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REGULARITIES OF OBTAINING, MORPHOLOGY AND PROPERTIES OF METAL-CONTAINING POLYMER-SILICATE MATERIALS AND POLYESTER COMPOSITES ON THEIR BASIS

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Abstract. The effect of the kind, concentration and introduction method of polymeric modifiers (polyvinyl alcohol and polyvinylpyrrolidone), as well as the kind of metal chloride on the physico-chemical regularities of the obtaining process of modified metal-containing polymer-silicate materials, their morphology and properties has been examined. Using instrumental methods of investigations it was established that obtaining of metal-containing polymer-silicate materials was accompanied by intermolecular interactions between active silicate groups and functional groups of a polymeric modifier. The effect of metal-containing polymer-silicate materials on the regularities of curing and properties of polyester composites has been studied.

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

1. Introduction

The polymeric composites with distinctive nanodimensionality of a filler [1] are gaining in importance. Among the significant amount of fillers used for the creation of composites the silicate materials of different kinds are of special attention [2, 3].

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. However, when creating polymer composites a problem associated with low technological compatibility of a filler and polymer matrix is arising [4]. 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 kinds or chemical reactions of the modifier with the surface groups of silicate fine filler [5]. Typically, these methods are labour-intensive, multistaged and demand specific modifiers and modification conditions [6].

At the same time the method including coprecipitation of water-soluble silicates and functional polymeric modifiers from aqueous solution has been developed [7]. It is without 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 [8, 9].

Moreover, from the viewpoint 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 [10]. Metal salts used as precipitants of sodium liquid glass extend the application area of obtained silicate materials [11].

Modified silicate materials are widely used as fillers to create polyester composites. Materials based on unsaturated polyester resins and silicate fillers are characterized by high hardness and moisture resistance, resistance to aggressive media and temperature, high adhesion to the surface of different kinds [12, 13].

The aim of this work is to establish physico-chemical regularities of obtaining metal-containing polymer-silicate materials based on water-soluble silicates and polymers under the action of different metal chlorides and interrelation with materials morphology and properties.

2. Experimental

Aqueous solution of sodium liquid glass (Na-LG) with concentration of 1 mol/l and modulus $n = 2.8$ was purified by filtration from soot, SiO_2 and Si colloidal particles. PVA 16/1 (Azot, Ukraine) and high-purified PVP with molecular weight of 28000 (AppliChem GmbH, Germany) were used as polymeric modifiers. Metals (Cu, Co, Ni, Ba, Zn) chlorides were of P.A.purity.

To obtain polymer-silicate materials the following solutions were previously prepared: PVA and PVP in Na-LG which were exposed to metals chloride action and solutions of metals chloride with dissolved PVA and PVP which acted upon Na-LG. PVA and PVP concentrations were varied from 0 to 0.4 base-mol/l. The precipitate was filtered, vacuumized and washed with distilled water to remove Cl^- and Na^+ ions and then dried in vacuum drier at 353–363 K.

To establish the physico-chemical regularities of obtaining polymer-silicate materials based on sodium liquid glass a series of instrumental analyses was carried out: gravimetry, sorption, photocolourimetry, IR-spectroscopy, EDS and SEM.

To carry out gravimetric analysis the scales Radwag XA 110/X was used with the precision of ± 0.0005 g. To determine PVA and PVP concentrations the standard solutions of PVA and PVP with iodine were prepared. The photocolourimeter 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 RES-106I scanning electronic microscope. To determine the sorption properties the photocolourimeter KFK-2 with methylene blue as an indicator were used. The material was stirred with the indicator at 298 ± 1 K for 1 h, then the solution was centrifuged and the optical density was measured.

To create polyester composites the unsaturated polyester resins Estromal 11LM-02 and Estromal A023 were used. The composites were cured at room temperature in the presence of cobalt naphthenate as an accelerator and methylethylketone peroxide in dibutylphthalate (Metox-50) as an initiator.

The regularities of unsaturated polyester resins curing were studied by the viscosimetric method using Rheomat-30 with the constant share rate of 28.5 s^{-1} in the measuring cell consisting of coaxial cylinders.

