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THE IMPACT OF TEMPERATURE ON FURAN RESIN AND BINDER STRUCTURE

1. INTRODUCTION

Furfuryl resins as well as those modified with furfuryl alcohol and used at foundries contain between 45% and 95% of furfuryl alcohol [1]. The addition of furfuryl alcohol accelerates resin curing, increases its setting ability, thus makes it possible to reduce the amount of binder added to the sands [2].

Furan resins can be cured as a result of their heating or the addition of a chemical agent. In the case of loose self-curing sands, the following acids are used as curing agents: orthophosphoric (V), sulfonic or blends of sulphuric (VI), and p-toluenesulfonic acids.

Sands based on furan resins are becoming more and more important in iron alloy casting [1]. The advantages of these sands include the ability to make moulds and cores of complicated shapes, highly precise in their dimensions, setting in ambient temperatures, and a small addition of binder relative to the matrix.

The disadvantage of furan sands comes from the noxiousness of gases emitted when liquid metal is poured and of waste sand, in particular of post-reclamation dust. Producers looking for more environmentally-friendly solutions are focusing their activities on two subjects [1]:

- reducing the content of noxious components (furfuryl alcohol, formaldehyde and phenol);
- reducing the sulphur content of curing agents.

The European Union requires reducing the proportion of furfuryl alcohol to 30%, it is suspected to be harmful to the human organism (suspected cancerogenicity). The practical consequence is that currently there are no resins on the market that meet these requirements [1, 3].

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Another weakness of these sands is their relatively high cost, while the mechanical reclamation used in practice is of poor effectiveness, giving a reason to use more expensive reclamation methods to get satisfactory results, i.e. high quality reclaimed material (e.g. the thermal method) [4].

As a result of exposure to high temperature, a series of structural changes occurs in binders used to prepare moulding and core sands. These may consist in the change to the character, the disappearance of, or the formation of new chemical bonds. These changes have a significant impact on the mechanical and technological properties of sands, but also on the environmental noxiousness of sands or the ability to reclaim the sand. Infrared spectroscopy offers a perfect tool for observing structural changes occurring in foundry binders. This article presents the results of analyses of changes taking place in the structure of selected furan resins and binders based on them, manufactured by various producers.

For many years, the Department of Casting Process Engineering has researched the use of infrared spectroscopy to test materials used in casting [5–10].

2. MATERIALS AND METHODS

2.1. Research materials

This research covered two furan resins sold by two different producers. They were used to make a binder by adding the curing agent specified by the producer.

2.2. Research methods

Structural analyses were carried out using an Excalibur FTIR spectrometer with a standard DTGS detector and the resolving power of 4 cm^{-1} . The spectra of samples tested at room temperature were produced using the transmission technique (KBr pellet). Changes occurring as a result of the temperature were analysed both in resins and binders, using an ATR temperature module able to heat up to $200\text{ }^{\circ}\text{C}$, fitted with a temperature controller. Samples were continuously heated and their infrared spectra were recorded at temperatures of $25\text{ }^{\circ}\text{C}$, $50\text{ }^{\circ}\text{C}$, $75\text{ }^{\circ}\text{C}$, $100\text{ }^{\circ}\text{C}$, $125\text{ }^{\circ}\text{C}$, $150\text{ }^{\circ}\text{C}$, $175\text{ }^{\circ}\text{C}$ and $200\text{ }^{\circ}\text{C}$.

3. RESEARCH RESULTS

Figure 1 shows the FTIR spectra of a furan resin (1) and a furan binder (1) obtained by the transmission technique at ambient temperature ($20\text{ }^{\circ}\text{C}$).

Figure 2 shows the FTIR spectra of the second furan resin (2) and a furan binder (2) obtained by the transmission technique at ambient temperature ($20\text{ }^{\circ}\text{C}$). Both furan resins have the same structure, which proves that their producers use the same components to produce them.

