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*V.Ye. Levytskyi, A.S. Masyuk, O.V. Suberlyak***PREPARATION AND PROPERTIES OF POLYMER-SILICATE COMPOSITES BASED ON HYDROPHILIC POLYMERS****Lviv Polytechnic National University**

In this work we have established the influence of the nature and content of polymer modifiers, polyvinyl alcohol and polyvinylpyrrolidone, on the physicochemical and technological characteristics of preparation of polymer-silicate composites based on sodium liquid glass under the influence of metal chlorides of different nature (Ba, Cu, Co, Ni, Zn, Fe). To ensure maximum efficiency of the modification and preparation of a polymer-silicate composite, the polyvinylpyrrolidone should be dissolved in sodium liquid glass solution, and polyvinyl alcohol should be dissolved in the solution of metal chloride, the optimum concentration of the polymer in the system being 0.2–0.3 base mol/dm³. Based on the results of scanning electron microscopy, elemental analysis, IR spectroscopic and sorption studies, we have stated that the fabrication of a polymer-silicate material is accompanied by intermolecular interactions between active silicate groups (sylandiolic, silanolic and siloxane) and functional groups of polymer, which contributes to the uniform distribution of macromolecules in silicones-oxygen carcass. The use of polymer modifiers, regardless of the nature of the metal, leads to a decrease in the number of active centers and the value of the active surface area of silicate formations. The specific active surface area and the number of active centers on it depend on the nature of the metal and decreases in the following range: Ni²⁺>Zn²⁺>Fe³⁺>Cu²⁺>Co²⁺>Ba²⁺. The values of the specific surface area and the number of active centers relative to methylene blue are 60–76 m²/g and (77–99)×10⁻⁶ mol/g, respectively; they depend on the nature of the polymer modifier.

Keywords: polyvinylpyrrolidone, polyvinyl alcohol, sodium liquid glass, modification, composite.

Introduction

The polymeric composites with distinctive nanodimensionality of filler [1,2] are increasingly gaining importance. Among the significant range of fillers used for the creation of composites the silicate materials of different nature deserve special attention [3,4].

It is advisable to use silicate fillers obtained by precipitation of water-soluble silicates, sodium liquid glass in particular, due to the simplicity of their preparation and availability of raw materials [5]. However, problems associated with low technological compatibility of filler and polymer matrix are arising during creation of polymer composites [6,7]. As a result, physical, mechanical and thermal properties of the composites become worse. In this regard, it is advisable to conduct a preliminary modification of silicate materials to enhance their technological compatibility with the composite matrix. Most

methods of fillers modification include adsorption of surfactants of different nature or chemical reactions of polymer modifier with the surface groups of silicate fine filler [8,9]. Typically, these methods are labour-intensive, multistage and demand specific modifiers and modification conditions [10].

At the same time, a method has been developed which includes coprecipitation of water-soluble silicates and functional hydrophilic polymers from aqueous solution [11]. It doesn't have the mentioned disadvantages. The advisability of using functional active high-molecular compounds to modify silicate fillers is confirmed by the fact that these polymers contain active groups and are characterized by high capability of reaction with proton-containing and high-polar molecules as well as inorganic polymers and ions. Moreover, from the point of starting materials rational use, technology efficiency and quantitative yield of polymeric-silicate material with

required properties, the use of polyvinylpyrrolidone (PVP) and polyvinyl alcohol (PVA) is advisable for modification [12–15]. Metal salts used as precipitants of sodium liquid glass extend the application area of obtained silicate materials.

Modified silicate materials are widely used as fillers to create polymer composites, sorbents, catalysts etc. The aim of this work is to establish physicochemical characteristics of obtaining polymer-silicate composites based on water-soluble silicates and hydrophilic polymers under the action of different metal chlorides and determine interrelation between materials morphology and properties.

Materials and methods

Aqueous solution of sodium liquid glass (Na-LG) with concentration of 1 mol/l and modulus of $n=2.8$ was purified by filtration from soot, SiO_2 and Si colloidal particles. PVA Gohsenol 58 B (Nippon Gohsei, Japan) and high-purified PVP with molecular weight of 28000 (AppliChem GmbH, Germany) were used as polymer modifiers. Metal chlorides (Cu, Co, Ni, Ba, Zn, Fe) were of P.A. purity.

