

ANALYSIS OF THE EFFECT OF CHALK MODIFICATION ON THE PECULIARITIES OF ITS INTERACTION WITH ACRYLIC FILM FORMER

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Методом ІЧ-спектроскопії досліджено процеси взаємодії в системах крейда (у вихідному стані та модифікована) – акриловий плівкоутворювач. Показано, що модифікація поверхні крейди метилсилікатом калію може викликати зміну характеру взаємодії в системах з плівкоутворювачем. Отримані дані підтверджують можливість взаємодії між згаданими компонентами за участю адсорбованої води і зв'язків С=О і С–О крейди

Ключові слова: кремнійорганічний модифікатор, поверхнева модифікація, акриловий полімер, міжфазна взаємодія, ІЧ-спектроскопія

Методом ИК-спектроскопии исследованы процессы взаимодействия в системах мел (в исходном состоянии и модифицированный) – акриловый пленкообразователь. Показано, что модификация поверхности мела метилсиликатом калия может вызвать изменение характера взаимодействия в системах с пленкообразователями. Полученные данные подтверждают возможность взаимодействия между упомянутыми компонентами при участии адсорбированной воды и связей С=О и С–О мела

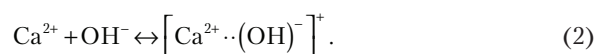
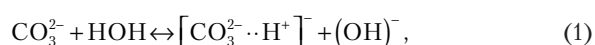
Ключевые слова: кремнийорганический модификатор, поверхностная модификация, акриловый полимер, межфазное взаимодействие, ИК-спектроскопия

1. Introduction

Treating the fillers with surface active substances (SAS) is one of the most effective methods for the modification of their properties, as well as for the intensification of processes in the production of paint and varnish materials. A wide experience of using surface-active modifiers for the creation of functional composite materials has been accumulated by chemical engineering [1].

In recent years, the task of the calcium carbonates modification, including chalk, has been quite relevant, which is linked to its cheapness and wide application in the polymeric industry [2].

At the surface of chalk, as a result of hydrolysis of surface compounds, there may be located the HCO_3^- ; CO_3^{2-} ; Ca_2^+ , CaHCO_3^+ ions, the OH hydroxyl groups and the molecules of H_2O . Due to its developed surface in these centers, chalk actively adsorbs moisture vapors whose binding and dissociation occurs according to the following schemes (1), (2) [3]:



According to the Langmuir theory of molecular adsorption, the absorption of non-polar polymer occurs not over the entire surface of adsorbent, but only at its active centers [4]. Hence, it follows that the intensification of processes of interaction in the systems of calcium carbonate (chalk) – polymer is possible due to the creation of additional organophilic groups over the active centers that are present on the surface of chalk. It is known that in the industry they use SAS for this purpose, in particular, organosilicone hydrophobizing liquids. The presence of an organic component in organosilicone materials creates conditions for the formation of reliable adhesive contact at the polymer – filler interface.

2. Literature review and problem statement

Article [5] demonstrated that improving the properties of composites based on styrene-butadiene latexes is possible

through their filling with the nanodispersed calcium carbonate, modified by silanes in waterless ethanol. In this case, silane agents displayed the highest effectiveness only at sufficiently high concentrations (to 5 % by mass). Also explored is the influence of calcium carbonate modification by the compound of stearin acid and silane on its interaction with polydimethylsiloxane. The method proposed in the work is rather energy-intensive because the process of modification occurs at high temperatures 105–125 °C [6].

Paper [7] examined a mechanism for the CaCO_3 activation in the interaction with SAS and the effect of this process on the foaming in aqueous dispersions. Positive effect is noted when anionic SAS are used. [8] described general patterns of influence of modifiers on the properties of paint and varnish materials, as well as enumerated and analyzed diverse methods for the modification. [9] investigated the modification and processes of interaction between the surface of CaCO_3 and SAS in more detail; this article, however, addressed the nanofillers only. There are also results of studies about the effect of treating the CaCO_3 particles surface with stearin acid by the Fourier infrared spectroscopy method [10].

