

Studies on thermal decomposition of phenol binder using TG/DTG/DTA and FTIR-DRIFTS techniques in temperature range 20–500 °C

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Abstract: This paper presents results of thermoanalytical and structural research on phenolic binder used in foundry for the preparation of moulding sand. The binder has been prepared based on resole type phenolic resin with the addition of ester hardener. The aim of the study was to determine the structural changes taking place in the phenolic binder under the influence of temperature. Results show that in the investigated range of temperatures, phenolic binder exhibits three exothermic thermal effects accompanying the decomposition process. The test results using the Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) technique show that the addition of a hardener stabilizes the binder structure within methylene bridges. The reduction in the reaction rate observed in the DTA curve at about 330 °C can be associated with the formation of gaseous products by decomposition of the binder or, as suggested by the literature data, the formation of triple bonds and CN-HCN groups.

Key words: phenolic resin; thermal decomposition; IR spectroscopy; thermal analysis; DRIFTS

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Various types of resins are used in the foundry industry, which, with a suitably selected hardener, constitute a binder for the preparation of a moulding sand. The moulding sands with organic resins are popular in the foundry industry due to many advantages such as the high surface quality of castings, high dimensional accuracy, adjustable setting time and a relatively easy way of preparation. The curing of the resin occurs due to the activity of physical or chemical agents. A common composition is a resole type phenolic resin cured with a liquid ester or a mixture of esters. Various physico-chemical changes will happen in the foundry binder at high temperatures. Thanks to the use of modern research techniques, it is possible to correlate physicochemical results with structural changes at the chemical bonds level.

Many research results are relevant to the phenolic

resins^[14], but it is difficult to find the results on foundry binders, which are the mixtures of resin and appropriately selected hardener. Literature dedicated to the foundry binder mainly concerns the analysis of gases which are released during thermal decompositions of binders^[15-20]. Structural studies on different types of binders were also carried out, including biopolymer binders^[21-24]. Research results indicated that the thermal decomposition of phenolic resins includes three temperature dependent stages: a low temperature stage (< 200 °C), an intermediate temperature stage (200–600 °C), and a high temperature stage (> 600 °C)^[1, 25]. Conley^[25] stated that thermo-oxidative processes take place regardless of whether the pyrolysis reaction occurs in an oxidative or inert atmosphere. He also studied the degradation process of phenolic resins in oxygen, nitrogen and in vacuum conditions in the temperature range of 100–200 °C. The structural changes were not found for phenolic resins pyrolyzed at 200 °C for 50 hours in nitrogen or in vacuum atmosphere, suggesting that degradation does not take place. However, in oxidizing atmosphere, products of oxidation were observed, therefore, the initial degradation stage was dependent on the presence of oxygen. It also shown that the IR spectra of resole and novolac resins obtained in the pyrolysis conditions were

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similar. Conley presented a hypothesis that the decomposition mechanisms under these conditions are similar for both types of phenolic resins, i.e., the degradation process takes place in the initial phase (low temperature) and is based on the thermo-oxidation process (Fig. 1) [1,25]. Lochte et al. [26] suggested that at elevated temperatures, the resin can act as a source of oxygen for the oxidation process. Jackson et al. obtained similar conclusions [27]. He stated that the oxygen which comes from the degradation products of the resin forms the carbonyl

bonds. Chang's [28] results on the phenol resin decomposition products indicate that in the second step (temperature higher than 200 °C), the decomposition of the resin occurs and the gaseous components such as water, carbon dioxide, methane, phenol, ammonia and compounds from the group BTEX are formed. The second stage is also related to the degradation of methylene bridges between the phenolic rings and the emission of volatile paraformaldehyde [1]. Table 1 shows the evolution temperature of each compound.

