

Structural Changes in the Furan Resins by UV Radiation and Atmospheric Air

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Abstract

In this paper, the results of research of structural changes that occur during in furan resins with different content of furfuryl alcohol by UV radiation and atmospheric air are presented. The research was carried out by transmission method (KBr pellets), using FTIR spectrometer Excalibur 3000 for the three samples of furan resins with different content of furfuryl alcohol. As a result of UV radiation and oxidizing atmosphere only the sample of the resin Kaltharz 8616 remained liquid. Two others (Kaltharz U 404 and Kaltharz 8117) were cured after 1 hour, and their chemical structure did not change with time.

Keywords: Furan resins, Furfuryl alcohol, Structural changes, Spectroscopy FTIR, Spectrum FTIR

1. Introduction

Moulding sands with furfuryl resins found wide applications in foundry iron casting industry. The addition of furfuryl alcohol accelerates resin curing, increases its setting ability and thus makes it possible to reduce the amount of binder added to sands [1].

Furan resins can be cured as a result of 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 [2].

The advantages of these sands include the ability to make complicated moulds and cores, 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.

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) [3].

European Union (EU Directive¹) requires reducing the proportion of furfuryl alcohol to 30%, it is suspected to be harmful to the human organism (suspected cancerogenicity) [2].

It happens that the resins during storage undergo a change of state from liquid to solid. Therefore, it is recommended that the resins were stored in places where there is no influence of solar radiation. As a result of exposure to UV radiation and oxidation atmosphere, a series of structural changes occurs in binders used to prepare moulding and core sands. These may cause a change of the chemical character, the disappearance of, or the formation of new chemical bonds. Infrared spectroscopy offers a perfect tool for observing structural changes occurring in foundry binders.

This article presents the results of analysis of changes taking place in the structure of selected furan resins with different furfuryl alcohol content under the influence of UV radiation and oxidizing atmosphere.

¹ Regulation (EC) No. 1272/2008.

2. Materials, test stand and methodology of investigations

The research covered three furan resins with different content of furfuryl alcohol. 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).

Table 1 shows the chemical characteristics and properties of furan resins with varying content of furfuryl alcohol.

Table 1. Chemical characteristics and properties of Kaltharz furan resins [4, 5]

Property	The resin		
	U404	8117	8616
Furfuryl alcohol free	71,0 – 72,0	-	23,5 – 24,75
Associated furfuryl alcohol	74,0 – 76,0	-	66,0 – 68,0
Formaldehyd frei	0,03 – 0,06	0,1-0,2	0,15 – 0,20
Nitrogen	3,0-4,0	0,35-0,50	2,5-3,2
Density in 20°C	1,155-1,165	1,155 $\pm 0,165$	1,180 – 1,190
Viscosity in 20°C	15-25	20-30	40-70

3. Results and their discussion

Figure 1 shows the FTIR spectra of furan resins with varying content of furfuryl alcohol obtained by the transmission technique at ambient temperature (20°C).

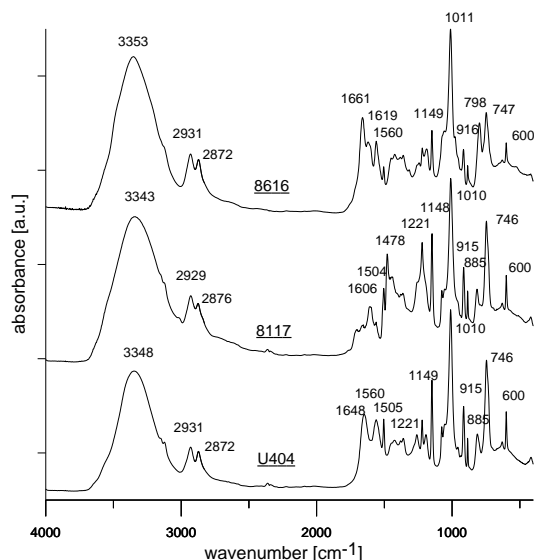


Fig. 1. FTIR spectra of furan resins with different furfuryl alcohol content.