The hardness of samples relative to conic flow point was measured at 293 K using Hepler consistometer. The steel cone with a lip angle of $58^\circ 08'$ and loading of 5.0 kg was pressed in the sample for 60 s.

3. Results and Discussion

The effect of modifier introduction method and the kind of precipitant on the efficiency of obtaining polymer-silicate materials (PSM) is represented in Table 1.

Irrespective of modifier introduction method the kind of precipitant essentially affects the process of PSM obtaining. Apparently, it is connected with the peculiarities of metal cation reaction with Na-LG in the presence of PVA and PVP macromolecules. At the same time the introduction of polymeric modifier into the reaction medium provides the 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 formation of soluble $\text{Ba}(\text{OH})_2$ in the reaction medium and steric obstacles connected with a large size of Ba^{2+} .

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

While using complex precipitants ($\text{BaCl}_2 + \text{ZnCl}_2$) it is possible to create metal-containing polymer-silicate materials with controlled content of various metals that extends the application area of resulting materials.

The increase in polymer concentration till 0.3–0.4 base-mol/l increases PSM yield. The change of PVP introduction method does not affect the yield of polymer-silicate products. If PVA is introduced, the increase in its concentration influences PSM yield depending on introduction method.

Table 1

Effect of modifier/precipitant kind and modifier introduction method on PSM yield

Polymeric modifier*	Introduction method	Precipitant				
		CuCl_2	CoCl_2	ZnCl_2	BaCl_2	$\text{BaCl}_2 + \text{ZnCl}_2$
Without modifier		194.9	184.7	178.6	167.2	173.0
PVP	into precipitant	276.5	251.4	234.4	148.9	276.3
	into Na-LG	279.7	254.5	234.7	165.4	280.1
PVA	into precipitant	229.1	211.1	175.6	159.2	170.4
	into Na-LG	218.5	196.6	181.9	149.3	170.5

Note: * $C_{pol} = 0.2$ base-mol/l

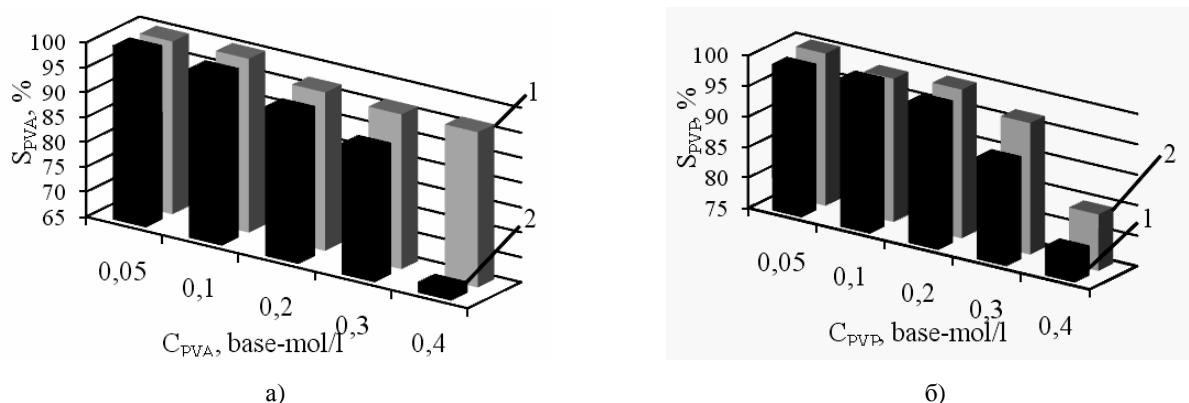


Fig. 2. Effect of polymer (PVP (a) and PVA (b)) concentration and its introduction method (into CuCl_2 (1) and into Na-LG (2)) on the degree of polymer precipitation S_{pol}

The active role of polymeric modifier in the intermolecular interactions is confirmed by photocolorimetric investigations of modified material filtrates which were used to determine the degree of polymer precipitation S_{pol} (Fig. 2).

