

FTIR SPECTROSCOPY OF WATER GLASS - THE BINDER MOULDING MODIFIED BY ZnO NANOPARTICLES

Received – Prispjelo: 2012-02-07
Accepted – Prihvaćeno: 2012-04-30
Preliminary Note – Prethodno priopćenje

The subject of the paper is the determination of the influence of the colloidal nanoparticles of zinc oxide on the structure of sodium water glass. Nanoparticles of zinc oxide in ethanol solvent were introduced into the water glass. The modification and structural changes were determined by means of the FT-IR absorption spectra.

In order to determine the kind of influence: binder-modifier the spectroscopic FTIR analysis of samples of a fresh binder and of a binder hardened for 24 h in the air was performed by means of the spectrometer Digilab Excalibur with a standard DTGS detector.

Key words: spectroscopy, sodium water glass, zinc oxide, colloidal nanoparticles, modification.

INTRODUCTION

One of the binders used in the molding and core sands is water glass. It is cheap, easily available and not toxic. However, unfavourable properties of sands with water glass are: brittleness, worse shakeout of moulds and reclamability.

The last decades has witnessed the development of nanoparticles of ceramic materials: SiO₂, Al₂O₃, Ca-SiO₃, ZnO etc.

Nanoparticles can be changing initial binder properties by physical or chemical influences. Not numerous results, presented in references, indicate the favourable influence of micro- and nanoparticles of MgO and Cr₂O₃ on the retained strength, which is related to the improvement of the knocking out property [1, 2].

The literature data concerning the water glass modification by nanoparticles of inorganic compounds are fragmentary and rather of a qualitative character.

An attempt to modify water glass with the zinc oxide nanoparticles was undertaken in the study.

MATERIALS AND TESTING METHODOLOGY

A binder modification was performed always with water glass:

- „R 145” of a module $M = 2,5$ and density $d_{20} = 1\,470\text{ kg/m}^3$, $\text{pH} = 11,2$

As a modifier was applied:

- colloidal suspension of ZnO nanoparticles of dimensions $< 10\text{-}100\text{ nm} >$ in ethanol: concentration of suspension: 0,3 M.

The water glass modification was performed by introducing of 3 and 5 mass % of the ethanol suspension of ZnO nanoparticles and homogenising the mixture.

In order to determine the kind of influence: binder-modifier the spectroscopic FTIR analysis of samples of a fresh binder and of a binder hardened for 24 h in the air was performed by means of the spectrometer Digilab Excalibur with a standard DTGS detector.

RESULTS AND THEIR DISCUSSION

Figure 1 illustrate the FTIR absorption spectra of samples of the fresh water glass (a) and after 24 h of hardening (b).

It is observed that whole spectrum (of the fresh and hardening water glass) can be divided into two sections: the first one comprises of the main sharp distinctive and characteristic absorption bands ranging from 400 – 1 400 cm⁻¹, which are due to main silicate network group

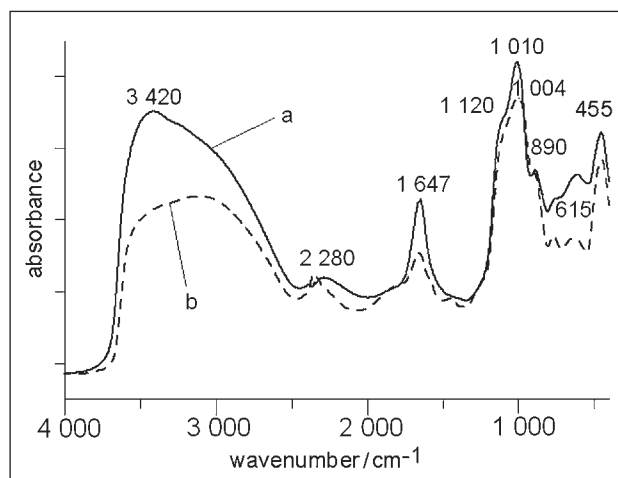


Figure 1 Absorption FTIR spectra of the fresh water glass (a) and the water glass after 24 h of hardening (b)

All authors from AGH - University of Science and Technology, Faculty of Foundry Engineering, Krakow, Poland

vibrations with different bonding arrangement and the second part, from 1 400 to 4 000 cm^{-1} obviously consists of vibrations due to water, hydroxyl, SiOH or similar groups. Table 1 summarize the band frequencies and corresponding vibration modes of silicate glass based on other research .

