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## APPLICATION OF FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR) TO INVESTIGATION OF MOULDING SANDS WITH FURAN RESINS HARDENING PROCESS

### ZASTOSOWANIE FOURIEROWSKIEJ SPEKTROMETRII W PODCZERWIENI (FTIR) DO BADANIA PROCESU UTWARDZANIA MAS Z ŻYWICAMI FURANOWYMI

There were investigated some initial structural transformations which take place in urea-furfuryl binding systems. They were investigated by FTIR spectrometry. There were also used two different techniques: transmission and diffuse reflection (DRS). The spectra were recorded within a range of 400–4000  $\text{cm}^{-1}$ .

The subjects of studies were two modified urea-furan resins (Kaltharz F700 and Kaltharz U404U) and the hardening process with two activators.

Changes in FTIR spectra during hardening of the resins were recorded after the time of 1, 2, 4, 8 and 24 hours. In comparison there were also examined mechanical properties (tensile strength and bending strength) of sands prepared with these resins.

Changes in the spectra of both resins with different activators were visible in the same range of 1400–1700  $\text{cm}^{-1}$  in about 2 hours since the moment of making the sand; then the number of the bands and their intensity were decreasing.

From the conducted tensile and bending tests of the sand it follows that the highest increase of these parameters takes place within the time of up to 2 hours; then the strength increases but only slightly. As it follows from the preliminary studies, FTIR spectroscopy, and DRS technique – in particular, can be helpful in assessment of the hardening degree of moulding sands with organic binders and in getting familiar with the mechanism of the hardening process of these binders. There are also needed further investigations, especially to identify all the peaks in obtained spectrums.

Przeprowadzono wstępne badania przemian strukturalnych zachodzących podczas procesu wiązania żywic mocznikowo-furanowych. Badania prowadzono stosując fourierowską spektrometrię w podczerwieni. Zastosowano dwie techniki pomiarowe: transmisyjną oraz technikę rozproszonego odbicia (DRS).

Widma były rejestrowane w zakresie 400–4000  $\text{cm}^{-1}$ . Przedmiotem badań były dwie modyfikowane żywice mocznikowo-furanowe (Kaltharz F700 i Kaltharz U404U). Widma FTIR podczas procesu utwardzania żywic były rejestrowane po czasie 1, 2, 4, 8 i 24 godzin. Równocześnie w tym samym czasie prowadzono badania właściwości wytrzymałościowych (wytrzymałość na roz-

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ciąganie i zginanie) mas z tymi żywicami przy dodatku dwóch różnych aktywatorów. Zmiany w widmach dla mas z obydwoma żywicami i różnymi aktywatorami były widoczne po ok. 2 godzinach od sporządzenia w tym samym zakresie  $1400\text{--}1700\text{ cm}^{-1}$ ; później intensywność pasm i ich liczba maleje.

Z przeprowadzonych testów wytrzymałościowych mas na rozciąganie i zginanie wynika, że największy wzrost tych parametrów ma miejsce również w okresie do 2 godzin, a następnie wytrzymałość wzrasta już nieznacznie.

Jak wynika z powyższych wstępnych badań metoda spektroskopii FTIR, a szczególnie technika DRS mogą być pomocne przy ocenie stopnia utwardzenia mas formierskich ze spoiwami organicznymi oraz w poznawaniu mechanizmu procesu utwardzania tych spoiw. Potrzebne są jednak dalsze badania, mające na celu identyfikację wszystkich pasm w uzyskanych widmach.

## 1. Introduction

Rapid development in the field of organic binders for moulding and core sands compels those who conduct research to use the most modern methods while investigating the binding mechanism of these binders. Moulding sand is composed of a base granular material (in most cases this is the silica sand), a binder (e.g. resin), and a hardener. In view of both the technological properties as well as ecological requirements, foundries become more and more convinced to the use of binders based on furfuryl alcohol, hardened with acid catalysts.