Despite the existing positive results of applying SAS for the treatment of carbonate fillers (including chalk), the influence of modification on their interaction in the aqueous polymer systems is examined fragmentarily. Furthermore, in most cases this question is of theoretical character. In particular, there are no data about studies on the nature of interaction between the carbonate fillers, modified by silanes, and the aqueous dispersions of polymeric binding agents. Development of new composite materials and regulation of their properties with the help of functional fillers requires detailed study of this question.

In the previous articles, influence of the physical-chemical properties of chalks on the processes of adsorbing the acrylic polymers was demonstrated [11]. Optimum concentrations of anionic modifiers (including potassium methylsiliconate) for increasing the polymerphilicity of chalks were also determined [12]. In the present work, we conducted research into the spectrum-energy characteristics of the systems chalk – organosilicon modifier – acrylic polymer.

3. The aim and tasks of the study

The aim of present research is to establish special features in the processes of interaction in the systems of calcium carbonate and organosilicon modifier, as well as acrylic film forming agent. This will make it possible to regulate the properties of paint and varnish materials by influencing the interphase interaction as a result of the modification of filler.

To achieve the set aim, the following tasks were to be solved:

- to conduct IR spectroscopy of systems of the starting and modified chalks, as well as their systems with acrylic film forming agent; to compare the obtained results;
- to analyze characteristic absorption bands in charge of the valence vibrations of reactive groups of chalk and polymer with whose participation the interaction between chalk and the film forming agent occurs;
- to compare quantitative parameters of the basic spectral characteristic bands in the systems of modified chalks with acrylic polymer.

4. Materials and methods of research

4.1. Materials that are used for obtaining the systems chalk – organosilicon modifier – acrylic polymer

As the samples for tests, we selected chalks MTD-2 and MMS-1, which have significant specific share in the structure of raw materials supply for the paint and varnish industry. As a film-forming agent, we used aqueous dispersion of the acrylic polymer Osakryl AB-20. As a modifier, we selected a hydroalcoholic solution of potassium methylsiliconate $\text{CH}_3\text{Si}(\text{OH})_2\text{OK}$. The choice of modifier is predetermined by the fact that the surface of chalk has a positive charge. In turn, potassium methylsiliconate is the anion-active SAS, which in the aqueous solutions dissociates into potassium hydroxide and organosilicon anion. The latter can interact with the surface of filler to form insoluble salts.

Improving effectiveness of the modifier is possible by using it for the preliminary mechanoactivation of the filler in the process of grinding. The modification of chalk was carried out in the laboratory ball mills by dispersion in the presence of 0.5 % by weight of potassium methylsiliconate. The time of modification was 45–50 min.

The systems of chalks with the acrylic polymer were also prepared by dispersion in the laboratory ball mills. Then the samples were dried to a constant mass at temperature 105 °C. After this, they were washed clean by water to remove the polymer not attached at the surface, and dried again.

4.2. The infrared-spectroscopic method of exploring the systems chalk – organosilicon modifier – acrylic polymer

An analysis of the processes of interaction between the components of the examined systems was carried out with the help of IR-Fourier spectrophotometer Avatar 370 PT-TR (USA) in the range 4000–400 cm^{-1} . As a carrier, we used dehydrated KBr. The mass of carrier and the examined samples remained constant and were 170 and 3 mg, respectively.

The existence and degree of interaction were estimated by the displacement of characteristic vibration bands, which correspond to OH-groups, carboxyl, aryl and alkyl groups of chalks, modifier and polymer [13].

5. Results of examining the interaction between chalk and the acrylic film forming agent

We carried out analysis of the starting materials in order to detect functional groups of the modifier and film-forming agent on the IR spectra of the examined systems.

IR spectral analysis of the acrylic film forming agent Osakryl AB-20 (Poland) allowed us to state the presence in its composition of groups OH (3448 cm^{-1}) and bonds C–H (2956.6; 2873.7; 1452 and 842.7 cm^{-1}), C=O (1733.1 cm^{-1}), C–O (1165.4 cm^{-1}) (Fig. 1, *a*). Clearly observed on the IR spectra of potassium methylsiliconate are characteristic bands in charge of groups OH, Si–O, Si–R, Si–OH and C–H modifier (Fig. 1, *b*).