PVP precipitation is more complete if it is previously dissolved in Na-LG. This peculiarity is conditioned by different types of intermolecular interactions in the system PVP–Na-LG and PVP–metal salt. PVA precipitation is more complete if it is previously dissolved in CuCl_2 . To our mind, this peculiarity is connected with partial hydrolysis of PVA acetate groups [14] caused by the presence of OH^- free ions in the sodium liquid glass. As a result, PVA solubility in the reaction medium is decreased. Moreover, a part of PVA molecules is precipitated as impregnated particles and participates in the modification process in a lesser degree.

The co-precipitation of Na-LG and PVA or PVP under the action of metal chlorides leads to the formation of material, where polymer macromolecules are uniformly distributed inside the silicate skeleton, but 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.

The most intensive bands within $1100\text{--}900\text{ cm}^{-1}$ typical of all samples are specified by internal vibrations of atoms in tetrahedrons $[\text{SiO}_4]$ [15], as well as by stretching asymmetric, symmetric and deformation vibrations of Si–OH bonds. Regardless of the modifier kind, the intensive bands corresponding to O–Si–O bonds are observed within $800\text{--}600\text{ cm}^{-1}$. Typical absorption bands of C–H bonds corresponding to $-\text{CH}_2$ groups are observed within $2840\text{--}2860\text{ cm}^{-1}$ for PVP-silicate composite and within $1450\text{--}1550\text{ cm}^{-1}$ – for PVA-silicate one. It should be also noted that typical vibrations of acetate groups were found: CH_3 – at 1458 cm^{-1} and C=O – at 1682 cm^{-1} (for PVA-silicate composite). For

PVP-silicate composite the vibrations of $-\text{N-C=O}$ group were observed at 1628 cm^{-1} and C=O – at 1677 cm^{-1} .

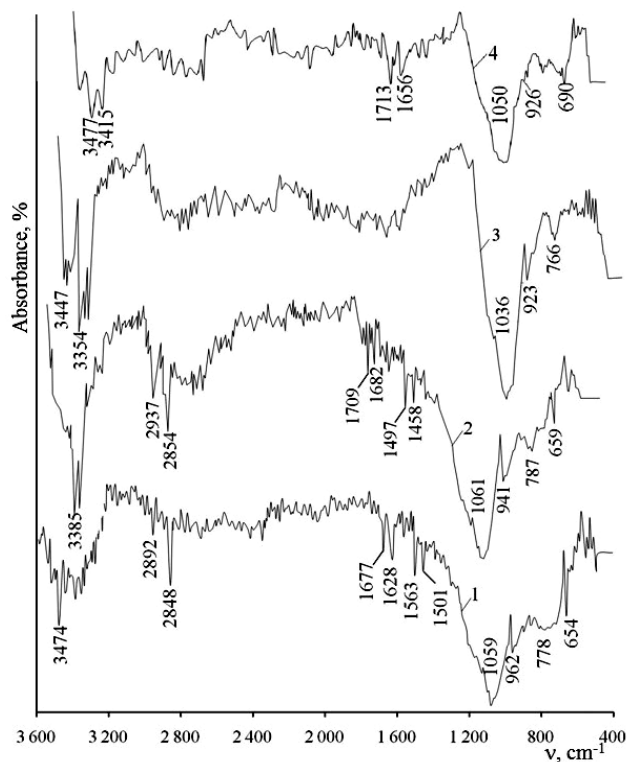


Fig. 3. IR-spectra of polymer-silicate materials: Cu-silicate material modified by PVP (1); Cu-silicate material modified by PVA (2); Cu-silicate material (3) and physical mixture of Cu-silicate material and PVP (4)

The shift of characteristic absorption bands of silicate materials caused by physical interaction between modifier functional groups and surface groups of silicium-oxygen skeleton is observed. In the case of non-modified silicate materials the appearance of intensive bands within

3200–3600 cm^{-1} , which correspond to the stretching vibrations of hydroxy group, are caused by the presence of hydration shell of capillary moisture. If silicate materials are modified, intensive peaks of hydroxy group vibrations are not observed. The reason is the enhancement of

silicium-oxygen skeleton hydrophobicity due to the modification.