To obtain polymer-silicate composites (PSC), the following solutions were previously prepared. PVA and PVP in Na-LG which were exposed to metal chlorides action and solutions of metal chlorides with dissolved PVA and PVP which were acting upon Na-LG. PVA and PVP concentrations varied from 0 to 0.4 base mol/l [11]. The precipitate was filtered, vacuumed and washed with distilled water to remove Cl^- and Na^+ ions and then dried in vacuum drier at 353–363 K.

To establish the physicochemical features of preparation of polymer-silicate composites based on sodium liquid glass, a series of instrumental analyses was carried out as follows: gravimetry, sorption, photocolometry, IR-spectroscopy, energy-dispersive X-ray spectroscopy (EDS) and scanning electron microscope (SEM).

The Radwag XA 110/X scales with precision of ± 0.0005 g were used to carry out gravimetric analysis. The standard solutions of PVA and PVP with iodine were prepared to determine PVA and PVP concentrations in the filtrate. The colorimeter KFK-2 MP was used for investigations. The spectrograph SPECORD 70 was used for IR-spectroscopy; the spectra were recorded within the range of 400–4000 cm^{-1} . SEM and EDS analyses were carried out using scanning electronic microscope RES-106I. Methylene blue, brilliant green and methylene blue as indicators were used to determine the sorption properties of polymer-silicate composites. The material was mixed with an indicator at 298 ± 1 K for 1 h, then the solution was centrifuged

and the absorbance was measured.

Results and discussion

To obtain highly dispersed PSC with particle sizes of 50–200 nm and a uniformly distributed polymer modifier, the concentration of aqueous solutions of Na-LG and metal chloride should vary within the range 10–15 wt.%, and the $\text{MeCl}_2/\text{Na-LG}$ [mole]/[mole] ratio should be equal to 0.8–1.

Irrespective the method of hydrophilic polymer modifiers introduction, the nature of precipitant slightly affects the process of PSC fabrication. Apparently, it is caused by the peculiarities of metal cation reaction with Na-LG in the presence of PVA and PVP macromolecules. At the same time, the introduction of polymer into the reaction medium provides an increase of process efficiency under the action of such precipitants as CuCl_2 , CoCl_2 , ZnCl_2 and NiCl_2 . The exclusion is BaCl_2 . The possible reasons are the formation of soluble $\text{Ba}(\text{OH})_2$ in the reaction medium and steric obstacles caused by large size of Ba^{2+} .

Obviously, two following processes proceed in the systems during the formation of polymer-silicate composite: (1) the formation of silicate nuclei with the contribution of siloxane bonds and metal cations; and (2) the interaction between silicate nuclei and with PVA/PVP macromolecules, i.e. between polymer functional groups and silanol/siloxane surface groups of the nearby nuclei.

The active participation of the polymer modifier in the redistribution of intermolecular interactions between the components of the reaction medium in the process of formation of PSC is confirmed by the data on photocolometric investigations of the modified materials filtrates. On this basis, we determined the effectiveness of modification PSC depending on the polymer method introduction (in Na-LG or in precipitant – CuCl_2) and its content in the reaction medium (Fig. 1).

The modification by PVP is more effective if it is previously dissolved in Na-LG. This feature is due to different type of intermolecular interactions in the system PVP–Na-LG and PVP–metal salt. The modification by PVA is more effective if it is previously dissolved in CuCl_2 . This feature might be connected with the partial hydrolysis of PVA acetate groups caused by the presence of free OH^- ions in the sodium liquid glass. As a result, PVA solubility in the reaction medium diminishes. Moreover, a part of PVA molecules is precipitated as drop particles and participates in the modification process in a less degree. An increase in the concentrations of polymer to 0.3–0.4 base mol/l results in a reduction of the modification efficiency for PVP by 5–15% and a reduction by 15–30% for PVA after the previous

introduction to Na-LG.

