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## THE EFFECT OF CHEMICAL STRUCTURE OF FOUNDRY BINDER DILUENT ON SURFACE PROCESSES AND SAND STRENGTH

### WPLYW CHEMICZNEJ STRUKTURY ROZCIEŃCZALNIKA W SPOIWIE NA PRZEBIEG PROCESÓW POWIERZCHNIOWYCH I NA WYTRZYMAŁOŚĆ MASY

The paper presents the results of investigations of the dynamics of wetting in a quartz-binder system. It has been proved that the two-stage process of wetting (unsteady state passing into the steady state) is important for the practice of moulding sands and depends on physico-chemical parameters of binder, especially on its viscosity.

A mathematical description of the wetting phenomena was given and it was demonstrated that the course of the wetting dynamics is determined by the viscosity which depends on the chemical structure and concentration of added diluent. The wetting dynamics is characterised by the difference  $\Delta\theta$  between the values of the initial  $\theta_0$  and equilibrium  $\theta_r$  contact angle and by the time  $\tau_r$  that the system needs to reach a steady state.

It has been shown that the dynamics of quartz wetting by the binder with diluent of a chain structure and high concentration is higher with simultaneous reducing of time  $\tau_r$ . It has been verified that the resistance of moulding sands with binder and the diluent of chain structure and high concentration is higher compared to the strength of the sands with diluent of another structure.

*Keywords:* dynamic contact angle, diluent, moulding sands

W pracy przedstawiono wyniki badań dynamiki zwilżania w układzie: kwarc-spoivo. Wykazano, że dwuetapowy proces zwilżania (stan niestacjonarny przechodzący w stan stacjonarny) ma znaczenie dla praktyki mas i uwarunkowany jest parametrami fizykochemicznymi spoiwa a zwłaszcza jego lepkością.

Przedstawiono matematyczny opis zjawiska zwilżania oraz wykazano, że na przebieg dynamiki zwilżania ma lepkość uwarunkowana chemiczną strukturą i stężeniem wprowadzonego rozcieńczalnika. Dynamikę zwilżania charakteryzuje różnica  $\Delta\theta$  pomiędzy wartościami początkowego  $\theta_0$  i równowagowego  $\theta_r$  kąta zwilżania oraz czas  $\tau_r$  dojścia układu do stanu stacjonarnego.

Wykazano, że dynamika zwilżania kwarcu przez spoiwa z rozcieńczalnikiem o strukturze łańcuchowej i wysokim stężeniu jest wyższa przy równoczesnym skróceniu czasu  $\tau_r$ . Zweryfikowano, że wytrzymałość mas ze spoiwem z rozcieńczalnikiem o strukturze łańcuchowej i wysokim stężeniu jest wyższa w porównaniu z wytrzymałością mas z rozcieńczalnikiem o innej strukturze.

### 1. Introduction

During foundry sand preparation, the surface processes that take place in a sand-binder system result in the formation of bonding bridges [1] of a geometrical structure that confers to the sand the required high mechanical properties [2, 3].

Detailed analysis of surface phenomena that occur in foundry sand mixtures has indicated that the type of coating formed by liquid binder on the sand grains (en-

veloped or unenveloped model), among others, depends on the binder viscosity and sand grains wettability [4].

It is the fact commonly known that the viscosity of binder can change in function of temperature, diluent addition in various concentrations, and chemical structure of particles [4].

Besides viscosity, another important parameter is wettability.

The high wetting dynamics (non-stationary state) results in quick spreading of the binder [5, 6], which soon reaches its contact point and starts forming bond-

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ing bridges characterised by a geometry corresponding to the unenveloped model with relatively short time required for the sand – binder system to reach its stationary state and low value of the equilibrium angle (the stationary state). This state can be obtained with proper diluent added to the binder.

Examining the related effects one can see that the wetting behaviour in both stationary and non-stationary condition depends not only on the chemical structure of binder but also on the chemical structure of the added diluent.

No studies have been undertaken so far on the subject of time-related changes in the contact angle of quartz – binder system and no attempt has been made to find a mathematical description of this process.

The theoretical investigations of a solid – liquid system started by T. D. Blake et al. [5, 6] indicated a formal relationship that is said to exist between the wetting dynamics and viscosity. The results of these investigations, confirmed further by XPS studies [7], stressed the importance of the chemical structure of diluent particles and proved that the wetting dynamics of quartz is higher when low viscosity binders are used, and that the system requires shorter time to reach the state of equilibrium.