All tested furan resins have similar structure. Bands typical for furfuryl alcohol can be observed in the spectrum of the resins. The following vibrations can be distinguished:

- a band at a wavenumber of about 3352 cm^{-1} is hydroxyl groups $-\text{OH}$ [6, 7],
- In the range $2931 - 2872\text{ cm}^{-1}$ there is C-H aliphatic bonds [7, 8, 9],
- at 1648 cm^{-1} is C=C vibration or OH group,
- 1560 cm^{-1} corresponding to C=C stretching in the furan ring [10],
- 1504 or 1505 cm^{-1} are C=C stretching vibration of the furan rings [6, 10],
- $1193, 915, 885\text{ cm}^{-1}$ from C-H deforming vibrations in the furan ring [6],
- 745 cm^{-1} a skeleton vibration [6],
- 600 cm^{-1} a deforming vibration of the entire furan ring [6].

In the range $1600-1700\text{ cm}^{-1}$ also deformation vibrations of $-\text{OH}$ groups [11], C=C vibrations in the aromatic ring [7] and vibrations of the C=O carbonyl [11] occur. It can also be seen band 1221 cm^{-1} of furan ring C-H [6].

Figure 2 shows the structural changes in the resin Kaltharz U404 after 1, 3 and 24 h of exposure to air and UV radiation impact.

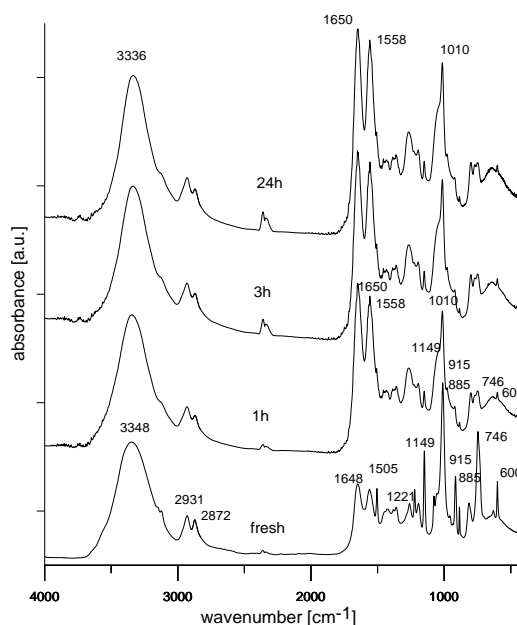


Fig. 2. FTIR spectra of furan resin Kaltharz U404 of fresh and after 1, 3 and 24 h

Already after one hour the intensity of the bands at wavenumbers $1505, 1221, 1149, 915, 885, 746$ and 600 cm^{-1} weakened. All of these bands correspond to bands of vibrations derived from furfuryl alcohol. The band at wavenumber 813 cm^{-1} is weakened and shifted to 800 cm^{-1} . The band 1622 cm^{-1} may be associated with vibration information while the OH groups of disappears band associated with stretching OH vibration is shifted toward lower wavenumbers. These changes may be due to the

evaporation of the alcohol in the resin. The process of complete curing of the resin occurs after 1 hour. After this time further structural changes were not observed.

On the basis of the FTIR spectra it can be concluded that the contact of the sample with external factors (UV radiation and atmospheric air) causes reconstruction of the structure of the resin. The result is dominated by the vibration of bonds in the aromatic ring (C = C) or skeletal vibration of the whole ring [7, 12]

Figure 2 shows the structural changes in the resin Kaltharz 8117 after 1, 3 and 24 h of exposure to air and UV radiation impact.

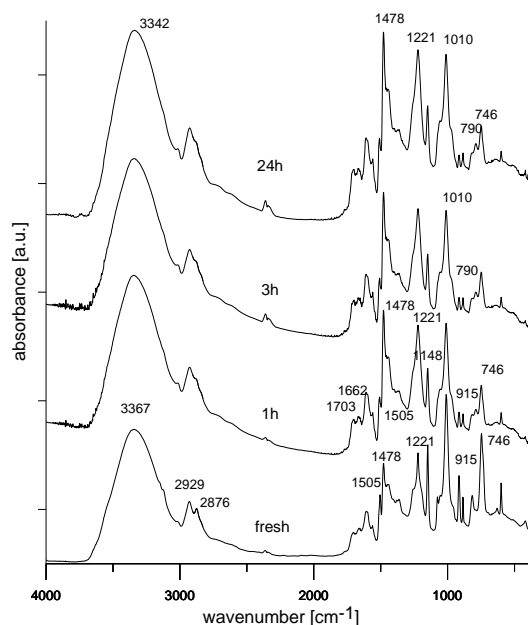


Fig. 3. FTIR spectra of furan resin Kaltharz 8117 of fresh and after 1, 3 and 24 h