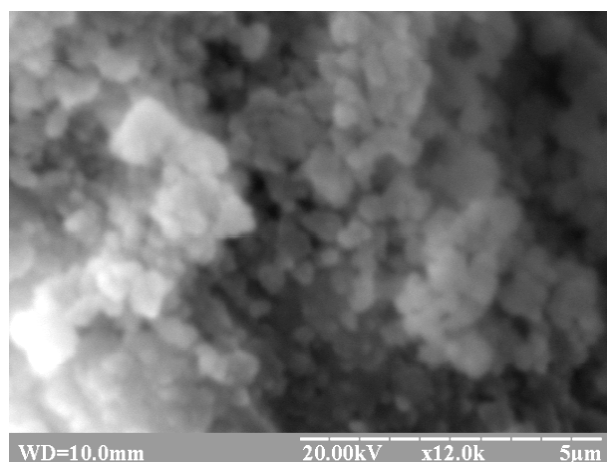
On the basis of elemental analysis the interrelation between the obtaining method and structural peculiarities of polymer-silicate materials was determined (Table 2).

Table 2

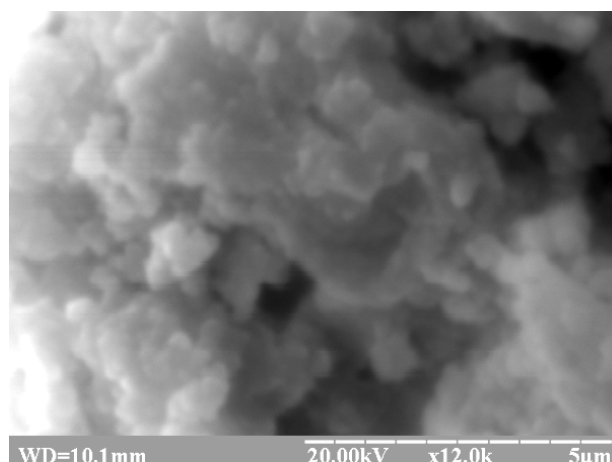
Elemental composition of resulting metal-containing polymer-silicate materials

Components of the reaction medium		Content of elements in the composite, atom%				Elements ratio	
Precipitant	Modifier	O	Si	Me		Me/Si-O	O/Si
CuCl ₂	–	57.95	27.3	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 *	–	59.01	25.58	Ba	Zn	0.18	2.30
				0.076	15.33		
BaCl ₂ +ZnCl ₂	–	71.15	20.84	3.49	4.52	0.08	3.41

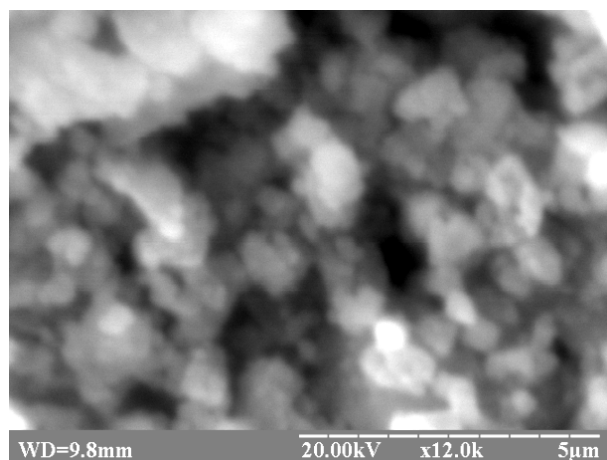
Note: *physical mixture of Ba- and Zn-silicate materials



