

# Effect of Water Glass Modification on Its Viscosity and Wettability of Quartz Grains

A. Kmita<sup>a\*</sup>, B. Hutera<sup>a</sup>

<sup>a</sup> AGH University of Science and Technology, Faculty of Foundry Engineering, Cracow, Poland

\*Contact for correspondence: e-mail: akmita@agh.edu.pl

Received 16.04.2012; accepted in revised form 02.07.2012

## Abstract

The aim of the present study was to develop a modifier for water glass. The method of thermal generation of metal oxide nanoparticles was adapted and used in the research. Nanoparticles of ZnO from the thermal decomposition of basic zinc carbonate were used. A method for the modifier introduction was developed, and the effect of modifier content and organic solvent type on the physico-chemical properties of binder (viscosity) and quartz wettability was determined. Binder viscosity was examined from the flow curves plotted with the help of a RHEOTEST 2 rotational rheometer equipped with proper software. Quartz wettability was determined examining time-related changes in the value of the contact angle in a quartz-binder system, until full stabilisation of the angle value has been achieved. Binder modification was carried out on sodium water glass designated as R"145". The water glass modifiers were suspensions of ZnO nanoparticles in propanol and methanol at a fixed concentration of  $c = 0.3$  M and with the size of nanoparticles comprised in a range of  $<61 - 981$  nm. Water glass modification with the suspensions of ZnO nanoparticles in methanol and propanol showed the effect of modifier on the water glass viscosity and quartz wettability. This effect depends on the type of alcohol used. The ZnO suspension in propanol (alcohol with a longer hydrocarbon chain) affects more strongly the viscosity of binder and quartz wettability than the methanol suspension.

**Keywords:** Water glass, Modification, Thermal synthesis of ZnO nanoparticles, Viscosity, Wettability

## 1. Introduction

Moulding sands with organic binders exhibit significant toxicity. This involves, on the one hand, the necessity of additional investments to ensure an adequate level of safety and proper working conditions in foundries, while, on the other, increases the sand cost, especially when it contains binders with furfuryl alcohol. These drawbacks forced the researchers to look for binders that do not show these characteristics.

One of such binders is water glass - cheap, readily available and nontoxic. However, the disadvantage of the sands with water glass is their brittleness, poor knocking out properties and low degree of reclamability. At the same time, the potentials of water glass as a binder for foundry sand moulds and cores are not fully utilised. This is because the technological process should simultaneously meet the following demands: ensure optimal conditions for the core and mould hardening, ensure the required

level of mechanical and physico-chemical properties (strength, hygroscopicity, brittleness, etc.) as well as the lowest possible residual strength of moulds and cores in a wide range of temperatures (300-1200°C), which will improve the knocking out properties of the sand and, last but not least, will improve the moulding and core sand reclamability.

Studies have shown that the most effective improvement in the quality of sands with water glass is obtained through modification of the binder [1-2]. So far, as modifiers, the multimolecular components have been used, such as e.g. polyphosphates and polyacrylamides, differing in the degree of polymerisation, in molar mass, and in the type and number of functional groups.

Recent decades have brought the development of a new family of materials known as nanoparticles. These are, among others, the nanoparticles of ceramic materials (e.g. SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CaSiO<sub>3</sub>, ZnO, aluminosilicates, etc. [3-8]). These nanoparticles, when introduced into the matrix (binder), create new systems,

called nanocomposites. Because of their similar molecular size and highly developed specific surface area, nanoparticles exhibit quite a unique and never observed in typical composites ability to interact with the binder matrix and modify the properties of binder in its interface layers. The improvement mainly consists in upgrading the mechanical and thermal properties (modulus of elasticity, breaking stress, hardness, adhesion, thermal stability, etc.). The improvement of nanocomposite properties depends on the following factors: the impact of nanofiller on the structure of the binder matrix, the size of nanofiller particles and their mutual arrangement.

Operating through chemical or physico-chemical effects, nanoparticles may alter the original properties of the binder. So far, most studies on the water glass modification have been focused on the use of organic compounds. Very scarce results reported in the literature suggest a positive impact of micro- and nanoparticles of MgO and Cr<sub>2</sub>O<sub>3</sub> on the residual strength, which is associated with an improvement of the sand knocking out properties [9].

In nanotechnology, there are two manufacturing techniques, called top-down and bottom-up [10-14]. The first technique consists in disintegration of the material to a very fine form, mainly by grinding and cutting. The bottom-up method produces larger structures from individual atoms or molecules. This technique includes the processes of chemical synthesis in liquid phase (e.g. sol-gel, precipitation methods) or in the gaseous phase (e.g. pyrolysis).

