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FTIR method in studies of the resol-type phenol resin structure in the air atmosphere over certain time intervals

Metoda FTIR w badaniach zmian struktury żywicy fenolowej typu rezolowego zachodzących w atmosferze powietrza w zadanym przedziale czasowym

Abstract

This paper presents the results of structural-type studies of resol phenolic resin used for the preparation of molding and core sands exposed to air. The FTIR study was carried out using a transmittance technique. Recorded changes in the IR spectra of resin can indicate a progressive polycondensation process, the consequences of which being changes in the aromatic rings of methylene bridges (among others).

Keywords: phenolic resin, resol type resin, FTIR, structural studies, cross-linking

Streszczenie

W artykule przedstawiono wyniki badań strukturalnych żywicy fenolowej typu rezolowego stosowanej do sporządzania mas formierskich i rdzeniowych, poddanej działaniu powietrza atmosferycznego. Badania prowadzono metodą FTIR z zastosowaniem techniki transmisyjnej. Zarejestrowane zmiany w widmach IR żywicy mogą świadczyć o postępującym procesie polikondensacji, którego konsekwencją są m.in. zmiany w obrębie mostków metylenowych pierścienia aromatycznego.

Słowa kluczowe: żywica fenolowa, żywica typu rezolowego, FTIR, badania strukturalne, sieciowanie

1. Introduction

Phenolic resins are widely used in many industries. Their principal advantage is their relatively low cost and simple production process. In a hardened state, they have stability, as they are resistant to moisture, acids, lubricants, and elevated temperatures. They are

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offered for a variety of applications, such as structural adhesives for wood, laminates, friction materials, abrasive products as well as binders for the production of molds, impregnated paper, and fabric for filters motor binder, for printing inks, producing tires, and many others [1].

Phenolic resins are formed by a reaction of phenol (or substituted phenol) with formaldehyde. The base of phenol-formaldehyde resin is obtained by the polycondensation reaction of phenol with formaldehyde (methanal – HCHO). Depending on the pH level and environment in which the synthesis of resin is performed, products of different properties are obtained. If polycondensation is carried out in an acidic environment, the reaction products are novolaks.

Products of reactions carried out in an alkaline environment with an excess of formaldehyde are known as resoles [2, 3]. Figures 1 and 2 show structural diagrams of two types of phenolic resins.

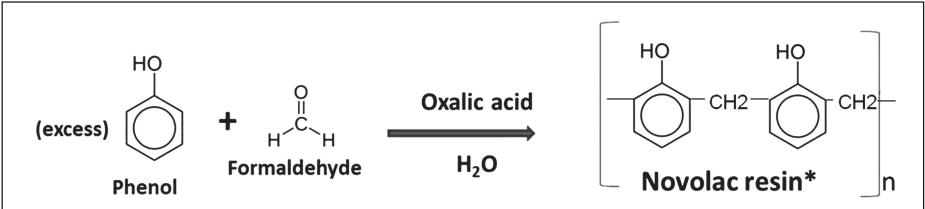


Fig. 1. Scheme of the formation of the novolak-type phenolic resin [1]

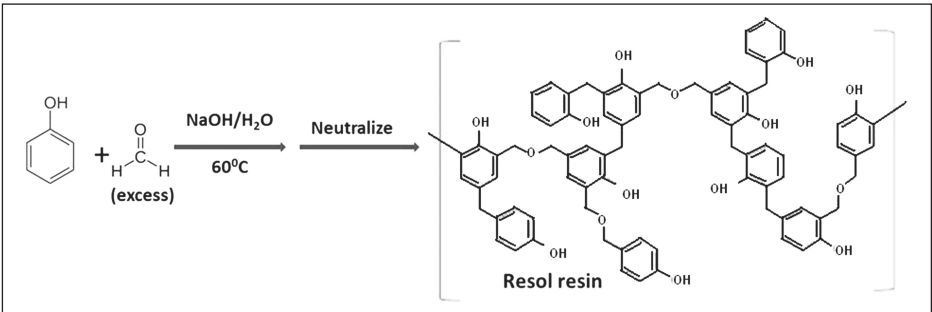


Fig. 2. Scheme of the formation of the resol - type phenolic resin [1]

In the foundry industry, these resins have been used in the preparation of core sand in the production of foundry cores. Industrially, the process of curing sand with phenolic resin followed by an intensive blowing performed by the stream of gaseous carbon dioxide leads to an almost immediate curing of the resin and provides the required strength of cores.

