

*Досліджені хімічний склад, фізико-хімічні, морфологічні і поверхневі властивості дисперсних наповнювачів на основі рослинної сировини: гречаного і вівсяного лушпиння, деревного борошна і борошна хвої. Потенціометричним методом вивчені якісні і кількісні характеристики кислотно-основних активних центрів на поверхні частинок наповнювачів. Встановлені закономірності зміни кислотно-основних характеристик центрів від хімічного складу та фізико-хімічних властивостей*

*Ключові слова: дисперсний наповнювач, рослинна сировина, композиційний матеріал, поверхневий активний центр, кислотно-основні властивості*

*Исследованы химический состав, физико-химические, морфологические и поверхностные свойства дисперсных наполнителей на основе растительного сырья: гречневой и овсяной шелухи, древесной муки и муки хвой. Потенциометрическим методом изучены качественные и количественные характеристики кислотно-основных активных центров на поверхности частиц наполнителей. Установлены закономерности изменения кислотно-основных характеристик центров от химического состава и физико-химических свойств*

*Ключевые слова: дисперсный наполнитель, растительное сырье, композиционный материал, поверхностный активный центр, кислотно-основные свойства*

UDC 691.175.2

DOI: 10.15587/1729-4061.2017.111350

# RESEARCH INTO SURFACE PROPERTIES OF DISPERSE FILLERS BASED ON PLANT RAW MATERIALS

**Yu. Danchenko**

PhD, Associate Professor\*

E-mail: u\_danchenko@ukr.net

**V. Andronov**

Doctor of Technical Sciences, Professor\*\*

**A. Kariev**

Postgraduate student\*

**V. Lebedev**

PhD, Associate Professor

Department of Technology of Plastics and

Biological Active Polymer

National Technical University "Kharkiv Polytechnic Institute"

Kyrpychova str., 2, Kharkiv, Ukraine, 61002

**E. Rybka**

PhD\*\*

**R. Meleshchenko**

PhD

Department of fire and rescue training\*\*\*

**D. Yavorska**

Department of Ecological Safety and Environmental Education

V. N. Karazin Kharkiv National University

Svobody sq., 4, Kharkiv, Ukraine, 61022

\*Department of General Chemistry

Kharkiv National University of

Civil Engineering and Architecture

Sumska str., 40, Kharkiv, Ukraine, 61002

\*\*Research Center\*\*\*

\*\*\*National University of Civil Protection of Ukraine

Chernyshevska str., 94, Kharkiv, Ukraine, 61023

## 1. Introduction

Thermoplastic wood-polymer composites (TWPC) based on secondary polyolefins – polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS), polycarbonate (PC) – are promising for the production of modern building materials for various purposes. The processing of composites into products is carried out by the methods of extrusion, injection molding, pressing, rotational formation. TWPC are used to make various building articles and structures, construction boards and floor boards, terraces, pipes, fences, sidings, wall panels, roof panels, products to clad building structures, etc. Compared with traditional materials, the benefits of products and structures from TWPC are high operational characteristics, durability, resistance to aggressive environments, ease of machining and environmental friendliness. Development of new TWPC solves

the task of rational use of secondary polymers and organic wastes of different industries.

## 2. Literature review and problem statement

One of the directions for creating TWPC with improved operational characteristics is the addition of dispersed fillers from the waste of plant origin. The main type of filler for TWPC based on primary and secondary polyolefins is traditionally wood flour – a by-product of processing different types of wood [1–6]. Recently, in addition to wood, using non-wood fillers has become widely popular. There are studies, for example, into utilization of wastes and products of processing of agricultural and woodworking industry. These are the products of processing grain crops – the husk of rice [7, 8], buckwheat [5, 6, 9, 10], oat [4–6], wheat [4].

The wastes of recycling certain vegetable crops are flax seed fiber [11], the stalks of cotton [12] and sunflower. The wastes of wood processing are needle flour [5, 6], palm [13] and pineapple leaves [14]. Household waste [15] and waste paper [4] were also used.

In paper [4], authors investigated the physical-mechanical properties of TWPC based on PE and PP. Wood dust and flour, chopped money waste paper, the husks and straw of wheat and oats served as fillers. The samples of composites were obtained by the methods of extrusion and hot pressing. It is established that at the content of fillers in the compositions of 50 %, the best indicators of strength at stretching and bending, impact viscosity and the modulus of elasticity were demonstrated by composites with wood fillers.

Authors of [5, 6] studied composites based on the recycled PP, filled with wood and coniferous flour and buckwheat and oats husk. The samples were made by the extrusion method. The best impact viscosity was demonstrated by composites with flour of pine needles, and strength at bending – by those with buckwheat husk. In both cases, the optimum content of filler in the composite is 60 %. In the course of the study, the authors established a correlation between chemical composition, structural-rheological properties of the fillers and physical-mechanical characteristics of the composites.

The authors of study [8] focused on the development of TWPC from rice husk and PVC. They examined the impact of size and the content of particles of rice husk on the mechanical properties and physical appearance of composites. Experimental results showed that impact viscosity typically decreases with an increase in the content of a filler. Composites with a larger size of particles have the highest impact viscosity. When loaded at stretching and bending, a larger modulus of elasticity and maximum strength were exhibited by composites with a filler content of up to 60 %. Beyond the limits of this concentration the examined indicators decrease due to the formation of agglomerates of rice husk. It was established that the particle size greater than 106  $\mu\text{m}$  is embedded into a matrix of PVC.