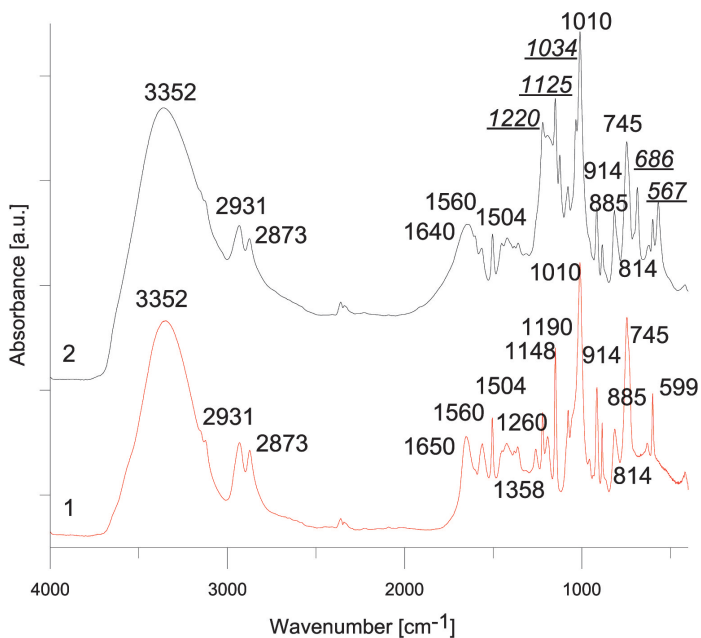


Fig. 1. Transmission spectra in the full range of wave numbers obtained by the transmission technique at the temperature of 20°C: 1 – furan resin (1), 2 – furan binder (1)

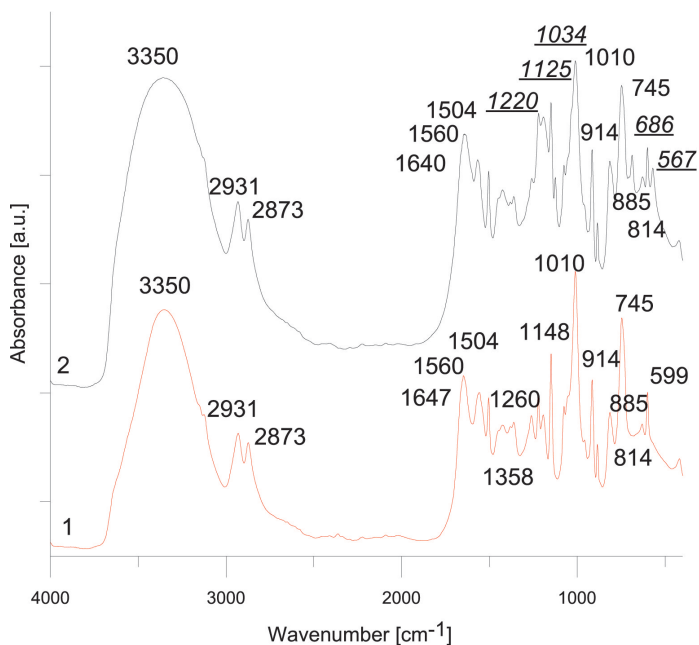


Fig. 2. Transmission spectra in the full range of wave numbers obtained by the transmission technique at the temperature of 20°C: 1 – furan resin (2), 2 – furan binder (2)

Bands typical for furfuryll alcohol can be observed in the spectrum of the tested resin and binder. The following vibrations can be distinguished:

- 3352 cm^{-1} (hydroxyl groups –OH) [11, 13],
- 2931, 2873 cm^{-1} (C-H aliphatic bonds) [12, 13, 14],
- 1504 cm^{-1} C = C stretching vibration of the furan rings [11, 15],
- 1190, 914, 885, 814 cm^{-1} C-H deforming vibrations in the furan ring [11],
- 599 cm^{-1} a deforming vibration of the entire furan ring [11].

