

# COHESION AND ADHESION PROPERTIES OF MODIFIED WATER GLASS WITH COLLOIDAL SOLUTIONS OF ZnO

Received - Primljeno: 2013-12-17

Accepted – Prihvaćeno: 2014-04-10

Original Scientific Paper – Izvorni znanstveni rad

The article discusses the issue of the influence of colloidal solutions of nanoparticles of ZnO obtained using original method on physical and chemical properties (cohesions, adhesion, wettability) of water glass. Adhesion and cohesion strength has been determined on the basis of own methodology of measurement using a special apparatus. The results of the above measurements have been supplemented with selected measurements of quartz wettability by the modified binder. Also, exemplary results have been presented of tests involving basic properties of moulding sands containing an addition of the aforementioned binder. In conclusions, the influence of binder modification on the properties of moulding sands have been presented.

*Key words:* nanoparticles ZnO, cohesion, adhesion, water glass, moulding sand

## INTRODUCTION

Moulding sands with water glass are an alternative for moulding sands with toxic organic binders widely used in foundry. The advantages of such moulding sands include: good flowability, small gas productivity, and very low toxicity. However, this is not generally used. Factors limiting its broad application include: high sensitivity to ambient conditions (hygroscopic properties of binder), low cohesion strength (which negatively affects the strength of moulding sand), poor knock-out properties, and regeneration capacity of sands containing it [1-5]. Therefore, attempts are made to modify water glass aimed at improvement of cohesion strength and wettability of the base by the binder. Most studies on modifications of water glass focused on application of organic compounds using their function groups [4-6]. The development of nanotechnology has allowed for water glass modification using nanoparticles [1, 7, 8], which due to their specific properties (multiplied specific surface, capacity of entering into chemical reaction with the binder) give favourable properties to the modified material. It should be emphasized that demonstrated significant changes in the physical-chemical properties of the modified binders may also affect the another moulding sand properties and in consequence such important technological processes as moulding sand preparation (for example reducing energy consumption in these processes) [4, 9, 10-12].

## MATERIALS, MEASUREMENT METHODOLOGY AND MEASUREMENT EQUIPMENT

Modification was performed on sodium water glass: R “145” with module  $M = 2,5$  and density  $d^{20} = 1\,470\text{ kg/m}^3$ ,  $\text{pH} = 11,2$ .

Modifiers were colloidal solutions of ZnO nanoparticles in propanol (modifier I - 5 mas. %) and in methanol (modifier II - 3 mas. %) with concentration of 0,3 M. Average diameter of nanoparticles  $d_n < 20\text{ nm}$ .

Methodologies for determining cohesion and adhesion strength were tested in prior studies on various binders [8, 9]. In the study, apparatus for adhesion and cohesion forces was used [8] with holders for cross samples. Load velocity on samples of 1 mm/min was applied.

The assessment of wettability of quartz by the binder was performed by analysis of wetting angle value in the quartz - binder system at thermostatic condition at 20 °C. Quartz surface was prepared by washing samples in distilled water [8].

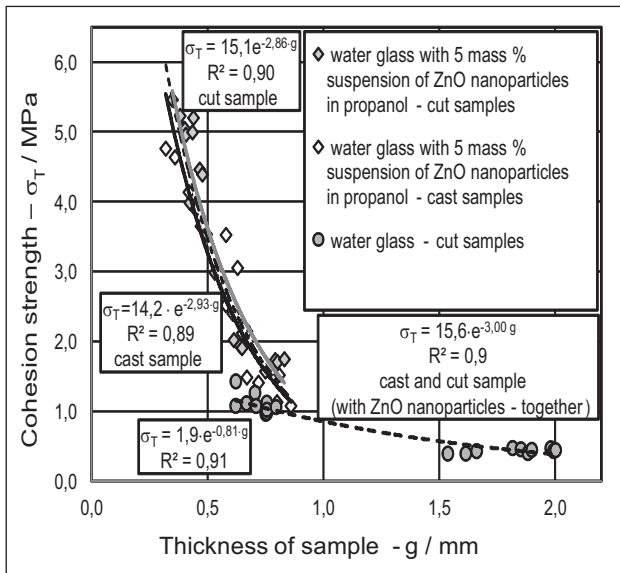
Verification of moulding sand strength was performed by testing tensile strength  $R_m''$  after 24 h of hardening.

Binder modification was performed by introduction of 3 and 5 % of colloidal solutions of ZnO nanoparticles in methanol or propanol.

## RESULTS OF THE STUDIES AND DISCUSSION

Figure 1 presents the results of the series of tests of cohesion strength of cast or cut samples. The material of samples was binder - water glass modified with colloidal solution of ZnO nanoparticles in propanol.