Papers [9, 10] studied physical-mechanical properties of composites based on PE of high density and buckwheat husks, its hydrolyzed lignin and the hydrolyzed ligning of wood. The samples were made by mixing in a melt using the extruder. It was found that for the composite with hydrolyzed lignin of buckwheat hulls, an increase in the content of a filler results in the growth of tensile strength at stretching while for other fillers a reverse dependence is observed.

In article [13], authors designed composites of palm leaves and polymeric wastes of PC, PS and PVC. Samples of the composites with a ratio of components of 1:1 were prepared by the extrusion method. They examined density, water absorption, hardness, modulus of elasticity (at stretching and bending), impact strength and the rate of linear combustion of the samples. It is established that the developed composites with shredded palm leaves are characterized by lower water absorption, combustion rate, and hardness. The larger density allows using composites for external structures.

Thus, the effect of fillers on the physical-mechanical, rheological, operational and other characteristics of composites is associated by researchers with many factors. The most important of them is the chemical nature, size, morphology and pretreatment of particles, as well as the content and the technique of adding a filler to the composite. However, as it was revealed, the nature and properties of surface of the fillers particles, which directly affect inter-phase interactions

in the composite material, and determine its properties, have practically been ignored.

In establishing the influence of the nature of the surface of fillers on the characteristics of composites, it is necessary to undertake research into physical-chemical and acid-base surface characteristics. Surface properties are predetermined by the chemical nature, conditions of storage, and the technique of chemical, physical or mechanical pretreatment. Organic fillers of vegetable origin have a complex chemical structure, unstable nature of the surface; studying the surface properties is one of the unresolved chemical-technological problems. The methods of preliminary indirect assessment of surface properties are qualitative and quantitative analyses [16, 17]. Information is also provided when determining the sorption properties of fillers particles relative to the substances of different chemical nature [18]. In this case, results of the experiments correlate with the properties of composites and a search for specific correlation dependences is conducted.

Special attention must be paid to studying the acid-base properties of the surface. The acid-base characteristics are important because in the compositions, when mixed, there may occur interactions between functional groups (functionals) of the filler's surface and the polymer's surface on the surface of inter-phases. There is a sufficient number of theoretical and experimental studies related to the acid-base nature of inter-phase interactions in the polymeric filled materials [19–26]. It is shown that the information about the acid-base properties of surface functionals makes it possible to predict interactions on the surface of interface between the filler and the polymer [19–21] and to control operational properties of composites [22–26].

The existence of functional groups at the surface of dispersed fillers of vegetable origin and the acid-base character is confirmed by studies [18]. The sorption properties were explored of buckwheat and sunflower husk relative to various organic and inorganic substances. It was found that pretreatment using the acid-alkaline technique [27] increases the adsorption capacity of husk particles from both species by 2.6–2.9 times. It is known that polymers based on polyolefins after recycling, due to the oxidation of hydrocarbons, may contain a certain number of functional groups [28, 29]. It was, for example, experimentally determined [28] that there are carboxylic groups with  $pK_a \approx 5.7$  on the surface of a PP fiber, which practically coincides with the acid strength of groups of acetic acid. Thus, in the presence of functional groups, there is a high probability of acid-base interactions at the inter-phase surface, which will substantially affect the properties and characteristics of composite materials.

To determine the acid-base properties of solid surfaces, most often used are the methods for measuring free surface energy and the components – dispersive and polar (acid-base) [30, 31]. Physical-chemical methods are also employed, such as potentiometric or spectral analysis [28, 29]. In this case, much of the research addresses the wood fillers, while data on other promising materials of vegetable origin are practically absent.

Thus, still lacking is the study into acid-base properties of the surface of fillers of vegetable origin that hold promise for the production of TWPC. Insufficiently explored and non-systemized are also relations between chemical composition, surface physical-chemical characteristics and acid-base properties of the surface of organic fillers.

### 3. The aim and objectives of the study

The aim of present work is to study acid-base properties of the surface of dispersed fillers of vegetable origin. This will make it possible to predict acid-base interactions between the filler and the polymeric matrix and to control the properties of polymeric composite materials.

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

- to explore chemical composition, surface and physical-chemical properties of the dispersed fillers of plant origin;
- to establish the relationship between chemical composition, physical-chemical characteristics and acid-base properties of the surface of fillers particles.

### 4. Materials and methods of research

We chose to study materials from the wastes after processing multi-tonnage agricultural products and woodworking industry, which are accumulated in large quantities in Ukraine. These include buckwheat husk (BH) and oat hulls (OH). In order to compare the properties, we selected wood flour (WF) and needle flour (NF). Materials of plant origin were crashed using the mill and dried under the same conditions in the drying chamber at a temperature of 105 °C until reaching a constant weight.

