COLLOID SILICA BINDERS WETTING PROPERTY MODIFICATION IN INVESTMENT CASTING

МОДИФИКАЦИЯ СМАЧИВАЕМОСТИ КРЕПИТЕЛЯ ИЗ, КОЛЛОИДАЛЪНОГО КРЕМНЕЗЁМА ДЛА ЛИТЕЛЙНЫХ ДЕЛ

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Abstract: *Wetting properties of colloidal silica, used in investment casting as a binder, were improved by addition of surfactants,and investigated using the shape analysis of pendant and sessile drops. The surfactants used were: perfluorononanonic acid (PFNA), the fluorinated surfactant Zonyl FSO-100 and the commercial surfactant Rokafenol RN8. Two binders were investigated: the 30% colloidal dispersion of silica in water and Sizol, the commercial binder. The size of the particles in these dispersions was determined by dynamic light scattering (DLS). Our investigations showed that the Zonyl FSO surfactant and its mixtures witch Rokafenol is effective in decreasing the dynamic contact angle, which attained 20*^{O}*. Such low values of contact angles represent an essential improvement of wetting properties of slilica binders used in investment casting.*

Keywords: CONTACT ANGLE, WETTING PROPERTIES, SILICA BINDERS

1. Introduction

The interfacial tension of liquid/liquid or liquid/gas interfaces is of great importance of many technological processes such as emulsification, emulsion coalescence and breakup, tertiary oil recovery from tar sands, extraction, detergency, froth flotation, etc. The interfacial tension also determines wettability of solid substrates by liquids, which has a major practical significance. For example, an efficient wetting of wax patterns by ceramic slurries produced from silica binders is critical for the investment casting industry in order to reduce the number of faulty parts. This is especially vital in the case of fine pattern details, which are hardly wetted by unmodified binders. Therefore, in order to improve wetting properties of binders and slurries, various surfactants are added, usually of a non-ionic character. However, the presence of colloid phase of large specific surface area may lead to a partial removal of surfactants due to adsorption, which results in less effective wetting. Despite of major significance of these problems, few systematic studies have been carried out in the literature, based on quantitative measurements of surface tension and the contact angles of binders on various interfaces.

In our previous work [1] we have performed surface tension measurements for silica binders using two model surfactants such as SDS (anionic type) and CTAB (cationic type). However, in that work, the contact angle of modified binders on solid substrates, which is a parameter of primary significance, was not determined.
Therefore, the primary aim of this work was to develop efficient methods for a quantitative characterization of wetting properties of silica binders used commonly in the investment casting industry. These methods are based on precise measurements of surface tension and the dynamic contact angles using the drop shape analysis method. In this way an optimum composition and concentration range of surfactants can be specified, enabling an essential improvements of wetting properties of binders, which was another goal of our work.

2. Materials and Methods

2.1. Materials

Surfactants used in the research:
-perfluorononanonic acid $CF_3(CF_2)_7COOH$ (PFNA), the product of 97% purity (Aldrich),
-Zonyl FSO-100 $(C_2H_4O)x(CF_2)yC_2H_5FO$ (Aldrich),
-Rokafenol RN8 (produced by the Rokita, Dolny Brzeg, Poland), which is a mixture of compounds synthesized by the nonylphenol/ethylene oxide polycondensation reaction with number of (-O-CH_2-CH_2-) groups ranging from 6 to 9
As binders we used the following, colloid silica based products:
-Silicon IV oxide, SiO_2 - 30%, a colloidal dispersion in water (Alfa Aesar) - AA
- Sizol, a commercial silica binder produced by the Rudniki factory, Poland

2.2. Experimental set-up

The surface tension and contact angle measurements were carried out using the drop shape analysis method shown in Fig. 1. Our apparatus exploits the video image processing system of a pendant drop for surface tension measurements. It is interesting to mention that this method enables one to perform also non-stationary (dynamic) surface tension measurements of surfactants over long times reaching hours. This is vital in the case of diluted solution, where the surface tension varies slowly with time due to diffusion of surfactants to the liquid/air interface.

