доцент Т.Н. Вахнина,
канд. техн. наук, доцент И.В. Сусоева*,
д-р техн. наук, профессор А.А. Титунин,
Костромской государственный
университет, г. Кострома, Россия

Key words: thermal-insulation boards; durability; static bend; thermal conductivity coefficient; water absorption; swelling; plant waste; urea-formaldehyde binder; hardener; extent of hardening

Ключевые слова: теплоизоляционные плиты; прочность; статический изгиб; коэффициент теплопроводности; водопоглощение; разбухание; растительные отходы; карбамидоформальдегидное связующее; отвердитель; степень отверждения

Abstract. Irreversible waste spinning flax and cotton are sent to landfill or incinerated, it adversely affects the environment, although it is desirable to use plant waste for production, which would be a very positive approach in terms of natural environment. Composite boards of irrecoverable waste from the processing of flax and cotton and urea-formaldehyde binder (UF) can be used as a thermal-insulation material, the development of this composite material is the purpose of this research.

The paper presents the results of laboratory research of indicators of composite thermal-insulation boards filled with irretrievable spinning flax and cotton. As the matrix of the composite used UF binder with various additives. UF binder has advantages and disadvantages: is cheaper but less waterproof than other synthetic binders. The work assessed the properties of the binder and the influence of the composition of the binder on the physical and mechanical properties of the thermal-insulating material. The IR spectrum of the binder, the dependence of the degree of curing of the UF binder on the type and proportion of the hardener additive are given. The results were obtained that the degree of curing and water resistance of the UF binder depends on the type and proportion of the hardener additive and the curing temperature.

The physical and mechanical properties and the coefficient of thermal conductivity of the boards on the UF binder were determined. It is shown that the type of additive in the UF binder affects the physical and mechanical properties of thermal-insulation composite boards from spinning flax and cotton. The paper summarizes the results of the determination of the physical and mechanical parameters of boards from plant waste, and proposed a rational combination of factors for the production of composites.

The type of additive in the binder does not have a significant effect on the thermal conductivity of the material. Composites have a coefficient of thermal conductivity required for thermal-insulation materials.

Аннотация. Невозвратные отходы прядения льна и хлопка отправляются на свалку или сжигаются, это негативно влияет на экологию, хотя растительные отходы желательно использовать для производства продукции, это было бы очень позитивным подходом с точки зрения естественной окружающей среды. Композиционные плиты из невозвратных отходов переработки льна и хлопка и карбамидоформальдегидного связующего (КФС) могут использоваться в качестве теплоизоляционного материала, разработка этого композиционного материала является целью данного исследования.

В работе представлены результаты лабораторных исследований показателей композиционных теплоизоляционных плит с наполнителем из невозвратных отходов прядения льна и хлопка. В качестве матрицы композита использовано КФС связующее с различными добавками. КФС связующее имеет достоинства и недостатки: оно является более дешевым, но менее водостойким, чем другие синтетические связующие. В работе дана оценка свойств связующего и влияния состава связующего на физико-механические свойства теплоизоляционного материала. Приведены ИК-спектр связующего, зависимости степени отверждения КФС связующего от вида и

Вахнина Т.Н., Сусоева И.В., Титунин А.А. Теплоизоляционные плиты из волокнистых растительных отходов и карбамидоформальдегидного связующего // Инженерно-строительный журнал. 2018. № 7(83). С. 136–147.

доли добавки отвердителя. Получены результаты, что степень отверждения и водостойкость КФС связующего зависит от вида и доли добавки отвердителя и температуры отверждения.

Определены физико-механические свойства и коэффициент теплопроводности плит на КФС связующем. Показано, что вид добавки в КФС связующее влияет на физико-механические показатели теплоизоляционных композиционных плит из отходов прядения льна и хлопка. В работе обобщены результаты определения физико-механических показателей плит из растительных отходов, предложено рациональное сочетание факторов производства композитов.

Вид добавки в связующее не оказывает значимого влияния на коэффициент теплопроводности материала. Композиты имеют коэффициент теплопроводности, необходимый для теплоизоляционных материалов.

1. Introduction

Development of effective materials with use of local raw materials and waste of the industry is an important task for the construction industry. The purpose of this work is justification of structure and properties of thermal-insulation board materials of construction appointment on urea-formaldehyde binder of irretrievable waste of spinning of linen and cotton fibers.

Secondary plant raw materials, along with primary waste of annual plant (such as flax shive, straw), it can be used for production of thermal-insulation elements of building constructions [1], especially in relation to wooden housing construction. A problem in development of material is creation of steady structure from plant filler and a matrix – binding.

The properties of the binder have a significant impact on the performance of composite materials, including the thermal-insulation boards [2, 3]. For thermal-insulation materials traditionally use phenol formaldehyde binder (PF) [4, 5]. Thermal-insulation boards most often make of plant fillers on the basis of inorganic binder or knitting [6–8].There are also developments of thermal-insulation board materials from cellulose hydrolysis lignin and lignocellulosic discrete wood particles, also developed, however, the complexity of the structure of the material, 90 % consisting of sawdust, is costly to manufacture [9].

The most large-capacity thermoreactive polymer in domestic and world practice is urea-formaldehyde, cost her is lower, than phenolic binder. According to G. Mantanis with colleagues, in the European industry for production of board materials are used (as use volumes) urea-formaldehyde binder (UF), melamine-urea-formaldehyde (MUF), phenol formaldehyde (PF) and polyisocyanates of PMDI (for OSB). A share of use of binder board materials in production (according to European federation of the particleboard): UF – 90 … 92 %, MUF– 6 … 7 % and PMDI – 1 … 2 %. More than 30 % of board materials are used in construction: about 20 % when finishing doors and laying floors, about 12 % – for production of panels [10].

The main lack of binder UF – adhesives occasionally exhibit some problems with long-term hydrolytic instability [11–12].

Are traditionally used for the production of insulating board materials. A significant advantage of the PF is the ability to combine with different fillers [13]. Materials based on the PF, in comparison with the composites of the urea-formaldehyde binders have higher water resistance, strength, elasticity and durability [14, 15].

In work the task of increase in water resistance of thermal-insulation composites from plant filler on UF by deepening of extent of polycondensation binding and increases in hydrolytic stability at the operating influence of technology factors of process of production of board materials is set.