Structural-rheological characteristics of fillers, namely, bulk density  $\rho_b$  and density after compaction  $\rho_{comp}$  were determined applying known techniques for dispersed materials. Specific surface to an accuracy of  $\pm 10\%$  was measured by the BET method of BETH (Brownauer, Emmett and Teller) by the adsorption of gaseous nitrogen at temperature – 196 °C. The samples were prepared by degassing for one hour at room temperature (25–30 °C) and a pressure of 0.01 mm Hg Art. Weighing of samples was carried out with to accuracy of 0.00001 g. Microscopic studies were carried out using the electron microscope Digital Microscope HD-color CMOS Sensor (China).

Potentiometric study of aqueous suspensions of fillers by the method of A. P. Nechyporenko [32] was carried out at room temperature (20–25 °C) using the portable pH-meter SX 711 with an accuracy of measuring the hydrogen index of  $\pm 0.001$  pH. In accordance with the procedure, we studied the pattern of change in the values of  $pH_{susp}$  over time  $\tau$ . We added 10 cm<sup>3</sup> of distilled boiled water with  $pH_0 = 6.8–7.0$  to the potentiometric cell with a glass and silver chloride electrodes. After stabilization of the potential of glass electrode (in 2–3 minutes at continuous agitation with a magnetic stirrer), we added a batch of the filler with a weight of (~0.2 g). We started a stopwatch simultaneously. Measurement of  $pH_{susp}$  was performed every 5 seconds over the first minute of contact between the filler and water and after each minute over the following 5 minutes. By the position of extrema on the constructed graph of dependence  $pH_{susp} = f(\tau)$  we assessed the instantaneous surface reaction, which indicates the type of active centers that dominate on the surface. Using the graph, we also determined the value of  $pH_{susp}^p$  in the state of chemical equilibrium  $pH_{susp}^p$ . The values of  $pH_{IIP}$  were calculated from formula:

$$pH_T = pH_0 + (pH_{susp}^p - pH_0) \cdot (pH_0 - 6). \quad (1)$$

In this case, it was assumed that pKa of active centers that dominate are in the range of  $pH_{susp}^p - pH$ .

### 5. Examining chemical composition, surface morphology, and physical-chemical properties of fillers

In order to characterize the fillers and to interpret results of the experiments, we obtained microscopic images and measured certain physical-chemical characteristics – bulk density  $\rho_b$ , density after compaction  $\rho_{comp}$ , the volume of voids  $V_0$  and specific surface  $S_{sp}$ .

The microphotographs received are presented in Fig. 1.

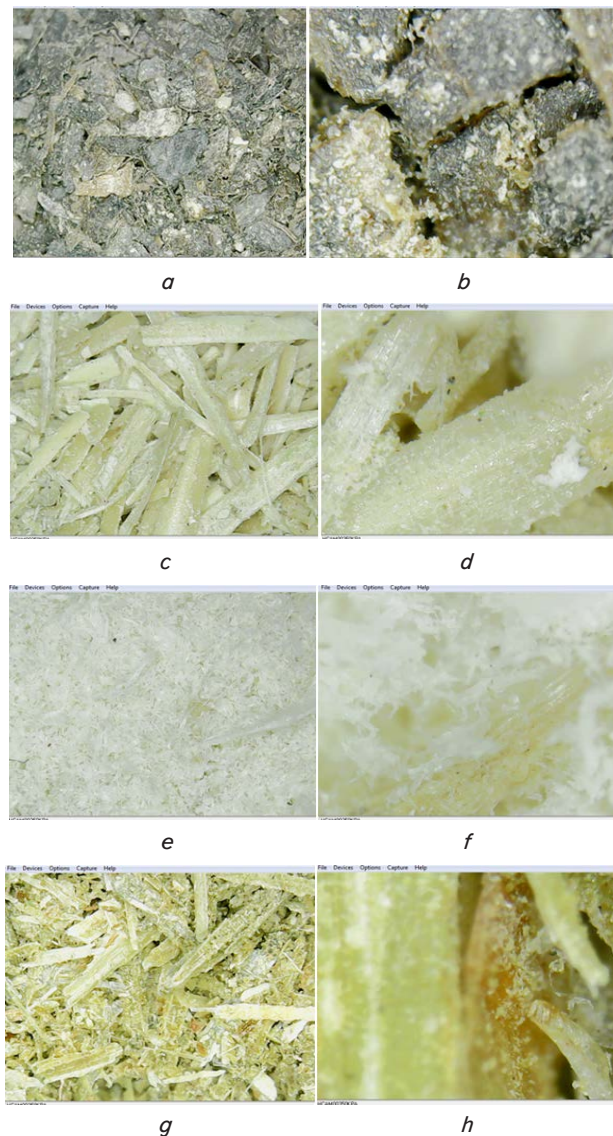


Fig. 1. Microphotographs of the particles: a, b – BH; c, d – OH; e, f – WF; g, h – NF, approximation: 100 % (a, c, e, g), and 500 % (b, d, f, h)

Results of the morphological studies, shown in Fig. 1, demonstrate that OH, WF and NF have a needle structure while BH is characterized by the laminar structure of particles. Particles of all fillers, except BH, are covered with resin or oily substances, as evidenced by the noticeable shine on microphotographs with large approximation (500 %). It should be noted that the range of particle size of BH and OH is, obviously, narrower than that of WF and NF, which, along with particles of a rather large size, contain particles, close in size to dust. Uneven distribution of particles by size results in a loose arrangement, and, consequently, reduces the bulk



density and density after compaction while increasing the volume of voids in the dispersed material. This assumption is confirmed by data on measuring the physical-chemical characteristics, given in Table 1.