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



**Figure 1** Correlation between cohesion strength  $\sigma_T$  and sample thickness  $g$ . Binder composition: water glass with 5 % modifier I and 3 % modifier II. Constant loading  $v = 1$  mm/min

On the basis of diagrams in Figure 1, one can state that the influence of the sample preparation method on cohesion strength results of the binder containing ZnO nanoparticles with propanol as solvent is marginal. This is testified to by trend line equations for both test series, where the coefficient values (Figure 1) for both cut and cast sample series are very similar. The differences are also small (from the point of view of measurement method accuracy) in the case of comparison of coefficient values -  $a$  for series of cast and cut sample series with trend line coefficients determined for the series comprising all measurement data for binder with ZnO nanoparticles (jointly).

The form of the binder did not significantly affect the occurrence of inhibited contraction in the samples, which could, in turn, cause contraction stress that reduces cohesion strength. At the same time, one can assume that during sample cutting in “flexible” state (in the appropriate moment – before turning to the state that can be referred to as “brittle”), there is no sample damage e.g. in the form of cracks that could reduce their cohesion strength. In both series of tests (cast and cut samples), in correlation of cohesion strength and sample thickness, one can assess the value of  $R^2$  coefficient as 0,9 (Figure 1).

The presented correlation can be described within the range of the experiments with general exponential equation (1):

$$\sigma_T = a \cdot e^{-b \cdot g} \quad (1)$$

where constant “ $a$ ” is the limit cohesion strength of the binder (for very small thickness  $g$  of sample). Constant “ $b$ ” expresses the rate of strength change in relation to thickness change.

Trend lines and constant “ $a$ ” values clearly point to the positive influence of nanoparticle addition to water glass – towards increased cohesion strength.

Observations in the study also included the influence of nanoparticle addition on physical-chemical status of the binder. With free pouring of binder layer on Teflon plate, one could obtain layers of smaller thickness (especially with propanol as solvent) as compared to non-modified water glass. This is confirmed with quartz wettability tests by the binder modified with colloidal solutions of nanoparticles of ZnO in methanol and propanol (Figure 2). All tested binders are characterized by decreasing (in time) of the contact angle –  $\theta$  from the maximum value –  $\theta_{max}$  to the value of the equilibrium –  $\theta_{eq}$ .

As shown (Figure 2), modification of the binder with suspensions in propanol is more effective as compared to the binder modified with ZnO modifiers in methanol. The change of contact angle in time are well described by equation (2):

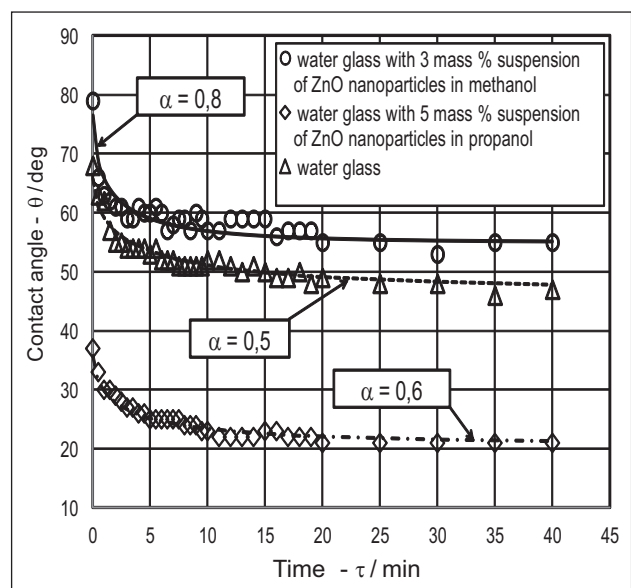
$$\theta = (\theta_{max} - \theta_{eq}) \cdot e^{-\alpha \sqrt{\tau}} + \theta_{eq} \quad (2)$$

The relative errors between measured and calculated values are not exceeded 5 %.

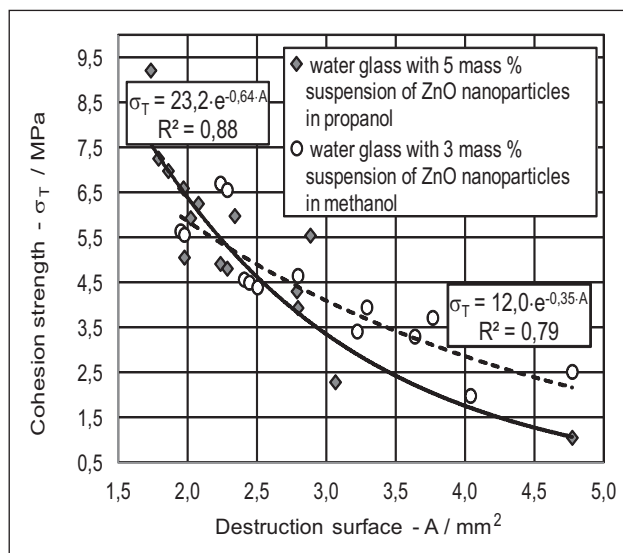
Properties of the binder modified with colloidal solutions of ZnO nanoparticles are also affected by the solvent used (Figure 3). These tests involved very long sample hardening, but this did not lead to very high increase in cohesion strength as compared to shorter hardening times.