The present study discloses the results of investigations concerning time-related changes in the contact angle (contact angle dynamics). The main aim of the investigations was:

- to prove that the double-stage process in which quartz is wetted by binder (the non-stationary and stationary condition) is important for the moulding sand practice,
- to check what effect an addition of diluent to binder can have on the sand strength in hardened state.

## 2. Research part

### 2.1. Materials, methods and equipment

The viscosity and wettability were measured on optically pure quartz, using as a binder:

– fine-molecule, diene, diepoxy resin (EPIDIAN 5), characterised by the following physico-chemical parameters:  $M_{cz}$  (300-600); LE (0.35-0.58);  $d^{25} = 1170 \text{ kg/m}^3$  (producer – Zakłady Chemiczne “Organik – Sarzyna”.

As resin diluents, organic compounds with chain and cyclic structure of particles were used.

The chain compounds were the following acetic acid esters:

- methyl acetate ( $M_{cz} = 74.08 \text{ g/mole}$ ;  $t_{wrz} = 57.5^\circ\text{C}$ ;  $d^{20} = 939.0 \text{ kg/m}^3$ ,  $\eta^{20} = 0.38 \text{ mPa}\cdot\text{s}$ ,  $\mu^{25} = 1.78\text{D}$  (dipole moment),

- butyl acetate ( $M_{cz} = 116.16 \text{ g/mole}$ ;  $t_{wrz} = 126.5^\circ\text{C}$ ;  $d^{20} = 881.3 \text{ kg/m}^3$ ,  $\eta^{20} = 0.69 \text{ mPa}\cdot\text{s}$ ,  $\mu^{25} = 1.84\text{D}$  (dipole moment).

The diluent with cyclic structure was cyclohexanone ( $M_{cz} = 98.15 \text{ g/mole}$ ;  $t_{wrz} = 155.5^\circ\text{C}$ ;  $d^{20} = 947.0 \text{ kg/m}^3$ ,  $\mu^{25} = 2.8\text{D}$  (dipole moment).

The resin hardener was triethylenetetramine (trade name Z-1).

Binder preparation consisted in mixing of constituents in predetermined weight proportions, homogenising the composition and thermostating to a preset temperature at an accuracy of up to  $\pm 0.2^\circ\text{C}$  (viscosity measurements)  $\pm 1^\circ\text{C}$  (wettability measurements). Measurements were taken in the temperature range of 10-50°C (raising the temperature by 10°C).

The viscosity of binder mixtures was determined with a RHEOTEST 2 rotation rheometer, plotting the respective flow curves.

To produce in quartz a surface layer characterised by constant value of the free surface energy (FSE), the quartz plates were rinsed with water and dried at 105-110°C. Onto thus prepared plates, a drop of binder was applied and changes in the contact angle were recorded along with changes in the drop image observed at predetermined time intervals until full stabilisation of the angle value has been obtained. The measurements were taken by a prototype wettability measuring device [8].

For XPS analysis, the quartz surface was prepared in the same way as for the wettability testing. On the quartz surface, a thin layer (up to 3 nm thick) of the examined binder (EPIDIAN 5 resin with 30 wt.% addition of diluent) was spread and hardened at 105÷110°C. The XPS examinations were carried out on pure quartz, on quartz mixed with resin, and on quartz mixed with resin compositions containing methyl acetate, butyl acetate and cyclohexanone, respectively.

The XPS examinations were carried out on a VSW spectroscope using AlK  $\alpha$  radiation of 1486.6 eV energy produced by an X-ray tube operating under a voltage of 13 kV and current of 10 mA. The operating pressure was up to  $2 \times 10^{-8} \text{ Tr}$  (1 Tr = 133.3 Pa).

### 2.2. Results and discussion

Figure 1 shows changes in the contact angle at 10°C observed in a quartz – epoxy resin binder system containing 20 wt.% of methyl acetate, butyl acetate and cyclohexanone.