Bands at wave numbers of 1560 cm^{-1} (C = C stretching in the furan ring [15], 1358 cm^{-1} (vibrations of the ring [13] or of the OH phenol deforming bond along the plane [17]), 1260 cm^{-1} (C-O stretching vibration [11, 16]), 745 cm^{-1} (the skeleton vibration [11]) also come from bonds found in furfuryl alcohol. The presence of a stretching vibration of the carbonyl bond (C = O) at the wave number of 1730 cm^{-1} can also be identified. The nature of the broad 1600–1700 cm^{-1} band shows that it is more complex, and this is the range in which deformation vibrations of –OH groups [18], C = C vibrations in the aromatic ring [13] and vibrations of the C = O carbonyl [18] occur.

The FTIR spectra of furan binders show that the curing agent influences the development of the foundry binder structure. One indicator of changes occurring during the setting process is the shift of the 1640 cm^{-1} band towards lower wave numbers. Adding the curing agent to the binder causes additional bands to appear at wave numbers of 1125, 1034, 686, 567 cm^{-1} .

Figures 3 and 4 show the spectra of tested furan resins subjected to the action of temperature ranging from 20 °C to 200 °C.

The FTIR spectra of furan resin obtained using the ATR high-temperature module differ from spectra obtained by the transmission technique in the location of certain bands (Fig. 1 and 2). These variations are due to the imperfections of the ATR technique, which does not produce a high quality spectrum in certain ranges of wave numbers.

At 50 °C, the spectra of both furan resins show no structural changes compared to the spectrum of the sample at room temperature. The most significant differences appear at 75 °C, where, as the temperature increases, the band corresponding to the deformation vibrations of the OH groups at 1640 cm^{-1} shifts towards higher wave numbers, and at 125 °C its intensity rises. In addition, the intensity of the 1504 cm^{-1} band (the C = C stretching vibration in the furan ring [11]) decreases compared to 1560 cm^{-1} . Simultaneously, the 1560 cm^{-1} band is shifted to 1540 cm^{-1} . Increasing temperature also causes the 808 cm^{-1} band (at 25 °C) to move to 738 cm^{-1} (at 150 °C). A similar behaviour was noted for the 1147 cm^{-1} and 915 cm^{-1} bands (the C-H deformation vibration [11]). At 175 °C, the vibrations of the furan ring clearly weaken (738 cm^{-1}) [15].

Figures 3 and 4 present the FTIR spectra of the produced furan binders heated within the 20 °C–150 °C range. Above this temperature, the binder hardens, making it impossible to obtain a spectrum using the ATR module.

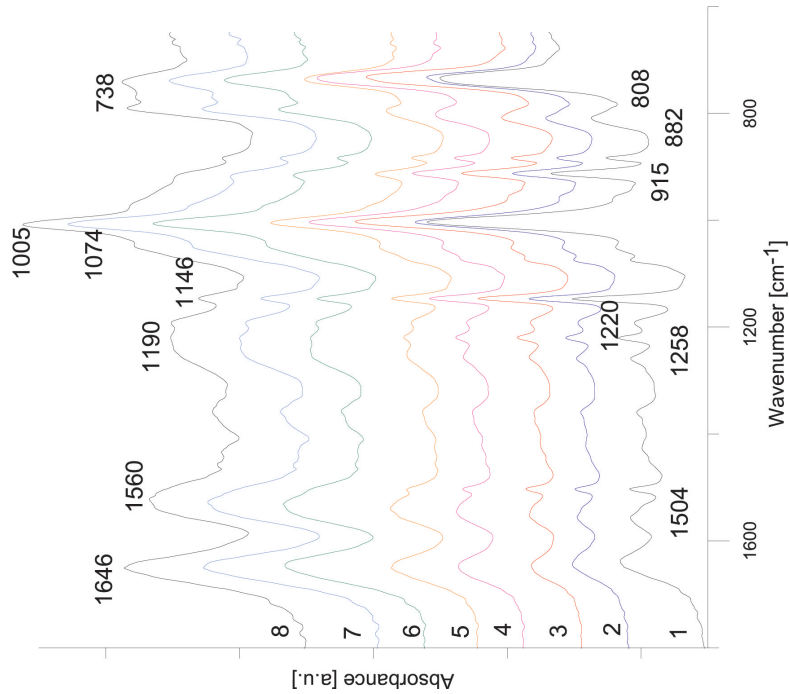


Fig. 3. FTIR spectra for the furan resin (1) obtained by the ATR technique at the temperatures of: 1 – 20 °C, 2 – 50 °C, 3 – 75 °C, 4 – 100 °C, 5 – 125 °C, 6 – 150 °C, 7 – 175 °C, 8 – 200 °C