In industry it is very important to quickly determine the technological properties (e.g. the tensile or bending strength) of the sand used in actual production. The main problem here is the sand hardening degree, which changes in time. The changing degree of hardening affects, on one hand, the technological properties of the sand while, on the other, it causes structural transformations in a binding system. Interrelating effectively these two phenomena should enable quick determination of the sand hardening ratio and more detailed knowledge of the binding mechanism acting in a particular type of binder.

Structural transformations, which take place in organic binding systems, were investigated by infra-red spectrometry (IR). Earlier even, Conley [1] and Hummel [2] used this method to describe the structure of phenol-formaldehyde and furfuryl-formaldehyde resins as well as furan compounds, while Janicka et al. [3] conducted research on urea furan and furfuryl resins. Rocznik et al. [4, 5] investigated the structure of phenol-formaldehyde-furfuryl resins. In all those works the structural examinations were made on infrared absorption spectra.

At that time, the measuring technique applied most commonly in the medium-range infrared studies was the transmission technique. Over past few years, the measuring technique developing most dynamically and applied most effectively in the examination of granular solid bodies within FTIR has been the Diffuse Reflection Spectroscopy (DRS) [6, 7, 8]. The spectrum of a sample is produced by an optical system of appropriate configuration, collecting the radiation diffused on this sample. The technique was used long ago in measurements of UV/VIS spectra, but starting with the 80-ties it has been applied in infrared spectra recording. First attempts at an application of this technique in investigation of moulding sands with furan resin were described in [9].

## 2. Methods of research

The spectra were prepared by transmission technique in the case of liquid components (applying a thin film onto the surface of a KBr tablet), and by DRS in the case of solid bodies. The spectra were recorded within a range of 400-4000  $\text{cm}^{-1}$  using a Digilab Excalibur FTS 3000Mx spectrometer equipped with a DTGS detector.

The subject of the studies was the process of hardening modified urea-furan resins (Kaltharz F700 and Kaltharz U404U made by Hüttenes-Albertus) using one of the two hardeners: p-toluenesulphonic acid (100T3) or benzenesulphonic acid (100T1) (Tab.). Changes in FTIR spectra during hardening of the resin were examined after the time of 1, 2, 4, 8 and 24 hours. In parallel, tests were conducted on the mechanical properties (tensile strength  $R_m$  and bending strength  $R_g$ ) of sands prepared with the examined resin.

TABLE  
Physicochemical parameters of resins

Parameter	Kaltharz U404U	Kaltharz F700
Density (20°C) [ $\text{g}/\text{cm}^3$ ]	1.145 – 1.155	1.175 – 1.195
Viscosity (20°C) [ $\text{mPa} \cdot \text{s}$ ]	10 – 20	40 – 80
Free formaldehyde [%]	0.15 – 0.20	0.15 – 0.25
Furfuryl alcohol [%]	75 ± 1	78 ± 1
N <sub>2</sub> [%]	0.8 – 1.2	1.1 ± 1

The mixtures based on standard 1K Szczakowa silica sand were prepared in a laboratory mixer of LM-2 type. The sand mixture composition was as follows: 100 parts by weight of sand, 1 part by weight of resin, 0.5 part by weight of hardener. The mechanical properties were tested on a LRu-1 apparatus.

## 3. Results of studies and discussion

The studies began with recording the spectra of the basic substrates, i.e. resins, hardeners, and sand (Fig. 1). The spectrums of Kaltharz F700 resin and Kaltharz U404U resin include bands of 600, 750, 800, 890, 920, 1012, 1148, 1500, 2872 and 2930  $\text{cm}^{-1}$ , typical of furfuryl alcohol. There are additionally the bands of free formaldehyde that is present in the mixture, and bands related with the resin modification process (urea-furan resin). These bands are present in the range of 1550-1700  $\text{cm}^{-1}$  and in the range of 1200-1500  $\text{cm}^{-1}$ .