Its appropriate selection is important due to possibility of occurrence of unfavourable physical-chemical phenomena. For example, application of a modifier in the form of colloidal solution of ZnO nanoparticles in methanol as solvent caused binder coagulation and small wettability of quartz – Figure 2 [7, 8].

Figure 3 presents results of the cohesion strength tests depending on the surface of destruction of the sample analysed



**Figure 2** Influence of the addition of colloidal solution of ZnO nanoparticles in propanol and methanol on wettability in the quartz - binder system;  $\alpha$  - values of coefficient in equation (2)



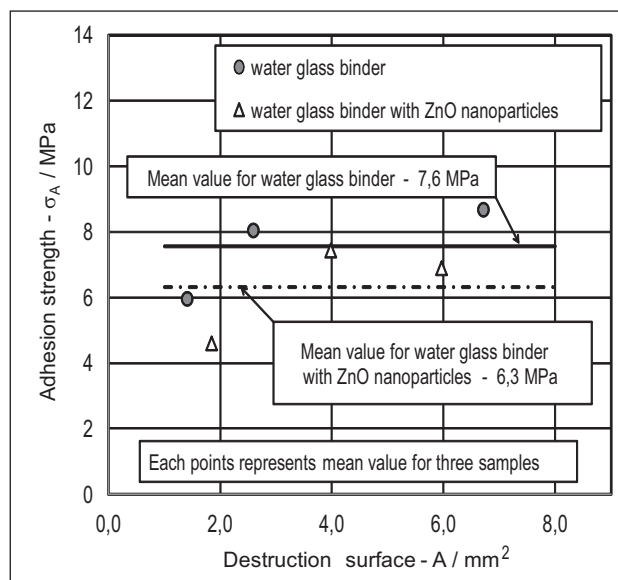
**Figure 3** Correlation between cohesion strength -  $\sigma_T$  and destruction surface area of the sample -  $A$ ; hardening time: 21 days, constant loading  $v = 1$  mm/min

Results of adhesion strength test on the destruction surface have been presented in Figure 4. Adhesion strength diagram  $\sigma_A$  has been made in the destruction surface function (specifically area of connection footage projection on plate surface). In the adopted methodology of sample preparation, determination of connection thickness would involve high measurement error. When performing cross samples, it is very difficult to stabilise the volume of binder dosed. Therefore, different connection destruction surface size was obtained. On the basis of preliminary tests, no material correlation was found between connection strength and their surface. Due to rather large range of measurement results.

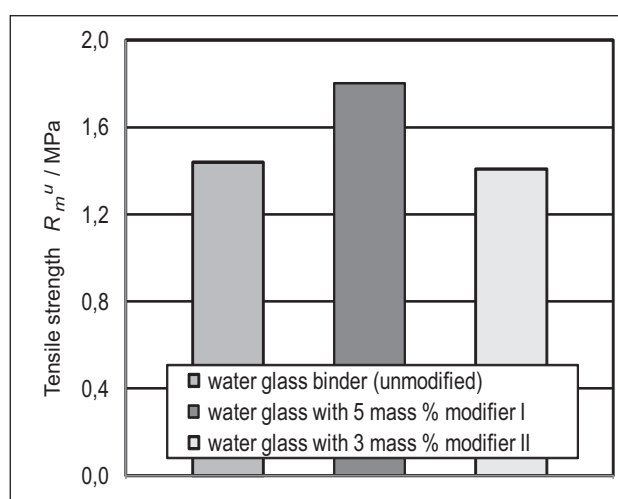
Figure 4 presents average values of adhesion strength of connections for both series of measurements. For the binder with nanoparticles, slightly lower average was obtained as compared to the binder without the addition. Reduced adhesion strength of the binder on the basis of water glass is favourable from the point of view of processes of regeneration and recovery of sand base [4-9].

On the basis of the comparison of average values with cohesion strength values (assessed on the basis of constants in regression equations), it can be stated that adhesion strength for water glass with nanoparticles are of the same order as cohesion strength values. In the case of non-modified water glass, the adhesion strength of connections is significantly higher than cohesion strength. Mean value of adhesion strength  $\sigma_A = 7,6$  MPa (Figure 4) and mean value of cohesion strength  $\sigma_T = 0,77$  MPa for samples thickness range -  $g$  from 0,62 to 2,0 mm (Figure 1).