Literature data on the water glass modification with nanoparticles of inorganic compounds are random and qualitative in nature [15]. There are no systematic studies that would interrelate the technique of modification with the modification effect, and structure of produced nanobinder (nanocomposite) with its properties.

## 2. Scope and purpose of the research

The purpose of the study was to develop a modifier for water glass.

For the purpose of the study, a method of thermal generation of metal oxide nanoparticles was adapted. Nanoparticles of ZnO were produced by thermal decomposition of the basic zinc carbonate.

A technique for the modifier introduction was developed, and studies were carried out on the effect of the type and content of an organic solvent on the physico-chemical properties of binder (viscosity) and quartz wettability.

## 3. Research methodology

### 3.1. Test materials

Binder modification was carried out on:

- sodium water glass grade R „145 ” characterised by the modulus  $M = 2,5$ , the density  $d^{20} = 1470 \text{ kg/m}^3$  and  $\text{pH} = 11,2$

Water glass modifiers were:

- suspensions of ZnO nanoparticles in propanol and methanol at a fixed concentration of  $c = 0.3 \text{ M}$  and with the size of nanoparticles comprised in a range of  $\langle 61 - 981 \text{ nm} \rangle$ .

### 3.2. Measurement apparatus and method

The size of nanoparticles was measured with a Philips XL30 SEM coupled with LINK ISIS EDX system and with a Philips ESEM with EBSD orientation imaging system.

Binder viscosity was examined from the flow curves plotted with the help of a RHEOTEST 2 rotational rheometer equipped with proper software.

Quartz wettability was determined examining time-related changes in the value of the contact angle in a quartz-binder system, until full stabilisation of the angle value has been achieved. The wettability was measured using a prototype device for the contact angle measurements [16].

Modification of "R145" water glass consisted in the introduction of 5wt.% of the alcohol-based, colloidal suspension of ZnO nanoparticles in propanol or methanol and in homogenising of the mixture next.

## 4. Results and discussion

Figures 1-6 show the effect of water glass modification on its viscosity (Figs. 1-3) and wettability of the quartz grains (Figs. 4-6). All the flow curves (Figs. 1, 2 and 3) are straight lines extending from the origin of a coordinate system ( $\gamma$ ,  $\tau$ ), which indicates a Newtonian nature of the binder with characteristic for this type of fluids rheological parameter - viscosity  $\eta$  (1):

$$\tau = \eta \cdot \gamma \quad (1)$$

where:

- $\tau$  – the tangent stress,
- $\eta$  – the absolute viscosity,
- $\gamma$  – the shear rate.

The presented results show that water glass modification with alcohol suspensions of nanoparticles affects the intermolecular phenomena. It manifests itself in an approximately 13% increase of viscosity after the modification with methanol suspension, or in an approximately 20% drop of this parameter as a result of modification with ZnO suspension of nanoparticles in propanol.

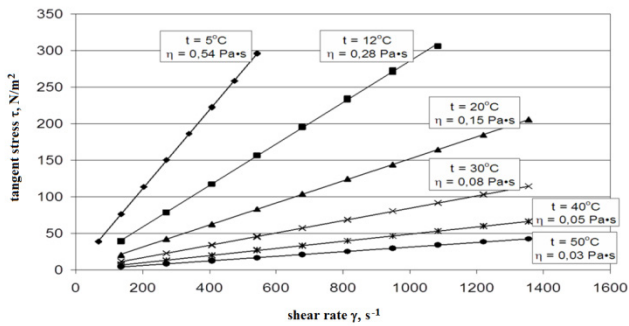


Fig. 1. Flow curves plotted for unmodified „R 145” water glass at different temperatures

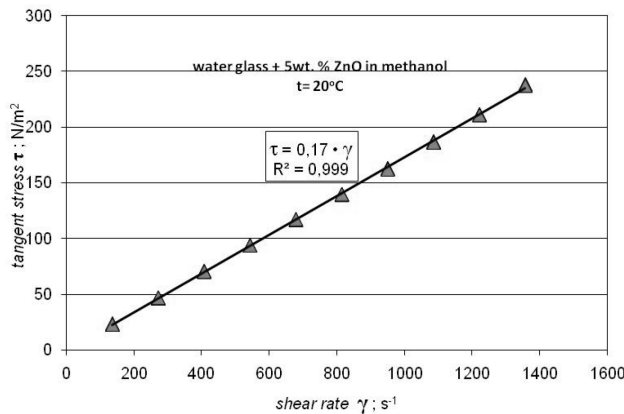


Fig. 2. Flow curve plotted for water glass modified with 5 wt.% suspension of ZnO nanoparticles in methanol. Measurement temperature: 20°C