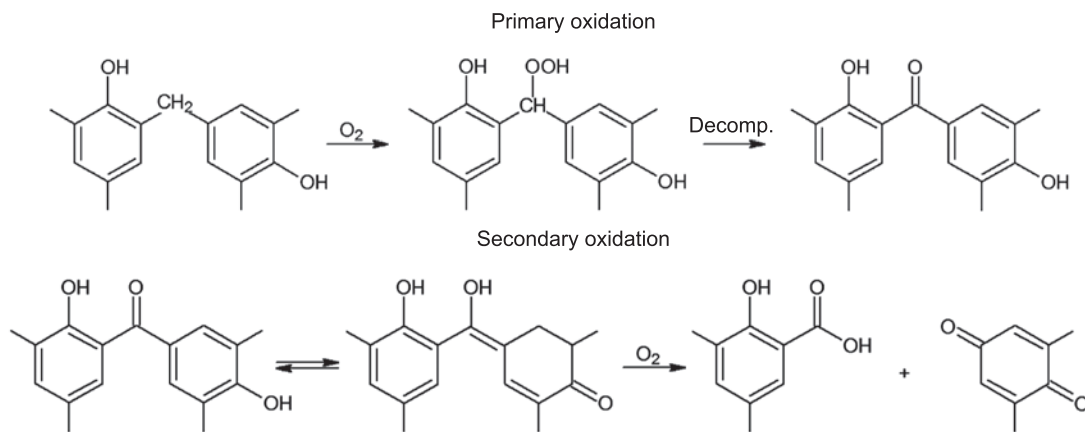


Fig. 1: Thermal degradation of phenolic resin at a low temperature as a result of thermo-oxidation [1,25]

Table 1: Gas emission caused by thermal decomposition of phenolic resin [28]

Temperature (°C)	Type of gas	Estimated loss of weight (%)
120	Water	0.8
145	Phenol	0.3
210	Water	4.4
	Phenol	1.8
	Methanol	1.2
	Carbon dioxide	0.4
270	Ammonia	2.7
370	Unidentified	0.3
420	Water	5.0
	Carbon dioxide	0.7
580	Water	5.7
	Carbon dioxide	1.3
650	Methane	3.8
	Benzene	3.4
	Toluene	2.7
	Xylens	1.3
	Trimethylbenzene	0.2
720	Phenol	4.1
	Crezol	2.6
	Dimethylphenol	1.1
	Trimethylphenol	0.1
	Carbon monoxide	6.1

The thermal decomposition of phenolic resins is still in the research interest and is not fully explained. The results of Ref. [29] show that the resin degradation may be based on the initial stage of releasing of low molecular compounds without a thermo-oxidation process. In the next stage, an emission of phenol,

crezol, and homologue occurs as a result of decomposition and bridging of methylene groups. In the final stage, a total destruction of the phenol structure takes place.

The results of Ref. [30,31] showed that the pyrolysis process of phenol resin includes three stages. The phenol is first formed as a product of condensation of functional groups, then a release of methane, hydrogen and carbon monoxide. In the final stage, the hydrogen atoms are released from the aromatic structure and removed in the form of hydrogen gas. Jiang H. et al. [32] stated that pyrolysis reactions are complex and difficult to separate into elementary reactions.

As mentioned above, the thermal degradation process of phenolic binders leads to the emission of gases. In casting technology, the emission of compounds from the BTEX group (Benzene, Toluene, Ethylbenzene, and Xylene) is a determinant of the harmfulness of molding and core sands [19,20,33]. The quality and quantity of emitted degradation products not only depend on the resin type used, but also its weight to sand ratio in moulding sand [34, 35]. Frequently, to accelerate the binding process, a hardener is introduced into the moulding sand, which may affect the final emissions. Moreover, in foundry practice, the reclamation process is carried out. The reclamation of spent moulding sands and the proportion of reclaimed sand in moulding sand can also affect the amount of emitted gaseous products during pouring by liquid metal. The exact knowledge of the thermal decomposition process for phenolic binder based on phenol resins is not only cognitive but also utilitarian. Proper temperature selection in the regeneration process directly translates into energy consumption and positively affects the economics of the foundry process.