On the IR spectra of starting chalks MMS-1 and MTD-2, we noted intensive absorption bands with maximums at 3200–3500 cm^{-1} . These bands are characteristic for the molecules of sorbed water and bound OH-groups at the surface of the filler, which confirms high activity of chalks in the initial state relative to water (Fig. 2).

A general regularity in the modification of chalks is an increase in the number of OH-groups at their surface. The absorp-

tion band half-width in the range 3449–3459 cm^{-1} increases to 431–454 cm^{-1} , and intensity – by 15.4–21.2 % (Table 1).

Table 1
Parameters of the IR bands of the starting and modified chinks

MMS-1 starting			MMS-1 modified			MTD-2 starting			MTD-2 modified		
Band	$\Delta\delta_{1/2}$ cm^{-1}	I_0/I	Band	$\Delta\delta_{1/2}$ cm^{-1}	I_0/I	Band	$\Delta\delta_{1/2}$ cm^{-1}	I_0/I	Band	$\Delta\delta_{1/2}$ cm^{-1}	I_0/I
3450,9	–	0,26	3449,3	431,8	0,33	3458,1	–	0,13	3459,3	454,5	0,15
2513,5	159,1	0,52	2514,3	56,8	0,55	2513,4	–	0,65	2513,2	34,1	0,26
1434,9	1340,9	10,43	1422,0	1000,0	9,62	1455,1	–	4,82	1428,9	840,9	9,38
874,8	56,8	7,60	875,9	56,8	7,70	874,8	–	5,33	874,8	45,4	3,83
712,5	22,1	2,33	712,0	22,7	1,26	712,5	–	3,50	712,4	11,4	1,17

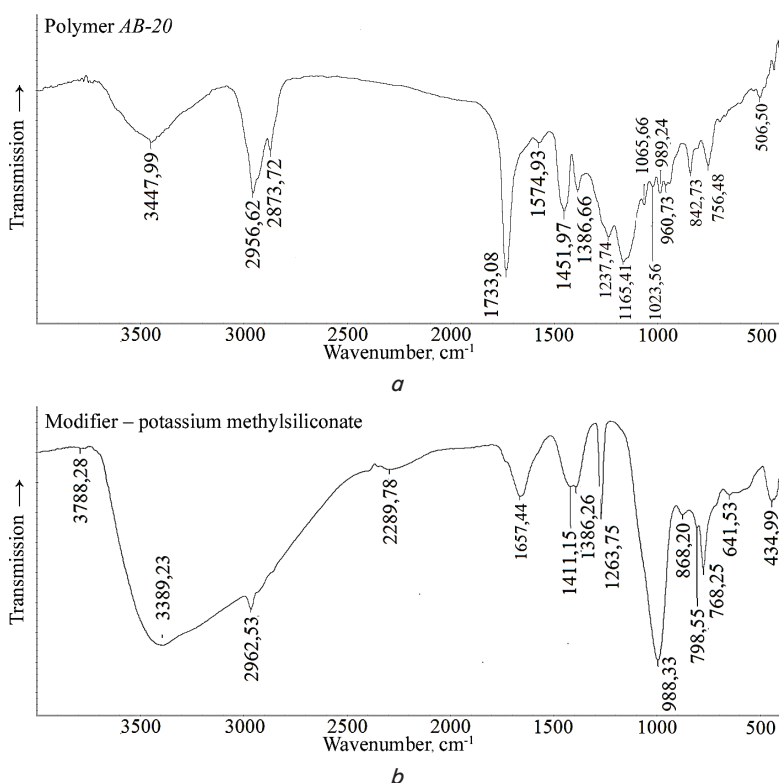


Fig. 1. IR spectra: *a* – acrylic polymer Osakryl AB-20; *b* – modifier potassium methylsilicate ($\text{CH}_3\text{Si}(\text{OH})_2\text{OK}$)