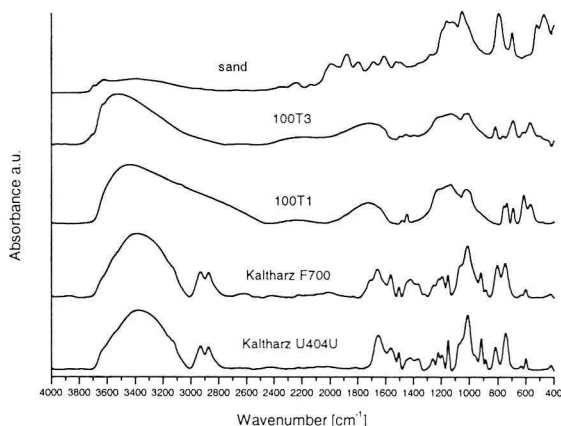


Fig. 1. Spectra of Kaltharz F700 resin, Kaltharz U404U resin, activators 100T1 and 100T3 (prepared by transmission technique) and spectrum of standard silica sand used as a base for moulding sands (prepared by DRS technique)

Then, the spectra of Kaltharz F700 resin with an addition of one of the hardeners (in non-hardened condition) were recorded (Fig. 2). The reactions, which have occurred between the resin and 100T1 or 100T3 activators, are on the obtained spectra manifested by disappearance of some bands and appearance of the other. The bands of the resin and hardener can be superimposed, thus creating the bands of increased intensity, e.g.  $810\text{ cm}^{-1}$  that can be made by applying bands coming from the furfuryl alcohol and benzenesulphonic acid. Due to the proceeding reactions, quite new bands, e.g.  $2913\text{ cm}^{-1}$  characteristic of C-H oscillations and  $1713\text{ cm}^{-1}$  that is characteristic band of C=O oscillations, can form as well.

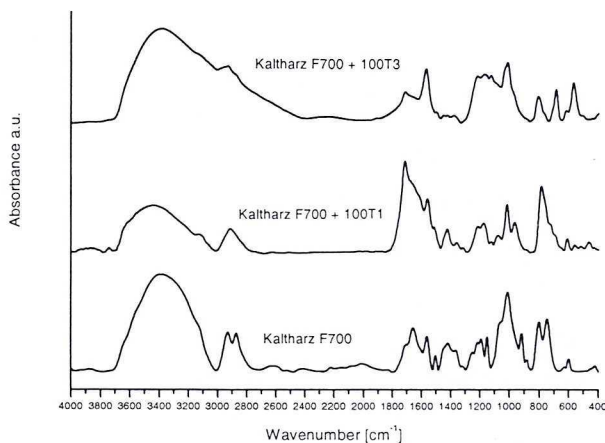


Fig. 2. Spectra of Kaltharz F700 resin and in combination with activators 100T3 and 100T1 (prepared by transmission technique)

Figure 3a shows the spectra of Kaltharz F700 obtained for a system containing 1 part by weight of resin and 0.5 part by weight of 100T3 hardener (p-toluenesulphonic

acid). Changes in the spectrum appeared in 2 hour after the binder components had been mixed, and they were appearing until hardening was completed. The changes in the spectra were most apparent within the range of  $1400\text{-}1700\text{ cm}^{-1}$ . In all cases there are shown the most important spectra: initial spectrum and the spectrum of arrangement after 24 hours. The band of  $1570\text{ cm}^{-1}$  is decreased after 24 hours. There are active bands coming from the tensile oscillations of non-saturated  $\text{C}=\text{C}$  systems in this region. Figure 3b shows changing the strength of sand during the time of 24 hours. Also in this case the greatest increase in the sand strength was noted during the first 2 hours, especially as regards the bending strength ( $R_g$ ).

