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AN EFFECT OF AROMATIC DILUENT ADDITION ON THE SELECTED PROPERTIES OF EPOXY RESIN

1. INTRODUCTION

The strength characteristics of moulding and core sands have an important effect on the quality of the ready castings. The results of numerous experimental and theoretical studies [8] indicate that a relationship exists between the obtained mechanical properties of foundry sands and the technique of their preparation. It is a well-known fact that in the process of preparing sand mixtures with liquid binders, attention should be paid to the sequence in which the liquid components are added, and to the time of mixing after each component has been introduced. A usual practice is to add the hardener first, and binder next. Introducing of individual components to the sand is accompanied by some physico-chemical phenomena taking place at the sand – hardener and sand – hardener + resin phase boundary. The surface phenomena depend on the sand grain parameters and binder behaviour. In the practical aspect of sand preparation, very important are the following effects: surface energy depending on the sand grains surface development and morphology, the sand grains wettability by the liquid, and the viscosity of binder. In an isothermal process, in the state of equilibrium, the wettability of a surface by a binder is characterised by an equilibrium contact angle, which depends on the value of energy at the solid body/gas – γ_{sg}, liquid/gas – γ_{lg}, liquid/solid body – γ_{ls} phase boundary. Full wettability of the solid body is possible when surface energy of the liquid is smaller than the energy of the surface onto which it has been applied. The problem of poor wettability can be solved by modification of the solid body surface, obtained through chemical or mechanical treatment. An improvement of the wettability can also be achieved by a thermal treatment of the binder, or by modifying its properties with an addition of diluent [10]. Another function of the diluent is to improve the utilisation properties of the binder by reducing its viscosity. Low viscosity of the binder stimulates formation in sand mixture of the, so called, envelope-free bonds

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between the sand grains and the binder [7]. The theoretical research and own experiments have proved that the presence of such bonds has a very beneficial effect on strength characteristics of the hardened sand.

The effectiveness of the applied diluent is determined by the chemical structure of its molecules. The diluents added to resins are usually organic compounds of chain or ring structure; among them one can distinguish aromatic or cyclic compounds. The type of the bond as well as the presence of a functional group confer to a molecule certain polarity, which determines how active the diluent will be.

The studies from the field of surface phenomena, published over the last decade [1, 2, 3, 11], have stressed the fact that the dynamic wetting, measured by changes in the contact angle, depends on the interactions which take place between the liquid and solid body. The intensity of these interactions, as proved by the conducted research, depends on the structure of the liquid, i.e. on the presence of polar or non-polar groups.

In this study an attempt has been made at investigating the dynamic wetting of the sand grains by a binder and establishing the role which temperature and non-active diluents (of low polarity) added to binder play in this phenomenon.

2. EXPERIMENTAL

2.1. Materials and equipment

The wettability of the sand grains was examined in a quartz – binder system, using:

- as a binder – fine-molecule epoxy resin, type EPIDIAN 5; density at 25^oC – 1170 kg/m^3; viscosity at 25^oC – 43.07 Pa s (produced by – Zakłady Chemiczne „Organik Sarzyna”),
- as a modifying agent (diluent) – xylene, which is a composition of isomers characterised by the density at 20^oC – 860 kg/m^3 and a boiling point of about 140^oC (produced by – OBR PR Płock).

As a base material optically pure quartz was used.

The contact angle was measured by a prototype apparatus described in technical literature [5].

2.2. The methodology

Since the surface condition of a solid body considerably affects the value of the contact angle θ, and in an attempt to relate the investigation to the practice of moulding sand preparation, the surface of the quartz grains was prepared for the examination by shaking the sample many time in demineralised water, followed by drying at a temperature from the range of 105–110^oC. Onto thus prepared surface a drop of the examined binder was applied. The dynamics of the wetting process was examined plotting in time, at an isothermal temperature, changes in the progressive angle θ with simultaneous recording of the drop image. The measurements were continued until an equilibrium value of the angle θ_r has been established, applying the following temperatures: 283 K, 293 K, 303 K, 313 K and 323 K, measured at an accuracy of up to ±1 K [6, 9]. On the other hand, in investigation of the effect of diluent on the examined parameters, 5, 20 and 30 percent by weight of xylene was added to EPIDIAN 5 resin.