In all graphs, two time intervals can be distinguished:

- first – dynamic, comprised in a range of  $0 \leq \tau \leq \tau_r$ , with angle changing from the starting value  $\theta_0$  to

an equilibrium value  $\theta_r$ , typical of a non-stationary condition of the quartz – binder system,

- second, comprised in a range of  $\tau_r \leq \tau < 2h$ , where values of the contact angle  $\theta_r$  are constant and correspond to a stationary state of the quartz – binder system.

Large drop in the contact angle value observed in the first interval is typical of high viscosity values. The theoretical research described in [9] has indicated that

this is due to a high value of the component of viscosity effects  $\Delta G^*$ , resulting from high cohesion of the liquid due to small intermolecular distances and an inherently low value of the component of interfacial effects  $\Delta G_S^*$ . This is why for large contact angles (obtained at high viscosities), a severe drop in the value of these angles should be expected, combined with weak interfacial effects.

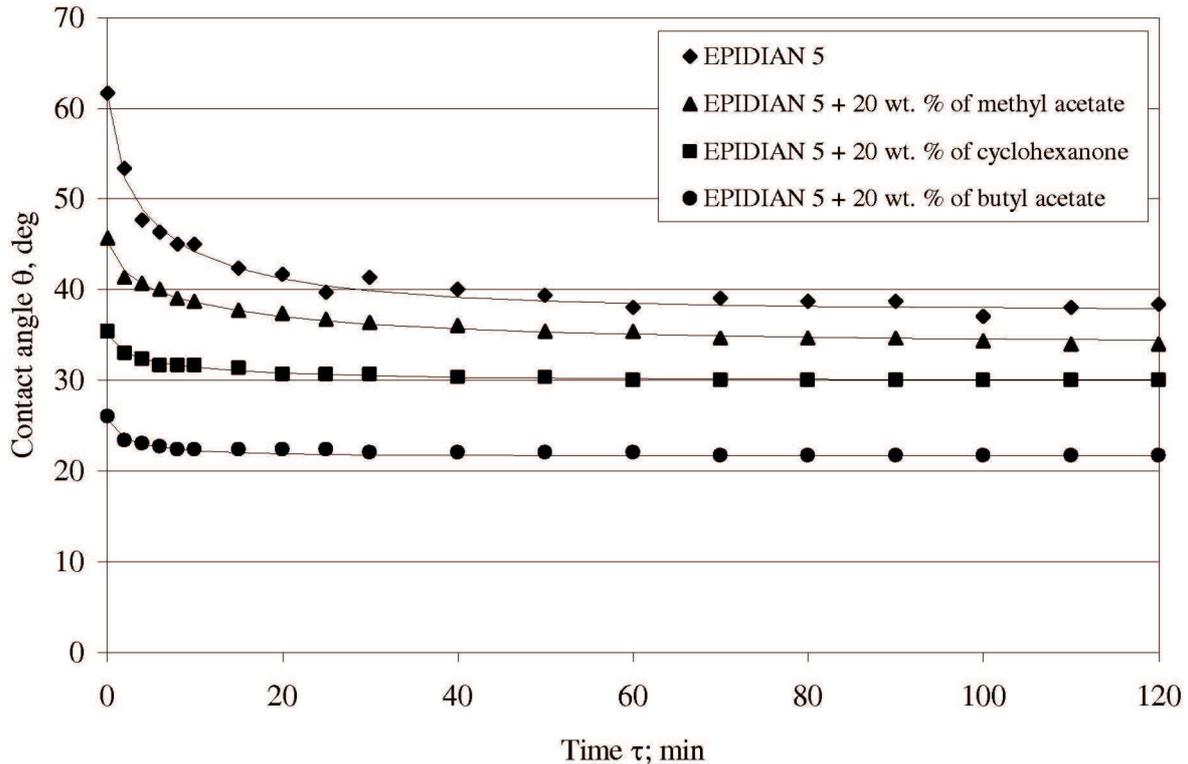


Fig. 1. Time-related changes in the contact angle  $\theta$  in a quartz – EPIDIAN 5 + diluent system; SEP – 62,7 mJ/m<sup>2</sup>; t = 10°C = const

Determined from the flowability curves (at 10°C), the viscosity of resin and its mixtures (20 wt.% addition) with methyl acetate, butyl acetate and cyclohexanone is 436.18 Pa·s, 0,31 Pa·s, 0.49 Pa·s, 2.14 Pa·s, respectively [9, 10]. The largest drop of contact angle in a quartz – binder system has been observed for resin mixed with methyl acetate.

