

Sorption Properties of Metal-containing Polymer-Silicate Fillers

Andrii Masyuk, Volodymyr Levytskyi

Department of Chemical Technology of Plastics,
Lviv Polytechnic National University, UKRAINE, Lviv,
S. Bandery street 12, E-mail: masyukas@gmail.com

Abstract – Sorption properties of metal-containing polymer-silicate fillers on regarding to different acid-base indicators have been investigated. The effect of the nature of metal and polymer modifier on the amount of active centers and specific active surface area of such material was determined. Moisture absorption of modified and not modified silicate materials has been found.

Key words – metal-containing polymer-silicate fillers, modifier, sorption, indicators, moisture absorption.

I. Introduction

Becoming increasingly important polymer composite materials based on nanoscale fillers. In particular, it is expedient to use metal-containing polymer-silicate fillers, which received by compatible precipitation of sodium liquid glass (Na-LG) and water-soluble functional polymers under the influence of metal chlorides (Ba, Cu, Co, Ni, Zn, Fe) [1]. The functional active polymers acting as a modifier and that allows to regulatet the properties of fillers and increase their technological compatibility with polymer matrix of composites [2].

An important characteristic of these modified materials is their surface adsorption properties that are directly related to the process of their modifying and nature of modifier.

As a modifiers was used water soluble, surface-active polymers: polyvinylpyrrolidone (PVP) and polyvinyl alcohol (PVA). The macromolecule of modifier uniformly distributed in the silica framework due to a compatible precipitation of water-soluble silicates and polymers from an aqueous solution [3]. The use of number of precipitant with different nature of metal increases the range of possible use such materials.

Therefore, the establishment of nature of precipitant and modifier on sorption properties of metal-containing polymer-silicate fillers is an urgent task.

II. Experimental

For obtaining the polymer-silicate fillers previously prepared solution of PVP in Na-LG, for which were acted by solution of metal chloride and prepared metal chloride solutions with dissolved there PVA, which acted on the Na-LG [1]. The resulting precipitate was filtered, evacuated and thoroughly washed with distilled water, then dried in a vacuum dryer at 80-90 °C

To install the sorption characteristics of these materials, such as the amount of active centers of sorption and specific active surface area, was elected a number of indicators with functional groups of different nature and pKa value.

Sorption ability of studied materials determined by photocolometry on photocolometer KFK-2. Concentration of indicators in aqueous or aqueous-alcoholic

solution was $(0,2-5) \cdot 10^{-4}$ M, and the mass of samples 0,25 g. Material stirred in solution of indicator for 1h. after that the solution was centrifuged and absorbance measurements were carried out.

To determine water absorption using vapor saturated solution of sodium dihydrogen phosphate with constant value of relative humidity of 95%.

III. Results and Discussion

On the basis of the results of sorption of methylene blue in metal-containing silicate materials can be argued that the ability to sorption in the studied material has a specific and selective nature and likely determined by the nature of metal (Table 1).

TABLE 1
THE EFFECT OF METAL NATURE ON THE SPECIFIC ACTIVE SURFACE AREA S_a AND AMOUNT OF ACTIVE CENTRES q_a

№	Metal nature	$q_a \cdot 10^6$ mol/g	S_a , m ² /g
1	Cu ²⁺	94,0	73,59
2	Ba ²⁺	77,8	60,94
3	Al ³⁺	94,6	74,06
4	Ni ²⁺	99,1	77,58
5	Zn ²⁺	96,4	75,46
6	Fe ³⁺	96,2	75,31
7	Co ²⁺	85,4	66,85

The lowest value of the specific active surface area and the number of active centers observed for systems where as precipitant were used barium and cobalt chlorides. This difference is related to structural features of the surface of such materials, and in the case of barium chloride with the possibility of the formation of soluble Ba(OH)₂ in the reaction medium and steric obstacles that are associated with large size of cation Ba²⁺. At the same time, the influence of valence metal on sorption ability of metal-containing silicate materials are not observed, apparently confirms the homogeneity of the surface of studied materials.

It is established that the number of active centers of sorption studied of metal-containing polymer-silicate fillers depends essentially on the nature of the indicator (Table 2).