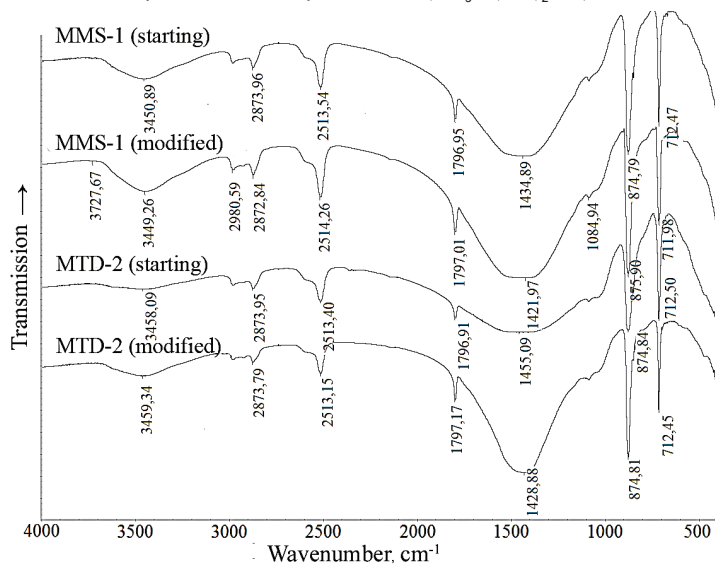


Fig. 2. IR spectra of the initial and modified chinks MMS-1 and MTD-2

The choice of the indicated groups for the estimation of effectiveness in the modification is caused by the presence of their significant quantity in the composition of potassium methylsilicate and by the fact that they are easy to identify against the background of IR spectra of calcium carbonate. Tracking other characteristic bands of the modifier (Si–O, Si–R, Si–OH and C–H) in the low-frequency part of the spectrum is impossible because of the disguising influence of carbonate-anion.

The application of methods of quantitative IR spectroscopy in the study of interaction between potassium methylsilicate during the process of dispersion with chinks allowed us to establish the following regularities (Fig. 2, Table 1):

- for MMS-1, which consists predominantly of calcite and aragonite, a disappearance of the characteristic absorption band of the latter is noted at 848.1 cm^{-1} ;

- the half-width of characteristic bands of calcites at 2513.5 and 1434.9 cm^{-1} decreases from 159.1 and 1340.9 to 56.8 and 1000 cm^{-1} , respectively, at an insignificant change in the intensities (I_0/I). A maximum change in the latter is observed for the band, predetermined by the presence of calcite at 719 cm^{-1} (from 2.33 to 1.26);

- it is necessary to note a shift in the band at 1434.9 cm^{-1} to 12, cm^{-1} in the region of lower frequencies. An even larger displacement (to 26.2 cm^{-1}) is observed for the chalk MTD-2, which contains predominantly aragonite (1455.1 cm^{-1}). Its intensity in this case grows almost by 2 times, and of the bands characteristic for calcite (2513.874 and 712 cm^{-1}) – decreases by 1.5–3 times.

To describe the processes of interaction between chinks and film forming agent, we employed the interpretation of changes in the parameters of bands characteristic for groups OH, C–H in the high-frequency part of the spectrum, C=O and C–O. The IR spectra of chinks of the MTD-2 and MMS-1 brands, in the starting state and after modification by potassium methylsilicate with acrylic polymer, are given in Fig. 3.

With the use of a film-forming agent, we registered a change in the intensity of bands at 1787–1790 cm^{-1} (decrease by 50 %). Moreover, this regularity is observed also after washing the excess of acrylic polymer, in contrast to the absorption bands of the adsorbed water. Somewhat different picture is observed in the systems based on the modified chalk and acrylic film-forming agent (displacement to 12 cm^{-1} towards lower frequencies and an increase in the intensity of absorption bands by 35 %).

The intensity of absorption bands of adsorbed water on IR spectrum of the system chalk MTD-2 (modified) – acrylic polymer is less by 25–30 % than when using the starting chalk. On the IR spectrum we also registered the appearance of new bands in the range 2996–2945 cm^{-1} . The intensity of bands in

charge of valence vibrations in compounds C=O falls by 50 % (Table 3).