Table 1

Physical-chemical characteristics of fillers

Filler	$\rho_b$ , kg/m <sup>3</sup>	$\rho_{comp}$ , kg/m <sup>3</sup>	$V_0$ , %	$S_{sp}$ , m <sup>2</sup> /g
BH	0.49	0.67	27	0.68
OH	0.27	0.48	45	0.75
WF	0.17	0.21	20	1.20
NF	0.20	0.32	37	0.92

The measured values of specific surface turned out to be the highest for particles of WF (1.2 m<sup>2</sup>/g) and NF (0.92 m<sup>2</sup>/g). This may indicate a large number of both the surface pores, openings and caverns and the centers absorption, which can include, among others, acid-base functional groups of organic molecules that come to the surface. The causes of increased capacity of particles for agglomeration and association is the presence of surface functionals and the acid-base interactions between them, for example, with the formation of hydrogen bonds. This leads to a decrease in the values of  $\rho_b$  and  $\rho_{comp}$ . The results given in Table 1 confirm these conclusions.

Surface functionals that can come to the surface of the particles are predetermined primarily by the chemical composition of a filler. Based on sources from the scientific literature, we compiled a comparative characteristic of approximate chemical composition of the examined fillers by some known components, given in Table 2.

Table 2

Chemical composition of fillers, % by weight

Filler	Cellulose	Lignin	Proteins	Lipids	Starch	Ash content
BH	29–39	30–35	1–5	1–5	1–2	4–5
OH	45–50	17–20	4–7	0.5–2	–	3–4
WF	65–70	22–28	–	–	–	0.2–2
NF	44–52	27–30	1–5	4–5	–	0.2–1.5

It follows from data in Table 2 follows that for all the examined fillers the main chemical components are the two kinds of organic matter: the polysaccharide cellulose and lignin – a mixture of aromatic polymers. Cellulose and lignin are not soluble and do not hydrolyze in water as a result of a large molecular weight and the formation of numerous intra- and intermolecular hydrogen bonds. Complex molecules of these substances contain a great number of different functional groups: hydroxyl, methoxyl, groups of simple and complex ethers, aldehydic, carbonyl. When emerging at the surface, the functionals create a wide range of active centers with a different function of acidity.

Cellulose and lignin are flammable substances, which is an essential disadvantage in terms of using the fillers of plant origin for producing TWPC. According to data from Table 2, the total content of cellulose and lignin in the examined fillers decreases in the series:

$$\text{WF (87–98 \%)} > \text{NF (71–82 \%)} > \text{BH (59–74 \%)} > \text{OH (62–70 \%)} \quad (2)$$

This series converges with the results of research into processes of thermo-oxidative destruction using the differential-thermal, differential-thermographic and thermogravimetric methods of analysis, which were derived in paper [33]. It was established that significant thermo-oxidative degradation of BH starts at a temperature of about  $T \geq 220$  °C, and that of OH at  $T \geq 200$  °C, with that of WF and NF at  $T \geq 160$ – $170$  °C. Thus, it was found that the particles of BH have a greater resistance to thermo-oxidative destruction than those of OH, NF and WF. This is obviously due not only to the reduced total content of cellulose and lignin, but also to the relatively larger number of inorganic components (ash content is 4–5 %) and the presence in the composition of BH of heat-resistant and non-combustible starch (1–2 %). Thus, it can be argued that when assessing resistance of the fillers of plant origin to high temperatures, one of the criteria can be a total content of cellulose and lignin.

Protein substances are contained in the composition of all fillers, except for WF. These are mostly difficult soluble fibrillary proteins, the bulk of which is represented by keratin [16, 17, 34, 35]. A typical type of bond in the protein molecules is the peptide bond, which is characterized by amphoteric character and can predetermine both acidic and basic properties of the surface.

The presence of insoluble lipids can provide basic properties of the surface. This is due to the presence in the molecules of fat of functional groups of complex ethers, which exhibit Lewis basicity.

The presence of pigments, insoluble in water (BH, NF), whose molecules contain polar functional groups (hydroxyl, phenolic, carbonyl, complex ethers, etc.) may also predetermine acidity of the surface of fillers.

According to data [16–18, 27, 34, 35], in addition to water-insoluble components, the examined fillers may contain small amounts of water-soluble organic compounds. These include, for example, free amino acids, tannins, gums, some pigments, pectins, organic acids (ascorbic, folic, etc.). Most of these compounds are characterized by acidic character. The presence of water-soluble substances can complicate interpretation of results derived from studies into aqueous solutions.

## 6. Discussion of results of potentiometric study into the acid-base properties of surfaces of the fillers of plant origin

The nature and acid-base properties of surface functional groups were studied in detail for the fillers of inorganic nature [32, 36, 37]. This is due to the fact that inorganic materials possess a more or less stable chemical composition and in most cases, a crystalline structure. The difficulty of research into materials of plant origin is caused by the requirement of simultaneous identification of a wide range of substances with different chemical nature. The characteristics of the components of fillers – density, molecular weight, molecular and supramolecular structure, decomposition temperature, solubility in solvents, heat capacity – have a very wide range. That is why most of the chemical and physical-chemical methods for studying surface properties of natural organic materials are not applicable.