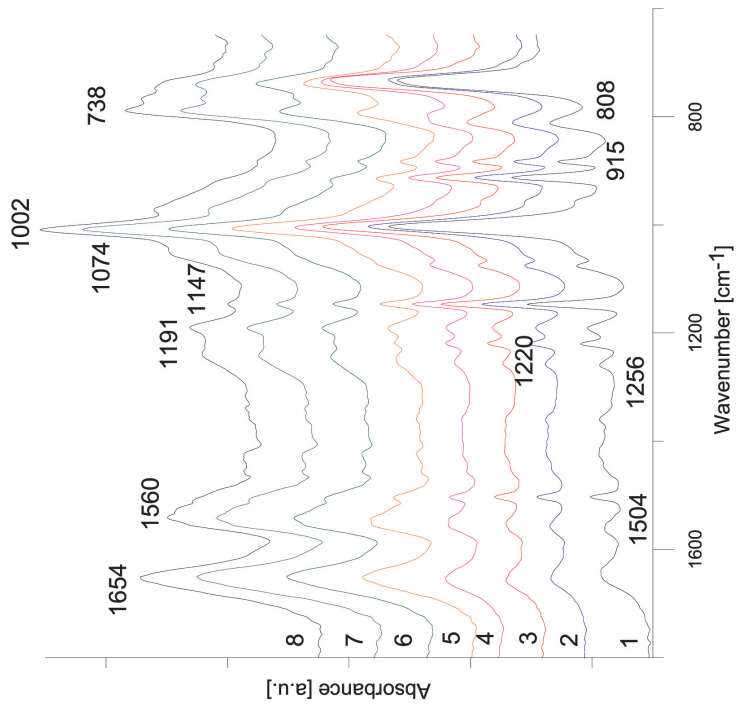


Fig. 4. FTIR spectra for the furan resin (2) obtained by the ATR technique at the temperatures of: 1 – 20 °C, 2 – 50 °C, 3 – 75 °C, 4 – 100 °C, 5 – 125 °C, 6 – 150 °C, 7 – 175 °C, 8 – 200 °C

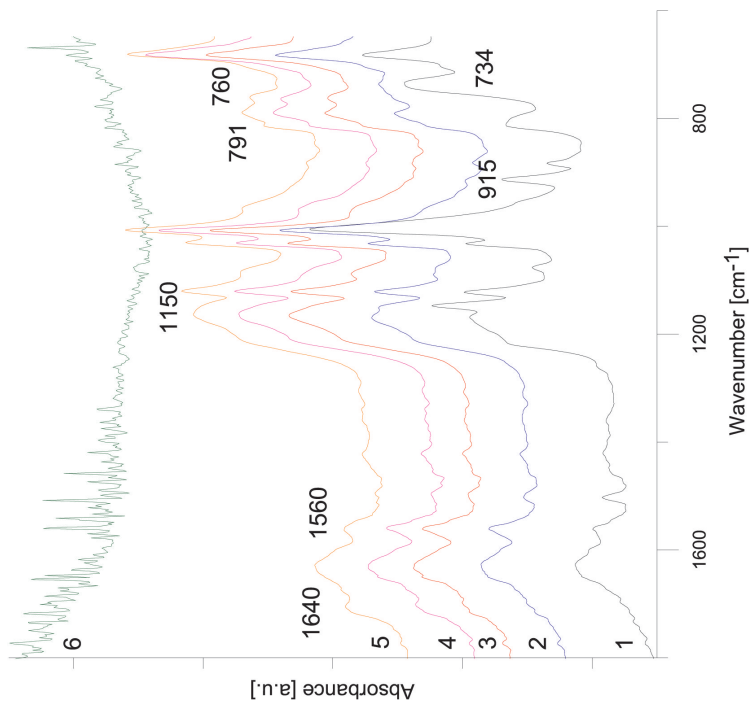


Fig. 5. FTIR spectra of the furan binder (1) obtained by the ATR technique at the temperatures of: 1 – 20 °C, 2 – 50 °C, 3 – 75 °C, 4 – 100 °C, 5 – 125 °C, 6 – 150 °C