The observed drop in the contact angle  $\Delta\theta$  is interrelated with a long time  $\tau_r$  that the quartz – binder system needs to reach a stationary state. For resins with 5 wt.% addition of methyl acetate and cyclohexanone, this time amounted to 40 and 25 minutes, respectively. Resin mixtures with butyl acetate were able to reach the stationary state almost immediately.

The driving force for the moving liquid is the force of interfacial effects  $F_A$  (the force of adhesion) balanced

by the force of surface tension  $\gamma_{LG}$ . The time taken by the system to reach a stationary state is a resultant of both forces (i.e. of the forces of adhesion and cohesion). The factors that reduce binder viscosity, e.g. an addition of diluent, force an increase in the energy of interfacial effects  $\Delta G_S^*$  (adhesion), on one hand, while – on the other – they reduce the energy of intermolecular effects  $\Delta G_V^*$  (cohesion). An outcome of the action of both these forces is the recorded drop in contact angle values. As soon as the system reaches a stationary state, i.e. when the forces of adhesion  $F_A$  are balanced by the forces of surface tension  $\gamma_{LG}$ , the movement of the liquid stops, and the measure of wettability in a stationary system is now the equilibrium contact angle  $\theta_r$ .

The effect of binder viscosity on changes in the contact angle in a non-stationary state and on the value of

parameters  $\theta_r, \tau_r$  is consistent with theoretical considerations put forward by T. D. Blake et al. [5, 6].

Changes in the contact angle value over time  $\tau$  are best expressed by the following general equation:

$$\ln [\cos \theta_r - \cos (\tau)] = -a\tau^{0,5} - \ln b \quad (1)$$

where  $a$  and  $b$  are constants related with the physico-chemical parameters of binder.

The constant  $a$  is related with surface tension ( $\gamma_{LG}$ ), while constant  $b$  is related with the viscosity of binder ( $\eta$ ) [9].

At a constant temperature of 10°C, for EPIDIAN 5 resin and its mixtures with 20 wt.% solvent addition, the relationship (1) is described by equations (2-5):

EPIDIAN 5

$$\ln [\cos 38 - \cos (\tau)] = -0,48\tau^{0,5} - 1,0455; R^2 = 0,9822 \quad (2)$$

EPIDIAN 5 with an addition of methyl acetate

$$\ln [\cos 34 - \cos (\tau)] = -0,317\tau^{0,5} - 2,0377; R^2 = 0,9915 \quad (3)$$

EPIDIAN 5 with an addition of butyl acetate

$$\ln [\cos 22 - \cos (\tau)] = -0,5542\tau^{0,5} - 2,8077; R^2 = 0,9937 \quad (4)$$

EPIDIAN 5 with an addition of cyclohexanone

$$\ln [\cos 30 - \cos (\tau)] = -0,7360\tau^{0,5} - 3,3085; R^2 = 0,9824 \quad (5)$$

