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THE EFFECT OF DYNAMIC WETTING IN A SAND – BINDER SYSTEM ON THE SAND MOULD STRENGTH

WPŁYW DYNAMIKI ZWILŻANIA W UKŁADZIE: OSNOWA PIASKOWA – SPOIWO NA WYTRZYMAŁOŚĆ MAS

The results of the investigations of quartz wetting by binders of different chemical structure of their molecules were presented. The following binders were used in the investigations:
– alkyd binders (containing long chains of the polyphtalic acid glycol esters),
– epoxy binders (containing functional epoxy group),
– sodium silicate.

The changes in the contact angle are best expressed by the exponential function (Equation 1) with constants related to physico-chemical parameters of the liquid binder, i.e. the viscosity and dynamic wetting. The high dynamics of the wetting process requires low viscosity of the binder and depends on the chemical structure of the binder molecule.

The following parameters were proposed as criteria for evaluation of the dynamic wetting process:
– $\Delta\theta = |\theta_r - \theta_0|$ where θ_0 is the starting contact angle, and θ_r is the value of equilibrium angle,
– τ_r which is the time taken by the system to reach the stationary condition.

The chain structure, typical of e.g. alkyd binder, favours quick adsorption on the sand grains surface and offers large energy of the phase interactions. This means short time necessary for the system to reach the stationary condition and small contact angles.

The high dynamics of the wetting process increases the probability of the formation in sand mixture of the bonding bridges, characterised by advantageous geometrical structure conferring high mechanical strength to the sand.

The proposed research methods enable better evaluation of the binder applicability in preparation of sands characterised by optimum mechanical properties.

Keywords: dynamic wetting, binders, sand mould

W pracy przedstawiono wyniki badań zwilżalności kwarcu przez spoiwa o zróżnicowanej chemicznej strukturze cząsteczki. Do badań zastosowano spoiwo:
– alkidowe (zawierające długie łańcuchy estrów poliglikoloftalowych),
– epoksydowe (zawierające funkcyjną grupę epoksydową),
– szkło wodne.

Zmiany kąta zwilżania w czasie najlepiej ujmuje funkcja wykładnicza (równ. 1) zawierająca stałe związane z parametrami fizykochemicznymi ciekłego spoiwa – lepkością i dynamiką zwilżania. Wysoka dynamika zwilżania uwarunkowana jest małą lepkością oraz chemiczną strukturą cząsteczki spoiwa.

Do oceny dynamiki zwilżania zaproponowano następujące parametry:
– $\Delta\theta = \theta_r - \theta_0$ gdzie θ_0 jest początkowym kątem zwilżania a θ_r wartością kąta równowagowego,
– τ_r czas dojścia układu do stanu stacjonarnego.

Struktura łańcuchowa (jaką odznacza się np. spoiwo alkidowe) sprzyja szybkiej adsorpcji na powierzchni osnowy i dużej energii oddziaływań międzyfazowych. Wskazują na to krótkie czasy dojścia układu do stanu stacjonarnego i małe wartości kąta zwilżania.

Wysoka dynamika zwilżania zwiększa prawdopodobieństwo powstania w masie mostków wiążących o korzystnej strukturze geometrycznej nadających jej wysoką wytrzymałość mechaniczną.

Zaproponowana metodyka badawcza umożliwia lepszą niż dotychczas ocenę przydatności spoiwa do sporządzania mas o optymalnych właściwościach wytrzymałościowych.

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1. Introduction

The physico-chemical phenomena that occur at the sand-binder interface have great impact on the quality of the ready moulding sand and its mechanical strength after hardening. In these processes, the parameters of the sand and liquid binder are of primary importance. Among numerous physico-chemical parameters, the key role is played by the binder viscosity and its capability of wetting the sand grains.

As follows from the theoretical studies [1, 2] and tests [3, 4], the viscosity of binder stimulates the formation in the sand mixture of adhesive (sand – binder) bonds, characterised by a definite geometrical structure corresponding to the, so called, enveloped and non-enveloped bonds [5]. The investigations carried out in this scope have proved that the use of low- viscosity binder increases the probability of the formation of non-enveloped bonds in the moulding sand, conferring to this sand high mechanical strength [3, 4]. Other positive practical aspects of the use of low-viscosity binders include:
– better utilisation properties of binders,
– reduced cost of the sand mixture preparation, while preserving the high level of mechanical properties and improved ecology.