In the study of surface acidity of inorganic dispersible materials, the potentiometric methods of research into aqueous suspensions were developed and are widely used [32]. In

order to assess the extent of integral (total) acidity of the surface of a solid body, the term “surface isostate” is applied. Isostate is an equilibrium steady state of inertia of the surface of a solid body in a solution, which is defined by the absence of mass transport of charged ions and is characterized by an isopoint (IP). At this point, over a certain time, the equilibrium is preserved between the ions of the hard surface and the ions in the solution. In terms of mass, there occurs the isoadsorption state (point of zero charge, PZC). In terms of charge, the system is characterized by the isoelectric state (isoelectric point, IEP).

We selected the *pH*-metric method for determining  $pH_{\text{susp.}}$  of aqueous suspensions by the technique of A. P. Nechyporenko to run a potentiometric analysis of the fillers of plant origin. The choice of the method for determining  $pH_{\text{susp.}}$  is due to the possibility of determining *pH* of the isoadsorption point (the point of zero charge)  $pH_{\text{IIP}}$ , that is, such a value of *pH* of the suspension, at which there is no a mass transfer of protoions from the solution to the surface of a solid body. A change in the values of  $pH_{\text{susp.}}$  over the time of contact between a solid body and a solution can be considered as the structure/property diagram. After a certain short period, the isoadsorption state of a solid surface is achieved, which is preserved over a certain long time. When considering the process and the patterns of change in  $pH_{\text{susp.}}$  over time, it becomes possible to determine the integral (total) acidity of the solid surface and the interface, as well as certain qualitative characteristics of the surface’s active centers. The value of  $pH_{\text{IIP}}$  indicates superiority of the surface’s acid or base active centers: the lower the acidic properties that characterize the surface in contact with an electrolyte, the larger the  $pH_{\text{IIP}}$  value in the given electrolyte. But it is necessary to take into account that the presence of water-soluble substances in the composition of fillers may complicate interpretation of the obtained results of experiments.

Results of the study into examined fillers employing the technique of A. P. Nechyporenko are shown in Fig. 2 and in Table 3.

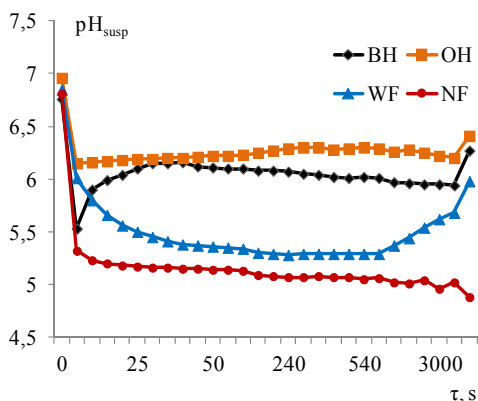


Fig. 2. Dependences of change in  $pH_{\text{susp.}}$  of aqueous suspensions on the duration of contact between fillers and water

When analyzing results shown in Fig. 2, it should be noted that at the moment of contact between the surface of fillers and water, *pH* of the suspension in all cases decreases dramatically, but the equilibrium is established after a while. The state of equilibrium in suspensions is preserved for 18–20 minutes. After this period, the values of  $pH_{\text{susp.}}$  change sharply. Over the period to 20 minutes, a change in *pH* of

the suspensions is related to the processes of absorption, hydration, dissociation, hydrolysis, and others, which occur on the surface of the particles of fillers. Probably, beyond this period, in the future, as a result of absorption of water molecules and ions and swelling, the processes will proceed inside the particles. Therefore, in order to analyze surface properties of the fillers of plant origin in aqueous suspensions, the observations are required over the first 20 minutes from the moment of contact with aqueous environment.

Table 3

Results of experimental determining of integral (total) acidity of the surface of fillers

Filler	$pH_0$	$pH_{\text{susp.}}^p$	$pH_{\text{IIP}}$	Time of reaching the equilibrium state, s
BH	6.76	5.53	5.83	40
	6.76	6.16	6.30	
OH	6.96	6.15	6.18	100
	6.96	6.30	6.32	
WF	6.85	5.29	5.52	180
NF	6.81	5.02	5.36	120

The duration of the period of time to establish the equilibrium state in a suspension can characterize the total quantity of acid-base surface’s active centers (functionals), which participate in the interactions with molecules of water. Indeed, the value of this period correlates with the indicators of specific surface of the fillers, and follows a directly proportional dependence: an increase in the specific surface results in the increased period of establishment of the equilibrium state in a suspension. In addition, based on data from Table 1, it can be noted that an increase in the period of establishing the equilibrium in a suspension leads to the increased capability of particles of a filler for agglomeration and association.