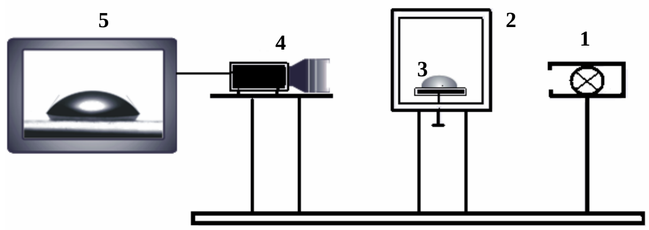


Fig.1 The scheme of the experimental apparatus for simultaneous surface tension and contact angle measurements

The main part of the apparatus, shown in Fig. 1, was the quartz-glass stalagmometer (2) made of a quartz capillary (3) of the outer diameter of 0.628 cm, placed in a thermostatic chamber, of regulated humidity to prevent drop evaporation during the measurement. The stalagmometer (2) was filled with the solution under investigation.

The size of colloidal particles was determined by the dynamic light scattering (DLS), using the Zetasizer Nano ZS Malvern instrument (measurement range of 0.6 nm to 6 μm). The Nano ZS instrument incorporates non-invasive backscatter (NIBS) optics. This technique measures the time dependent fluctuations in the intensity of scattered light that occur because the particles undergo Brownian motion. From the autocorrelation function one can calculate the diffusion coefficient *D* of silica particles. Knowing *D* one can calculate the hydrodynamic radius of particles R_H from the Einstein relationship [2,3]

$$D = \frac{kT}{6\pi\eta R_H} \qquad (2)$$

where: *k* – is the Boltzmann constant, *T* - is the absolute temperature, η - is the viscosity of the solution, R_H - hydrodynamic radius of particles.

It is interesting to mention that in the case of nearly spherical particles, the hydrodynamic radius corresponds to the geometrical radius of the particle

3. Results and discussion

One of the most important characteristics of the binders is the particle size, which was determined via the DLS measurements of the particle diffusion coefficient. From these measurements it was found that the average hydrodynamic radius of silica particles of the AA binder was 15 nm, which corresponds to average particle size of 30 nm. In the case of Sizol, the primary particle size was significantly smaller, equal to 24 nm. Surface tension measurements were also performed for the surfactants used, to determine the concentration range of their adsorption on the air/solution interface, inducing significant decrease in this parameter. In order to increase the precision of these measurements, the dynamic surface tension dependence on the time for each surfactant solutions of appropriate concentration was determined. Then, these results were extrapolated to the infinite time as have been done before in Refs.[4], which produced equilibrium values of the surface tension

Additionally, the surface tension and contact angles for these unmodified binders have been measured. The 30% AA silica exhibited the surface tension of 72.4 mN m^{-1} (dyn cm^{-1}), which practically coincides with the surface tension of triple distilled water used in our studies to produce solutions. This indicates that the AA silica dispersion was of a very high purity, containing no organic contaminants. The contact angle of AA silica drop on the pure paraffin surface was 109^o (see Table 1) which results from the hydrophilic character of the binder. This high value indicates very poor wetting of hydrophobic surfaces being, therefore, unacceptable from the point of view of the investment casting.

Surface tension measurements showed that the fluorinated surfactants studied in this work can be used to effectively reduce surface tension of silica dispersions.

The results obtained for pure PFNA in water, AA and Sizol indicate that in the case of the AA silica dispersion, the effectiveness of the surfactant was even higher than in the case of pure water. This behavior indicates that adsorption of this anionic surfactant on negatively charged silica surface was negligible. High concentration of PFNA decreases also the surface tension of Sizol. In the case of Zonyl the surface tension vs. surfactant concentration dependence was practically the same for both the pure water and for the AA silica dispersion. This indicates that in this case, adsorption of Zonyl on silica particles was practically negligible. The addition of Zonyl to Sizol dispersion, exerted a rather limited effect on its surface tension.

The results obtained for RN8 in AA were less satisfied. The decrease of the surface tension is low and comparable with results obtained for water solution.