On the other hand, good wettability (i.e. low value of the equilibrium angle) helps the quartz - binder system to quickly reach the stationary condition, promotes easy penetration of the binder to the contact points, combined with the formation of non-enveloped bonds, beneficial for the sand mixture properties. It is the fact generally known that good wettability can be achieved only when the free surface energy (FSE) of the surface layer (WW) of the sand grains gains a high value.

The theoretical studies initiated for a solid – liquid system by T. P. Blake et al. [6, 7] indicated the existence of a formal relationship between the dynamic wetting and viscosity. Detailed analysis of the results described in those studies as well as own investigations [8 - 11] have proved that the dynamic wetting of silica grains by a binder is stronger when the binder has low viscosity; also the time taken by the system to reach the state of equilibrium is shorter.

This study gives the results of the investigations concerning the time-related changes of the contact angle (the dynamic contact angle) in a quartz – binder system. The main aim of the investigations was:
– to compare the dynamic contact angle for binders of different viscosities assigned for practical application in foundries,
– to prove the existence (in a non-stationary state) of functional relationships between the dynamic contact angle and viscosity.

2. Research part

2.1. Materials and equipment

The measurements of viscosity and wettability were carried out on the following binders:
— low molecular-weight diepoxy diane resin (EPIDIAN 5), characterised by the following physico-chemical parameters: M_{cz} (300 - 600); LE – chemical equivalent/100 g (0,35 – 0,58); d^{25} = 1170 kg/m^3; η^{20} = 67,61 Pa·s (producer – Zakłady Chemiczne „Organik – Sarzyna"),
— – alkyd resin (LT – 72): the density of d^{20} = 1115 kg/m^3; the viscosity at 20°C – 1,4 Pa·s (producer – Przedsiębiorstwo Polimer),
— sodium silicate: modulus M = 2,5; the density of d^{20} = 1467 kg/m^3, SiO_2 + Na_2O content – 40,666 wt.%; the content of water-insoluble matter – 0,042 wt.%; the viscosity at 20°C – 0,027 Pa·s.

The base material was optically pure quartz.
For the measurements of viscosity, a modified rotational rheometer with computer program (RHEOTEST 2 type) was used.
The wettability was measured on a prototype apparatus for the measurement of contact angle, equipped with a thermal chamber [11].

2.1.1. Methods of investigation

The viscosity of each binder was measured basing on the experimentally determined relationship: shear rate ($\dot{\gamma}$), shear stress (τ) $\tau = f(\dot{\gamma})$, that is, on the plotted flow curve [2]. The examined sample was thermostated at a preset temperature and with an accuracy of ±0,2 K. The characteristics of the viscosity at different temperatures were always determined on the same sample.
The dynamic wetting $\theta = f(\tau)$ was determined from the contact angle θ measured for a quartz – binder system on a quartz plate washed three times with demineralised water, roughly dried with absorbing paper first, and held in a drier at 378 - 383 K next. On thus prepared quartz surface, a drop of the examined binder (of appropriately small volume) was placed, and changes of the contact angle θ were plotted in time τ under the isothermal conditions, recording the drop image until full stabilisation of the contact angle θ was achieved. The measurements of wettability were carried out in the atmosphere of air, in a chamber with the thermostated temperature maintained at a preset level with an accuracy of ±1 K. On each specimen, 3 to 7 measurements of the contact angle were taken in time.

FSE – Free surface energy was determined using method Owens'a and Wendt'a [13].

The viscosity and wettability were examined in the temperature range of 283 - 323 K.

2.2. Results and discussion

Figure 1 shows changes of the contact angle θ in time τ (at 283 K) for the three different binders applied on the surface of a quartz plate prepared by the technique as described above. The solid line marks the course of changes determined from a theoretical equation (Equation 1).

On the curves plotted in Figure 1 for the function $\theta = f(\tau)$, one can distinguish two time intervals:

— the first interval, comprised in a range of $0 \leqslant \tau < \tau_r$, characterised by large changes of the contact angle starting with the angle θ of a value corresponding to the time $\tau = 0$ (the instant when the binder is dropped onto the quartz plate surface)

and going up to an equilibrium value of the angle θ_r corresponding to the time $\tau = \tau_r$ (the instant when the system has reached the stationary state),

— the second interval, comprised in a range of $\tau > \tau_r$, when the values of the contact angle remain constant (or nearly constant; $\theta = \theta_r$).

The first interval was charaterised by the following parameters: $\Delta\theta = |\theta_r - \theta_0|$ and τ_r.

In the second interval, the measure of the wettability was the equilibrium angle θ_r.