The aim of this paper is to capture structural changes in this type of resole phenolic resin as a result of contact with atmospheric air. In view of the CO₂ presence in atmospheric air, phenolic resin can undergo chemical changes at the time. It is assumed that, on a structural-analysis basis, it is possible to either indicate changes in the resin construction showing its cross-linking process or further cure core sand. Structural changes will be determined in a given time interval (24 hours).

2. Material

The tests were performed for the resol-type phenolic resin, which is known under the trade name Carbophen 6240 and produced by the Hüttenes-Albertus company.

3. Apparatus and research method

Studies were carried out using an Excalibur 3000 FTIR spectrometer with a standard DTGS detector. Spectra were recorded in a range of 4000–400 cm⁻¹, with a resolution of cm⁻¹. The spectra of samples tested at room temperature were produced by means of the transmission technique (KBr pellet).

The resin sample was applied to the surface of pellets in the form of a thin film. Spectra were recorded for the sample in its fresh state (immediately after application) as well as after the sample exposition to atmospheric air. Additional spectra were recorded within 24 hours; i.e., after 1, 3, and 24 hours.

4. Results and discussion

Figure 3 shows the IR spectrum of the resol-type phenolic resin Carbophen 6240 in the fresh state and after 1, 3, and 24 hours of atmospheric air impact, in the full wavenumber range.

The IR spectrum of the resin in the initial state has the most intensive band. The maximum recorded at wave-number 3400 cm⁻¹ is related to the stretching vibrations of OH in the aromatic ring (C–OH). This can also indicate weak bands derived from stretching vibrations of CH bonds in the aliphatic arrangement at 2941 and 2911 cm⁻¹, which are surely related to the methylene group –CH₂– present in the phenolic resin structure between the aromatic rings [4–11].

Band 1645 cm⁻¹ is related to vibration within the carbonyl bond C=O. This band is derived from monomer residues (formaldehyde), which did not completely enter into a polycondensation reaction with the phenol molecules. In turn, band 1600 cm⁻¹ is derived from the C=C vibration in the aromatic ring, while wave-number 1447 cm⁻¹ band is a vibration scissor of CH₂. After 1, 3, and 24 hours, a band of wave-number 1472 cm⁻¹ occurs and shows an additional vibration of the aromatic ring. The 1351 cm⁻¹ band can be

attributed to deformation vibrations of phenolic OH groups in a plane. Vibration bonds alkyl-phenol can be attributed to band 1288 cm^{-1} , while the band at 1080 cm^{-1} is a result of the deformation vibration of bonds CH of the aromatic ring [4–11].

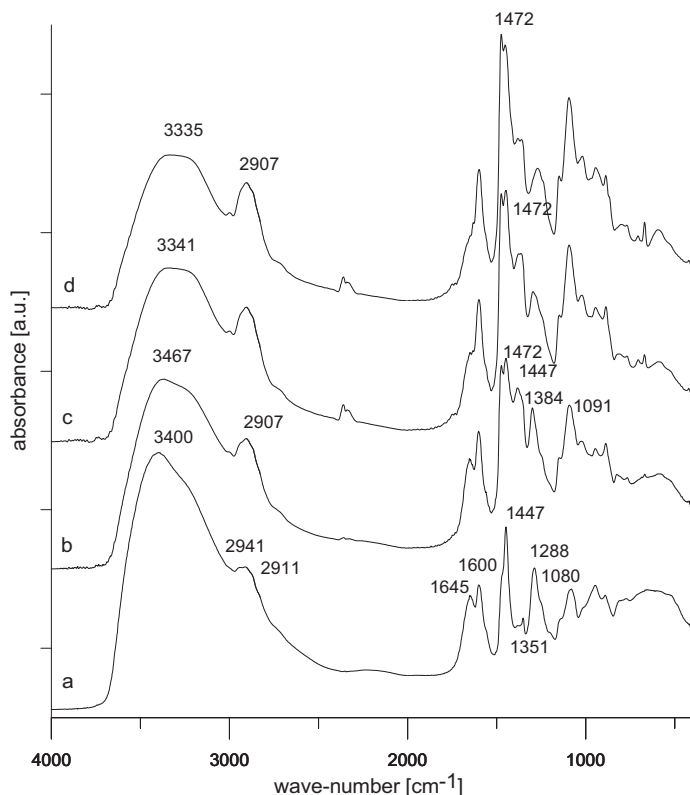


Fig. 3. IR spectra of the resol-type phenolic resin in the initial state (a) and after 1 (b), 3 (c), and 24 (d) hours of atmospheric air impact in the full wave number range of $4000\text{--}400\text{ cm}^{-1}$

Exposure of the sample to atmospheric air means that, already after 1 hour, a reduction of band intensity in OH groups at 3400 cm^{-1} can be seen. Such a change may be interpreted as the release of OH groups resulting from progressive polycondensation. The product of transformations of this kind of resin is water.