Table 3

Parameters of IR bands of the systems based on chalks and acrylic polymer

MMS-1 (starting) – acrylic polymer		MMS-1 (modified) – acrylic polymer		MTD-2 (starting) – acrylic polymer		MTD-2 (modified) – acrylic polymer	
Band	I ₀ /I	Band	I ₀ /I	Band	I ₀ /I	Band	I ₀ /I
3442,2/3443,9*	0,12/0,15*	3443,6/3444,1*	0,16/0,14*	3446,1	0,24	3445,6	0,11
2959,2/2959,4	0,54/0,62	2959,8/2959,4	0,43/0,52	2959,4	0,37	2959,2	0,56
2874,1/2874,6	0,56/0,48	2874,0/2874,3	0,44/0,45	2874,1	0,33	2874,4	0,41
2514,0/2514,4	0,88/0,58	2514,1/2514,1	0,76/0,64	2514,2	0,56	2514,4	0,59
1419,3/1418,4	3,75/4,83	1420,5/1428,5	2,53/2,68	1426,4	4,64	1419,6	2,56
875,5/874,3	3,07/2,09	875,9/875,2	2,60/2,36	874,4	2,56	874,0	2,09
712,1/711,5	1,67/1,16	712,2/712,0	1,79/1,38	711,7	1,39	711,6	1,45

Note: * – denominator contains the values for models after washing by water

As a result of analysis of obtained data, it is possible to unambiguously establish the following:

- in the systems chalk – acrylic binding agent, independent of the presence of modifier and subsequent washing, an existence of the absorption bands is registered characteristic for bonds S=O and S–O;

- a quantity of compounds C–H (by the ratio of I₀/I intensities of bands in the range 2959–2874 cm⁻¹) grows by 2–3 times in comparison with the starting material for the system MMS-1 – acrylic film forming agent, and by 8 times in the case of system MDT-2 – potassium methylsiliconate – acrylate after washing;

- the concentration of OH-groups in the process of interaction with acrylic binding agent changes insignificantly (I₀/I values are within 0.12–0.16) for MMS-1; 0.1 – analogous, washed clean, and 0.24 – modified and washed clean;

- a presence of modifier in the system contributes to subsequent improvement in the structure of calcium carbonates. Along with calcite, we registered the appearance of dolomitized calcites (absorption band at 1418–1420 cm⁻¹);

- the intensity of absorption bands characteristic for calcite in the process of interaction with acrylic binding agent decreases from 0.76–3.07 to 0.58–2.36, while that of dolomitized calcite grows from 2.53–3.75 to 2.68–4.83 for MMS-1.