It was revealed in the course of research that there are two types of active centers at the surface of BH: weakly-acidic ( $pK_a \approx 5.53-5.83$ ) and almost neutral ( $pK_a \approx 6.16-6.30$ ). The surface of OH is of a character close to the neutral with an acidic strength of active centers of  $pK_a \approx 6.15-6.32$ . The surfaces of WF and NF are of total weakly-acidic character with centers  $pK_a \approx 5.29-5.52$  and  $pK_a \approx 5.02-5.36$ , respectively. In general, integral acidity of the surface of fillers decreases in the series:

$$NF > WF > BH > OH. \tag{3}$$

By comparing the obtained series – expressions (2) and (3), one can pay attention to the fact that both patterns are virtually the same. The exception is the greater acidity of the surface of NF than that of WF at a smaller total content of cellulose and lignin. The higher acidic character of the NF suspension can be explained by the presence of essential oils in the composition. Essential oils contain a mixture of various water-soluble substances of acidic character: water-soluble free amino acid, ascorbic and folic acid, pectin [34].

Thus, by summarizing the obtained results of potentiometric studies, it can be argued that the total acidity of the surface of fillers of plant origin depends in a greater extent on the total contents of basic components. It was established that an increase in the sum of basic components of cellulose and lignin results in the growth of surface acidity of the particles of fillers.

## 7. Conclusions

1. We conducted experimental studies into surface and physical-chemical properties of dispersed fillers of plant origin – buckwheat husk, oats husk, wood flour and pine needle flour. Microscopic studies have allowed us to determine morphology of the surface and a range of distribution of particles by size. A comparative characteristic of the chemical composition of fillers is considered. Based on the assumption that the functional groups of organic components can come to the surface of particles, an analysis was performed regarding a potential acid-base character of the surfaces. A correlation was found between a chemical composition and the physical-chemical characteristics of fillers. It is shown that the total content of cellulose and lignin can be one of the criteria for evaluating resistance of fillers to high temperatures. It was established that a decrease in the content of cellulose

and lignin leads to an increase in the resistance of fillers to high temperatures.

2. Employing a potentiometric analysis of aqueous suspensions by the technique of A. P. Nechyporenko, we investigated acid-base properties of the surface of fillers. It is shown that the use of this method makes it possible to accurately characterize the total relative quantity and acidic strength of the surface's functionals (active centers), which dominated on the surface of particles. It was revealed that the surface of BH is dominated by two types of active centers: weakly-acidic ( $pK_a \approx 5.53-5.83$ ) and almost neutral ( $pK_a \approx 6.16-6.30$ ). The surface of OH is of a character close to the neutral with an acid strength of active centers of  $pK_a \approx 6.15-6.32$ . The surfaces of WF and NF are characterized as the weakly-acidic with centers  $pK_a \approx 5.29-5.52$  and  $pK_a \approx 5.02-5.36$ , respectively. It was established that the acidity of the surface is directly proportional to the total content of cellulose and lignin in the composition of fillers.