In the resin spectra after 1, 3, and 24 hours of sample exposure to air, a progressive decline in the intensity of band 1645 cm^{-1} is observed. The disappearance of bands in this region is associated with the re-activation of groups $\text{C}=\text{O}$ from formaldehyde and their reaction with the hydroxyl groups (OH), present in the aromatic rings. Thus, the progressing polycondensation reaction continues. At the same time, the adjacent band 1600 cm^{-1} ($\text{C}=\text{C}$) does not change its position and does not reduce its intensity.

With exposure time increasing, a wide band at 3400 cm^{-1} (OH) outlines the clearly highlighted band 2907 cm^{-1} . The $-\text{CH}_2-$ methylene groups remain in the resin structure between phenolic rings and do not change during the curing process. To make a detailed analysis of the obtained spectra, Figure 4 shows the IR spectrum of the phenol resin Carbophen 6240 wave-number range of $2000\text{--}400\text{ cm}^{-1}$.

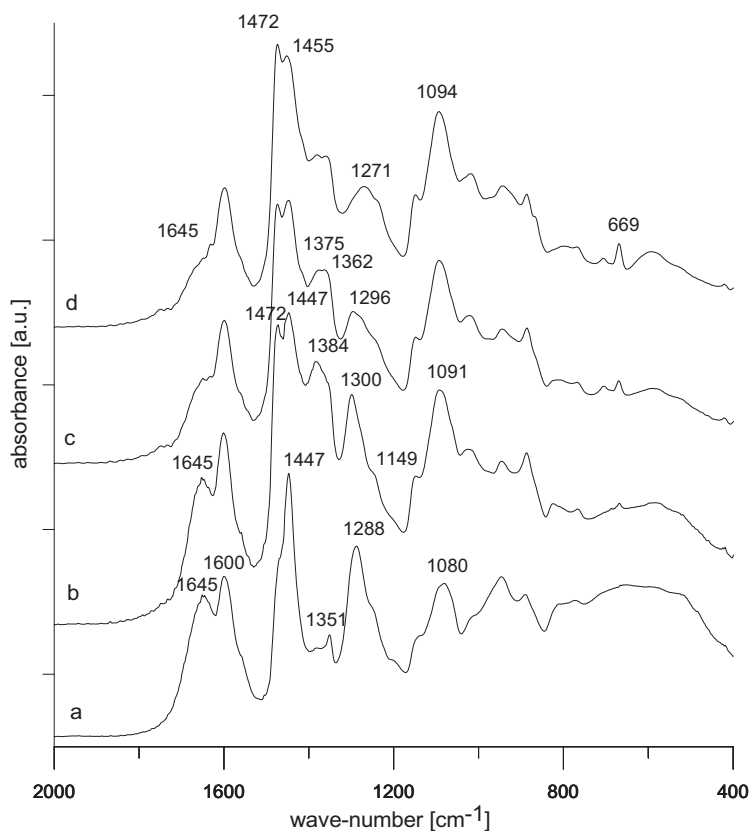


Fig. 4. IR spectra of the resol-type phenolic resin in the initial state (a), and after 1 (b), 3 (c), and 24 (d) hours of atmospheric air impact in the wave-number range of $2000\text{--}400\text{ cm}^{-1}$

As apparent in Figure 4, the band found in the resin in its initial state at wave-number 1447 cm^{-1} after 1 hour undergoes a separation into two bands corresponding to wave-numbers 1472 and 1447 cm^{-1} . With the passage of time, a progressive change in the intensity of the relationship between two bands is observed. Initially (for approximately one hour), there is a higher intensity characterized by band 1447 cm^{-1} . After 3 hours of exposure to ambient air, the intensity is aligned, while after 24 hours, a higher intensity characterized by band 1472 cm^{-1} occurs.