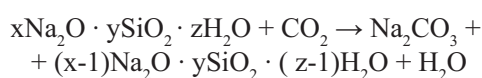
It can be observed, that the absorption spectra of the fresh water glass, in the 400-1 400 cm^{-1} region, have the most pronounced band located at 1 010 cm^{-1} with two shoulders at ca. 1 120 and 890 cm^{-1} and less intense band at 615 and 455 cm^{-1} . The most intense component at 1 010 cm^{-1} lies in the middle bands (1 020 and 1 000 cm^{-1}), respectively attributed to Si-O stretching vibration of $[\text{SiO}(\text{OH})_3]^-$ and partly undissociated $[\text{SiO}_2(\text{OH})_2]^{2-}$, (this is Q^1 and Q^2) species [3]. The shift main band towards higher wavenumbers ca. 1 100 cm^{-1} corresponds to increase the activity Q^3 species. While, the lower wavenumbers ca. 900 cm^{-1} is attributed to Q^1 species. The shoulder at ca. 850 cm^{-1} is associated with the asymmetric vibration of isolated Q^0 species. The lower frequency envelope between 600-400 cm^{-1} are attributed to the rocking motion of Si-O-Si bridges connecting various Q^n species [3], (Table 1). According to above, the main bands observed at 1 010 cm^{-1} and 890 cm^{-1} indicate, the presence of $[\text{SiO}(\text{OH})_3]^-$ and $[\text{SiO}_2(\text{OH})_2]^{2-}$ (Q^1 and Q^2) species as main silicate network group, in fresh water glass of a module 2,5.

In the second frequency range (1 400 – 4 000 cm^{-1}), the characteristic strong adsorption band with maximum at 3 440 cm^{-1} , and narrow at 1 647 cm^{-1} are observed. In addition, there is a small shoulder at 2 280 cm^{-1} . The bands ca. 3 440 cm^{-1} and 1 640 cm^{-1} are attributed to constitutional water molecules and OH – bending and stretching modes. The band within the range 2 400 – 2 100 cm^{-1} corresponds to vibrations of hydrogen bridges between $\text{Si}(\text{OH})_4$ and the silicate lattice.

After 24 h of hardening, the small changes and shift of several bands in the absorption spectrum of water glass are observed. In wave number correspond to silicate network group vibration, the main band at 1 010 cm^{-1} is shifted to 1 004 cm^{-1} .

The bands related to vibration molecules of water and OH group at 3 440 cm^{-1} and 1 640 cm^{-1} are shift to 3 352 cm^{-1} and 1 658 cm^{-1} (not bonded water). In addition, there is the band (1 435 cm^{-1}), corresponding to asymmetric stretching vibration of O-C-O bonds [8].

These changes indicate the binding of carbon dioxide (from air) in accordance with in the classical, total reaction:



This reaction is generally accepted as reaction in water glass hardening process with CO_2 .

Figures 2 and 3 illustrate the influence of ZnO additions (3 mass. % suspension of ZnO nanoparticles) on the FTIR spectrum of fresh and hardened water glass. It

can be seen a small shift of some bands in the spectra of both samples, fresh and hardened. The change reveals itself in the wave number range related to OH groups, it means: 3 600 – 3 400 cm^{-1} , where the band is shifted from 3 440 cm^{-1} to 3 520 cm^{-1} , in the direction corresponding to stretching vibrations of OH groups. The main band Si-O-Si originated from asymmetric stretching vibrations of Si-O at the wave number 1 010 cm^{-1} is not shifted, but its intensity decreases in relation to the OH band. Small shifting in the lower wave numbers direction is seen in the band of 891 cm^{-1} (885 cm^{-1}), which can be connected with the increase asymmetric vibration isolated Q^0 species [3]. Similarly, the band at 615 cm^{-1} is shifted to 600 cm^{-1} , which can indicate the tendency of ions reduction in the system too [4].

After 24 h of hardening (Figure 3), the additions band at 1 813 cm^{-1} emphasize in the spectrum. This band is in the vicinity of the band related to stretching vibrations in carbonates coordinated by metal cations in

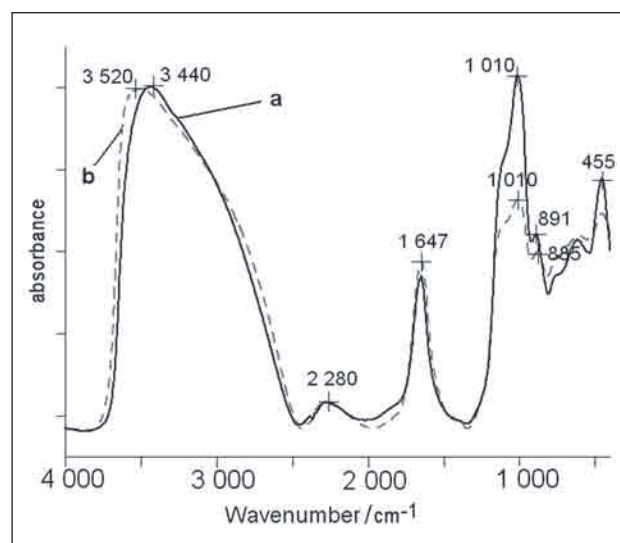


Figure 2 Absorption FTIR spectra of the fresh water glass (a) and the modified by suspension ZnO nanoparticles (3 mass %) (b)