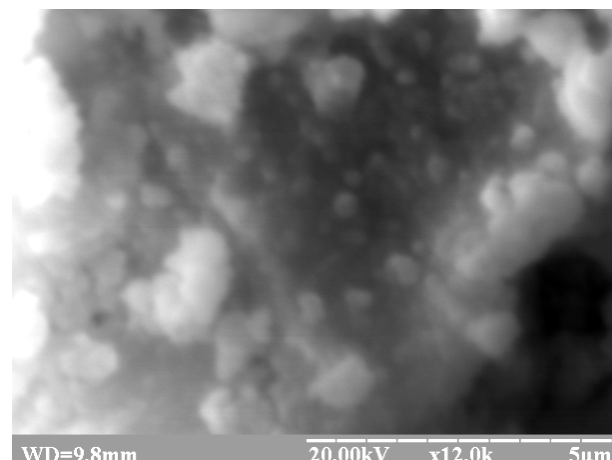
a)



b)



c)



d)

Fig. 4. SEM images of Cu-silicate materials with different modifiers: without modifier (a); PVA (b); PVP (c) and physical mixture of PVP and Cu-silicate material

Table 3

Effect of metal and modifier kinds on the number of active centers q_a and specific area of active surface S_a of polymer-silicate materials

Kind of metal	Modifier	$q_a \cdot 10^6$, mol/g	S_a , m ² /g
Cu	–	94.00	73.59
	PVP	80.75	63.21
	PVA	87.10	68.18
Ni	–	99.10	77.58
	PVP	94.15	73.70
	PVA	97.20	76.09

During co-precipitation the metals in silicate skeleton are distributed uniformly. Due to directed control of initial parameters (concentration and mixing method) it is possible to develop necessary ratio between metals in the polymer-silicate material, depending on the final goal. The increase in oxygen : silicon atomic ratio is observed in the modified materials indicating the transfer from three-dimensional to two-dimensional skeleton silicates – chain, band or layered. This transfer is connected with PVP/PVA and silicate materials interaction at the stage of nucleation and growth.

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

One can see that 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 that is connected with peculiarities of macromolecules conformational characteristics and, hence, with type of interaction.

While using the physical mixture of PVP and Cu-containing silicate materials we observe considerably greater dispersion of the particles and availability of large monolithic irregular particles. It should be noted that resulting polymer-silicate composites are agglomerates composed of the particles with the size of 50–200 nm.

To determine surface characteristics of metal-containing polymer-silicate materials we investigated the sorption of indicator – methylene blue – capable to be adsorbed on the surface due to the physical interaction with acid centers. It was determined that the kind of modifier also influences specific area of active surface of metal-containing polymer-silicate materials (Table 3).

The modification decreases the value of specific area of active surface relative to methylene blue regardless of metal kind. At the same time the modification effect of PVP is higher. The reason is the blocking of active surface groups of silicate materials as a result of reaction with modifier functional groups.

The resulting polymer-silicate materials may be effectively used as filler-modifiers for the composites on

their basis, polyester composites in particular, due to high technological compatibility with thermoplastics and thermosetting plastics. Therefore we conducted investigations concerning the effect of metal-containing polymer-silicate materials on the regularities of unsaturated polyester compositions curing and their properties.

The formation of network polymer is accompanied by occurrence of structural heterogeneities, which in turn, provide the occurrence of residual stress in the composite matrix and affect its strength. The introduction of metal-containing polymer-silicate filler into the structure of polyester composite influences the crosslinking of binding agent due to the formation of boundary layer with the lower crosslinking degree. In addition, it becomes possible to control the operational properties, namely the values of surface hardness.

The effect of metal-containing polymer-silicate fillers on the surface hardness is represented in Fig. 5.

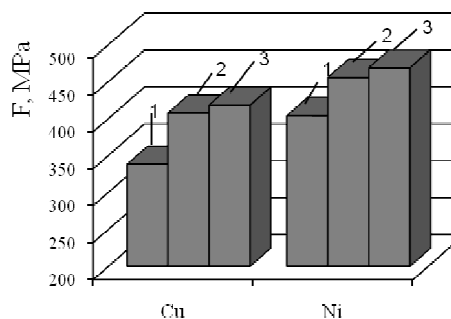


Fig. 5. Effect of filler kind on the surface hardness of polyester composite: without modifier (1); PVP (2) and PVA (3)

It should be noted that introduction of Ni- and Cu-containing polymer-silicate materials into polyester composite increases the value of surface hardness. The similar effect of polymer modifier on the surface hardness is observed for any kind of metal but composites on the basis of metal-silicate materials modified by PVA have higher values of surface hardness.