The series of measurements taken with the diluent added consisted in examining the effect of various xylene additions on the wetting dynamics (the addition of 5, 20 and 30 wt. % of xylene was used) and the type of interaction that this diluent is said to have with the resin structure. The measurements were taken by an infra-red spectroscopy, using a Digilab Excalibur FTS 3000 Mx spectrometer with an electrically cooled DTGS detector. The system additionally offers a HATR attachment with ZnSe crystal for multiple reflection and a transmission device.

2.3. The results and discussion

The results of the wettability investigation conducted in a quartz – EPIDIAN 5 resin system at different temperatures were disclosed in previous studies [6, 9]. The results of those studies are summed up in Figure 1. From the data given in this drawing it follows that wetting is proceeding within the two, easily distinguishable, time intervals. The first interval (up to 20 min) is characterised by a large drop in the angle value, corresponding to the decreasing wetting dynamics; the second (20–120 min) is characterised by small changes in the angle θ and reaching by the angle θ_r a value of equilibrium. For analysis of the phenomenon, the first time interval was adopted.

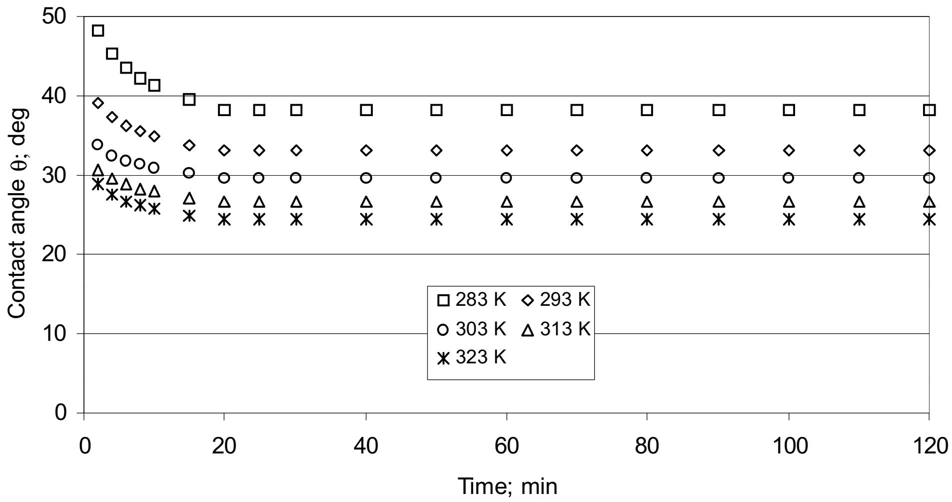

Fig. 1. *Effect of time and temperature on the values of contact angle θ in a quartz – EPIDIAN 5 system (according to equation (1))*

Changes in the angle θ over time t, i.e. the dynamics of the wetting process, can be described by a logarithmic function

$$\theta = -A \ln t + B_0 \tag{1}$$

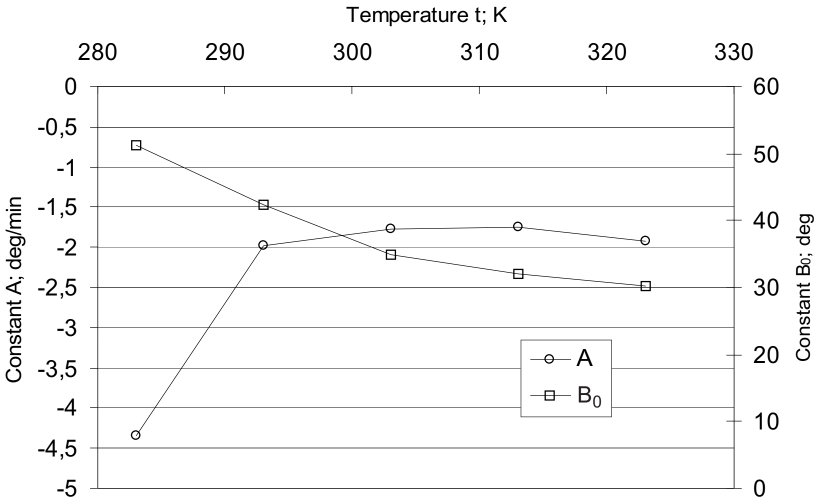

Fig. 2. *Effect of temperature on the values of constants A and B_0 in equation (1) for a quartz – EPIDIAN 5 system*