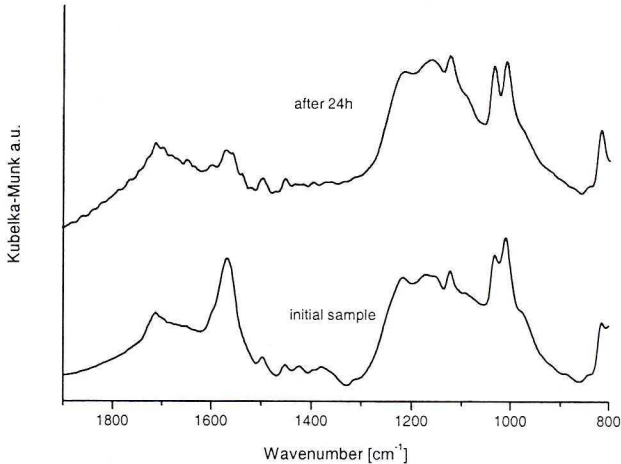


Fig. 3a. Changing the spectra during the time for the hardening process of arrangement: Kaltharz F700 resin – activator 100T3 in the weight ratio of 1:0,5 (prepared by DRS technique)

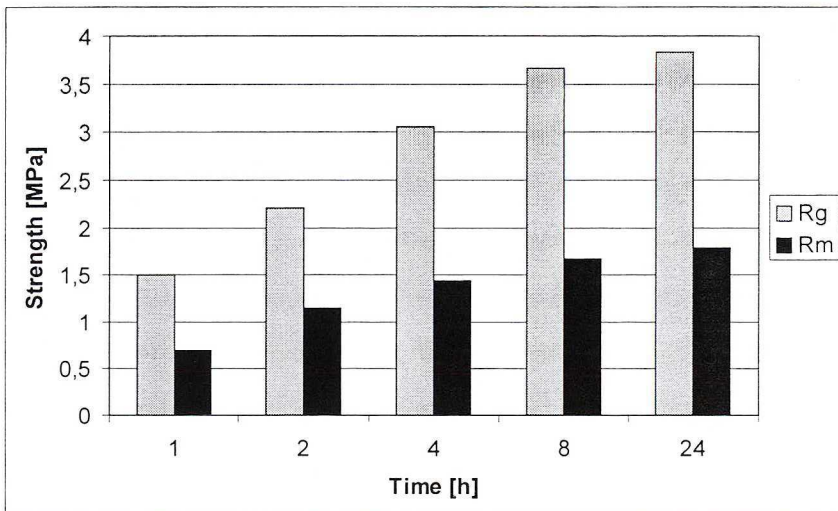


Fig. 3b. Changing the strength of sand (made from Kaltharz F700 resin and activator 100T3, based on the silica sand, in the weight ratio of 1:0,5:100) during the time ( $R_g$  – bending strength,  $R_m$  – tensile strength)

The same tests were made for the resin Kaltharz F700 with 100T1 activator (benzenesulphonic acid). The results are shown in Figures 4a (FTIR spectra) and 4b (changes in the sand mechanical properties). In this case changes in the spectra are less visible. There is only change in the intensities of bands: 1713 and 1670  $\text{cm}^{-1}$ .

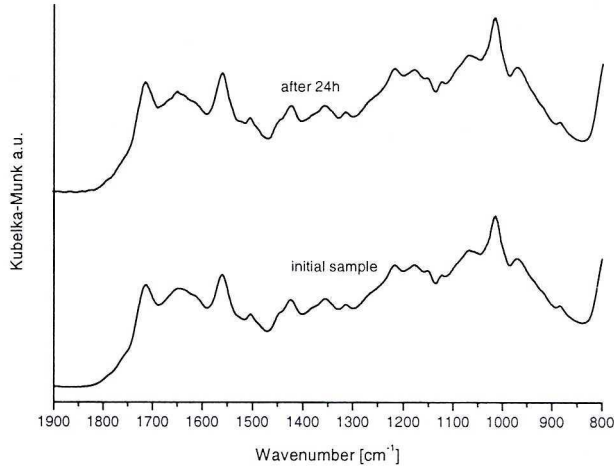


Fig. 4a. Changing the spectra during the time for the hardening process of arrangement: Kaltharz F700 resin – activator 100T1 in the weight ratio of 1:0,5 (prepared by DRS technique)