Zaimatul Aqmar Abdullah used in the work a way of increase in hydrolytic stability of UF by additives of compounds of sulfur, acrylamide and PMDI, and the best results were yielded by additive of acrylamide [16]. The results in the improvement of the water resistance of thermal-insulation materials obtained by using for their production combined urea-phenol-formaldehyde binders are also known [5]. UF is generally used for production of the made foam plastic. Both the Russian, and foreign researchers note that use urea-formaldehyde binder for production of the construction materials operated under variable temperature and moist conditions is limited owing to their low water resistance [17, 11].

The gluing ability of UF glues depends on number of metilolny groups $-CH_2OH$, however a part them remains not connected in cured binder. Low hydrolytic stability of UF is due to the presence in the cured polymer of free methylolgroups – CH_2OH. Scientists of the whole world deal with problems of assessment of hydrolytic stability of UF glues for construction [16]. According to L.F. Mubarakshina, operational technical characteristics of polymeric construction materials on the basis of UF binders can be improved by their modification [8].

The lower the degree of polycondensation of the binder, the more it contains free methylol− CH_2OH groups. In additionto gidroliticheski unstablemethylol − CH_2OH groups, the polymer matrix contains UF resistant to hydrolysis methylene groups − CH_2 − and partially hydrolysable methylene-ether groups− CH_2−O−CH_2−, which can degrade under the influence of moisture and temperature.

According to M. Dunky, extent of hardening of UF glues depends on a formaldehyde share at synthesis of binder [11]. According to O. F. Shishlov with colleagues, extent of hardening binder depends on the speed of heating and a type of plant filler [18]. However except a molar ratio of UF and above the listed factors, on stitching degree and consequently and hydrolytic stability of UF glues is influenced by both a look and amount of hardener.

As UF hardeners of glues in Europe persulphate of ammonium $(NH_4)_2SO_4$ and nitrate of ammonium NH_4NO_3, NH_4Cl are used have been forbidden for the ecological reasons [10, 11], however in many countries about 20 years ago (Russia, Indonesia, etc.) chloride ammonium is still used for hardening of UF glues [19].

2. Methods

In this paper, we studied the indicators of UF resin and thermal-insulation composite boards of plant filler and UF binder.

Fiber boards by wet way of production were used as an analogue (EN 13986:2004 Wood-based panels for use in construction, Russian Standard 4598-2018).

The samples of composite thermal-insulation boards from wastes of spinning of flax and cotton fibers and binding of urea-formaldehyde binder and hardeners – the ammoniynykh salt shave been made in the work. Composite board materials were made with an average density of 370 … 410 kg/m^3, the expense of binding made 10 – 30% of the mass of plant filler. Boards were made by wet way of production. Plant wastes were mixed with water, a binder (UF resin and hardener), and molded, extra water was squeezed out. Composites were dried at a temperature of T = 100 °C and T = 170 °C to a humidity of 8 ± 0.5 %. After exposure, the physical and mechanical characteristics of the samples of the boards were determined.

Composite samples were tested for strength under static bending to EN 310. To determine the strength of the samples, a testing machine 2166 R-5 was used (division price 0.1 N). Samples were installed on the supports of the testing machine. The load was applied at a constant rate until the test specimen was destroyed. The destruction of the sample occurred within (60 ± 30) s. The maximum load was recorded with an accuracy of 0.1 N, the tensile strength of the samples during static bending was determined, MPa.

The swelling of the boards in thickness after 24 hours in water was determined. The thickness of the samples was measured before and after their stay in the water, and the thickness swelling was determined, %. The water absorption of the boards, % after 24 hours in water was determined by the weight method.

The value of the coefficient of heat conductivity of material was determined with on the help of the measuring instrument of heat conductivity of ITP-MG4. The IR spectra of the binder and composites were taken on a NETZSCH STA 449 F3 Jupiter synchronous thermal analysis unit, combined with an IR Fourier transform. For the manufacture of composites used polycondensation UF resin of the brand UFN-66-P (urea-formadehyde, non-vacuumed, for board production) was used. The manufacturer’s normalized resin indicators:

- specific gravity 1.19 … 1.22 g/m^3;
- mass fraction of free formaldehyde no more than 0.1 %;
- level pH 6.5 … 7.5.

To determine the degree of curing of the binder used the following method. Samples of polymeric materials were cured, dried up in a drying cabinet at T = 105 °C, weighed with an accuracy of 0.0002 g and were located on a steam bath. Steaming was carried out during 3 h, at the same time not cured part of the binder absorbed water, samples of polymeric materials were washed out by steam. After steaming samples were dried up to the constant weight. The extent of hardening of polymeric samples of Q was determined by the formula:

$$Q = 100 - [(G_1 - G_0)]100\ \%,$$

where G_1 – the mass of a sample of polymer before extraction, g;

G_0 – the mass of a sample after extraction, g.

A physical and chemical analysis of particles from spinning flax and cotton was performed. The content of cellulose, lignin, ash content and the proportion of water-soluble substances were determined using classical methods [23].

3. Results and Discussion

Figure 1 presents the IR spectrum of the urea-formaldehyde resin, hardened at 100 °C. The spectrum is filmed at the setting of the simultaneous thermal analysis NETZSCH STA 449 F3 Jupiter, combined with the prefix FT-IR. The position and the reference of bandwidths are given in Table 1. The results showed that the transmission in the frequency domain 1002 cm^{-1} and 1128 cm^{-1}, characterizing metrolinie and methyleneimine group, has a broad intense band of complex shape and the shoulder, due, apparently, to the in-phase vibrations of the group – OH [20]. The high content of methynol groups - CH_2OH in the cured resin (transmission intensity 0.35 %) causes low hydrolytic stability of UF resin.

To increase hydrolytic stability of UF, i.e. to reduce the quantity of free metilolnykh groups in the hardened binder, is possible by deepening the extent of polycondensation of the binder. It will allow to increase the water resistance of composites. The completeness of hardening of the binder depends on the initial indicators of the pitch [21], the temperature of hardening, the type of the catalyst of reaction of polycondensation (hardener) [22].