According to the proposed mathematical model (Equation (1)), the experimentally determined constants A and B_0 stand for, respectively, the changes in angle θ in a time unit, and the starting value of this angle (after the binder has been applied onto the surface of quartz). For a quartz – EPIDIAN 5 resin system, at the examined temperatures, the changes in the values of constants A and B_0 have been graphically plotted in Figure 2, and analytically described by Equations (2a) and (2b).

$$A = 15.6 \ln T - 91.6 \tag{2a}$$

$$B_0 = 2156.4 e^{-0.0134T} \tag{2b}$$

Figure 3, on the other hand, depicts a relationship between the rate of changes in angle θ (expressed by derivative $\frac{d\theta}{dt}$) and inverse of time $\frac{1}{t}$

$$\frac{d\theta}{dt} = -A \frac{1}{t} \tag{3}$$

As it follows from the plotted curves, at constant temperature, the relationship assumes a rectilinear course and expresses the dynamics of the wetting process, constant A in Equation (3) being the factor of proportionality. According to the disclosed relationships, the wetting rate $\frac{d\theta}{dt}$ is assuming a linear increase with time from the value $\frac{d\theta}{dt} = -A$ (characteristic of a given temperature for time t = 1) up to a value equal to zero, that is, $\frac{d\theta}{dt} = 0$ (corresponding to the state of equilibrium).

On the other hand, the exponential character of changes in coefficient B_0 (Equation (2b)) with temperature is similar to the temperature-related changes in viscosity [4, 10], thus proving a relationship which is said to exist between the constant B_0 and this property of the binder.

As we all know, the viscosity of plastic bodies in liquid state is related with rheological parameters, like molecular mass, chain branching and rigidity, and forces of molecular attraction [10]. An increase of temperature causing drop of viscosity is best revealed in the, so called, mean coefficient of dynamic viscosity ξ, which rapidly decreases due to the reduced internal friction, which reflects viscosity and counteracts the segments movement.

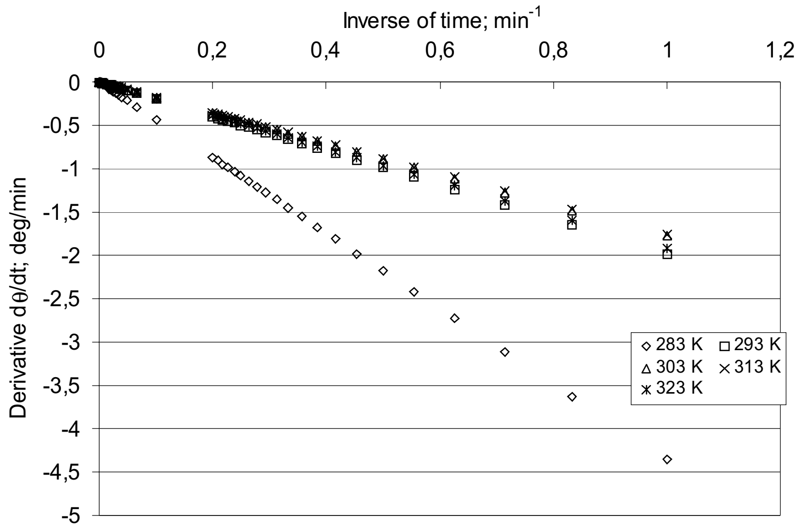

Fig. 3. *Relationship between derivative* $d\theta/dt$ *and inverse of time in a quartz – EPIDIAN 5 system at different temperature values*