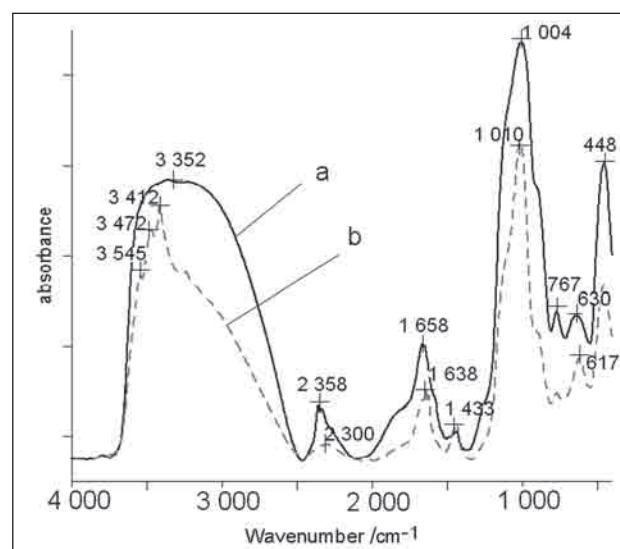


Figure 3 Absorption FTIR spectra of the hardened water glass (a) and the modified by suspension ZnO nanoparticles (3 mass %) (b), after 24 h.

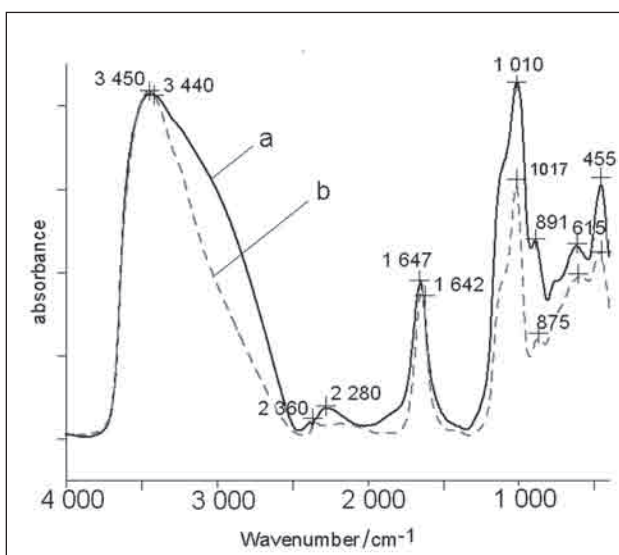


Figure 4 Absorption FTIR spectra of the fresh water glass (a) and the modified by suspension ZnO nanoparticles (5 mass %) (b)

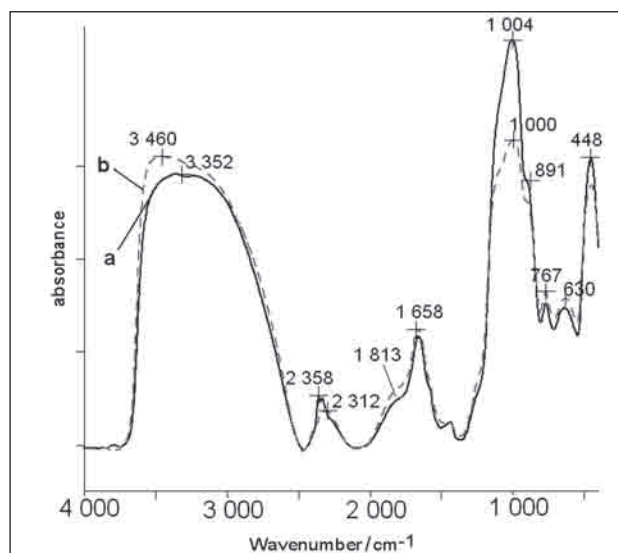


Figure 5 Absorption FTIR spectra of the hardened water glass (a) and the modified by suspension ZnO nanoparticles (5 mass %) (b), after 24 h

bridging bidentate complexes [5]. The location and intensity of the band ($1\,435\text{ cm}^{-1}$), corresponding to asymmetric stretching vibration of O-C-O bonds in carbonate complexes monodentate [8], do not change.

Due to the very strong Si-O-Si band in the obtained spectra, it is not possible to indicate the band characteristic for the Si-O-Zn band, which usually occurs in the range $1\,161 - 1\,153\text{ cm}^{-1}$ [3].