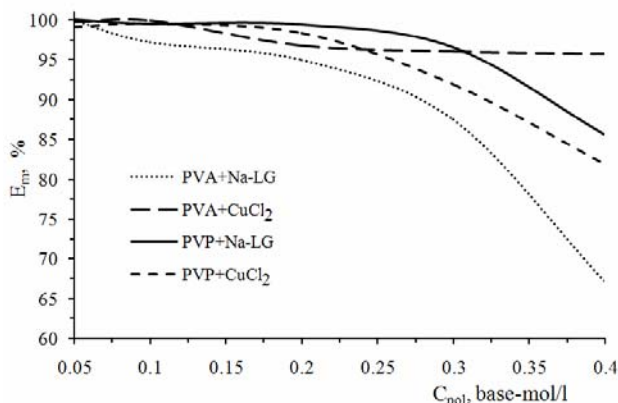


Fig. 1. Influence of the concentration of polymer C_{pol} and the method of its introduction on the effectiveness of modification (E_m) of PSC

The nature of metal insignificantly affects the PSC modifying efficiency by polyvinylpyrrolidone (Fig. 2,a), the lowest values were observed for Co- and Zn-containing PSC (82–86 and 90–93%, respectively).

For PVA (Fig. 2,b), the modification efficiency is slightly lower than for PVP, while introducing a polymer in a solution of Na-LG reduces modification efficiency by 10–20% for all types of precipitants.

The coprecipitation of Na-LG and PVA or PVP under the influence of metal chlorides leads to the formation of material, in which polymer macromolecules are uniformly distributed inside the silicate skeleton, not just adsorbed over the surface. This distribution is caused by physical interaction of

polymer macromolecules with functional silicate groups. The results of IR-spectroscopy (Fig. 3) confirm this conclusion.

All materials, regardless of the nature of the polymer and metal, have absorption bands with the greatest intensity, that are caused by major internal vibrations of atoms in a tetrahedron $[\text{SiO}_4]^-$, bound in silicon-oxygen frame and valence asymmetric, symmetric and deformation vibrations of Si–O bonds in the range of 1100–900 cm^{-1} and vibrations O–Si–O bonds in the range of 800–600 cm^{-1} . For polymer-silicate composite, the following shifts of typical absorption bands of PVP and PVA were detected: $-\text{CH}_2-$ 2840–2860 cm^{-1} and 1450–1550 cm^{-1} , CH_3- 1458 cm^{-1} , $-\text{C}=\text{O}$ 1682 cm^{-1} , $-\text{N}-\text{C}=\text{O}$ 1628 cm^{-1} and $-\text{C}=\text{O}$ 1677 cm^{-1} , which indicates their participation in the modification process. In case of physical mixture of PVP and silicate material (Fig. 3, curve 3), the absorption peak of N–C=O groups (1652 cm^{-1}) is higher than for the PSC obtained by compatible precipitation due to the presence of «free» PVP carbamate groups and their smaller impact on intermolecular interactions in the system. For polymer-silicate composite, unlike unmodified, there is no intense vibration peaks of hydroxyl groups of hydration membranes in the region of 3200–3600 cm^{-1} which is caused by redistribution of intermolecular interactions in the system with direct participation of functional groups or PVP and PVA macromolecules and silicon-oxygen frame.

The interrelations between the preparation method and structure of polymer-silicate composites were determined on the basis of elemental analysis (Table 1).

The metals in silicate frame are uniformly distributed during coprecipitation. Due to directed