Figure 4 illustrates time-related changes in contact angle θ for EPIDIAN 5 resin with an addition of 5 wt. % of xylene at temperatures of 283 K; 293 K; 303 K; 313 K and 323 K. As we can see, the shape of the curves plotted in this drawing is similar to the shape of the curves plotted in Figure 1, i.e. for the resin without an addition of xylene, which makes the use of the same mathematical model possible (Equation (1)). Graphically, the changes in constants A and B_0 in function of temperature were plotted in Figure 5; analytically they are expressed by Equations (4a) and (4b), analogically as for the resin without an addition of xylene:

$$A = 15.2 \ln T - 89.4 \tag{4a}$$

$$B_0 = 3297.6 e^{-0.0153T} \tag{4b}$$

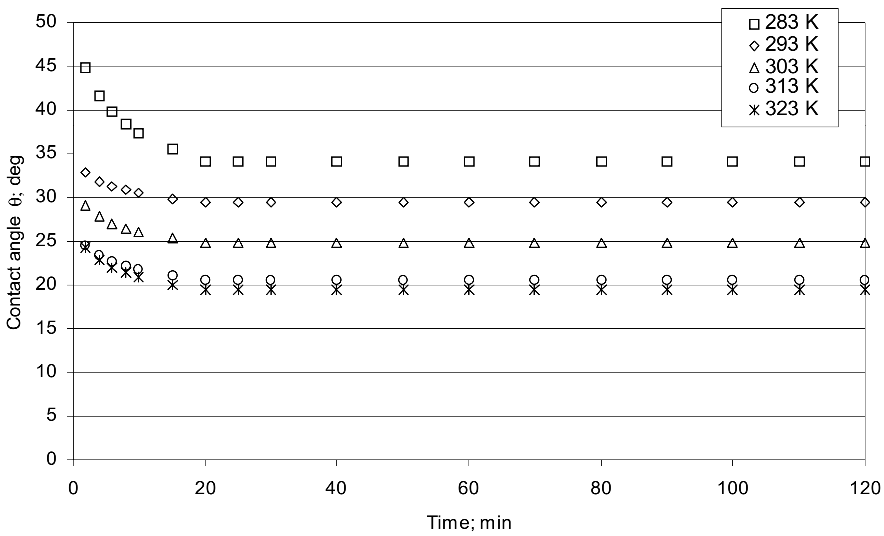

Fig. 4. *Effect of time and temperature on the values of contact angle θ in a quartz – binder system (according to equation (1)); binder composition (in percentage by weight): EPIDIAN 5 – 95; xylene – 5*

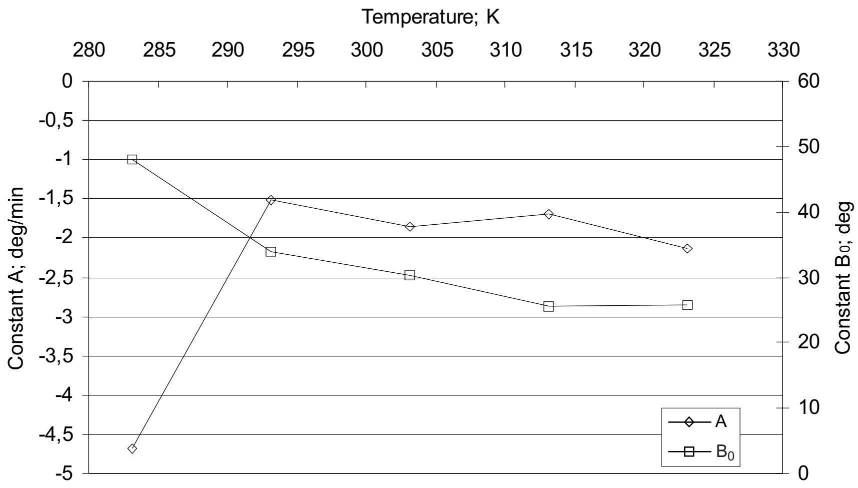

Fig. 5. *Effect of temperature on the values of constants A and B_0 in equation (1) for a quartz – binder system; binder composition (in percentage by weight): EPIDIAN 5 – 95; xylene – 5*

The analysis of the value of constant A, expressing the dynamic wetting at different temperatures, indicates that 5% addition of xylene to EPIDIAN 5 resin has no significant effect on this value. This is well illustrated by relationship $\frac{d\theta}{dt} = f(t)$ plotted in Figure 6, described also by means of a linear function (Equation (3)).