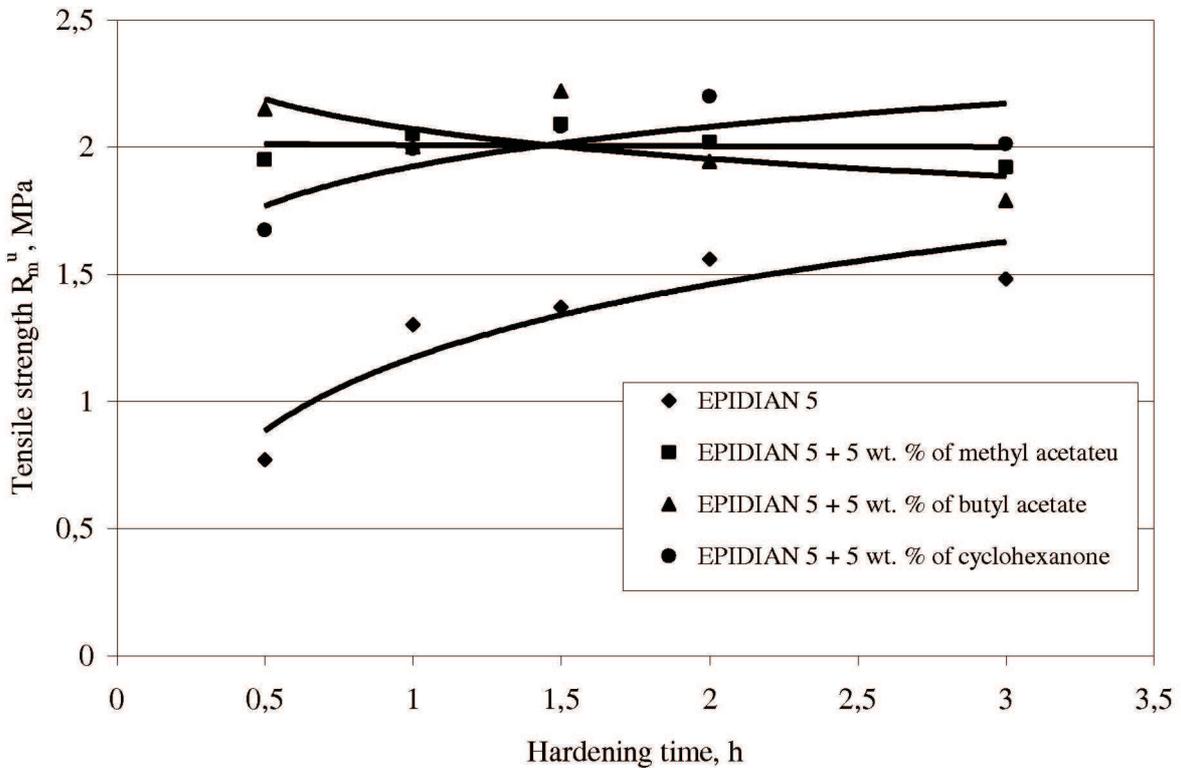


Fig. 2. Effect of hardening time on the tensile strength  $R_m''$  of sand with an addition of binder: EPIDIAN 5 resin; EPIDIAN 5 + 5 wt.% methyl acetate, EPIDIAN 5 + 5 wt.% butyl acetate, EPIDIAN 5 + 5 wt.% cyclohexanone. Mixing conditions: 1) sand + binder 1,5 min, 2) sand + binder + hardener – 1,5 min, sand compacted by vibrations, hardening temperature – 100°C

The relations obtained between the physico-chemical parameters, i.e.  $\Delta\theta$ ,  $\theta_r$ ,  $\eta$ ,  $\gamma_{LG}$ , were verified on sand – binder systems actually used by foundries.

Figure 2 shows changes in the tensile strength  $R_m''$  of a sand mixture with epoxy resin binder hardened at 100°C with 10% addition of Z-1 hardener (calculated in respect of resin). Curve 1 is corresponding to the

strength of the sand containing resin without diluent, i.e. characterised by a viscosity of about 75,99 Pa·s (0,7 part by weight of resin/100 parts by weight of sand), while other curves show changes in the  $R_m''$  values of sands containing binder modified with 5 wt.% of diluent (Table 1).

TABLE 1

Comparison of the tensile strength  $R_m^u$  values obtained in sands hardened for 30 min at 100°C and of the  $\theta_0$  and  $\eta$  parameters of the currently used binders (at 20°C)

Tensile strength $R_m^u$ [MPa]	Binder composition [% wag.]	Contact angle $\theta$ of quartz wetted by binder [deg]	Binder viscosity $\eta$ [Pa.s]
0,8	EPIDIAN 5-100 diluent – “0”	47	75,99
1,9	EPIDIAN 5-100 diluent – “0” (at 50°C)	32 (at 50°C)	0,78 (at 50°C)
1,9	EPIDIAN 5-95 methyl acetate – 5	44	4,88
2,1	EPIDIAN 5-70 methyl acetate – 30	39	0,028
1,9	EPIDIAN 5-95 ethyl acetate – 5	44	6,20
2,1	EPIDIAN 5-70 ethyl acetate – 30	33	0,034
2,1	EPIDIAN 5-95 butyl acetate – 5	39	6,05
2,3	EPIDIAN 5-70 butyl acetate – 30	20	0,055
1,7	EPIDIAN 5-95 cyclohexanone – 5	41	12,78
0,79	EPIDIAN 5-70 cyclohexanone – 30	27	0,176

Figure 2 shows that the tensile strength  $R_m^u$  of sands containing diluent-modified binder (curves 2-4) is higher compared with the tensile strength  $R_m^u$  of sands with non-modified resin (curve 1).