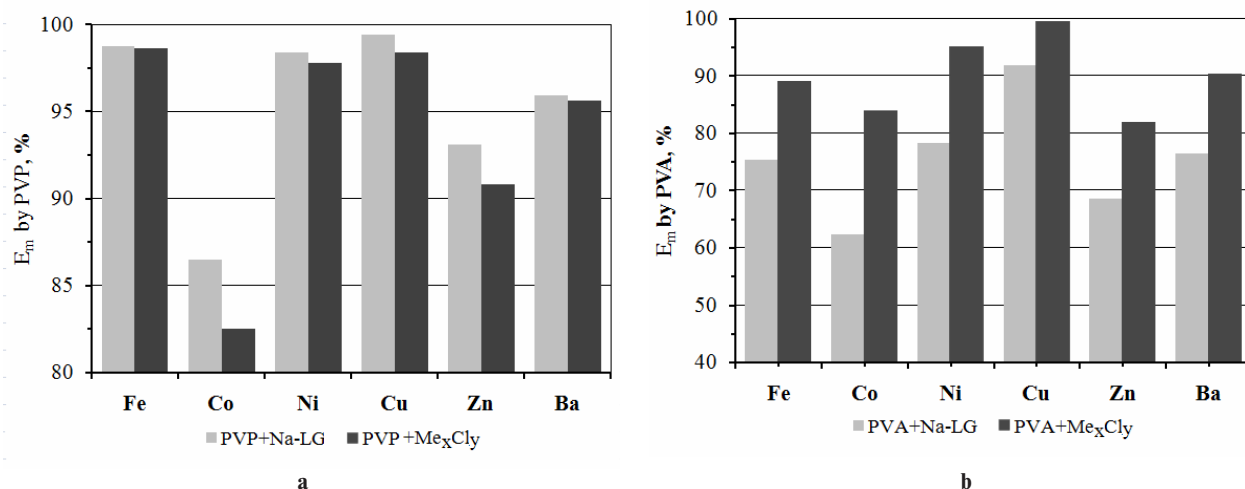


Fig. 2. Influence of metal nature on the PSC modifying effectiveness (E_m): a – PVP; b – PVA; $C_{pol}=0.2$ base mol/l

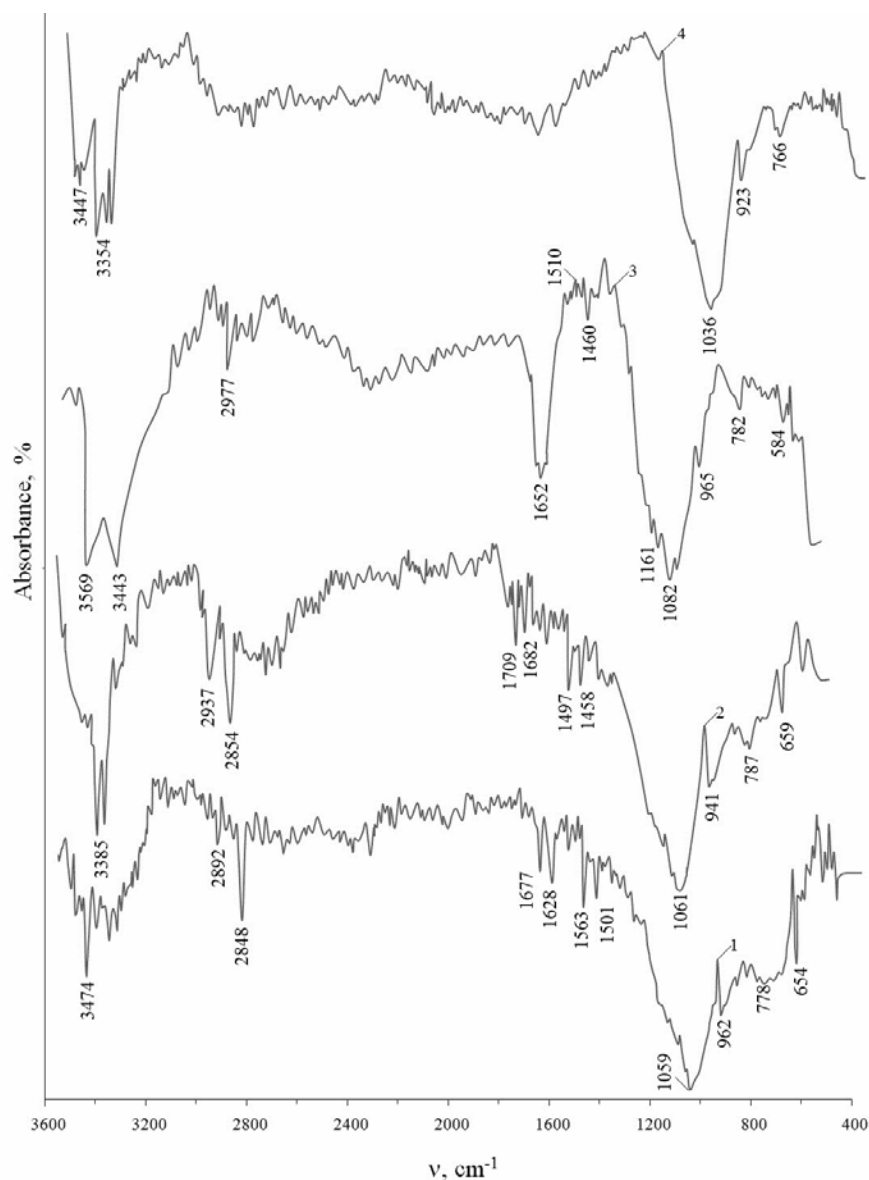


Fig. 3. IR-spectra of polymer-silicate composites: Cu-silicate material modified by PVP (1); Cu-silicate material modified by PVA (2); physical mixture of Cu-silicate material and PVP (3); unmodified Cu-silicate material (4)