The aim of this study was to connect the thermal effects

accompanying the process of heating a cured phenolic binder with structural changes in the temperature range of 20–500 °C, (simulating the conditions in the mould after pouring). In this temperature range, the biggest changes in the DTG curve were recorded, to correlate thermal effects (endo- and exothermic) with structural changes in the cured foundry binder. The overview of research [36–38] indicates that at a higher temperature (about 600 °C), the thermal effect associated with the complete carbonization of resin can be expected. The total carbonation of the binder is associated with the loss of binding strength. This phenomenon occurs in the immediate contact of moulding sand with hot metal. As a result, the grains of the sand matrix are free from residues of the used binder. Determining the occurrence temperature of this effect may suggest at what distance from the hot metal the self-regeneration of molding sand could be observed.

1 Materials

Phenolic binder used for preparation of moulding sands in the Alphaset technology was investigated. The binder was prepared based on phenolic resin Estrofen and hardener PR6 (hardener/resin 1:20). The ratio of resin/hardener was selected on the basis of manufacturer binder recommendations. Estrofen resin is a kind of alkaline phenolic resin, resole type, offered by Prec-Odlew Company.

Such resins are obtained by a condensation of phenol (1 mol) with an excess of formaldehyde (1.5 mol) (or the furfuryl alcohol). As a hardener, a liquid ester or mixture of esters were used. According to our observations, the obtained binder sample is characterized by high hardness. Then, the sample of hardened binder was crushed to a fine powder before investigations.

2 Experimental

The temperature range and characteristic temperature points were determined on the basis of thermal analysis carried out earlier. It showed that in the 20–500 °C temperature range, the thermal effects associated with degradation reactions of Estrofen binder can be observed. Testing was performed using a thermal analyzer, produced by Jota. The structural studies were carried out by means of the transmission technique (FTIR spectroscopy) and reflection technique of Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS).

The DRIFTS was used for the sample in a condensed-phase, fine powder. In order to obtain good quality IR spectra, the cured binder sample powder was mixed with potassium bromide (KBr). Potassium bromide does not give spectrum in mid-infrared range, therefore, it does not affect the obtained spectrum and it is a transparent background for the sample. Infrared radiation was directed to the sample containing a mixture of the test material with KBr, and was reflected from the individual grains. Scattered, weakened portion of the IR radiation was captured by the optical system and directed to the detector. The optical system collects simultaneously the scattered radiation passing

by the gaseous medium above the sample, where the atmosphere above the sample begins to change due to the formation of new compounds in the gas phase. The detector can also obtain signals from the vibration of molecules in the gaseous state. Research was carried out with this method without changing the sample – the test sample is heated continuously within a specified temperature range, which allows the recording of spectra with structural changes occurring in the test sample. This is a reflex technique that is ideally suited for testing powders and rough surfaces. It is also used in investigations of polymorphic/crystal samples, because the grinding material can lead to changes in its polymorphic form.

Structural changes in the cured phenolic binder were also observed by the transmission method (at the points where thermal effects associated). Binder samples were placed in the ceramic crucibles and heated in the oven to the set temperature. Heating rate was the same as in the case of thermal analysis (10 °C·min⁻¹). After cooling to room temperature, the Fourier-transform infrared (FTIR) investigation was carried out. Approximately 200 mg of KBr is mixed with about 2 mg of the test sample, and then, in a special matrix, the pellets were made using a laboratory press. The prepared sample (in pellet) was placed in a pellets holder in the spectrometer to perform the IR spectrum.

The spectra were recorded using the Pro Resolution software. DRIFT spectra were recorded with a resolution of 8 cm⁻¹, in the range of 4,000–600 cm⁻¹, because under 600 cm⁻¹, there are interferences with the features of the accessory, which is not suitable for analysis. DRIFTS results were supplemented by transmission techniques. Spectra made using the transmission technique (KBr pellets) were recorded in the full mid-infrared range (4,000–400 cm⁻¹), with a resolution of 4 cm⁻¹.

Infrared structural studies using a spectrometer Excalibur 3000 FTIR with a standard detector DTGS were also carried out.

3 Results and discussion

Figures 2 and 3 show the curves of the TG/DTG/DTA recorded in the temperature range of 20–500 °C for a sample of the cured phenolic binder – Estrofen resole type.