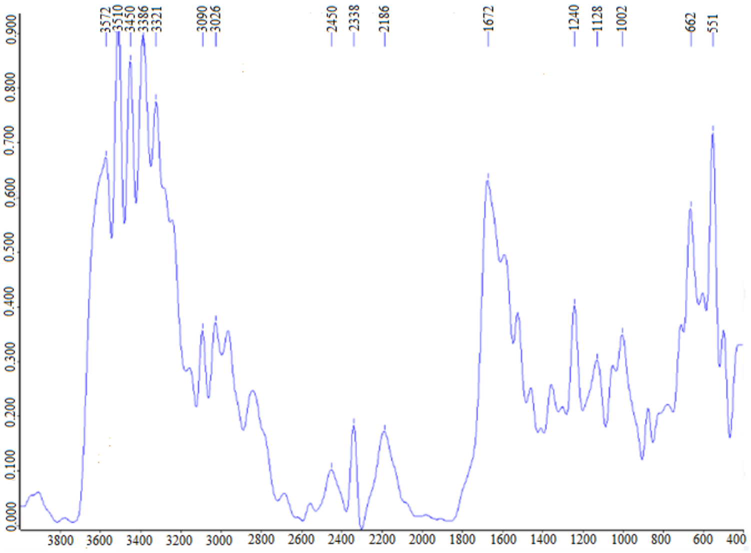

Figure 1. IR spectrum of the urea-formaldehyde resin

Table 1. Bandwidth of the urea-formaldehyde resin

Position band, cm^{-1}	Intensity transmittance, %	Allocation of band width*
3572	0.68	Intra - and intermolecular H-bonds
3510	0.9	Intra - and intermolecular H-bonds
3450	0.85	Intra - and intermolecular H-bonds
3386	0.9	Intra - and intermolecular H-bonds
3321	0.78	Intra - and intermolecular H-bonds
3090	0.37	SVcommunications in groups-C-OH and -C-H
3026	0.38	SVcommunications in groups-C-OH and -C-H
2450	0.11	SVcommunications in groups-C-OH and-C-H
2338	0.19	SVcommunicationsN-H
2186	0.18	SVcommunicationsN-C
1672	0.65	SVcommunicationsC-O andC-N
1240	0.4	DVcommunications N-HandC=O
1128	0.3	SVcommunicationsC-Oin-H_2C-O-CH_2-and -C-OH
1002	0.35	SVcommunicationsC-Oin groups-CH_2OH
662	0.58	DVcommunicationsC-H in groupsCH_2
551	0.74	DVcommunicationsC-H in groupsCH_2

* Notatio conventions: SV – stretching vibrations, DV – deformation vibrations

The extent of hardening of UF[1] cured at temperatures 100 °C and 170 °C has been investigated in the work. Ammoniyny salts: NH_4Cl ammonium chloride; urea-ammoniyny $NH_4NO_3–(NH_2)_2CO–H_2O$ nitrate; nadsernokisly ammonium $(NH_4)_2S_2O_8$; hydrophosphate of ammonium $(NH_4)_2HPO_4$ were used as hardeners.

The minimum and maximum values of the degree of curing of the UF binder with NH_4Cl cured at 100 °C are given in Table 2. Dependences of the degree of UF hardening on the proportion of additives of hardeners, constructed from the average values, are shown in the Figure 2 (curing at a temperature T = 100 °C) and in the Figure 3 (T = 170 °C).

Table 2. Curing degree of UF binder with NH_4Cl, cured at 100 °C

NH_4Cl,%	0.8		1.0		1.2		1.4		1.6		2.0	
Q,%	91.57	92.1	94.74	95.27	94.61	93.87	92.68	93.24	92.16	92.39	90.32	91.60

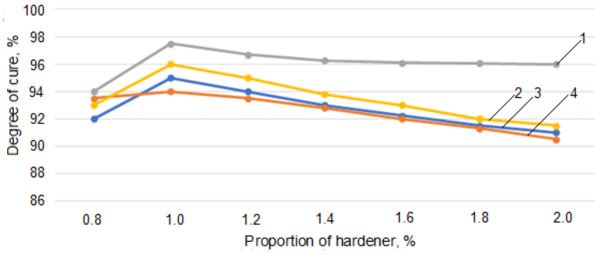

Figure 2. Dependence of the degree of curing of the urea-formaldehyde binder on the proportion of additive curing agents (the curing temperature T = 100 °C):
1 – $(NH_4)_2S_2O_8$; 2 – $(NH_4)_2HPO_4$; 3 – NH_4Cl;4 – $NH_4NO_3–(NH_2)_2CO–H_2O$

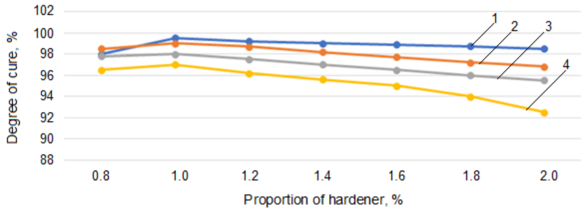

Figure 3. Dependence of the degree of curing of the urea-formaldehyde binder on the proportion of additive curing agents (the curing temperature T = 170 °C):
1– NH_4Cl; 2 – $NH_4NO_3–(NH_2)_2CO–H_2O$; 3 – $(NH_4)_2S_2O_8$; 4 – $(NH_4)_2HPO_4$

At the curing temperature of the UF binder at 100 °C, the best cure rate is provided by the use of an ammonium nitrate $(NH_4)_2S_2O_8$ additive in the amount of 1 % by the resin weight. At a curing temperature of 170 °C, the maximum cure is given by the addition of ammonium chloride in the amount of 1 %. These experimental results make it possible to choose the composition of the adhesive composition for the production of composite boards, but it is necessary to take into consideration the effect of the plant filler on the board indicators. The fractional composition of the filler from waste spinning was determined by sieving in a sieve analyzer and weighing a part of the fraction. The determination results of the fractional composition of the filler are shown in Table 3.

Table 3. Results of determination of fractional composition of filler

Fraction	Share of fraction for cotton waste i_{fr}, %	Share of fraction for flax waste i_{fr}, %
–/10	0.059	0.339
10/7	0.285	0.020
7/5	0.339	0.045
5/2	0.229	0.106
2/0.5	0.042	0.266
Pallet	0.043	0.216

Non-returnable waste of spinning and cotton has an average length:

- for cotton 4.76 mm;
- for flax 4.12 mm.

---

[1] The research was carried out by magister Mochalov A.N.

The average length of the waste products of flax and cotton spinning is longer than the length of the wood fiber used in the production of fiberboards (2 mm for coniferous fibers, about 1.2 mm for hardwood fibers). So we have come to the conclusion that it is possible to use non-returnable waste of spinning of flax and cotton as a filler of soft boards produced by the technology of heat-insulating fiberboard. At comparable average lengths, flax spinning waste contains about 34 % of long fiber-like particles (fraction - / 10), capable of participating in creating a composite structure by felting.