The cause of varying results of the measurements can include: complex stresses in the bond (difficult to entirely eliminate even despite the application of toggle connections in holders), differences in accuracy of quartz plate preparation, difficulties in precisely symmetrical (central) placement of binder drop, placement of too much binder on the plate.



**Figure 4** Correlation between adhesion strength -  $\sigma_A$  and destruction surface -  $A$



**Figure 5** Influence of water glass modification on tensile strength  $R_m^u$  of moulding sands

The aforementioned limitations also affect variable thickness of bond layer between the plates. This parameter is difficult to control with satisfactory accuracy. In publications, this factor is deemed very important for adhesion strength [8, 10].

Figure 5 illustrates the influence of water glass modification on tensile strength ( $R_m^u$ ) of moulding sand after 24 hours of hardening. Sand base - 100 weight parts, binder - 3 weight parts; modifier I: 5 % of colloidal solution of ZnO nanoparticles in propanol, modifier II: 3 % of colloidal solution of ZnO nanoparticles in methanol (calculated to the binder).

Compacted by vibrations. Hardening conditions: time - 24 h, ambient temperature -  $t_a = 22$  °C, relative humidity -  $RH \approx 39$  %.

Significant increase in tensile strength was determined (by approx. 26 %) after binder modification with 5 % of colloidal ZnO suspension in propanol (modifier I).

## SUMMARY

The study performed revealed favourable influence of modifications on cohesion and adhesion properties, and wettability of quartz surface in the aspect of usefulness for moulding sands. The several - fold increase in cohesion strength was accompanied with preservation of constant level of adhesion strength.

The modification improves the binder capacity to wet the quartz base. Modifier I more effectively improves wettability than modifier II.

The above physical - chemical studies correlate with the strength of moulding sands. The positive influence of the colloidal solutions of ZnO in the alcohols (especially in propanol) results from the acid-base interactions (Lewis acids) between oxygen atoms from ZnO and the OH groups from the alcohol and water glass [11-16]. These interactions cause the creation of hydrogen bonds which are responsible for physico-chemical properties of the binder and as a result the strength of the moulding sand.

The final result is improvement of the cohesion properties of binder and wettability, as well as generation of bridges in the moulding sand with favourable geometric structure [2-10].

## Acknowledgments

The study was performed within the "Dean's Grant No. 15.11.170.419.

## REFERENCES

- [1] B. Stypuła, J. Banaś, T. Habdank-Wojewódzki, H. Krawiec, M. Starowicz, Method for obtaining micro- and nano particles of metal oxides. Polish Patent 369 320, 2004.
- [2] J. Zych, Foundry Journal of the Polish Foundrymen's Association (in Polish) 3 (2005) 2, 88-97.
- [3] J. Zych, Journal of the Polish Foundrymen's Association (in Polish) 4 (2005) 12, 782-792.
- [4] J. Wang, Z. Fan, H. Wang, X. Dong, N. Huang, China Foundry 4 (2007) 1, 26-30.
- [5] Z. Chun-xi: China Foundry 1 (2007) 4, 13-17.
- [6] E. Popatowa, M. Grahn, A. Holmgren, J. Hedlund, Journal of Colloid and Interface Science 354 (2010) 2, 96-102.
- [7] A. Bobrowski, B. Stypuła, B. Hutera, A. Kmita, D. Drożyński, M. Starowicz, Metalurgija 51 (2012) 4, 477-480.
- [8] A. Kmita, B. Hutera, Archives of Foundry Engineering 12 (2012) 3, 59-62.
- [9] E. Ziolkowski, R. Wrona, K. Smyksy, Archives of Metallurgy and Materials 4 (2010) 55, 953-961.
- [10] I. Izdebska-Szanda, A. Baliński, Engineering Procedia 9 (2011) 10, 887-893.
- [11] S. A. Bernal, J. L. Provis, V. Rose, Ruby Mejia de Gutierrez, Cement & Concrete Composites 33, (2011) 1, 46-54.
- [12] H. Roggendorf, W. Grond, M. Hurbanic, Glass Sci. Technol. 69 (1996) 7, 216-230.
- [13] A. Argawal, M. Tomozawa, Journal of Non Crystalline Solids 209 (1997) 3, 166-174.
- [14] M. Bailly, et al.: Journal of Catalysis 5 (2005) 235, 413-418.
- [15] D. Lincot, MRS Bulletin 5 (2010) 35, 778-789.
- [16] S. Peulon, D. Lincot, Advances Materials 8 (1996) 2, 166-170.

**Note:** The responsible translator for English language: "ANGOS" Translation Office, Cracow, Poland