Analysis of the TG/DTG/DTA curves shows that the binder based on phenolic resin Estrofen exhibits a slow and steady

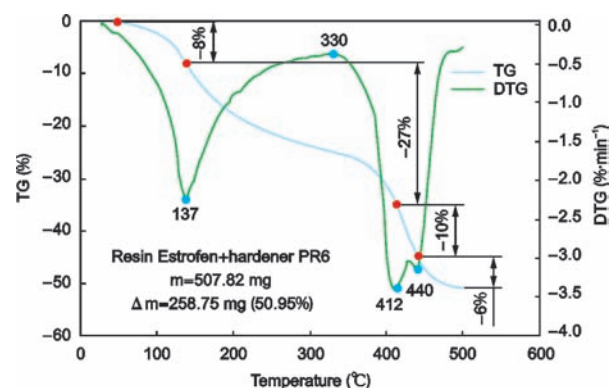


Fig. 2: TG/DTG curves of phenol binder Estrofen

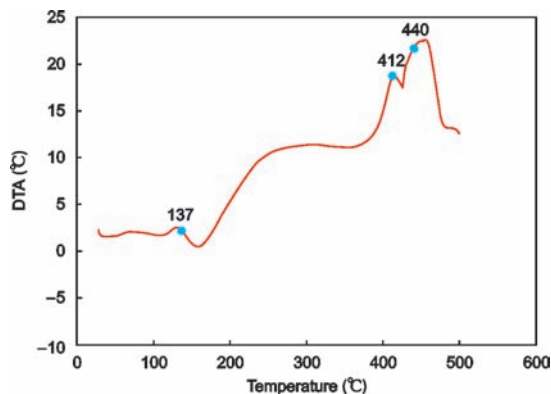


Fig. 3: DTA curve for phenol binder Estrofen

weight loss in the initial stages of heating, but without any accompanying thermal effects. In the DTA, the beginning of the thermal effect with a maximum at 137 °C, can be noticed, but this is not a rapid reaction. Maybe there is a release of water, unreacted phenol or other volatile substances, which results in a stepwise weight loss of the sample. At a temperature in the range of 160–170 °C in the DTA curve, endothermic reaction was observed, which is probably due to achieving the vaporization temperature of the binder volatiles. Above this temperature, the progresses of the exothermic reaction with the temperature increasing is recorded. As the DTG curve shows, at a temperature of about 330 °C, the heat-releasing was temporarily stopped, and then, the beginning of a significant two-stage weight loss of the sample was observed. The first stage, at 412 °C, corresponds to the weight loss of 35%, and the second (at 440 °C), weight loss of about 45%. In these two temperature points, binder has the highest intensity of decomposition, and in the DTA, two distinct exothermic effects were recorded.

Thermal analysis was performed at the selected temperatures at which there was a significant change in the sample mass, and the significant thermal effects of the degradation process also occurred. For the designated temperatures, the DRIFT spectra of the cured binder and transmission spectra for the samples heated in oven were recorded. Figures 4 and 5 show the spectra of the cured binder heated to the temperature indicated in the thermal

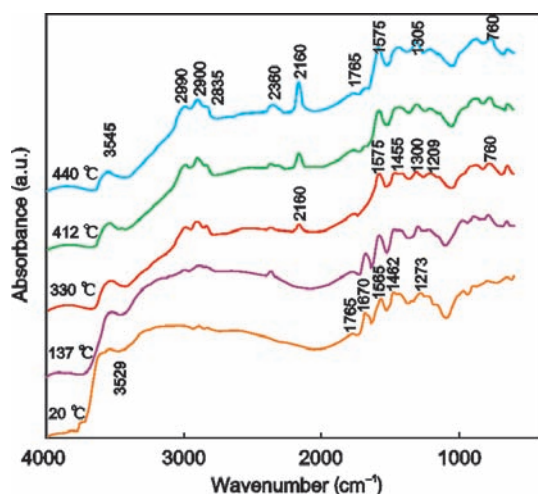


Fig. 4: DRIFT spectra of phenol binder Estrofen in temperature range of 25 – 500 °C