## References

1. Klesov, A. A. Drevesno-polimernye kompozity [Text] / A. A. Klesov. – Sankt-Peterburg: Nauchnye osnovy i tekhnologi, 2010. – 736 p.
2. Dikobe, D. G. Effect of filler content and size on the properties of ethylene vinyl acetate copolymer–wood fiber composites [Text] / D. G. Dikobe, A. S. Luyt // Journal of Applied Polymer Science. – 2006. – Vol. 103, Issue 6. – P. 3645–3654. doi: 10.1002/app.25513
3. Polyolefin composites [Text] / D. Nwabunma, T. Kyu (Eds.). – John Wiley & Sons, Inc., 2007. – 603 p. doi: 10.1002/9780470199039
4. Shkuro, A. E. Poluchenie i izuchenie drevesno-polimernykh kompozitov s napolnitelyami iz othodov rastitel'nogo proiskhozhdeniya [Text] / A. E. Shkuro, V. V. Gluhih, N. M. Muhin // Lesnoy vestnik. – 2016. – Issue 3. – P. 101–105.
5. Kariev, A. I. Perspektyvy vykorystannia roslynnykh vidkhodiv u vyrobnytstvi polimernykh kompozitiv [Text] / A. I. Kariev, Yu. M. Danchenko // Materialy IX Mizhnarodnoi naukovy-tekhnichnoi WEB-konferentsii «Kompozitsiini materialy». – Kyiv, 2016. – P. 81–82.
6. Kariev, A. I. Vplyv pryrody dyspersnykh orhanichnykh napovniuvachiv na fizyko-mekhanichni vlastyvyosti kompozitiv z vtorynnoho polipropilenu [Text] / A. I. Kariev, Yu. M. Danchenko // Materialy II Mizhnarodnoi naukovy-tekhnichnoi Internet-konferentsyi «Resursozberezhennia ta enerhoefektyvnist inzhenernoi infrastruktury urbanizovanykh terytoriy ta promyslovykh pidpriemstv». – Kharkiv: KhNUHKh im. A. N. Beketova, 2016. – P. 104–107.
7. Zini, E. Green composites: An overview [Text] / E. Zini, M. Scandola // Polymer Composites. – 2011. – Vol. 32, Issue 12. – P. 1905–1915. doi: 10.1002/pc.21224
8. Petchwattana, N. Effects of Rice Hull Particle Size and Content on the Mechanical Properties and Visual Appearance of Wood Plastic Composites Prepared from Poly(vinyl chloride) [Text] / N. Petchwattana, S. Covavisaruch // Journal of Bionic Engineering. – 2013. – Vol. 10, Issue 1. – P. 110–117. doi: 10.1016/s1672-6529(13)60205-x
9. Lim, L. A. Poluchenie lignocellyuloznykh polimernykh kompozitov na osnove grechnevoy sheluhi i poliehtilena [Text] / L. A. Lim, D. A. Makeich, N. A. Prishchenko, A. M. Zaboltnaya, V. A. Reutov, E. V. Kovaleva // Mezhdunarodnyy zhurnal prikladnykh i eksperimental'nykh issledovaniy. – 2015. – Issue 6. – P. 514–514.
10. Reutov, V. A. Vliyanie sostava napolnitelya na svoystva lignocellyuloznogo polimernogo kompozitsionnogo materiala [Text] / V. A. Reutov, L. A. Lim, A. M. Zaboltnaya, N. A. Prishchenko, A. V. Anufriev, E. V. Pustovalov // Sb. materialov Vtorogo mezhdisciplinarnogo molodezhnogo nauchnogo foruma s mezhdunarodnym uchastiem «Novye materialy». – Moscow: Interkontakt nauka, 2016. – P. 69–71.
11. Yan, L. Flax fibre and its composites – A review [Text] / L. Yan, N. Chouw, K. Jayaraman // Composites Part B: Engineering. – 2014. – Vol. 56. – P. 296–317. doi: 10.1016/j.compositesb.2013.08.014
12. Bajwa, S. G. Properties of thermoplastic composites with cotton and guayule biomass residues as fiber fillers [Text] / S. G. Bajwa, D. S. Bajwa, G. Holt, T. Coffelt, F. Nakayama // Industrial Crops and Products. – 2011. – Vol. 33, Issue 3. – P. 747–755. doi: 10.1016/j.indcrop.2011.01.017
13. Binhussain, M. A. Palm leave and plastic waste wood composite for out-door structures [Text] / M. A. Binhussain, M. M. El-Tonsy // Construction and Building Materials. – 2013. – Vol. 47. – P. 1431–1435. doi: 10.1016/j.conbuildmat.2013.06.031
14. Kengkhetkit, N. A new approach to “Greening” plastic composites using pineapple leaf waste for performance and cost effectiveness [Text] / N. Kengkhetkit, T. Amornsakchai // Materials & Design. – 2014. – Vol. 55. – P. 292–299. doi: 10.1016/j.matdes.2013.10.005
15. Mattos, B. D. Properties of polypropylene composites filled with a mixture of household waste of mate-tea and wood particles [Text] / B. D. Mattos, A. L. Misso, P. H. G. de Cademartori, E. A. de Lima, W. L. E. Magalhães, D. A. Gatto // Construction and Building Materials. – 2014. – Vol. 61. – P. 60–68. doi: 10.1016/j.conbuildmat.2014.02.022
16. Zemnuhova, L. A. Neorganicheskie komponenty solomy i sheluhi ovsy [Text] / L. A. Zemnuhova, V. V. Budaeva, G. A. Fedorishcheva, T. A. Kaydalova, L. N. Kurilenko, E. D. Shkorina, S. G. Il'yasov // Himiya rastitel'nogo syr'ya. – 2009. – Issue 1. – P. 147–152.