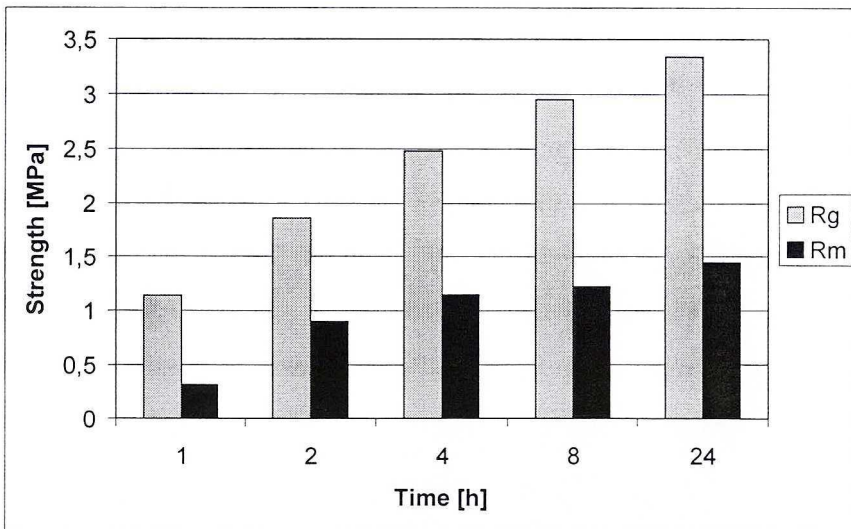


Fig. 4b. Changing the strength of sand (made from Kaltharz F700 resin and activator 100T1, based on the silica sand, in the weight ratio of 1:0,5:100) during the time ( $R_g$  – bending strength,  $R_m$  – tensile strength)

Then, the spectra of Kaltharz U404U resin with an addition of one of the hardeners (in non-hardened condition) were recorded (Fig. 5). For this resin we can observe no bands at 1713  $\text{cm}^{-1}$  as it was for Kaltharz F700.

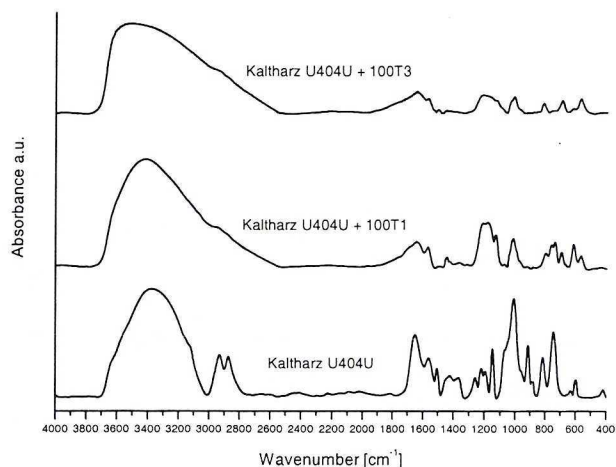


Fig. 5. Spectra of Kaltharz U404U resin and in combination with activators 100T3 and 100T1 (prepared by transmission technique)

The test results for the resin Kaltharz U404U with activator 100T1 are shown in figures 6a and 6b, and for the resin Kaltharz U404U with activator 100T3 are shown in figures 7a and 7b.