Photographs of flax fiber spinning waste and a composite of flax waste made by the authors using the Quanta 3D FEG FEI Company microscope are shown in Figure 4.

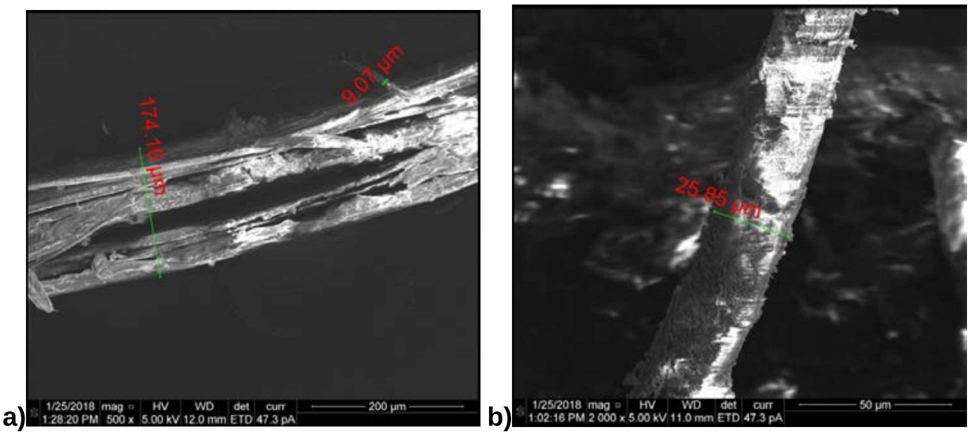

Figure 4. Photo of waste of spinning of linen fiber and composite:
a – waste of spinning of linen fiber; b – composite

Filler particles from waste spinning have significant damage and a large specific surface, so the binder covers only part of the filler surface (Figure 4 b).

In Table 4 presents the results of the determination of the physical and chemical analysis of the composition of waste from the processing of plant fibers.

Table 4. Composition of plant materials, %

Irretrievable waste of spinning	Cellulose	Lignin	Ash	Water-soluble substance *
cotton	44.0	22.7	17.0	0.01
flax	54.0	24.9	5.0	0.02

* soluble in hot water

The lignin content in the irretrievable plant waste of flax and cotton is comparable to that for wood raw materials. The pulp content in cotton waste is the same as in wood. Cellulose content in flax production wastes is significantly higher than for wood raw materials. Water-soluble substances waste flax and cotton contain less than wood raw materials. Plant waste from flax and cotton has significant ash, the reason for this is contaminated waste.

Despite the increased ash content, irretrievable waste of flax and cotton can be used for the production of insulation boards. The high content of cellulose in plant waste allows you to create a composite structure due to hydrogen bonds between the particles and chemical bonds with the binder.

Glue from UF resin and hardeners used for the production of composites from flax and cotton waste.

The content of lignin in the irretrievable plant waste of flax and cotton is comparable to the indicator of wood raw materials; the same can be noted for the cellulose content in cotton waste, for flax waste, the cellulose content is much higher than for wood raw materials. Water-soluble substances waste of flax and cotton contain less than wood raw materials. It should be noted the significant ash content of the filler particles from the irretrievable waste, the reason for this is the contamination of the waste. In general, we can say that the use of technology for the production of fiberboards for plant fiber-like particles with a high content of cellulose makes it possible to create a structure of a soft thermal-insulation composite due to hydrogen bonds between particles, chemical bonds with a binder, and a felting effect.

Glutinous compositions of UF binder and hardeners, the degree of curing of which has been researched, was used for the production of thermal-insulation boards from the waste products of flax and cotton. The mass fraction of the hardener for each composition was taken in the amount that provides the maximum degree of cure at the drying temperature of the composite.

In Tables 5–7 the results of definitions of the strength of boards at a static bend, the swelling in thickness and the water absorptions of composites are given. In Table 8 the results of definitions of the coefficient of heat conductivity of board materials are given.

Table 5. Strength of composites at a static bend, MPa

Filler	Type of hardener, share of UF additive, %											
	Ammonium chloride NH_4Cl			Nadsernokisly ammonium $(NH_4)_2S_2O_8$			Karbamido-ammoniyny nitrate $NH_4NO_3–(NH_2)_2CO–H_2O$			Hydrophosphate of ammonium $(NH_4)_2HPO_4$		
	10	20	30	10	20	30	10	20	30	10	20	30
	- temperature of drying of samples T = 100 °C											
Cotton waste	0.27	0.32	0.4	0.41	0.56	0.81	0.23	0.3	0.36	0.29	0.35	0.42
Flax waste	0.4	0.55	0.67	0.54	0.71	0.88	0.38	0.5	0.58	0.41	0.65	0.76
	- temperature of drying of samples T = 170 °C											
Cotton waste	0.44	0.58	0.84	0.29	0.35	0.42	0.31	0.39	0.44	0.23	0.3	0.36
Flax waste	0.57	0.75	0.9	0.44	0.59	0.7	0.43	0.68	0.79	0.38	0.5	0.58

Table 6. Swelling on thickness for 24 h composites, %

Filler	Type of hardener, share of UF additive, %											
	Ammonium chloride NH_4Cl			Nadsernokisly ammonium $(NH_4)_2S_2O_8$			Karbamido-ammoniyny nitrate $NH_4NO_3–(NH_2)_2CO–H_2O$			Hydrophosphate of ammonium $(NH_4)_2HPO_4$		
	10	20	30	10	20	30	10	20	30	10	20	30
	- temperature of drying of samples T = 100 °C											
Cotton waste	6.2	5.4	4.3	5.6	4.8	4.1	7.5	6.8	5.6	6.5	5.9	5.1
Flax waste	5.5	5.3	4.4	5.2	4.5	3.8	6.1	5.3	4.2	5.8	5.6	4.8
	- temperature of drying of samples T = 170 °C											
Cotton waste	5.3	4.4	3.8	6.0	5.1	4.2	6.2	5.6	4.7	7.2	6.4	5.3
Flax waste	5.0	4.1	3.3	5.2	5.0	3.8	5.5	5.3	4.4	6.0	5.2	3.9