The changes described above can be a result of the structural transformation of the resin within methylene bridges. A significant decrease in the intensity of bands appearing in the range of 1270–1300 cm^{-1} may be a consequence of a systematic weakening of the stretching vibration of C–O. With the systematic shifting of bands at 1080 cm^{-1} in the direction of higher wave-numbers, an increase in intensity at wave 669 cm^{-1} can be noticed. Both bands are related to aromatic ring vibrations. An advancing cross-linking process may also be limiting valence vibrations for the benefit of deformations due to a decrease in the distance between phenolic rings.

5. Conclusions

On the basis of the structural analysis, the following conclusions can be drawn:

- The resol-type phenolic resin in the presence of atmospheric air undergoes a chemical transformation within 24 hours. Visible changes in the spectra indicate a progressive polycondensation reaction.
- The reason for significant weakening of the intensity of the OH stretching vibration bands (from phenolic groups) as well as vibrations of bands within the carbonyl group (C=O) may be the secondary polycondensation reaction involving the unreacted residues of formaldehyde. The polycondensation reaction product is water, and its eventual removal can be done by physical means, through evaporation.
- The resol-type phenolic resin also causes structural changes within methylene bridges and the aromatic ring. Changes of band intensities related to the vibrations of CH_2 and C=C with an increasing time of exposure can be the result of decreasing the distance between the mers of the polymer, thereby limiting the freedom of stretching alkyl vibrations. Thus, an increase in the intensity vibration of the phenyl ring is observed and, at the same time, a weakening of alkyl phenol bond vibrations.

References

- [1] <http://polymerinnovationblog.com/the-winding-road-to-renewable-thermoset-polymers-part-4-phenolic-resins/23.09.2015>
- [2] Lewandowski J.L.: Masy formierskie i rdzeniowe [Molding and core sand]. Wydawnictwo Naukowe PWN, Warszawa, 1991
- [3] Bobrowski A.: Badania wpływu temperatury na proces utwardzania spoiwa fenolowego z wykorzystaniem spektroskopii fourierowskiej w podczerwieni (FTIR-ATR) [Investigation of temperature influence on curing process of phenol binder using FTIR-ATR spectroscopy]. In: Ł. Mika (ed.): Jakość i innowacyjność w procesach odlewniczych, obróbce cieplnej i plastycznej oraz w wytwarzaniu materiałów kompozytowych [Quality and innovation in foundry, heat treatment and plastic and in the production of composite materials], Monograph 494. Cracow University of Technology, Krakow, 2015, 7–18
- [4] Costa L., Roosi di Montelera L., Comino G., Weil E.D., Pearce E.M.: Structure-charring relationship in phenol-formaldehyde type resins. *Polymer Degradation and Stability*, 56 (1997), 23–35

- [5] Zhiqin Ch., Yangfei Ch., Hongbo L.: Pyrolysis of Phenolic Resin by TG-MS and FTIR Analysis. *Advanced Materials Research*, 631–632 (2013), 104–109
- [6] Jiang H., Wang J., Wu S., Yuan Z., Hu Z., Wu R., Liu Q.: The pirolysis mechanism of phenol formaldehyde resin. *Polymer Degradation and Stability*, 97 (2012), 1527–1533
- [7] Zhao Y., Yan N., Feng M.W.: Thermal degradation characteristics of phenol-formaldehyde resins derived from beetle infested pine barks. *Thermochimica Acta*, 555 (2013), 46–52
- [8] Elsayed M.A., Hall P.J., Heslop M.J.: Preparation and structure characterization of carbons prepared from resorcinol-formaldehyde resin by CO₂ activation. *Adsorption*, 13 (2007), 299–306
- [9] Poljanšek I., Šebenik U., Krajnc M.: Characterization of Phenol-Urea-Formaldehyde Resin by Inline FTIR Spectroscopy. *Journal of Applied Polimer Science*, 99 (2006), 2016–2028
- [10] Alonso M.V., Oliet M., Dominguez J.C., Rojo E., Rodriguez F.: Thermal degradation of lignin-phenol-formaldehyde and phenol-formaldehyde resol resins. Structural changes, thermal stability, and kinetics. *Journal of Thermal Analysis and Calorimetry*, 105 (2011), 349–356
- [11] Chauhan N.P.S.: Thermal curing and degradation kinetics of terpolymer resins derived from vanillin oxime, formaldehyde and p-chloro-/p-methylacetophenone. *Korean Journal of Chemical Engineering*, 32, 3 (2015), 552–562