Iryna Lutsyuk, Yaroslav Vakhula, Volodymyr Levytskyi and Liliya Zhuk

ADSORPTIVE MODIFICATION OF HIGH-DISPERSED MAGNESIUM HYDROSILICATE

Lviv Polytechnic National University
12, S. Bandery str., 79013 Lviv, Ukraine

Abstract. The modification action of polyvinylpyrolidone (PVP) on morphological peculiarities of magnesium hydrosilicate powder has been investigated. PVP modification mechanism has been studied depending on its introduction method to the system. The most effective modification method is observed during joint precipitation of the system liquid components and PVP.

Keywords: high-dispersive powder, magnesium hydrosilicate, polyvinylpyrolidone, modification.

1. Introduction

Among the variety of mineral powders used in the industry, the high-dispersed silicate powders are considered to be the effective ones [1, 2]. Magnesium hydrosilicates are widely used as fillers in lacquer-varnish, building, polymeric, paper, ceramic, and other industries due to their large specific surface. Moreover, sorption properties of magnesium hydrosilicates are promising for solving the ecological problems, namely the elimination of oil pollutions and biodiesel purification [2, 3].

In many cases it is advisable to modify the structure of mineral powders by water- and alcohol-soluble polymers with functional groups to improve the sorption properties. The used polymers are: polyvinylpyrolidone (PVP), polyvinyl alcohol (PVA), sodium salt of carboxymethytlcellulose (Na-CMC), and polyvinylbutyral (PVB) [4, 5]. PVP is the most promising material with high capability of complexation with silicate groups. It was established in [6, 7] that the efficiency of modifiers depends on the conditions of their introduction into the system.

Therefore the aim of this work was to investigate the modifier effect on morphological peculiarities of magnesium hydrosilicate (MHS) depending on the method of its introduction.

2. Experimental

2.1. Methods of Analyses

X-ray analysis of the synthesized powders was carried out using diffractometer DRON-4-07. The used regime was: CuKα radiation; range of 2θ angles – from 18 to 38°; $U = 40$ kV; $I = 30$ mA; measuring step – 0.1°; time of impulses measurement – 8 s. Electron-microscopic investigations were carried out using JEOL JCM 5000 NeoScope electron microscope. IR-spectra were obtained by means of Specord M-80 spectrophotometer in the range of 3700–300 cm^{-1} using KBr and KRS-5 plates.

2.2. Synthesis of MHS Modified Powders

The modified MHS was obtained in accordance with the following procedure. Sodium liquid glass (module $n = 2$, concentration $C = 1$ mol/l) and magnesium chloride hexahydrate MgCl$_2$K·6H$_2$O ($C = 1$ mol/l) were used as the initial components. The solutions were blended with MgCl$_2$: liquid glass ratio of 1:1 (v/v). PVP was used as a modifier. The modification was carried out by two different methods.

1. Mechanical stirring in the solid state of the previously obtained powder of MHS and PVP in the amount of 5 mas % (regime 1).

2. Co-precipitation in the solution. PVP concentration was 0.2 mol/l. The precipitation was carried out at room temperature using magnetic stirrer. Components were blended by two ways:

a) the solution of magnesium salt was added gradually to the liquid glass and then PVP was added (regime 2);

b) PVP was added to the liquid glass, the mixture was stirred till its complete dilution and then the solution of magnesium salt was added gradually (regime 3).

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As a result, a white loose deposit was formed (regimes 2 and 3), which was sustained for 24 h. Then it was boiled for 15 min, washed from Cl⁻ anions by distilled water and dried at 383–388 K. The white powders of modified MHS were obtained according to the developed technology.

3. Results and Discussion

To determine the morphological peculiarities of the powders modified by PVP, the complex of instrumental investigation methods was used: X-ray, IR-spectroscopy, differential thermal, and electron-microscopic analysis.