Table 7. Water absorption of composites, %

Filler	Type of hardener, share of UF additive, %											
	Ammonium chloride NH_4Cl			Nadsernokisly ammonium $(NH_4)_2S_2O_8$			Karbamido-ammoniyny nitrate $NH_4NO_3–(NH_2)_2CO–H_2O$			Hydrophosphate of ammonium $(NH_4)_2HPO_4$		
	10	20	30	10	20	30	10	20	30	10	20	30
	- temperature of drying of samples T = 100 °C											
Cotton waste	180	168	142	171	159	134	193	185	176	187	181	163
Flax waste	91	79	68	87	73	60	101	89	81	98	85	76
	- temperature of drying of samples T = 170 °C											
Cotton waste	168	155	132	178	164	139	185	179	160	190	182	173
Flax waste	85	71	58	88	77	65	96	83	72	97	86	78

Table 8. Coefficient of heat conductivity of composites, W/(m·K)

Filler	Type of hardener, share of UF additive, %											
	Ammonium chloride NH_4Cl			Nadsernokisly ammonium $(NH_4)_2S_2O_8$			Karbamido-ammoniyny nitrate $NH_4NO_3–(NH_2)_2CO–H_2O$			Hydrophosphate of ammonium $(NH_4)_2HPO_4$		
	10	20	30	10	20	30	10	20	30	10	20	30
	- temperature of drying of samples T = 100 °C											
Cotton waste	0.090	0.091	0.091	0.086	0.086	0.087	0.092	0.092	0.093	0.088	0.088	0.089
Flax waste	0.064	0.064	0.065	0.060	0.061	0.062	0.066	0.067	0.068	0.062	0.062	0.064
	- temperature of drying of samples T = 170 °C											
Cotton waste	0.085	0.086	0.088	0.089	0.090	0.091	0.087	0.088	0.089	0.091	0.093	0.095
Flax waste	0.058	0.060	0.060	0.062	0.063	0.065	0.060	0.062	0.063	0.064	0.065	0.067

The strength of the boards during static bending is influenced by the drying temperature and the type of additive in the binder. For each drying temperature, a hardener is recommended, which provides the maximum degree of curing of the binder.

At a board drying temperature of 100 °C, it is recommended that the additive as a hardener of UF ammonium binder is used. If the boards are produced at a temperature of 170 °C, it is necessary to use ammonium chloride. This provides the best physical and mechanical properties of boards from plant waste.

The results of physical and mechanical tests of the boards are in good agreement with the results of determining the degree of curing of the binder at these temperatures. In the Figures 5 and 6 you can see the IR spectra of composites from flax and cotton waste on a UF binder made at a drying temperature of T = 100 °C.

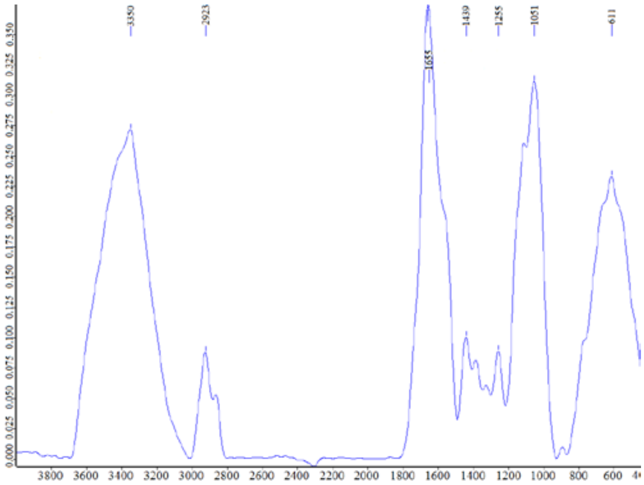

Figure 5. Composite IR spectrum from waste of cotton and UF binding with hardener $(NH_4)_2S_2O_8$ (temperature of drying of samples of T = 100 °C)

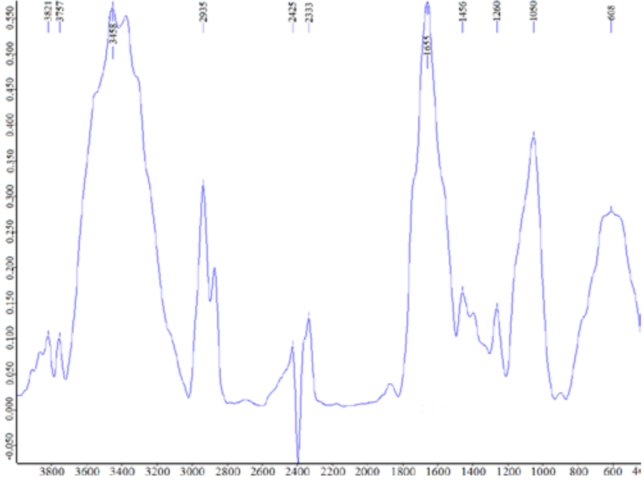

Figure 6. Composite IR spectrum from waste of flax and UF binding with hardener $(NH_4)_2S_2O_8$ (temperature of drying of samples of T = 100 °C)

While manufacturing the composites, according to the chosen values of the factors, a large number of hydrogen bonds is provided, as it is can be seen by a broad absorption band (3350 cm^{-1} for a composite of cotton waste, 3458 cm^{-1} for a composite of flax waste). The water presented in the composites is strongly bound, which can be indicated by an absorption band of 1655 cm^{-1}. Methyl groups (absorption band (1002 cm^{-1}) in composites are absent.

To create a hydrolytically board composite structure from plant waste flax and cotton and a UF binder, it is necessary to increase the degree of curing of the binder.

There are rather labor-consuming ways of assessment of extent of hardening binding. So D. Brown and G. Sherdron with colleagues estimated extent of polycondensation of a low-molecular product, binding on allocation, – waters [24]. Z. Virpsha and Ya. Brzezinski determined extent of hardening of binders by change of level pH [25]. A. A. Leonovich and A. V. Sheloumov also estimated hardening of urea-formaldehyde binding on a share of allocation of by-products and also on change pH systems [21]. Authors in general note that "… because of existence of collateral chemical reactions it is difficult to interpret characteristics of hardening of UF" [21]. Z. Virpsha and Ya. Brzezinski have also developed a definition method "… sufficiency of hardening" on resistance of aminoplastics to effect of the boiling water [25]. However, this method is difficult to apply to composites with plant filler. After boiling the board on the UF binder is completely destroyed.

In this work dependences of extent of hardening of UF with additive the ammoniynykh of salts are experimentally received from temperature of hardening and a share of additive of hardeners. Zh.-Zh. Vilnav notes that it is in fact rather difficult to receive "the correct stitching" [26]. He offers for increase in extent of hardening of a message reaction at high temperature under pressure. However and here he notes a problem: if to use temperature above 100 °C, the "foamy" seam with a low mechanical durability [26].