The resin Kaltharz 8117 after 1 hour reduced the intensity of the bands 915, 885, 816, 746 and 600 cm^{-1} associated with the presence of furfuryl alcohol and there is a new peak at 790 cm^{-1} . OH band moves, which occurs in a fresh sample at a wavenumber 3367 cm^{-1} moves towards the 3342 cm^{-1} and strip 2876 cm^{-1} is weakened vibrations associated with the C-H bonds. As regards the $1800\text{-}1500\text{ cm}^{-1}$ band split up and creates 1700 and 1663 cm^{-1} . Followed by a clear change in the relationship between the amount of bands 1505 and 1478 cm^{-1} . The band 1478 cm^{-1} begins to grow, and decreases the intensity of the band in 1148 and 1010 cm^{-1} . There is also a weakening of the intensity of bands at 1505 cm^{-1} wave numbers.

It can be assumed that as a result of contact of the sample with external factors with the participation of the OH groups, has weakened the intensity of vibrations at wavenumbers 3342 and 1010 cm^{-1} band compared to 1148 cm^{-1} corresponding to vibrations of the aliphatic C-H [13].

Figure 3 shows the structural changes in the resin Kaltharz 8616 after 1, 3 and 24 h of exposure to air and UV radiation impact.

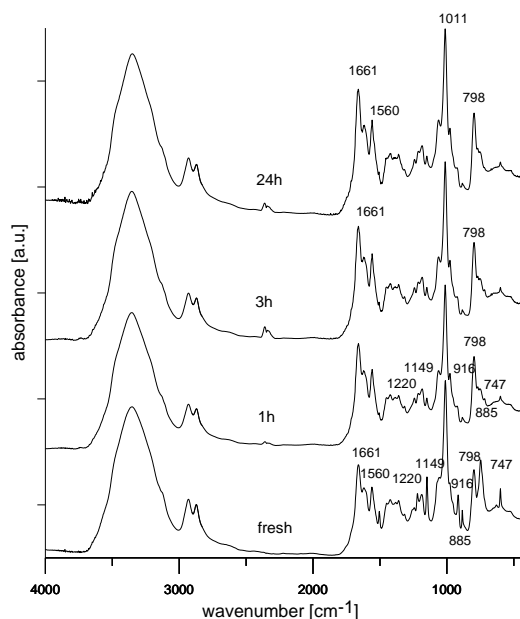


Fig. 4. FTIR spectra of furan resin Kaltharz 8616 of fresh and after 1, 3 and 24 h

The smallest structural changes under the influence of UV radiation and oxygen in the air are observed in the resin Kaltharz 8616. They consist mainly of the weakening of the intensity of the bands 1221 , 1149 , 916 , 885 , 748 , 600 cm^{-1} . Kaltharz 8616 resin with the lowest amount of free furfuryl alcohol was the only resin which remained fully cured under the conditions of testing, and remained liquid even after 24 hours. The remaining samples cured in approximately 1 hour.

4. Conclusions

Based on extensive investigations, you can draw the following conclusions can be made:

- As a result of UV radiation and oxidizing terms the largest changes were observed in the structure of the resin with the highest amount of furfuryl alcohol (Kaltharz U-404).
- As a result of the curing process of the resin Kaltharz U404 structural changes occurred, which were characterized by the predominance bands associated with the C = C vibration in an aromatic ring.
- Exposition of 8117 Kaltharz resin samples to external factors cause a marked increase in the intensity of the band associated with aliphatic CH vibrations while weakening the intensity of the bands corresponding to the vibrations of OH.
- The sample with the highest resistance to UV radiation and atmospheric air is the resin having the smallest quantity of furfuryl alcohol (Kaltharz 8616). It did not cure despite prolonged exposure to external factors. It can therefore be concluded that it should be easier to store and have a longer shelf life.

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