The results of X-ray analysis show that the structure of the obtained powders is amorphous because two amorphous "halo" are observed in the range of 2θ = =19–25 and 33–37° (Fig. 1).
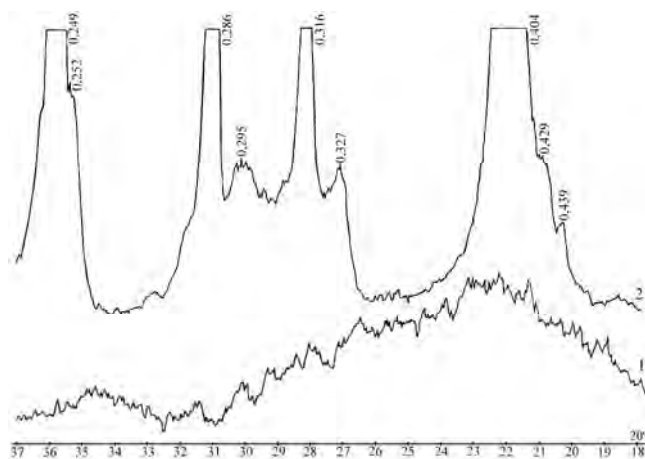
**Fig. 1.** Diffractogram of MHS powders after thermal treatment at the temperatures of 378–388 K (1) and 1153 K (2)

The modified powders obtained by regime 1 (Fig. 2a) have the non-uniform structure and polydis-persive particles. In some cases there are PVP inclusions. The size of new formations is 40–600 nm. PVP introduced at the stage of MHS obtaining (regime 2, Fig. 2b) forms uniform structure with the size of spherical particles 60–70 nm; the size of their aggregates is 300–400 nm. It should be noted that the powder obtained by regime 3 is characterized by larger size of the primary particles 80–90 nm and aggregates 600–700 nm. At the same time the individual phases enriched by PVP molecules are not observed.

To our mind it is connected with the fact that primary particles of MHS-PVP are formed at the initial stages of liquid glass and polymer macromolecules precipitation from sol under the action of magnesium chloride. Since the size of PVP ball in the solution of sodium liquid glass are greater by several times than that of sol particles of liquid glass [8, 9], it is obvious that PVP macromolecule is capable to adsorb simultaneously at the surface of few particles. At the same time the following stage of precipitation is connected with the formation of nanoparticle aggregates with adsorbed polymer layer, from which siliceous skeleton with uniformly distributed PVP inclusions is formed. Such physico-chemical regularities of PVP-silicate matter formation are confirmed by derivatographic and IR-spectroscopic investigations.

In our previous investigations [10, 11] we established that the synthesized powders are greatly hydrated. The water loss is 31. 5 % due to the heating to 1053 K, the temperature at which matter dehydration is completed.