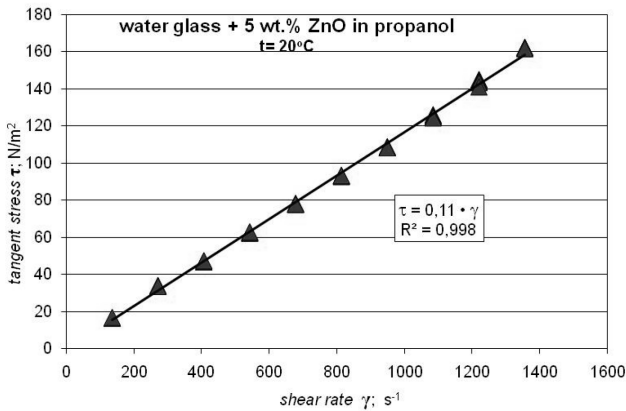


Fig. 3. Flow curve plotted for water glass modified with 5wt.% suspension of ZnO nanoparticles in propanol. Measurement temperature: 20°C

Wetting of quartz by unmodified water glass (Fig. 4) is taking place with the dynamics that has the highest value of the initial angle  $\theta_0$  (about 45 deg.) and equilibrium angle  $\theta_r$  (about 33 deg.), and the longest time necessary for the system to reach the steady state  $\tau_r$  (about 20 min.). Binder modification with the ZnO suspension in methanol (Fig. 5) improved the wettability of quartz

grains reducing the above mentioned parameters, i.e.  $\theta_0$ ,  $\theta_r$ ,  $\tau_r$  to 33 deg, 22 deg, 7 min., respectively. The best wettability was achieved by binder modification with the ZnO suspension in propanol (Fig. 6). The symptom of improvement was a significant drop in the value of both angles  $\theta_0$  and  $\theta_r$  to 20 deg. and 5 deg., respectively. Attention also deserves much shorter time lapse necessary for the system to reach its steady state (about 2 min.).

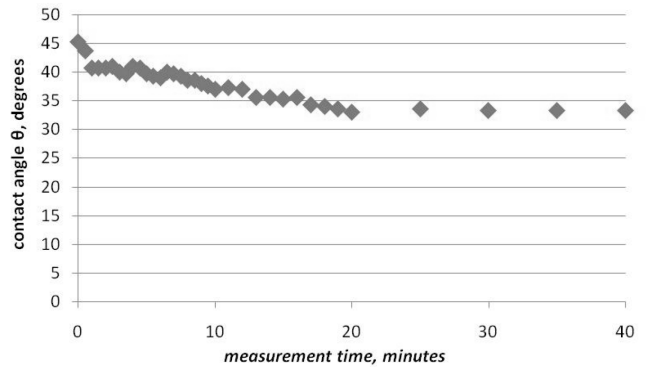


Fig. 4. Time-related changes in the value of contact angle in a quartz-unmodified water glass system. Measurement temperature: 20°C

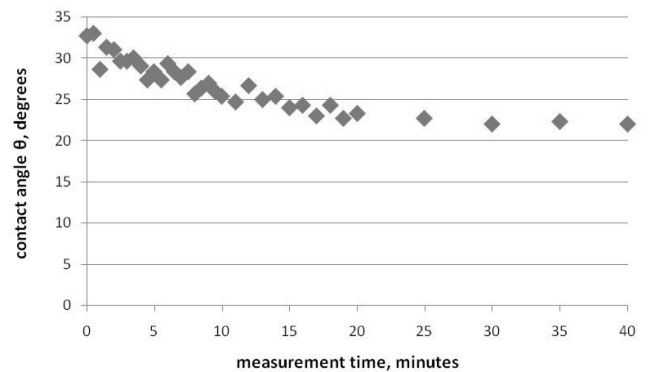


Fig. 5. Time-related changes in the value of contact angle in a quartz-modified water glass system (5wt.% suspension of ZnO nanoparticles in methanol). Measurement temperature: 20°C

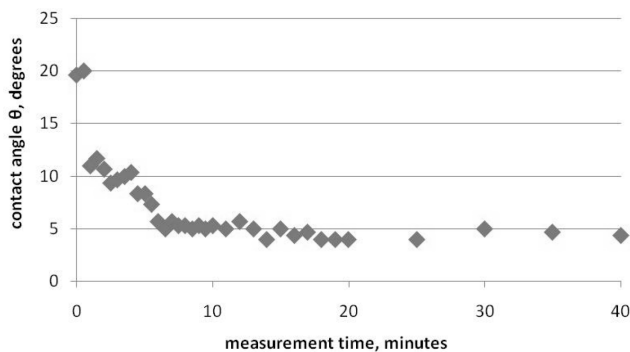


Fig. 6. Time-related changes in the value of contact angle in a quartz-modified water glass system (5wt.% suspension of ZnO nanoparticles in propanol). Measurement temperature: 20°C

## 5. Summary

Water glass modification with the suspensions of ZnO nanoparticles in methanol and propanol shows the effect of modifier on the viscosity of binder and wettability of quartz grains in a quartz - binder system.