Z. Akmer used in the work a way of increase in hydrolytic stability by additives of compounds of sulfur, acrylamide and PMDI, and the best results were yielded by acrylamide additive. The scientist used a similar method of assessment of depth of polycondensation and hydrolytic stability of UF. The cured binder was not steam flushed, but in water. This, in his opinion, changes the structure of the UF [16]. Binding it is possible to refer neurotoxicity of acrylamide to shortcomings of this method of increase in hydrolytic stability.

It has already been mentioned in this work, the best physical and mechanical properties of composite fibrous insulating boards from plant wastes at a drying temperature of 100 °C were obtained by adding ammonium sulfate as a curing agent, at a temperature of 170 °C, using ammonium chloride. This is consistent with the results of determining the degree of curing of the binder at the given temperatures. The coefficient of thermal conductivity of the boards 0.05 – 0.07 W/(m·K).

Ammonium sulfate (ammonium peroxodisulfate) is a highly active hardener. In the processes of board production, it allows a third to reduce the duration of pressing. This is due to the acceleration of the UF polycondensation reaction.

It is necessary to consider the features of persulphate of ammonium at temperature influence – when heated to 120 °C it decays with release of oxygen, forming pyrosulphate:

$$2(NH_4)_2S_2O_8 \rightarrow 2(NH_4)_2S_2O_7 + O_2.$$

This process is well illustrated by the curve of the extent of gelatinization of peroxodisulphate of ammonium at the temperature of 170 °C. The degree of curing of UF with the addition of persulphate does not exceed 96–98% due to the release of oxygen. When this begins the process of oxidative destruction of the binder. For these reasons, the physical and mechanical characteristics of boards made with the addition of ammonium persulfate with a drying mode of 170 ° C have low values.

Ammonium chloride has a thermal stability above 250 ° C, when it interacts with the formaldehyde of the binder, hemethylenetetramine and hydrogen chloride are formed:

$$4NH_4Cl + 6CH_2O \rightarrow 4HCl + (CH_2)_6N_4 + 6H_2O.$$

Due to the release of HCl, the pH of the binder decreases. In this case, cross-links are formed between the chains of the macromolecules of the UF oligomer. This is due to the binding of free methyl groups (bandwidth in the IR spectrum of 3090, 3026 and 2450 cm^{-1}) between themselves and with amide groups.

Urea ammonium nitrate provides the lowest values of the extent of hardening at the temperature of 100 °C and high values at the temperature of 170 °C. The temperatures of phase transition of nitrate of ammonium are 32-33 °C; 84.2 °C; 125.2 °C. Mechanism of decomposition of nitrate of ammonium can change depending on the temperature and structure of the composition. At the temperature above 110 °C nitrate of ammonium dissociates on NH_3 ammonia and HNO_3 nitric acid. Nitric acid interacts with free CH_2O formaldehyde of the binding, accelerating the hardening process.

Some part of nitric acid interacts with formaldehyde with the release of N_2 nitrogen and oxide of CO_2 carbon fabrics (IV). The urea of urea ammonium. $NH_4NO_3–(NH_2)_2CO–H_2O$ nitrate is the weak basis. For this reason, in his presence, the curing rate of the binder slows down. Theoretically the urea of urea ammonium nitrate can react with free formaldehyde. However in acidic environment at small time of interaction only mono-connections will be formed of possible mono-metilol urea. It should also be borne in mind that in a strongly acidic environment (pH<3) the formed metilol urea at once are exposed to dehydration, giving the methyleneurea having amorphous structure and not participating in the process of hardening of the binder. All this is the reason that when urea ammonium nitrate is used as hardener at temperature of 170 °C less durable boards turn out, than when chloride ammonium is added.

The research showed that the type of additive in the urea-formaldehyde binder affects the physical and mechanical properties of composites made from flax and cotton waste. This is achieved by choosing an additive in a binder that ensures the maximum degree of curing of the polymer at a given temperature.

The coefficient of thermal conductivity of the material depends on the factors of production of the composite – the drying temperature, the proportion of the binder additive and the type of plant filler – flax/cotton.

The coefficient of thermal conductivity of composite boards is more affected by the mass fraction of the binder than the type of plant filler. The value of thermal conductivity for UF – 0.1–0.12 W/(m·K), for cotton – 0.05 W/(m·K), for flax – 0.04 W/(m·K). The difference in thermal conductivity of the filler is explained by the structure of discrete plant particles. In the elementary cotton fiber there is a large internal cavity (as opposed to flax fiber). Also, as noted by the authors, part of the flax particles has closed ends [27], and the presence of closed pores significantly affects the thermal conductivity of the material.

4. Conclusions

1. Thus, it is possible to increase the water resistance of a thermal-insulation board composite from waste of spinning of plant fibers and urea-formaldehyde binder due to increase in extent of hardening binding by the operating influence of technology factors of process of production of material.

2. For increase in hydrolytic stability at the choice of structure binding on the basis of the urea-formaldehyde binder for production of thermal-insulation board material from waste of spinning of plant fibers it is necessary to be guided by value of temperature parameter of process of drying of a composite.

3. The type of additive in urea-formaldehyde binder exerts impact on physical and mechanical indicators of heat-insulating composite boards from waste of spinning of a flax and cotton. This factor doesn't exert significant impact on coefficient of heat conductivity of material.

4. The best physical and mechanical indicators of composite fibrous thermal-insulation boards from the plant waste made at a temperature of drying of 100 °C are provided by additive as hardener of ammonium dust, and at a temperature of drying of 170 °C – additive of chloride ammonium.