While the tensile strength  $R_m^u$  of sands with non-modified resin was growing slowly, reaching its maximum after about 2 h hardening (about 1,5 MPa), the sand with an addition of modified binder was able to reach its constant and maximum strength level after about 0,5 h hardening (Table 1).

### 3. Summary

The sand strength can be improved by modification of the physico-chemical properties of binder, its viscosity and wettability in particular.

The ultimate sand strength depends on numerous physico-chemical effects that occur during sand preparation and hardening and often are of a coinciding and overlapping nature.

The effects that take place during sand preparation result in the formation of bonding bridges, the geometry of which depends on the wetting dynamics and binder viscosity.

### 4. Conclusions

1. The wettability investigations carried out on a quartz – binder system (for  $FSE = 62,7 \text{ mJ/m}^2 = \text{const.}$ ,  $t = \text{const.}$ ) enabled determination of a formal relationship that is said to exist between the wetting dynamics ( $\Delta\theta$ ) and binder viscosity ( $\eta$ ):

$$\ln [\cos \theta_r - \cos (\tau)] = a\tau^{0.5} - \ln b$$

2. Low viscosity of binder resulting in high wetting dynamics favours the probability of the formation of bonding bridges of a beneficial geometrical structure, which will confer high strength to the sand.
3. It has been observed that the quartz wetting dynamics is favourably affected by the chemical structure of the added diluent. The analysis of the wetting process has indicated a favourable effect of the diluents of a chain structure.

### REFERENCES

- [1] E. Zi ó ł k o w s k i, R. W r o n a, K. S m y k s y, Some Aspects of Monitoring of Foundry Moulding Sands Preparation Process. Archives of Metallurgy and Materials **54**, 2, 399-411 (2009).
- [2] B. H u t e r a, J.L. L e w a n d o w s k i, K. S m y k s y, Wybrane aspekty teoretyczne wytrzymałości mas oraz

znaczenie niektórych parametrów osnowy i żywicy dla tej właściwości. Materiały XIII Konferencji Sprawozdawczej PAN pt. "Polska metalurgia w latach 1998-2002", s. 141-146, Krynica (2002).

- [3] B. H u t e r a, The Effect of Dynamic Wetting in a Sand – Binder System on the Sand Mould Strength. Archives of Metallurgy and Materials **54**, 2, 413-419 (2009).
- [4] B. G r a b o w s k a, M. H o l t z e r, Structural Examination of the Cross-Linking Reaction Mechanism of Polyacrylate Binding Agents. Archives of Metallurgy and Materials **54**, 2, 427-437 (2009).
- [5] T.P. B l a k e, Y.P. S h i k h m u r z a e v, Dynamic Wetting by Liquids of Different Viscosity. Journal of Colloid and Interface Science **253**, 196-202 (2002).
- [6] T.P. B l a k e, J. D e C o n i n c k, The influence of solid – liquid interactions on dynamic wetting. Advances in Colloid and Interface Science **96**, 21-36 (2002).
- [7] B. H u t e r a, Oddziaływania międzyfazowe w układzie: kwarc – spoiwo epoksydowe. Archiwum Technologii Maszyn i Automatykacji **28**, 3, 49-56 (2008).
- [8] B. H u t e r a, K. S m y k s y, J.L. L e w a n d o w s k i, D. D r o ż y Ń s k i, Wybrane aspekty oznaczania zwilżalności osnowy przez materiały wiążące stosowane w masach formierskich. Archiwum Technologii Maszyn i Automatykacji, **23**, 1, 63-70 (2003).
- [9] B. H u t e r a, Znaczenie rozcieńczalnika w spoiwie dla przebiegu zjawisk powierzchniowych w układzie: osnowa piaskowa – materiał wiążący. Wyd. Naukowe "Akapit", Kraków 2008 (ISBN 978-83-60958-13-1).
- [10] B. H u t e r a, Wpływ wybranych czynników na lepkość żywicy epoksydowej stosowanej jako spoiwo mas formierskich. Archiwum Technologii Maszyn i Automatykacji **23**, 1, 53-61 (2003).