TABLE 2
AMOUNT OF ACTIVE CENTERS OF CU-CONTAINING POLYMER-SILICATE FILLER

Indicator	pKa	Modifier	$q_a \cdot 10^6$, mol/g
Brilliant green	1,3	–	8,64
		PVP	7,84
		PVA	5,00
Bromophenol blue	4,2	–	6,36
		PVP	6,63
		PVA	–
Bromocresol purple	6,4	–	1,71
		PVP	0,88
		PVA	1,17
Methylene blue	9,7	–	94,00
		PVP	80,75
		PVA	87,10
Indigo carmine	12,8	–	2,28
		PVP	0,55
		PVA	1,58

As in the case of modified materials and not modified the highest activity shows up on methylene blue and brilliant green, and the lowest - bromocresol purple. At the same time, the sorption of methyl orange is not happening at all.

Found that the use of polymeric modifiers leads to a reduction of the specific active surface area and the amount of active centers on it. This feature as a result of blocking the active groups on silicate structures due to interaction with the functional groups of the polymer modifier. Should be noted that for most of indicators PVP impact is more significant than the PVA. This difference is related to greater conformational parameters of PVP macromolecules and presence of more sophisticated functional groups.

Established that the modifiers also affect the specific active surface area (Fig. 1).

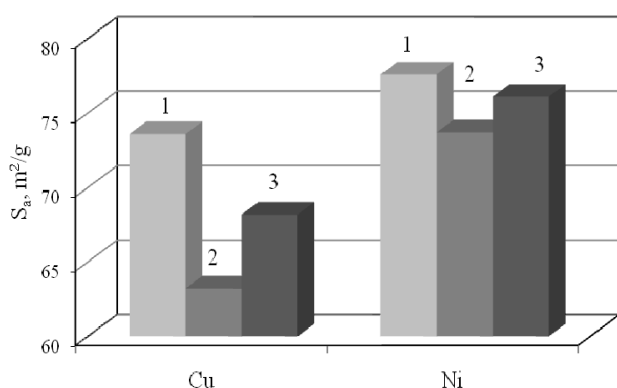


Fig. 1. The effect of modifier on the specific active surface area: 1 – without modifier; 2 – PVP modifier; 3 – PVA modifier

The established regularities of effect of the nature of polymer and metal on the surface characteristics to some extent confirmed by the results of the moisture adsorption studies which are shown in the Table. 4.

TABLE 4
MOISTURE ABSORPTION OF METAL-CONTAINING
POLYMER-SILICATE FILLERS

Modifier	Precipitant			
	CuCl ₂	BaCl ₂	ZnCl ₂	CoCl ₂
	Moisture absorption, %			
Without modifier	52,4	20,2	37,5	39,5
PVP	25,5	12,6	17,3	16,2
PVA	28,9	7,2	32,7	32,3

Based on these data we can conclude that the obtained materials are characterized by a developed surface.

The modified silicate materials characterized by significantly lower values of moisture absorption than unmodified. This confirms the ability to block of silicate surface groups by macromolecules of polyvinylpyrrolidone and polyvinyl alcohol and reduced the porosity of fine particles.

The nature of metal differently affects on the absorption values of water, which is due to the peculiarities of interaction of metal with Na-LG during the reaction of obtained of metal-containing polymer-silicate materials.

Conclusion

In this paper established the effect of polymer modifier and the nature of metal on the sorption characteristics of metal-containing polymer-silicate fillers. Found that the specific active surface area and the amount of active centers in it depends on the nature of metal, for Ba²⁺ and Co²⁺ observed a significant reduction of these values.

At the same time, the use of polymeric modifiers, regardless of the nature of metal and indicator, reduces the amount of active centers and specific active surface area, which is associated with the blocking surface active groups of silicate structures due to interaction with the functional groups of the polymer modifier.

The modified silicates materials is observed a significantly lower moisture absorption values than unmodified, due to the blocking of silicate structures surface groups by macromolecules of polyvinylpyrrolidone and polyvinyl alcohol and reduced of the porosity of fine particles.

References

- [1] A. S. Masyuk, R. V. Nechypor, V. Ye. Levytskyi "The effect of nature of polymer and metal chloride on regularities of obtaining of polymer-silicate composite," Bulletin of the NU LP, № 787, pp 429-434, 2014.
- [2] V. Levytskyj, V. Kochubei, A. Gancho "Influence of the silicate modifier nature on the structure and properties of polycapromide," Chemistry & Chemical Technology, vol. 7, pp 169-173, 2013.
- [3] A. S. Masyuk, V. Ye. Levytskyi "Regularities of obtaining of polymer-silicate composites from water-soluble silicates and polymers," Eastern-European Journal of Enterprise Technologies № 6/6 (72), pp 29-33, 2014.