Table 1

Elemental composition of polymer-silicate composites

Components of the reaction medium		Content of elements in the composite, at.%				Elements ratio	
Precipitant	Polymer	O	Si	Me		Me/Si-O	O/Si
CuCl ₂	–	57.95	27.30	14.75		0.17	2.12
	PVP	67.30	17.25	15.45		0.18	3.90
	PVA	65.64	25.28	9.08		0.09	2.59
CoCl ₂	–	54.08	18.77	27.15		0.37	2.83
	PVP	76.26	19.63	4.11		0.04	3.88
BaCl ₂ +ZnCl ₂ *	PVP	59.01	25.58	Ba	Zn	0.18	2.30
				0.08	15.33		
BaCl ₂ +ZnCl ₂	PVP	71.15	20.84	3.49	4.52	0.08	3.41

Note: * – physical mixture of Ba- and Zn-silicate composites.

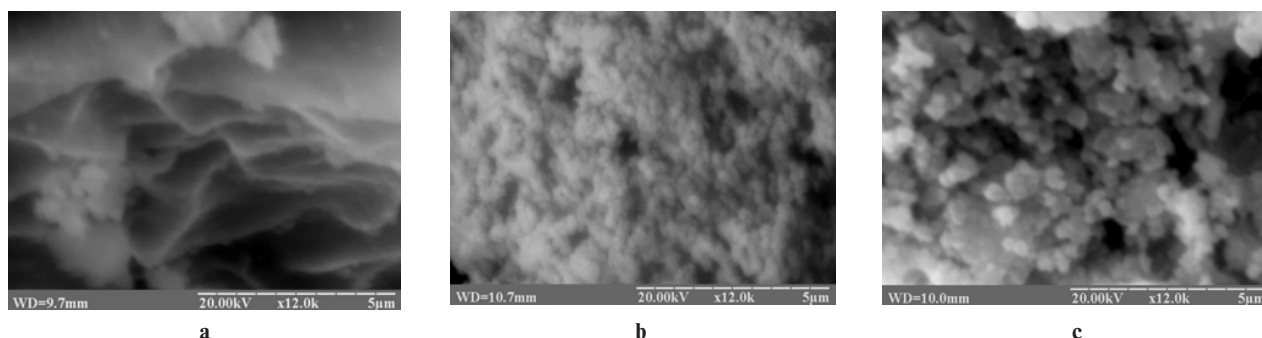


Fig. 4. SEM images of Cu-silicate materials with different polymer modifiers: without polymer (a); PVP (b); PVA (c)

control of initial parameters (concentration and mixing method), it is possible to establish necessary ratio of metals in polymer-silicate composites, depending on the final goal. The increase in oxygen/silicium atomic ratio is observed in the modified materials indicating the transfer from three-dimensional to two-dimensional silicate frames—chain, ribbon or layered. This transfer is caused by the interaction of PVP/PVA and silicate materials at the stage of nucleation and growth.

The use of modifiers decreases the metal content in the composite. The maximum content of metal is observed for the systems with CoCl_2 as a precipitant. The possible reason is a specific interaction of Co^{2+} with silicate nuclei at the beginning of silicate materials formation. The effect of polymer nature on morphology of PSC is confirmed by SEM images (Fig. 4).

The introduction of modifier leads to the formation of silicate materials with particles which are homogeneous by both shape and size. While using PVA, the particles are more monolithic which is caused by peculiarities of macromolecules' conformational characteristics. It should be noted that resulting polymer-silicate composites are agglomerates composed of the particles with the size of 50–200 nm.