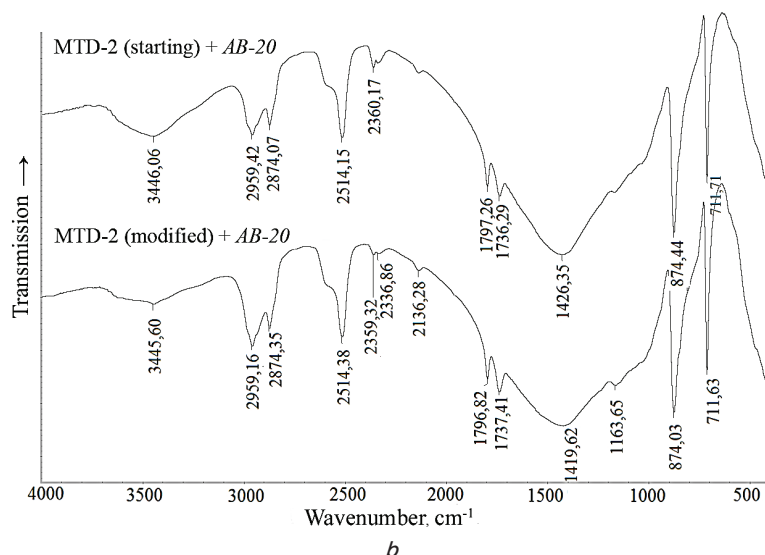
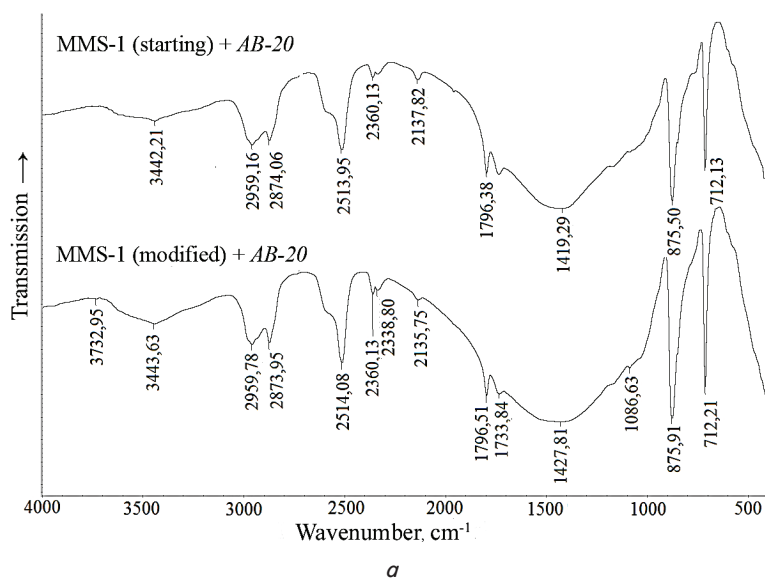


Fig. 3. The IR spectra of systems chalk – acrylic film forming agent: a – based on chalk MMS-1 after washing; b – based on chalk MTD-2 after washing

6. Discussion of research into the interaction between modified chalk and acrylic film forming agent

Infrared-spectroscopic analysis was carried out to analyze the interaction between modified chalk and acrylic film forming material. We compared characteristic spectrum bands of chalks in the starting and modified states, as well as the systems of these chalks with the film-forming agent.

Infrared-spectroscopic analysis of the system chalk – potassium methylsiliconate – acrylic film forming agent revealed that the interaction of these components occurs by means of the adsorbed water, bonds C=O and C–O of chalks. We also noted intensive inculcation of polymer (by the intensity of bands characteristic for bonds C–H) by 2–8 times as a result of modification.

The existence of the above-described changes in the parameters of basic bands of the absorption of structure-forming bonds of calcium carbonates can be explained by their interaction with the potassium ions. Moreover, this occurs

most intensively in the case of modification of aragonite in the composition of chalks, which has the loosest structure. A substitution of calcium by potassium contributes to the formation of a denser structure of the calcite type. In this case, we do not rule out additional formation of potassium carbonate.

7. Conclusions

1. We obtained the IR spectra of the starting, modified chalks and their systems with an acrylic film forming material. The IR spectra of the original chalks are characterized by intensive absorption bands with maximums at 3400–3500 cm⁻¹, in charge of the molecules of sorbed water at the surface of filler. This indicates high activity of chalks in the initial state towards water. For the modified chalk MMS-1, we observed a shift in the characteristic bands of adsorbed water and OH-groups up to 40 cm cm⁻¹ to the side

of high frequencies. Their intensity also decreases by 30 %. A decrease in the region of lower frequencies is also characteristic for the bands of calcites. A substitution of calcium by potassium contributes to the formation of a denser structure of the calcite type.

2. It is established that the processes of interaction between chalks MTD-2 and MMS-1, modifier (potassium methylsiliconate) and acrylic film forming agent occur with the participation of adsorbed water and bonds C=O and C–O of chalks.

3. The IR spectra of systems of the modified chalk with acrylic polymer are characterized by the decrease in the intensity of absorption bands of adsorbed water by 25–30 % in comparison with the starting chalk. A number of the C–H bonds, as a result of the modification of chalk, grows by 2–3 times for the system MMS-1 – acrylic polymer, and up to 8 times for the system MTD-2 – acrylic polymer, which indicates an increase in the interaction of chalks with the film forming agent.