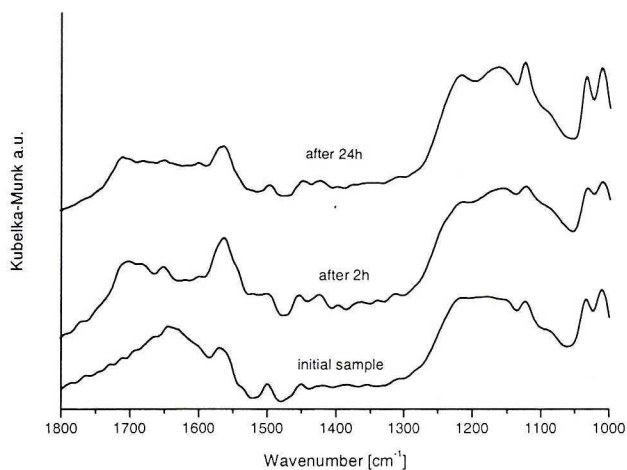


Fig. 6a. Changing the spectra during the time for the hardening process of arrangement: Kaltharz U404U resin – activator 100T3 in the weight ratio of 1:0,5 (prepared by DRS technique)

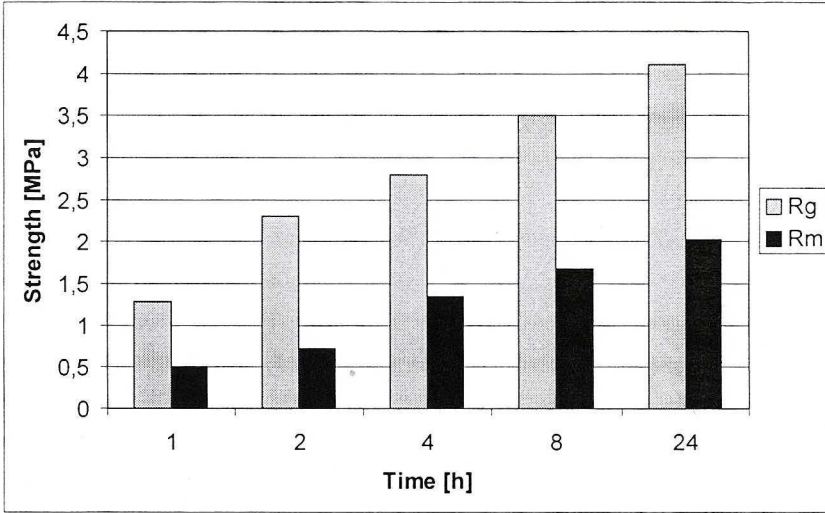


Fig. 6b. Changing the strength of sand (made from Kaltharz U404U resin and activator 100T3, based on the silica sand, in the weight ratio of 1:0,5:100) during the time ( $R_g$  – bending strength,  $R_m$  – tensile strength)

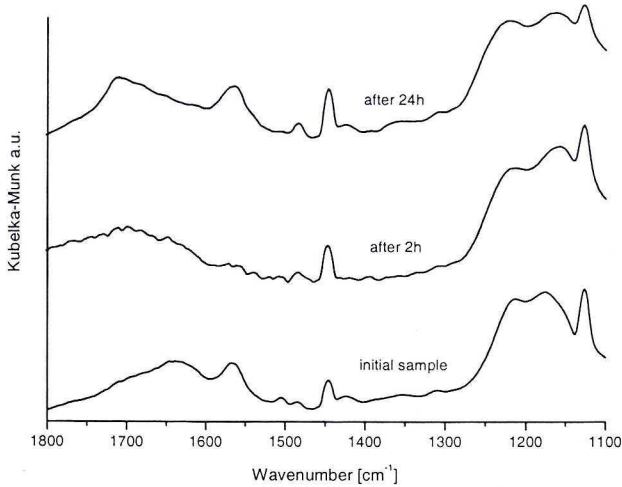


Fig. 7a. Changing the spectra during the time for the hardening process of arrangement: Kaltharz U404U resin – activator 100T1 in the weight ratio of 1:0,5 (prepared by DRS technique)