The significant endothermal effect is observed at DTA curves while heating to 493 K. The reason is the separation of physically-bounded water. For the modified powders exoeffects are observed within the temperature range of 573–893 K. They are caused by intensive elimination of the organic matter. Within 1043–1133 K the exothermal effect is observed connected with crystallization of enstatite $MgO \cdot SiO_2$ (*d/n* 0.317; 0.287 and 0.249) and partially SiO_2 (*d/n* 0.404; 0.285 and 0.249) (Fig. 1).
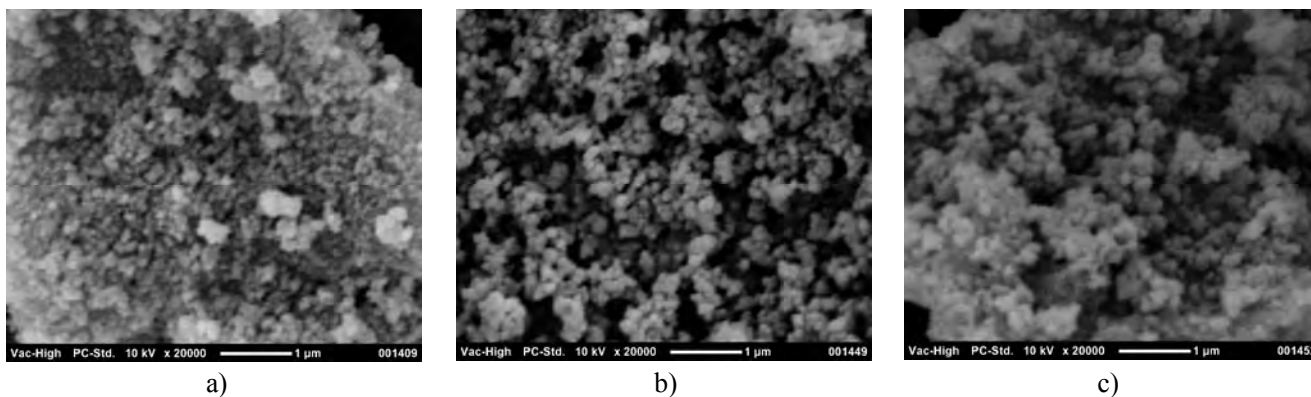
Fig. 2. SEM-images of the synthesized powders depending on modification method: regime 1 (a); regime 2 (b) and regime 3 (c)
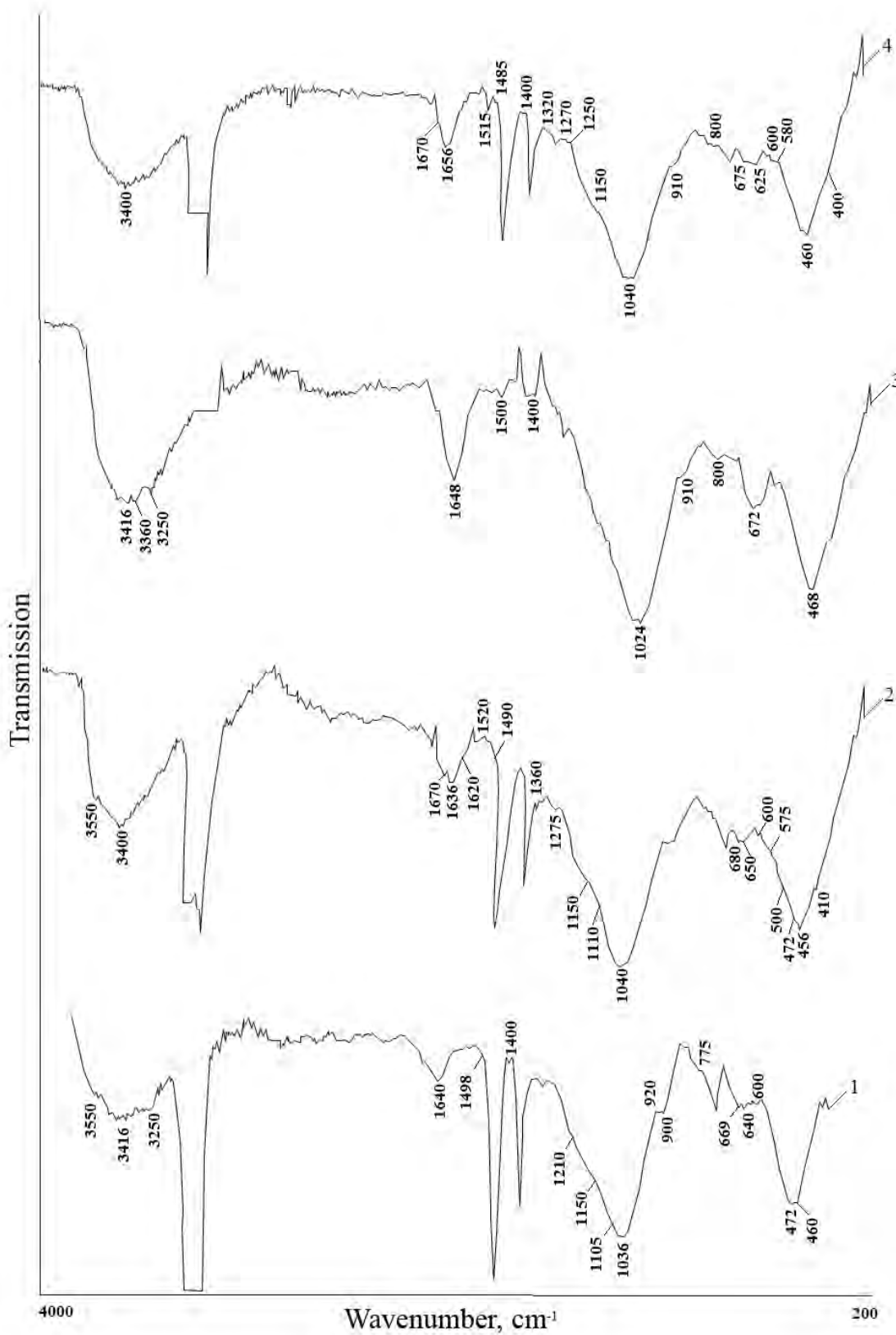
Fig. 3. IR-spectra of pure (1) and modified (2-4) powders

The structural peculiarities of the synthesized powders were studied by IR-spectroscopy. Fig. 3 represents IR absorption spectra of pure and modified MHS.