This effect depends on the type of alcohol used. The ZnO suspension in propanol (alcohol with a longer hydrocarbon chain) affects more strongly the viscosity of binder and quartz wettability than the methanol suspension.

## Acknowledgements

The studies were performed under the „Dean’s Grant” 2012 No. 15.11.170.419

## References

[1] Kmita, A., Hutera, B. & Drożyński, D. (2010). Effect of sodium silicate modification on selected properties of loose self-setting sands. *Archives of Foundry Engineering*, vol. 10 issue 4, pp. 93–96.

[2] Hutera, B., Stypuła, B., Kmita, A. & Nowicki, P. (2011). Modification of water glass with colloidal slurries of metal oxides. *Archives of Foundry Engineering*, vol. 11, issue 4, pp. 51–54.

[3] Avella, M., Bondioli, F., Cannillo, V., Errico, M.E., Ferrari, A.M., Focher, B., Malinconico, Manfredini, M.T. & Montorsi, M. (2004). Preparation, characterisation and

computational study of poly( $\epsilon$ -caprolactone) based nanocomposites. *Materials Science and Technology*, vol. 20, pp.1340 – 1344. DOI:10.1179/026708304225022278.

[4] Chaisan, W., Yimnirun, R. & Ananta, S. (2008). Preparation and characterization of ceramic nanocomposites in the PZT-BT system. *Ceramic International*, pp. 1-4. DOI: 10.1016/j.ceramint.2008.10.032.

[5] Wang, H., Bai, Y., Liu, S., Wu, J. & Wong, C.P. (2002). Combined effects of silica filler and its interface in epoxy resin. *Acta Materialia*, 50, pp. 4396-4377. DOI: 10.1016/S1359-6454(02)00275-6.

[6] Odegard, G.M., Clancy, T.C. & Gates, T.S. (2005). Modelling of the mechanical properties of nanoparticle/polymer composites. *Polymer*, 46, pp. 553-562. DOI:10.1016/S0266-3538(03)00115-5.

[7] Wentzel, B., Haupter, F. & QiuZhang, M. (2003). Epoxy nanocomposites with high mechanical tribological performance. *Composites Science and Technology*, 63, pp. 2055-2067.

[8] Kacperski, M. (2004). Wstępne badania nad wpływem rodzaju modyfikatora na właściwości nanokompozytów epoksydowych. *Kompozyty*, 4, vol. 9, pp. 28-32.

[9] Ji-na, W., Zi-tian, F., Hua-feng, W., Xuan-pu, D.H. & Nai-yu. (2007). An improved sodium silicate binder modified by ultra-fine powder materials. *China Foundry*, vol. 4. No. 1, pp. 26-30, DOI: 1672-6421(2007)01-026-05.

[10] Darezereshki, E., Alizadeh, M., Bakhtiari, F., Schaffie, M. & Ranjbar, M. (2011). A novel thermal decomposition method for the synthesis of ZnO nanoparticles from low concentration ZnSO<sub>4</sub> solutions. *Applied Clay Science*, 54, pp. 107–111. DOI: 10.1016/j.clay.2011.07.023.

[11] Fan, H., Song, B., Liu, J., Yang, Z. & Li, Q. (2005). Thermal formation mechanism and size control of spherical hematite nanoparticles. *Materials Chemistry and Physics*, 89, pp. 321–325. DOI: 10.1016/j.matchemphys.2004.09.021.

[12] Jajarmi, P. (2009). Fabrication of pure ZnO nanoparticles by polymerization method. *Materials Letters*, 63, pp. 2646–2648. DOI: 10.1016/j.matlet.2009.08.062.

[13] Reverchona, E., Della Portaa, G. & Torinoa, E. (2010). Production of metal oxide nanoparticles by supercritical emulsion reaction. *J. of Supercritical Fluids*, 53, pp. 95–101. DOI: 10.1016/j.supflu.2009.11.007.

[14] Wu, R., Xie, C., Xia, H.J., Hu, Wang, A. (2000). The thermal physical formation of ZnO nanoparticles and their morphology. *Journal of Crystal Growth*, 217, pp. 274–280.

[15] Chun-xi, Z. (2007). Recent advances in waterglass sand technologies. *China Foundry*, vol. 4, No. 1, pp. 13-17 DOI: 1672-6421(2007)01-013-05.

[16] Hutera, B. (2008). *Znaczenie rościączalnika w spoiwie dla przebiegu zawisk powierzchniowych w układzie osnowa piaskowa-material wiążący*. Kraków: Wydawnictwo Naukowe AKAPIT.