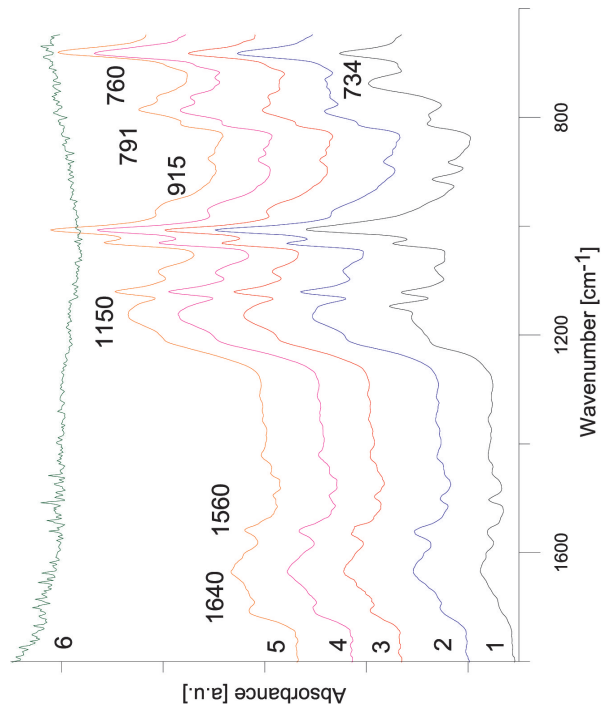


Fig. 6. FTIR spectra of the furan binder (2) obtained by the ATR technique at the temperatures of: 1 – 20 °C, 2 – 50 °C, 3 – 75 °C, 4 – 100 °C, 5 – 125 °C, 6 – 150 °C

The changes taking place in the studied binders observed in the infrared mainly concern the furan ring. Already at 50 °C, one can observe the increasing intensity of bands associated with the vibrations of the C-H bonds (e.g. 1560, 1150, 915 cm⁻¹). In the place of the band at the wave number of 734 cm⁻¹ (the skeleton vibration of the furan ring [15]), a new one appears at the wave number of 791 cm⁻¹ (the ring deformation vibration outside the plane [17]). The temperature going up further to 75 °C causes a band to be distinguished at the wave number of 760 cm⁻¹ (ring deformation [17]). Then, increasing the temperature still more (100 °C–125 °C) leads to a drop in the intensity of the 1560 cm⁻¹ band (C = C bonds in the furan ring [15]).

The ATR technique used in this research project can be applied to liquid materials. Figures 5 and 6 justify the claim that the binder hardened completely (transformed into the solid phase) at the temperature of 150 °C (spectrum 'f').

4. SUMMARY

Both analysed resins behave in the same way at higher temperatures. At the 20 °C–50 °C temperature range, it is mainly the intensity of bands associated with C-H bond vibrations that change. A further increase of the temperature causes the structure of the resin to be modified within the range corresponding to furan ring vibrations. The location and intensity of bands within the range in which OH group vibrations occur also change.

A very characteristic change in furan resin spectra is the gradual decrease in the intensity of the band characteristic for the C = C bond in the furan ring (1504 cm⁻¹), which starts at 125 °C. In the case of the binders, in turn, the addition of a curing agent causes bonds within this band to stabilise more.

The analysis of infrared spectra of the studied furan resins has shown that in the initial condition they are not structurally different. Also, their behaviour when heated is the same, which is due to the same components being used to produce them.

It should also be noted that the action of the temperature accelerates the curing of the binder. To observe structural changes at a higher temperatures, a different research method has to be applied.

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