The time-related course of changes in the contact angle of quartz wetted by the binder is best described by the exponential function given below:

$$\cos\theta_r - \cos\theta(\tau) = A \cdot e^{-B\sqrt{\tau}} \tag{1}$$

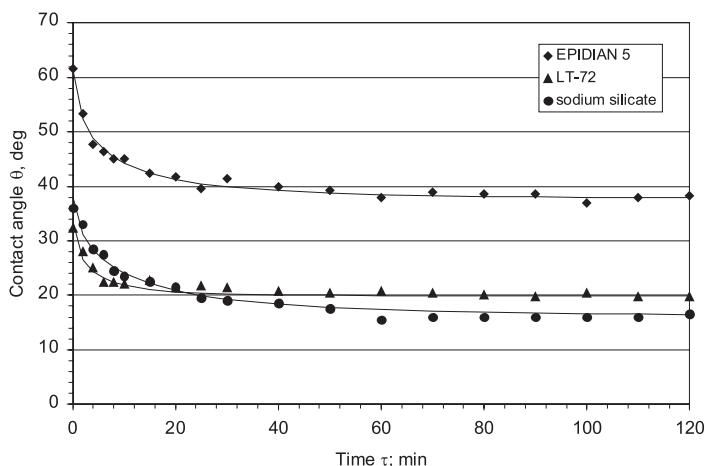where A, B and θ_r are constants related with the physico-chemical parameters of a quartz – binder system.

Fig. 1. Changes of the contact angle θ in a quartz – binder system; the temperature of measurement t = 283 K = const.; quartz washed with water; FSE = 62,7 mJ/m^2 = const

Figure 2 illustrates the time-related changes of the contact angle θ observed in the examined binder (at 283 K) and described with functional relationships given below:

$$\ln[\cos 38 - \cos\theta(\tau)] = -0,4853\tau^{0,5} - 1,0465; R^2 = 0,9822 \text{ (for EPIDIAN 5 resin)} \tag{2}$$

$$\ln[\cos 20 - \cos\theta(\tau)] = -0,4152\tau^{0,5} - 2,6391; R^2 = 0,9004 \text{ (for LT}-72 \text{ resin)} \tag{3}$$

$$\ln[\cos 17 - \cos\theta(\tau)] = -0,5052\tau^{0,5} - 1,4746; R^2 = 0,9739 \text{ (for "145" sodium silicate)} \tag{4}$$

The dynamic wetting capability of the examined binders is characterised by different angles of inclination of the straight lines in equations (2 - 4) and by different values of $\Delta\theta$ and τ_r.

As follows from the straight lines presented in Fig-

ure 2 and from equations (2 - 4), the type of the functional group present in resin (of ester or epoxy type) affects the dynamic wetting behaviour.

Dynamic wetting determine the slope of the graph (Fig. 2), equation (2 - 4).

The highest dynamic wetting reveals the alkyd resin; lower values have been found in epoxy resins and sodium silicate.
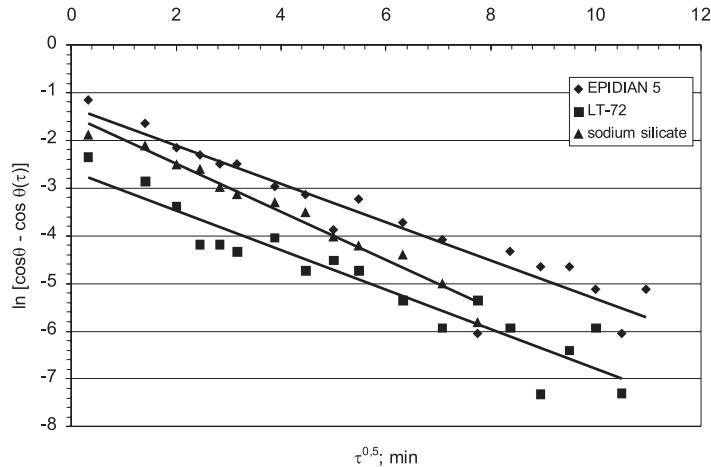
Fig. 2. A relationship between changes of the contact angle and time in a quartz - binder system; the temperature of measurement t = 283 K = const.; quartz washed with water; FSE = 62,7 mJ/m2 = const.