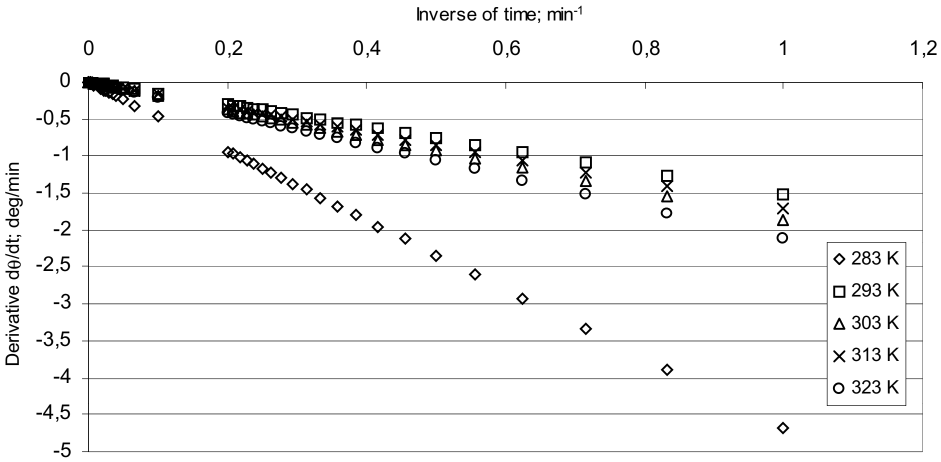

Fig. 6. *Relationship between derivative* $d\theta/dt$ *and inverse of time* $\frac{1}{t}$ *in a quartz – binder system at different temperature values; binder composition (in percentage by weight): EPIDIAN 5 – 95; xylene – 5*

The value of constant B_0 changing with the changes of temperature for a 5% addition of xylene indicates a relationship that is said to exist between this constant and the viscosity of binder.

The examinations of the dynamic wetting of EPIDIAN 5 resin with 20 wt. % and 30 wt. % of xylene indicated that the state of equilibrium was reached almost immediately (at the investigated temperatures) with similar values of the angle θ_r. In practice, this means that it is possible to considerably reduce the time necessary for sand preparation.

The results of the carried out investigation are illustrated in Figure 7. The run of changes in angle θ_r with temperature can be, with some approximation, expressed by a straight-line Equation: $\theta_r = -AT + B$ (a mild-slope curve – $A \approx 0.2\frac{d\theta}{dT}$), which means that the effect of temperature on the dynamic wetting of resin with this diluent is practically very small.

The examinations made by infra-red spectroscopy on EPIDIAN 5 resin indicated that after introducing 5 wt. % or 20 wt. % of xylene no important changes occurred as regards shifting of absorption bands and changes in their shape. This is illustrated by the spectra shown in Figure 8 for resin alone, for xylene, and for resin with the above mentioned additions of xylene.

The analysis of the spectra confirms that the effect of xylene added to EPIDIAN 5 resin is of physical nature, which means that there is no chemical reaction between the diluent and resin. The physical effect of xylene, which belongs to the group of aromatic compounds, is due to its low polarity (the presence of two methyl groups in benzene ring). Therefore, it is included into the family of non-active diluents [12].

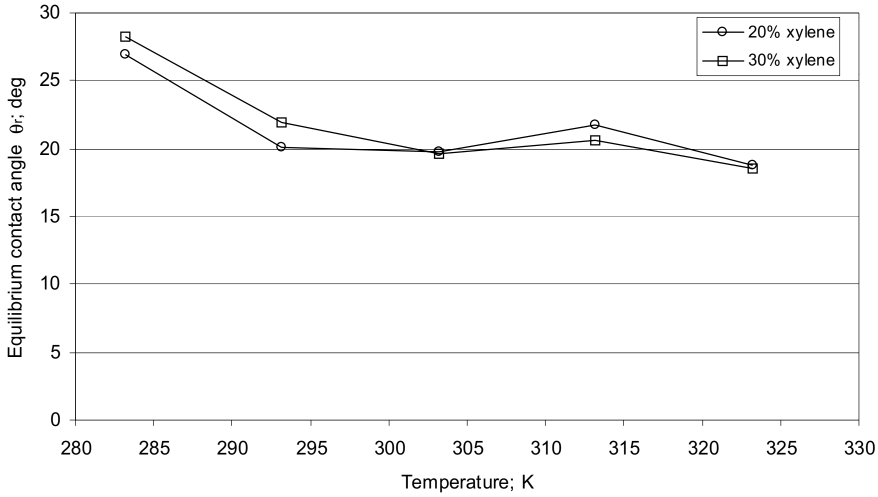

Fig. 7. *Relationship between equilibrium contact angle* θ_r *and temperature in a quartz – binder system (binder composition: EPIDIAN 95 + xylene 5)*