References

1. Talbert, R. *Paint technology handbook* [Text] / R. Talbert. – New York: CRC Press, 2007. – 217 p. doi: 10.1201/9781420017786
2. Merezhko, N. Expanding of raw material base of mineral fillers for waterdispersion paints in Ukraine [Text] / N. Merezhko, V. Sviderskyi, V. Komakha, O. Shulga; R. SalernoKochan (Ed.) // *Commodity Science in Research and Practice – Nonfood products' quality and innovations*. – Cracow: Polish Society of Commodity Science, 2014. – P. 113–117.
3. Goldschmidt, A. *BASF Handbook on Basics of Coatings Technology* [Text] / A. Goldschmidt, H.J. Streitberger. – 2-nd ed. – Munster/Germany: Vincentz Network, 2007. – 769 p.
4. *Handbook of Surface and Colloid Chemistry* [Text] / K. S. Birdi (Ed.). – 4-nd ed. – New York: CRC Press, 2015. – 708 p. doi: 10.1201/b18633
5. Zhiyuan, Y. Surface modification of CaCO₃ nanoparticles with silane coupling agent for improvement of the interfacial compatibility with styrenebutadiene rubber (SBR) latex [Text] / Y. Zhiyuan, T. Yanjun, Z. Junhua // *Chalcogenide Letters*. – 2013. – Vol. 10, Issue 4. – P. 131–141.
6. Xu, X. Influence of surfacemodification for calcium carbonate on the interaction between the fillers and polydimethylsiloxane [Text] / X. Xu, X. Tao, Q. Zheng // *Chinese Journal of Polymer Science*. – 2008. – Vol. 26, Issue 02. – P. 145. doi: 10.1142/s0256767908002777
7. Cui, Z.-G. Aqueous foams stabilized by in situ surface activation of CaCO₃ nanoparticles via adsorption of anionic surfactant [Text] / Z.-G. Cui, Y.-Z. Cui, C.-F. Cui, Z. Chen, B. P. Binks // *Langmuir: the Acs journal of surfaces and colloids*. – 2010. – Vol. 26, Issue 15. – P. 12567–12574. doi: 10.1021/la1016559
8. Brok, T. *Evropejskoe rukovodstvo po lakokrasochnym materialam i pokrytijam* [Text]: *spravochnik* / T. Brok, M. Grotjeklaus, P. Mishke. – Moscow: Standart, 2007. – 548 p.
9. Song, E. Surface modification of CaCO₃ nanoparticles by alkylbenzene sulfonic acid surfactant [Text] / E. Song, D. Kim, B. J. Kim, J. Lim // *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. – 2014. – Vol. 461. – P. 1–10. doi: 10.1016/j.colsurfa.2014.07.020
10. Deshmukh, G. S. Effect of uncoated calcium carbonate and stearic acid coated calcium carbonate on mechanical, thermal and structural properties of poly(butylene terephthalate) (PBT)/calcium carbonate composites [Text] / G. S. Deshmukh, S. U. Pathak, D. R. Peshwe, J. D. Ekhe // *Bulletin of Materials Science*. – 2010. – Vol. 33, Issue 3. – P. 277–284. doi: 10.1007/s12034-010-0043-7
11. Komaha, V. O. *Procesy vzajemodii' v systemi «modyfikovanyj karbonatnyj napovnjuvach – plivkoutvorjuvach»* [Text] / V. O. Komaha, V. A. Sviders'kyj // *Tovary i rynky*. – 2015. – Issue 1. – P. 135–141.
12. Komaha, V. O. *Energetychnyj stan poverhni modyfikovanyh karbonatnyh napovnjuvachiv* [Text] / V. O. Komaha, V. A. Sviders'kyj // *Visnyk Chernigivs'kogo derzhavnogo tehnologichnogo universytetu. Serija «Tehnichni nauky»*. – 2015. – Issue 1 (77). – P. 43–49.
13. Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds* [Text] / K. Nakamoto. – 6-th ed. – Canada: Wiley, 2008. – 432 p. doi: 10.1002/9780470405840