Having compared the results for pure and modified powder it becomes obvious that spectra have the similar character with definite deviation in some areas. There are 6 main absorption bands (cm^{-1}): 3600–3000, 2000–1500, 1550–1400, 1300–900, 600–400, and 670–640 corresponded to vibrations of valence OH-groups, deformation OH-groups, deformation bonds Si–O, deformation bonds Si–O, and valence bonds Mg–O, respectively.

The vibrations of valence OH-bonds in the area of 3600–3000 cm^{-1} for the modified samples are less intensive and shifted to the area with lower frequency. This fact is explained by the decrease of OH-groups amount due to MHS modification by PVP.

In the spectra of the synthesized powders the wide band at 1640 cm^{-1} is observed, the intensity of which decreases for the modified powders. The band is typical of OH-groups deformation vibrations.

The absorption band at 1090 cm^{-1} is typical of asymmetric stretching vibrations Si–O. However we observe the band shift to 1040–1024 cm^{-1}, which is in agreement with the data [12-14]. The change of vibration frequency may be connected with asymmetric vibrations of Si–O bond in Si–O–Mg bridge groups. Moreover, in this area the absorption band at 900–910 cm^{-1} is present, which should be referred to asymmetric vibrations Si–OH [14].

The absorption band at 669 cm^{-1} is typical of Mg–O bond stretching vibrations. The same vibrations are observed at 640 cm^{-1} for pure MHS and for the hydrosilicate modified by regime 1 this band becomes wide and blurred; it shifts to 680–650 cm^{-1}. For the hydrosilicate modified by regimes 2 and 3 the intensity of Mg–O stretching vibrations considerably increases and band shifts to 675 cm^{-1}, which is explained by strain of MgO_6 octahedrons. The wide band at 1400–1500 cm^{-1} confirms the strain of octahedrons for MHS.

The band with the maximum at 472 cm^{-1} should be referred to the vibrations of Si–O–Mg bond, which is in agreement with [13]. It should be noted that for the modified powders this band shifts to the area of lower frequencies (468–460 cm^{-1}). In accordance with [15] such shift may be explained by break of silica-oxygen skeleton and the increase of number of Si–O–Mg bonds.

Moreover, for modified MHS the absorption bands at 1670–1653 cm^{-1} are observed typical of PVP. The formation of intermolecular bonds between the groups of siliceous skeleton and carbamate groups of PVP is confirmed by the shift of absorption bands to the area of lower frequency and appearance of own absorptions bands at 600–650 cm^{-1} [16, 17].

4. Conclusions

The investigation results testify to different mechanism of PVP modifying action relative to siliceous matter. Apparently, the joint precipitation of sodium liquid glass and PVP under the action of magnesium chloride forms the material where PVP macromolecules are not only adsorbed over the surface, but uniformly distributed inside the skeleton due to their physical interaction with functional siliceous groups. This fact is confirmed by electron-microscopic, IR-spectroscopic, and derivatographic investigations.

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АДСОРБЦІЙНЕ МОДИФІКУВАННЯ ВИСОКО-ДИСПЕРСНОГО МАГНІЮ ГІДРОСІЛІКАТУ

Анотація. *Досліджено модифікуючу дію полівініл-піролідону (ПВП) на морфологічні особливості порошку магнію гідросилікату. Вивчено механізм модифікування ПВП, який залежить від способу його введення в систему. Найбільш ефективний спосіб модифікування спостерігається під час сумісного осадження рідких компонентів системи і ПВП.*

Ключові слова: *високодисперсний порошок, магнію гідросилікат, полівінілпіролідон, модифікування.*