References

1. Soldatov, D.A., Hozin, V.G. Teploizolyacionnye materialy na osnove solomy [Heat-insulating materials on the basis of straw]. News of the KSUAE. 2013. No. 1(23). Pp. 197–201. (rus)
2. Alentiev, A.Y., Yablokov, M.Yu. Svyazuyushchie dlya polimernyh kompozicionnyh materialov [Binders for polymeric composite materials]. Moscow, 2010. 69 p. (rus)
3. Askadsky, A.A., Popova, M.N., Kondrashenko, V.I. Fiziko-himiya polimernyh materialov i metody ih issledovaniya [Physical chemistry of polymeric materials and methods of their research]. Moscow, 2015. 408 p. (rus).
4. Makarov, V.P., Nedzelsky, I.A. Kompleksnoe svyazuyushchee dlya izgotovleniya plit iz bazal'tovoj vaty na osnove biopolimerov [Complex binder for the production of slabs of basalt wool on the basis of biopolymers]. Vestnik KRSU. 2012. Vol. 12. No. 6. Pp. 102–105.
5. Kanashov, S.S. Svyazuyushchie dlya proizvodstva teploizolyacionnyh materialov i izdelij [Binder for manufacturing heat-insulating materials and products] [Electronic resource] URL:http://center-science.ru/files/adhesive.pdf (date of reference: 10.11.2017). (rus)
6. Uglova, T.K., Novoselova, S.N., Khodakova, N.N., Tatarintseva, O.S. Svyazuyushchie dlya teploizolyacionnyh voloknistyh plit [Binders for insulating fiber board]. Polzunovskij vestnik. 2010. No. 4–1. Pp. 258–261. (rus).
7. Safin, R.G., Petrov, V.I., Ignat'eva, G.I., Stepanov, V.V. Halitov, R.A. Ispol'zovanie othodov lesozagotovok i derevoobrabotki dlya proizvodstva teploizolyacionnyh materialov [Use of waste timber and wood for production of heat-insulating materials]. News of higher educational institutions. Energy problems (KGEU). Kazan. 2012. No. 3–4. Pp. 94–100. (rus).

Литература

1. Солдатов Д.А., Хозин В.Г. Теплоизоляционные материалы на основе соломы // Известия КГАСУ. 2013. № 1(23). С. 197–201.
2. Алентьев А.Ю., Яблокова М.Ю. Связующие для полимерных композиционных материалов. М., 2010. 69 с.
3. Аскадский А.А., Попова М.Н., Кондращенко В.И. Физико-химия полимерных материалов и методы их исследования. М., 2015. 408 с.
4. Макаров В.П., Недзельский И.А. Комплексное связующее для изготовления плит из базальтовой ваты на основе биополимеров // Вестник КРСУ. 2012. Т. 12. № 6. С.102–105.
5. Канашов С.С. Связующие для производства теплоизоляционных материалов и изделий. [Электронный ресурс] URL:http://center-science.ru/files/adhesive.pdf (дата обращения 12.04.2018)
6. Углова Т.К., Новоселова С.Н., Ходакова Н.Н., Татаринцева О.С.. Связующие для теплоизоляционных волокнистых плит // Ползуновский вестник. 2010. № 4–1. С. 258–261.
7. Сафин Р.Г., Петров В.И., Игнатьева Г.И., Степанов В.В., Халитов Р.А. Использование отходов лесозаготовок и деревообработки для производства теплоизоляционных материалов // Известия высших учебных заведений. Проблемы энергетики (КГЭУ). Казань. 2012. № 3–4. С. 94–100.
8. Мубаракшина Л.Ф., Абдрахманова Л.А., Крадинова А.Е. Суперконцентраты для усиления строительных материалов на основе карбамидоформальдегидных смол // Известия КГАСУ. 2013. № 4. С. 240–245.
9. Halahmi I., Gross M., Iacobs L., Kadosh G. Strong durable low cost composite materials made from treated cellulose and plastic. Patent № 6863971. US6066680 B

8. Mubarakshina, L.F., Abdrahmanova, L.A., Kradinova, A.E. Masterbatches for strengthening building materials based on urea-formaldehyde resins. News of the KSUAE. 2013. No. 4. Pp. 240–245. (rus).
9. Halahmi, I., Gross, M., Iacobs, L., Kadosh, G. Strong durable low cost composite materials made from treated cellulose and plastic. Patent № 6863971. US6066680 B [Electronic resource] URL :http://www.google.tm/patents/US6066680 (date of reference: 10.11.2017).
10. Mantanis, G.I., Athanassiadou, E.Th., Barbu, M.C., Wijnendaele, K. Adhesive systems used in the European particleboard, MDF and OSB industries. Wood material science & engineering. 2017. No. 9. Pp. 1–13.
11. Dunky, M. Urea-formaldehyde (UF) adhesive resins for wood // International Journal of Adhesion & Adhesives. 1998. No. 18. Pp. 95–107.
12. Pizzi, A., Mittal, K.L. Handbook of Adhesive Technology. 2 edition Second. — Revised and Expanded. Marcel Dekker, Inc. 2003. 999 p.
13. Burdonov, A.E. Kineticheskie osobennosti vspenivaniya termoreaktivnyh polimerov pri poluchenii teploizolyacionnyh materialov v prisutstvii mineral'nogo napolnitelya [Kinetic features of foaming thermosetting polymers in the preparation of thermal insulation materials in the presence of mineral filler]. Magazine of Civil Engineering. 2014. No. 3(47). Pp. 9–16. (rus)
14. Varankina, G.S., Chubinsky, A.N. Formirovanie nizkotoksichnyh kleenyh drevesnyh materialov [The formation of low-toxic laminated wood materials]. SPb.:Spbgltu, 2014. 148 p. (rus).
15. Mamza, P.A.P., Ezeh, E.C., Gimba, E.C., Arthur, D.E. Comparative study of phenol formaldehyde and urea formaldehyde particleboards from wood waste for sustainable environment. International journal of scientific & technology research. 2014. Vol. 3. No. 9. Pp. 51–63.
16. Abdullah, Z.A., Park, B.-D. Hydrolytic stability of cured urea-formaldehyde resins modified by additives. Journal of Applied Polymer Science. 2009. No. 14. Pp. 1011–1017.
17. Sergienko, A.V., Yatsun, V.I. Vybor tipa svyazuyushchego dlya innovacionnogo teploizoliruyushchego drevesnogo materiala [Select the type of binders for thermal insulation innovative wood material]. Bulletin of science and education. 2015. No. 10(12). Pp.14–16. (rus)
18. Shishlov, O.F., Dozhdikov, S.A., Gluhih, V.V. Izuchenie vliyaniya vida napolnitelya na kinetiku otverzhdeniya kompozicionnyh materialov na osnove fenolkardanolformal'degidnyh novolachnyh smol [The influence of extender type on cure kinetics in composite materials based on fenol-kardanol-formaldegidtnovolac resins] Chemistry of vegetable raw materials. 2014. No. 4. Pp. 219–227. (rus)
19. Nuryawan, A., Risnasari, I., Sucipto, T., HeriIswanto, A., Rosmala Dewi, R. Urea-formaldehyde resins: production, application, and testing // Innovation in polymer science and technology. 2016. Pp. 1–10.
20. Bell, R.J. Vvedenie v Fur'e-spektroskopiyu [Introduction to Fourier spectroscopy]. M: Mir, 1975. 380 p. (rus).
21. Leonovich, A.A., Sheloumov, A.V. Issledovanie prevrashchenij komponentov drevesnyh plit. 1. Termogravimetricheskoe izuchenie prevrashchenij karbamidoformal'degidnogo oligomera [The study of the transformations of the components of wood panels. 1. Thermogravimetric study of the transformations of urea-formaldehyde oligomer]. Khimiyarastitelnogosyrya. 2010. No. 2. Pp. 169–176. (rus).
22. Azarov, V.I., Burov, A.V., Obolenskaya, A.V. Himiya drevesiny i sinteticheskih polimerov [Chemistry of wood and synthetic polymers]. SPb.:Lan', 2010. 624 p. (rus).