Fig. 2. A relationship between changes of the contact angle θ and time τ in a quartz – binder system; the temperature of measurement t = 283 K = const.; quartz washed with water; FSE = 62,7 mJ/m^2 = const

The alkyd resin (as a product of condensation of the phthalic acid and glycerine) is probably a mixture of the three-dimensional gliptal residues connected by long chains of the polyphtalic acid glycol esters [12], while epoxy resin having a functional epoxy group has a much weaker effect on the dynamic wetting. This is proved by lower values of the equilibrium angle θ_r and shorter time τ_r observed in alkyd resins.

The next graph (Fig. 3) shows changes in the values of the constant A from temperature T for epoxy and alkyd binders, and for sodium silicate. A linear character of changes of the constant A in function of temperature satisfies the Arrhenius relationship, and as such can be described by the following equation:

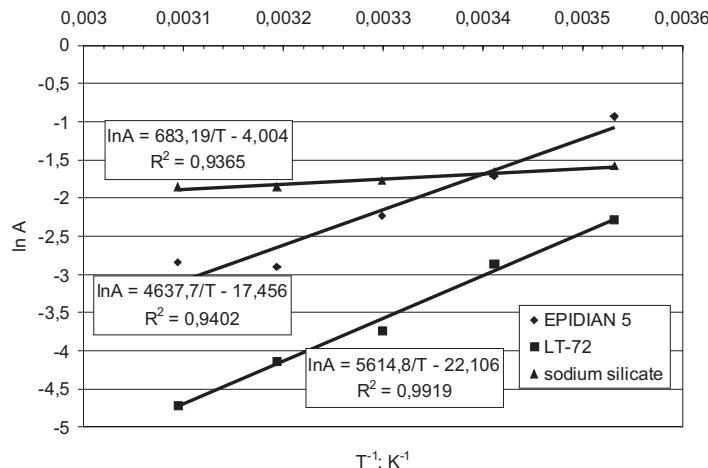$$\ln A = \frac{a}{T} - b \qquad (5)$$

Fig. 3. A relationship between the logarithm of constant A and inverse temperature for the following systems: quartz – epoxy binder, quartz – alkyd binder, quartz – sodium silicate; FSE of quartz 62,7 mJ/m^2 = const

The same temperature-related relationship has also been found to occur in the case of viscosity (Fig. 4), which would suggest a relationship between the constant A and the viscosity of binder. This is confirmed by graphs plotted for the examined binders in Figure 5, by general empirical equation (6), and by more specific equations (6a - 6c):

$$\ln A = k_1 \ln \eta - k_2 \tag{6}$$

$$\ln A = 0,3242 \ln \eta - 2,9521; \ R^2 = 0,9493 \ \text{(epoxy binder)} \tag{6a}$$

$$\text{in } A = 0,1465 \ln \eta - 3,1887; \ R^2 = 0,9878 \ \text{(alkyd binder)} \tag{6b}$$

$$\ln A = 0,1465 \ln \eta - 1,3633; \ R^2 = 0,9516 \ \text{(sodium silicate)} \tag{6c}$$
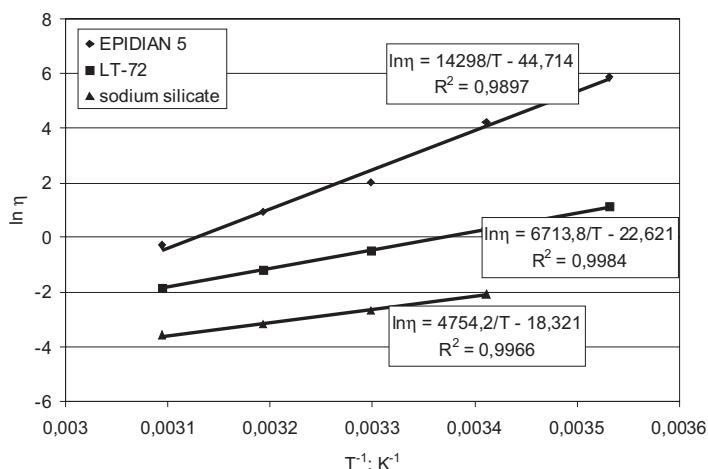