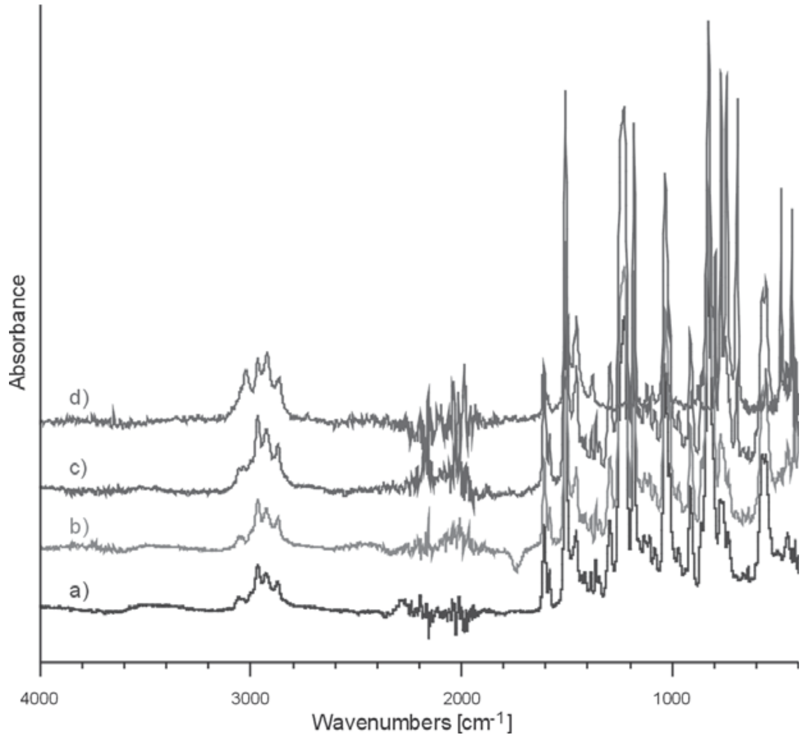

Fig. 8. *FT-IR spectra of: a) EPIDIAN 5; b) EPIDIAN 5 + xylene 5%; c) EPIDIAN 5 + xylene 20%; d) xylene*

In the practical aspect of moulding sand preparation, the low initial viscosity of binder (obtained due to the addition of a diluent) is very beneficial, since it improves the utilisation properties of this binder and enables its steady and uniform spreading on the surface of the sand grains as well as reducing the amount added to the sand. Additionally, the lack of any reaction between the resin and diluent makes removal of the binder from the system very easy, e.g. during compaction or hardening (with the requirements of environmental protection duly observed).

3. CONCLUSIONS

The changes observed in contact angle θ within the time interval of 1–20 min, that is, the investigation of the dynamic wetting of quartz grains by an epoxy binder, have indicated that the run of this process depends on the volume of the diluent added and on the chemical structure of its molecules.

The dynamic wetting of quartz by pure EPIDIAN 5 resin or by the same resin with an addition of 5 wt. % of xylene is described with best approximation by a logarithmic function (Equation (1)).

The constants A and B_0 (Equation (1)), determined by experiments, depend on the temperature with:

- constant A showing a logarithmic increase with temperature and being a measure of the wetting dynamics,
- constant B_0 showing an exponential decrease with temperature, which proves its relation with the viscosity of binder.

In EPIDIAN 5 resin with an addition of 20 wt. % and 30 wt. % of xylene the state of equilibrium is reached immediately, and in practice this means that the time of mixing can be considerably reduced (with good wetting of the sand grains still preserved).

The course of relationship: $\theta_r = f(T)$ for EPIDIAN 5 resin with this diluent shows a very small effect of temperature (the value of constant $A \neq 0$).

The infra-red spectroscopy has proved the absence of any reaction between EPIDIAN 5 resin and the added xylene, which is due to an aromatic nature of this diluent (low polarity of its molecules). The investigated physical interactions between the resin and xylene are very beneficial to the practice of moulding sand preparation.

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