17. Zemnuhova, L. A. Issledovanie aminokislотного состава v othodah proizvodstva risa, grechihi i podsolnechnika [Text] / L. A. Zemnuhova, N. V. Makarenko, L. Ya. Tishchenko, E. V. Kovaleva // Himiya rastitel'nogo syr'ya. – 2009. – Issue 3. – P. 147–149.
18. Yamansarova, E. T. Issledovanie sorbtsionnykh svoystv materialov na osnove rastitel'nogo syr'ya po otnosheniyu k organicheskim i neorganicheskim primesyam [Text] / E. T. Yamansarova, N. V. Gromyko, M. I. Abdullin, O. S. Kukovinec, O. B. Zvorygina // Vestnik Bashkirskogo universiteta. – 2016. – Vol. 21, Issue 1. – P. 73–77.
19. Li, F.-Z. Surface interaction energy simulation of ceramic materials with epoxy resin [Text] / F.-Z. Li, Z.-L. Lu, Z.-H. Yang, K. Qi // Polimery. – 2015. – Vol. 60, Issue 07/08. – P. 468–471. doi: 10.14314/polimery.2015.468
20. Danchenko, Yu. M. Regulation of free surface energy of epoxy polymer materials using mineral fillers [Text] / Yu. M. Danchenko // Polymer materials and technologies. – 2017. – Vol. 3, Issue 2. – P. 56–63.
21. Glazkov, S. S. Poverhnostnye ehnergeticheskie karakteristiki kompozitov na osnove prirodnykh polimerov [Text] / S. S. Glazkov, V. A. Kozlov, A. E. Pozhidaeva, O. B. Rudakov // Sorbtsionnye i hromatograficheskie processy. – 2009. – Vol. 1, Issue 1. – P. 58–66.
22. Starostina, I. A. Kislотно-osnovnye vzaimodeystviya i adgeziya v metall-polimernykh sistemah [Text] / I. A. Starostina, O. V. Stoyanov. – Kazan': Izd-vo Kazan. gos. Tekhnol. un-ta, 2010. – 200 p.
23. Barabash, E. S. Vliyaniye modifitsiruyushchih dobavok na adgeziionnyuyu sposobnost' ehpoksiaminnykh svyazuyushchih k alyumoborsilikatnomu steklu i stali [Text] / E. S. Barabash, Yu. V. Popov, Yu. M. Danchenko // Naukovyi visnyk budivnytstva. – 2015. – Issue 4 (82). – P. 122–128.
24. Danchenko, Yu. M. Vplyv kyslотно-osnovnykh vlastyvostei poverkhni poli mineralnykh napovniuvachiv na strukturu ta kharakterystyky epoksykompozitiv [Text] / Yu. M. Danchenko, Yu. V. Popov, O. S. Barabash // Voprosy himii i himicheskoy tekhnologii. – 2016. – Vol. 3 (107). – P. 53–60.
25. Andronov, V. A. Efficiency of utilization of vibration-absorbing polymer coating for reducing local vibration [Text] / V. A. Andronov, Yu. M. Danchenko, A. V. Skripinets, O. M. Bukhman // Scientific Bulletin of National Mining University. – 2013. – Issue 6. – P. 85–91.
26. Osipchik, V. S. Issledovanie vliyaniya poverhnostnykh svoystv bentonita na processy otverzhdeniya ehpoksiaminnykh kompozitsiy [Text] / V. S. Osipchik, R. A. Yakovleva, Yu. M. Danchenko, M. P. Kachomanova, R. A. Bykov, I. A. Posohova // Uspekhi v himii i himicheskoy tekhnologii. – 2007. – Vol. XXI, Issue 6 (74). – P. 40–43.
27. Yamansarova, E. T. Issledovanie sorbtsionnykh svoystv materialov na osnove rastitel'nogo syr'ya po otnosheniyu k neftyanym zagryazneniyam vody [Text] / E. T. Yamansarova, N. V. Gromyko, M. I. Abdullin, O. S. Kukovinec, O. B. Zvorygina // Vestnik Bashkirskogo universiteta. – 2015. – Vol. 20, Issue 4. – P. 1209–1212.
28. Lysak, I. A. Issledovanie kislотно-osnovnykh svoystv poverhnosti polimernykh voloknistykh materialov [Text] / I. A. Lysak, G. V. Lysak, T. D. Malinovskaya, L. N. Skvorcova, A. I. Potekaev // Pis'ma o materialah. – 2013. – Vol. 3, Issue 4. – P. 300–303.
29. Baranova, N. V. Vzaimosvyaz' himicheskoy struktury poverhnosti polimerov vinilovogo ryada s poverhnostnyimi kislотно-osnovnymi karakteristikami [Text] / N. V. Baranova, L. A. Pashina, E. G. Osipova // Vestnik Kazanskogo tekhnologicheskogo universiteta. – 2013. – Vol. 16, Issue 21. – P. 171–175.
30. Zenkiewicz, M. Methods for the calculation of surface free energy of solids [Text] / M. Zenkiewicz // Journal of Achievements in Materials and Manufacturing Engineering. – 2007. – Vol. 24, Issue 1. – P. 137–145.
31. Hejda, F. Surface free energy determination by contact angle measurements – a comparison of various approaches [Text] / F. Hejda, P. Solar, J. Kousal // WDS'10 Proceeding of Contributed Papers. – Prague, 2010. – P. 25–30.
32. Ikonnikova, K. V. Teoriya i praktika rN-metricheskogo opredeleniya kislотно-osnovnykh svoystv poverhnosti tverdyykh tel [Text] / K. V. Ikonnikova, L. F. Ikonnikova, T. S. Minakova, Yu. S. Sarkisov. – Tomsk: Izd-vo Tomsk. politekhn. un-ta, 2011. – 85 p.
33. Kariev, A. I. Vlastyvosti orhanichnykh napovniuvachiv derevno-polimernykh kompozitiv budivelnogo pryznachennia [Text] / A. I. Kariev, Yu. M. Danchenko, D. H. Yavorska // Naukovyi visnyk budivnytstva. – 2016. – Vol. 86, Issue 4. – P. 160–164.
34. Osadchuk, L. S. Vmist terpenovykh vuhlevodniv u khvoi sosny zvychainoi riznoi katehoryi smoloproduktyvnosti [Text] / L. S. Osadchuk // Naukovyi visnyk NLHU Ukrainy. – 2015. – Issue 25.3. – P. 16–21.
35. Mitrofanov, L. Yu. Izuchenie himicheskogo sostava vodnogo ehkstrakta solomy ovsya (AVENA SATIVA L.) i issledovanie ego rostoreguliruyushchih svoystv [Text] / L. Yu. Mitrofanov, V. N. Zolotuhin, V. V. Budaeva // Polzunovskiy Vestnik. – 2010. – Issue 4-1. – P. 174–179.
36. Tarasevich, Yu. I. Poverhnostnye yavleniya na dispersnykh materialah [Text] / Yu. I. Tarasevich. – Kyiv: Nauk. dumka, 2011. – 390 p.
37. Danchenko, Yu. Investigation into acid-basic equilibrium on the surface of oxides with various chemical nature [Text] / Yu. Danchenko, V. Andronov, E. Rybka, S. Skliarov // Eastern-European Journal of Enterprise Technologies. – 2017. – Vol. 4, Issue 12 (88). – P. 17–25. doi: 10.15587/1729-4061.2017.108946