We investigated the sorption of several indicators (methylene blue, diamond green and bromocresol purple) to determine the surface characteristics of polymer-silicate composites. These indicators have different nature of functional groups and value of pK_a and are capable of being adsorbed on the surface due to the physical interaction with acid centers. It was determined that the nature of modifier also influences specific area of active surface of polymer-silicate composites (Table 2).

We found that the sorption capacity for the studied material has a specific and selective nature and is determined by the nature of polymer modifier and metal. The number of active centers q_a is reduced

in the following range: $\text{Ni}^{2+} > \text{Zn}^{2+} > \text{Fe}^{3+} > \text{Cu}^{2+} > \text{Co}^{2+} > \text{Ba}^{2+}$ based on determined patterns of sorption. Both for modified materials and for unmodified ones, the highest activity is observed for methylene blue, and bromocresol purple displays the lowest activity. At the same time, the adsorption of methyl orange does not occur at all. For indicators with pK_a within the range of 4.2–12.8, the more influence have PVP than PVA. This difference is probably related to larger conformational parameters of PVP macromolecules and their increased ability to form complexes.

Table 2

The influence of metal and polymer nature on the number of active centers q_a of polymer-silicate composites

No	Indicator	pK_a	Polymer	$q_a \times 10^6, \text{mol/g}$	
				Nature metal	
				Cu	Ni
1	Diamond green	1.3	–	8.64	1.37
			PVP	7.84	1.09
			PVA	5.00	0.85
2	Bromocresol purple	6.4	–	1.71	0.66
			PVP	0.88	0.50
			PVA	1.17	0.44
3	Methylene blue	9.7	–	94.00	99.10
			PVP	80.75	94.15
			PVA	87.10	97.20

Polymer modifiers also influence the specific surface area of the active of PSC S_a (Fig. 5), in particular, lead to some reduction of its value.

The use of polymer modifiers, such as PVP and PVA, leads to the formations of fewer active centers due to the blocking of active groups of silicate surface formations (sylandiolic, silanolic and siloxane) resulted from the interaction with the functional groups of the polymer.

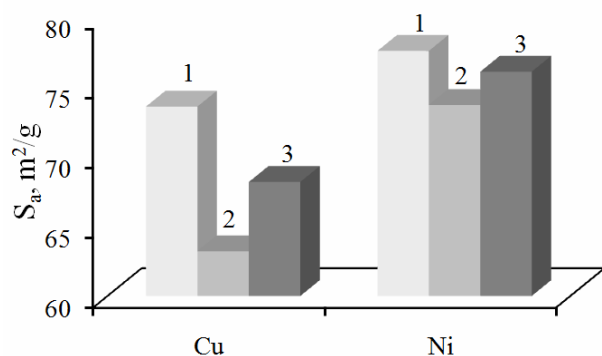


Fig. 5. The influence of polymer nature on the specific surface active area of PSC (S_a): 1 – without polymer; 2 – PVP; 3 – PVA

Conclusions

Physicochemical features of the preparation of polymer-silicate composites resulted from PVA or PVP and sodium liquid glass coprecipitation under the influence of metal chlorides of different nature were determined. The effects of precipitant nature, polymer introduction method, polymer nature and concentration on the modification efficiency and morphology of polymer-silicate composites were stated.

It was found that PVP should be dissolved in the solution of sodium liquid glass and PVA should be dissolved in the solution of metal chloride. This provides the maximum degree of polymer precipitation, high modification efficiency and yield of precipitated polymer-silicate composites. The polymer optimal concentration was found to be 0.2–0.3 base mol/l.

The fabrication of polymer-silicate composite is accompanied by intermolecular interactions between active silicate groups and functional groups of polymer providing uniform distribution of macromolecules in the silicium skeleton.

Irrespective of metal nature, the presence of polymer modifiers decreases the number of active centers and specific area active surface. The reason is the blocking of active surface groups of silicate materials resulted from the reaction with modifier functional groups. The obtained polymer-silicate materials can be effectively used as filler-modifiers for the composites on their basis, thermoplastic and thermoset composites in particular, due to high technological compatibility with thermoplastics and thermosetting plastics.

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V.Ye. Levytskyi, A.S. Masyuk, O.V. Suberlyak

Lviv Polytechnic National University, Lviv, Ukraine

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