Fine metal-containing polymer-silicate materials change kinetic dependencies of polyester composite hardness which were determined in the present work by viscosimetry. The results are present in Fig. 6.

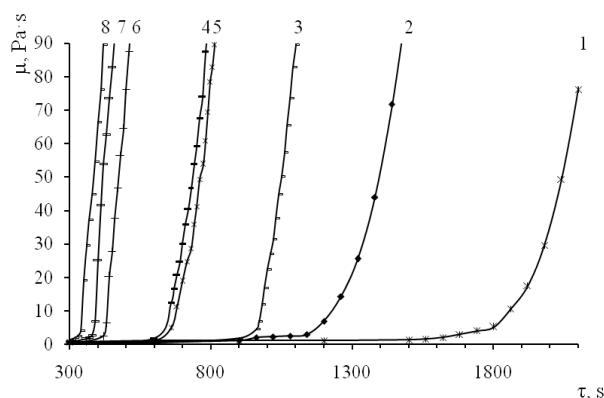


Fig. 6. Kinetic dependencies of viscosity for polyester composites based on Estromal 11LM-02 resin (1-4) and Estromal A023 (5-8) during their curing in the presence of Ni-containing polymer-silicate fillers (2 wt %): without filler (1, 5); filler without polymer modifier (2, 6); filler modified by PVA (3, 7) and filler modified by PVP (4, 8)

Ni-containing polymer-silicate fillers in the reaction medium accelerate polyester composites curing. Polymer modifier accelerates the crosslinking of polyester matrix. It is connected with the enhancement of technological compatibility between composite components and blocking of silicate material functional groups by PVP carbamate groups or PVA hydroxy groups. At the same time PVP accelerates crosslinking to a greater extent compared with PVA.

The determined physico-chemical and technological regularities of the obtaining metal-containing polymer-silicate materials as a result of PVA or PVP and sodium liquid glass co-precipitation under the action of different metal chlorides open up new possibilities to control properties and structure of the resulting materials.

4. Conclusions

Physico-chemical regularities of the obtaining metal-containing polymer-silicate materials as a result of PVA or PVP and sodium liquid glass co-precipitation under the action of metal chlorides of different kinds were determined. The effect of precipitant kind, polymer introduction method, polymer kind and concentration on the modification efficiency and morphology of polymer-silicate materials was studied.

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

Using EDS, SEM and IR-spectroscopy it was established that obtaining 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 kind, the polymer modifiers decrease the number of active centers and specific area of active surface. The reason is the blocking of active surface groups of silicate materials as a result of reaction with modifier functional groups.

Fine metal-containing polymer-silicate materials affect the kinetic dependencies of unsaturated polyester resins curing and properties of the composites on their basis.

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ЗАКОНОМІРНОСТІ ОДЕРЖАННЯ, МОРФОЛОГІЯ І ВЛАСТИВОСТІ МЕТАЛОВІСНИХ ПОЛІМЕР-СИЛІКАТНИХ МАТЕРІАЛІВ ТА ПОЛІЕСТЕРНИХ КОМПОЗИТІВ НА ЇХ ОСНОВІ

Анотація. Встановлено вплив природи, концентрації і способу введення полімерного модифікатора (полівініловий спирт та полівінілпіролідон) та природи хлориду металу на фізико-хімічні закономірності процесу одержання модифікованих металовісних полімер-силікатних матеріалів, на їх морфологію та властивості. На підставі інструментальних досліджень встановлено, що процес одержання металовісних полімер-силікатних матеріалів супроводжується міжмолекулярними взаємодіями між активними силікатними групами та функційними групами полімерного модифікатора. Досліджено вплив металовісних полімер-силікатних матеріалів на закономірності тверднення та властивості поліестерних композитів.

Ключові слова: композит, натрієве рідке скло, полівініловий спирт, полівінілпіролідон, осаджувач, модифікування, поліестерний композит.