Fig. 4. A relationship between the logarithm of viscosity η and inverse temperature for epoxy binder, alkyd binder and sodium silicate
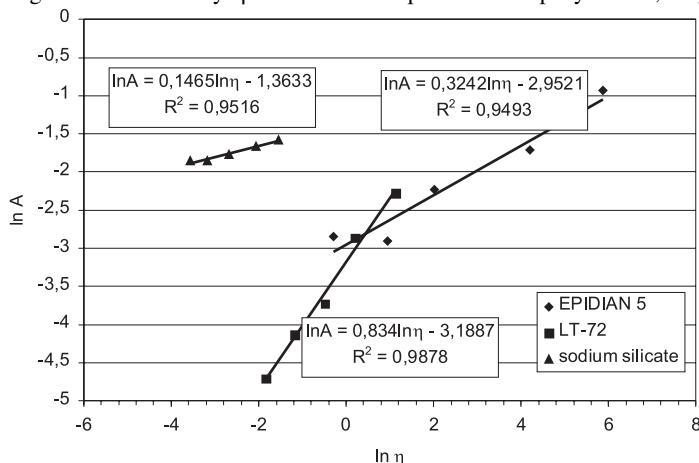

Fig. 5. A relationship between the constant A and the viscosity for epoxy binder, alkyd binder and sodium silicate; FSE of quartz – 62,7 mJ/m^2

Figure 6 illustrates the course of changes in the tensile strength R_m^u for the sand mixtures with epoxy binder, alkyd binder and sodium silicate, hardened for 3 hours at 323 K.

As the diagram shows, the highest tensile strength was obtained by the mixture with alkyd binder, characterised by the highest dynamic wetting properties ($\Delta\theta \approx 22$ deg; $\tau_r \approx 25$'); consequently, the sand mixtures

with epoxy binder, characterised by the lowest dynamic wetting properties ($\Delta\theta \approx 40$ deg; $\tau_r \approx 40$'), had the lowest strength.

The alkyd binder with a chain group (HOR'OH) present in its molecule has been observed to exert a definitely stronger effect on both the dynamic wetting and time taken for the system to reach the stationary condition. Binders characterised by strong chemical affinity to quartz (e.g. sodium silicate) have had much weaker effect on both the dynamic wetting and sand mixture strength (Fig. 6). In other hand, impetuosity decrease tensile strength (in 323 K) is probably produce by dehydratation sodium silicate and formation plastic or semisolid.
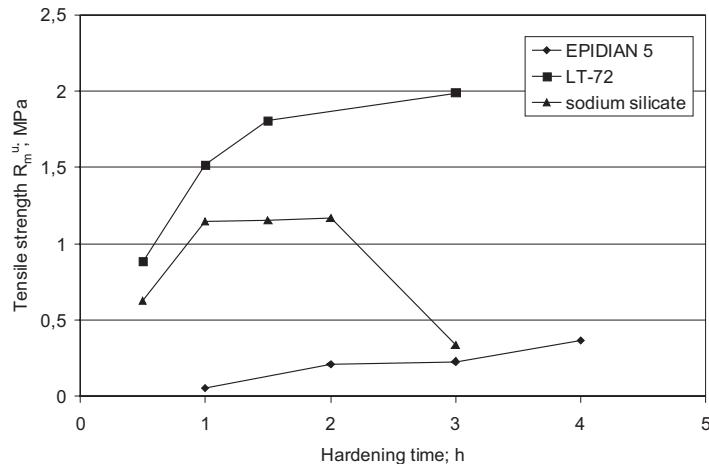

Fig. 6. Tensile strength R_m^u vs hardening time of the sand. The sand mixture composition was as follows: the sand from „Szczakowa" mine; epoxy binder (EPIDIAN 5 resin + Z-1 hardener); alkyd binder (LT-72 resin + PMI hardener – 1); "145" sodium silicate + flodur 1 hardener. Mixing conditions: sand + hardener – 1,5 min + resin – 5 min. Vibration compaction. Test conditions - ambient temperature

The dynamic wetting, depending on the physico-chemical parameters of the liquid binder, causes quick penetration of this binder to respective contact points with the successive formation of the bonding bridges of a configuration corresponding to the, so called, non-enveloped bonds [5]. The presence of these bonds in a moulding sand confers to this mixture high mechanical properties. The bonding bridges developed during the sand preparation are hardened in the process of the sand hardening.

3. Summary

The results of the carried out investigations have proved that binder viscosity η has some effect on the dynamic wetting behaviour. Hence, the general dynamic wetting equation (Equation 1) assumes the form:

$$\ln[\cos\theta_r - \cos\theta(\tau)] = k_1 \ln\eta - k_2 - B\sqrt{\tau}$$

Binders of lower viscosity are characterised by higher power of the dynamic wetting of the sand grains. This promotes the formation in a foundry sand mixture of the bonding bridges of an unenveloped character with a geometrical structure beneficial for the moulding sand properties.

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