[Электронный ресурс] URL: http://www.google.tm/patents/US6066680 (дата обращения: 12.04.2018).

10. Mantanis G.I., Athanassiadou E.Th., Barbu M.C., Wijnendaele K. Adhesive systems used in the European particleboard, MDF and OSB industries // Wood material science & engineering. 2017. № 9. Pp. 1–13.
11. Dunky M. Urea-formaldehyde (UF) adhesive resins for wood // International Journal of Adhesion & Adhesives. 1998. № 18. Pp. 95–107.
12. Pizzi A., Mittal K.L. Handbook of adhesive technology. 2 edition Second. Revised and Expanded. MarcelDekker, Inc. 2003. 999 p.
13. Бурдонов А.Е. Кинетические особенности вспенивания термореактивных полимеров при получении теплоизоляционных материалов в присутствии минерального наполнителя // Инженерно-строительный журнал. 2014. №3(47). С. 9–16.
14. Варанкина Г.С., Чубинский А.Н. Формирование низкотоксичных клееных древесных материалов. СПб.: СПбГЛТУ, 2014. 148 с.
15. Mamza P.A.P., Ezeh E.C., Gimba E.C., Arthur D.E. Comparative study of phenol formaldehyde and urea formaldehyde particleboards from wood waste for sustainable environment // International journal of scientific & technology research. 2014. Vol. 3. № 9. Pp. 51–63.
16. Abdullah Z.A., Park B.-D. Hydrolytic stability of cured urea-formaldehyde resins modified by additives // Journal of Applied Polymer Science. 2009. № 14. Pp. 1011–1017.
17. Сергиенко А.В., Яцун И.В. Выбор типа связующего для инновационного теплоизолирующего древесного материала // Вестник науки и образования. 2015. № 10(12). С. 14–16.
18. Шишлов О.Ф., Дождиков С.А., Глухих В.В. Изучение влияния вида наполнителя на кинетику отверждения композиционных материалов на основе фенолкарданолформальдегидных новолачных смол // Химия растительного сырья. 2014. № 4. С. 219–227.
19. Nuryawan A., Risnasari I., Sucipto T., HeriIswanto A., Rosmala Dewi R. Urea-formaldehyde resins: production, application, and testing // Innovation in polymer science and technology. 2016. Pp. 1–10.
20. Белл Р.Дж. Введение в Фурье-спектроскопию. М: Мир, 1975. 380 с.
21. Леонович А.А., Шелоумов А.В. Исследование превращений компонентов древесных плит. Термогравиметрическое изучение превращений карбамидоформальдегидного олигомера // Химия растительного сырья. 2010. № 2. С. 169–176.
22. Азаров В.И., Буров А.В., Оболенская А.В. Химия древесины и синтетических полимеров. СПб.: Лань, 2010. 624 с.
23. Сусоева И.В., Вахнина Т.Н., Свиридов А.В. Химический состав и способ утилизации отходов производства хлопковых и льняных волокон // Химия растительного сырья. 2017. № 3. С. 211–220.
24. Браун Д., Шердрон Г., Керн В. Практическое руководство по синтезу и исследованию свойств полимеров. Пер. снемец. М: Химия, 1978. 256 с.
25. Вирпша З., Бжезиньский Я. Аминопласты. Пер. с пол. М: Химия, 1973. 345 с.
26. Вильнав Ж.-Ж. Клеевые соединения. Пер. с франц. М: Техносфера, 2007. 384 с.
27. Сусоева И.В., Вахнина Т.Н., Титунин А.А., Асаткина Я.А. Показатели композитов из растительного сырья при изменениях температуры и влажности // Инженерно-строительный журнал. 2017. № 3(71). С. 39–50.

23. Susoeva, I.V. Vakhnina, T.N., Sviridov, A.V. Himicheskij sostav i sposob utilizacii othodov proizvodstva hlopkovyh i l'nyanyh volokon [Chemical composition and way of recycling productions of cotton and linen fibers] Khimiyarastitelnogosyrya. 2017. No. 3. P. 211–220. (rus).
24. Braun, D., Sherdron, G., Kern, V. Prakticheskoe rukovodstvo po sintezu i issledovaniyu svojstv polimerov [Practical guidance on synthesis and a research of properties of polymers]. Moscow: Himiya, 1978. 256 p. (rus)
25. Virpsha, Z., Bzhezin'skij, Y.A. Aminoplasty [Aminoplastics]. Moscow: Himiya, 1973. 345 p. (rus).
26. Vil'nav, Zh.-Zh. Kleevye soedineniya [Gluejoint]. Moscow: Tekhnosfera, 2007. 384 p. (rus).
27. Susoeva, I.V. Vakhnina, T.N., Titunin, A.A., Asatkina, J.A. The performance of composites from vegetable raw materials with changes in temperature and humidity. Magazine of Civil Engineering. 2017. No. 3(71). Pp. 39–50.

Tatiana Vahnina,
+7(960)748-64-71; t_vachnina@mail.ru

Irina Susoeva,*
+7(915)903-86-70; i.susoeva@yandex.ru

Andrey Titunin,
+7(910)804-55-75; titunin62@mail.ru

Татьяна Николаевна Вахнина,
+7(960)748-64-71;
эл. почта: t_vachnina@mail.ru

Ирина Вячеславовна Сусоева,*
+7(915)903-86-70;
эл. почта: i.susoeva@yandex.ru

Андрей Александрович Титунин,
+7(910)804-55-75; эл. почта: titunin62@mail.ru