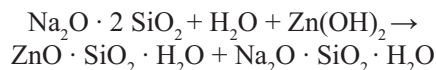
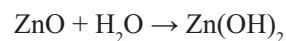
Larger differences in the spectra of the water glass modified by additions of 5 % ZnO in ethanol (Figures 4, 5) are seen after 24 hours of hardening (in the same direction) in all characteristic ranges.

Table 1 Results of the FTIR analysis of water glass not modified and modified by the suspension of ZnO nanoparticles (like in literature data)

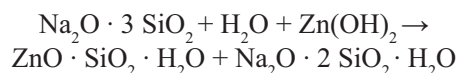
Wave number/cm ⁻¹	Binding
800-400	Bending vibrations of [O-Si-O] bands, pseudo-crystal lattice vibrations [3]
950	Monomers, oligometries originated from O-Si-O bands [6], [7]
1 010-1 000	Asymmetric stretching vibrations of Si-O-Si [3]
1 120	Asymmetric vibrations of three-dimensional bands originated from Si-O-Si [3]
1 161-1 153	Vibrations originated from Si-O-Zn bands [3]
1 028-1 003	Stretching vibrations originated from Si-O bands [3]
1 443-1 440	Vibrations originated from carbonate bands O-C-O [8]
1 640	Constitutional water [8]
1 535	Vibrations originated from asymmetric, carboxylic bands [6]
1 663	Not bonded water H-HO [8]
1 711	Vibrations originated from vibratory carboxylic groups in oleic acid [6]
2 400-2 000	Water vibrations and vibrations of hydrogen bonds between Si(OH) ₂ and silicon lattice, and vibrations originated from asymmetric CO ₂ bands [9-11]
3 100-2 700	Overlapping stretching vibrations of the Cx type [9-11]
3 600-2 700	Stretching vibrations of -OH group and molecular water [12]

The most visible effect of the ZnO addition, apart from bands shifting is significant decrease in intensity in OH and water stretching region between $3\,600 - 2\,700\text{ cm}^{-1}$ and bands originated from Si-O-Si bonds ($1\,200 - 400\text{ cm}^{-1}$). This indicate the participation of ZnO nanoparticles in the hardening by dehydration of water glass.

The dehydration may be proceeds according to general reactions:



and / or



SUMMARY

- The introduction of ZnO nanoparticles to the water glass in the form of colloidal suspension of alcohol changes the shape of FTIR absorption spectra (at spectral features in the whole wave number region). The most marked differences in the spectra (especially after 24 h) are observed with addition of 5 mass. % ZnO nanoparticles in ethanol;
- Significant differences are visible in the intensity of each of the main bands (water, silicate);
- The nanoparticles accelerates the hardening process, probably by participation in dehydration reactions.

The research was done within the framework of the Project No. N N508 47 5538

REFERENCES

- [1] Wang Ji-na, Fan Zi-tian, Wang Hua-feng, Dong Xuan-pu, Huang Nai-yu, China Foundry 4 (2007) 1, 26-30,
- [2] Zhu Chun-xi, China Foundry 4 (2007) 1, 13-17

- [3] M. Yuan, J. Lu, G. Kong, Ch. Che, *Surface & Coatings Technology* 205 (2011) 4466-4470,
- [4] H. S. Liu, *Materials Chemistry and Physics* 50 (1997), 1-10,
- [5] H. Wijnja, C.P. Schulthess, *Spectrochimica Acta Part A* 55 (1999), 861-872,
- [6] P. Roonasi, X. Yang, A. Holmgren, *Journal of Colloidal and Interface Science* 343 (2010), 546-552,
- [7] E. Popatowa, M. Grahn, A. Holmgren, J. Hedlund, *Journal of Colloid and Interface Science* 354 (2010), 96-102,
- [8] S. A. Bernal, J. L. Provis, V. Rose, Ruby Mejia de Gutierrez, *Cement&Concrete Composites* 33, (2011), 46-54,
- [9] H. Roggendorf, W. Grond, M. Hurbanic, *Glass Sci. Technol.* 69 (1996) 7, 216 – 230,
- [10] A. Argawal, M. Tomozawa, *Journal of Non Crystalline Solids* 209 (1997), 166-174,
- [11] M. Handke, W. Mozgawa, M. Nocuń, *Journal of Molecular Structure* 325 (1994), 129-136,
- [12] Y. Liu, J. Shen, Z. Chen, L. Yang, Y. Liu, Y. Ha, *Applied Catalysis A: General* 403 (2011), 112-118,

Note: The responsible translator for English language: „ANGOS”
Translation Office, Kraków, Poland