The dependence of the equilibrium contact angle of the AA silica dispersion and Sizol binder modified by addition of the surfactants were also determined. For pure binders the contact angles were 109^o and 46^o respectively. For the low concentration range, 10^{-6} - 10^{-4} M, Rokafenol was the most efficient surfactant in the reduction of the contact angle to the limiting value of about 40^o. For this concentration range the PFNA and Zonyl were less effective, probably because of their significant adsorption on the paraffin surface. However, the Zonyl surfactant at higher concentrations, exceeding 10^{-4} M, induced a more significant decrease in the contact angle than Rokafenol, down to the value of 30^o. Interestingly, the Zonyl was even more efficient, reducing further the contact angle to about 20^o, in higher concentrations which practically means a complete wetting of the paraffin surface by the modified silica drop.

Table 1
Contact angles of Alfa Aesar (AA) binder on the paraffin substrate determined for various surfactants.

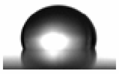
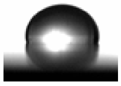
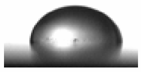
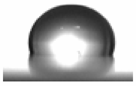
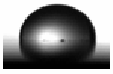
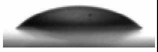
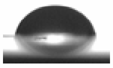
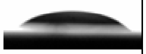
Concentration [mol/dm³] / Surfactant	10^{-5}	10^{-4}	10^{-3}
$C_8F_{17}COOH$	 $\vartheta=109^0$	 $\vartheta=100^0$	 $\vartheta=80^0$
Zonyl FSO - 100	 $\vartheta=109^0$	 $\vartheta=56^0$	 $\vartheta=30^0$
Rokafenol N8	 $\vartheta=93^0$	 $\vartheta=42^0$	
Mixture Zonyl/RokafenolN8	 $\vartheta=79^0$	 $\vartheta=22^0$	 $\vartheta=18^0$

Table 2
Contact angles of Sizol binder on the paraffin substrate determined for various surfactants

Concentration [mol/dm³] / surfactant	10^{-5}	10^{-4}	10^{-3}
$C_8F_{17}COOH$	 $\vartheta=50^0$	 $\vartheta=47^0$	 $\vartheta=32^0$
Zonyl FSO - 100	 $\vartheta=46^0$	 $\vartheta=28^0$	 $\vartheta=17^0$
Rokafenol N8	 $\vartheta=46^0$	 $\vartheta=44^0$	 $\vartheta=35^0$

The influence of surfactant mixtures on the surface tension of the AA silica dispersions was also studied. The results indicate that the best effect was observed for the Zonyl/Rokafenol mixture. However, the minimum surface tension of AA and Sizol dispersion was practically the same as for pure Zonyl, i.e.,22 mNm[1].

For sake of convenience, the actual drop shapes on paraffin films and values of contact angles determined for various surfactants are collected in Table 1 and 2.

Results of analogous measurements were performed for the Sizol (Table 2). As can be noticed, also in this case, a significant reduction of the contact angle was induced by all surfactants. For example, in the case of PFNA, the contact angle as low as 23^o was achieved for a relatively high surfactant concentration of $3x10^{-3}$ M. An analogous effect was attained in the case of Zonyl at lower concentration of 10^{-4} M.

Hence, these measurements proved unequivocally that a the surfactants studied in our works can be used for major improvements of wetting properties of both pure silica dispersion and a commercial colloid silica binder, used in investment casting

4. Conclusion

Our investigations showed that the fluorinated non-ionic surfactant Zonyl-FSO and its mixture with Rokafenol effectively reduced the surface tension of colloid silica (AA) and the commercial silica binder to the low value of 20 mN m^{-1}. Because of surfactant adsorption, the dynamic contact angle of binders on paraffin films was decreased, attaining to the minimum value of 18^o at the bulk surfactant concentration of about 10^{-3} M (0.07%). Such low contact angles represent an essential improvement in comparison with ordinary binders used commonly for producing casting forms in the investment casting industry.

5. References

[1] Z.Adamczyk , G.Para , A.Karwiński, Tenside.Surf.Det. 38 (1998) 261-264.
[2] Z.Adamczyk, Academic Press, Elsevier (2006) 214-219.
[3]Z.Adamczyk, K.Sadlej, E.Wajnryb, M.Nattich, M.L.Ekiel-Jeżewska, J.Bławzdziewicz, Adv. Colloid Interface Sci, 153 (2010) 1-29..
[4]G.Para , E.Jarek., P.Warszyński, *Advances in Colloid Interface Sci*.122 (2006) 39-55.