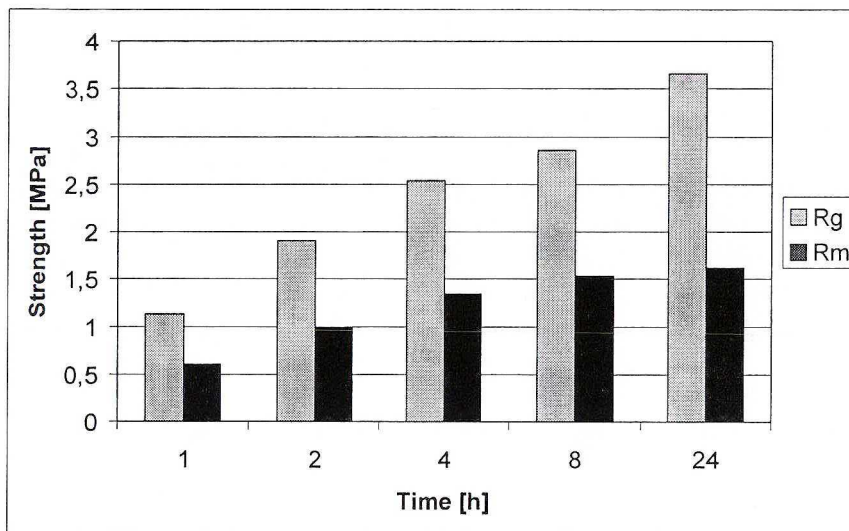


Fig. 7b. Changing the strength of sand (made from Kaltharz U404U resin and activator 100T1, based on the silica sand, in the weight ratio of 1:0,5:100) during the time ( $R_g$  – bending strength,  $R_m$  – tensile strength)

As we can observe at Fig. 6a the band of  $1713\text{ cm}^{-1}$  that wasn't visible after mixing the resin with activator is present after 24 hours, but the band of  $1640\text{ cm}^{-1}$  is disappeared. This effect appears in 2 hours after mixing the ingredients and is present still after 24 hours. The same effects are visible for the resin Kaltharz U404U mixed with activator 100T3 (Fig. 7a). The spectra of the examined binding systems were characterised by a complex structure which was due to superpositioning of absorption bands of different compounds, groups and bonds developed during hardening.

The band of  $1713\text{ cm}^{-1}$  is present in the spectrum of resin alone as well as in the spectra obtained after the binder has been hardened. It is typical of the tensile oscillations induced by the  $C=O$  group. The presence of this band can also prove a transformation of furfuryl alcohol into  $\gamma$ -diketone which is in equilibrium with the diene form or levulin acid [4].

#### 4. Summing up

The first changes in the spectra of the examined binding system were visible in about 2 hours since the moment of making the sand within a range of  $1400\text{--}1700\text{ cm}^{-1}$ , until the moment when the hardening was completed (after 24 hours) (Figs. 3a, 4a, 6a, 7a).

From the conducted tensile and bending tests of the sand it follows that the highest increase\* of these parameters takes place within the time of up to 2 hours; then the strength increases but only slightly.

In spite of the fact that for two resins hardening two different activators were used, i.e. p-toluenesulphonic acid and benzenesulphonic acid, and that the obtained spectra of binders in non-hardened state differed from each other (Fig. 2, 5), on hardening, changes in

the spectra were visible for both systems within the same range of 1400-1700  $\text{cm}^{-1}$  (Fig. 3a, 4a, 6a, 7a). Within this range, most active were, first of all, bands coming from the tensile oscillations of non-saturated C=C systems in this region. Besides as it is shown in Figures 6a and 7a the band of 1640  $\text{cm}^{-1}$  is fading while the new band of 1713  $\text{cm}^{-1}$  (C=O) is appearing.

As it follows from the previous studies, FTIR spectroscopy, and DRS technique - in particular, can be helpful in assessment of the hardening degree of moulding sands with organic binders and in getting familiar with the mechanism of the hardening process of these binders [8].

There are also needed further investigations, especially to identify all the bands in obtained spectra.

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