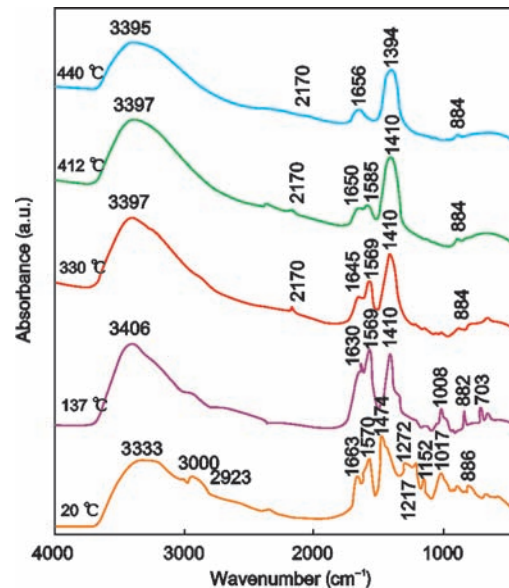


Fig. 5: IR spectra of cured phenolic binder Estrofen at selected temperatures associated with thermal effects

analysis (characteristic points), respectively by the DRIFT and FTIR investigations.

On the DRIFT spectrum (Fig. 4) and the FTIR spectrum (Fig. 5) obtained for the cured phenolic binder at 20 °C, the characteristic band for the occurrence of stretching bond vibrations of hydroxyl group (-OH) can be identified. This is confirmed by the broad band in the wavenumbers range of 3,600–3,300 cm^{-1} [8,10]. The peaks in the range of 1,670–1,550 correspond to the C=C aromatic ring vibrations. The appearance of a band at wavenumber 1,765 cm^{-1} is interpreted as stretching vibration of C=O [9,10,12]. Bands in the range of 1,470–1,390 cm^{-1} are derived from vibrations of C-H group [8,9,10,13]. The bands in the range of 1,300–1,150 cm^{-1} indicate the presence of vibrations within the C-O bond [8,9,10,12,13]. The spectrum of the cured sample also contains the characteristic band for deformation vibrations of hydroxymethyl aliphatic C-OH (1,017 cm^{-1}) bonds and the C-H bonds out of plane (in the range of 900–750 cm^{-1}) [8,10].

It is apparent from Fig. 4 that with an increasing temperature, there is a systematic decrease of the intensity of bands related to -OH vibrations, which simultaneously result in a separation of the bands derived from the C-H vibrations (2,990–2,835 cm^{-1}), which do not decompose within the adopted temperature range. Changes in the region of hydroxyl groups (decrease of intensity) and increase of intensity bands at 1,575 cm^{-1} assigned to aromatic compounds could be related to the formation of a cyclic structure form of xanthenes with the participation of hydroxyl groups [8], according to the diagram shown in Fig. 6.

The appearance of bands at 2,360 cm^{-1} is assigned to carbon dioxide (CO_2) [39]. The recorded increase in the intensity of this band indicates that there is an increasing emission of this gaseous product above 400 °C. Carbon dioxide emitted during the degradation is adsorbed on the surface of the sample, and the characteristic band that appeared in the spectrum confirmed its presence. The band of 2,160 cm^{-1} appears in the

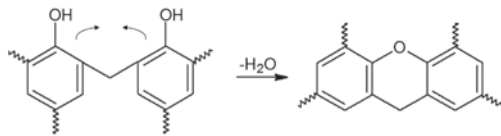


Fig. 6: Possible cyclization reaction with participation of hydroxyl groups [8]

DRIFT spectrum at a temperature of about 330 °C. Its intensity increases with an increasing temperature and it can be related to the formation of carbon oxide (CO) as a result of incomplete combustion and its adsorption on the surface of the sample. This is observed at the same time as an elimination of the band at a wavenumber 1,670 cm⁻¹, associated with the vibration of the carbonyl bond C=O.

The appearance of additional bands is probably associated with the separation of CO and CO₂ (which can be a result of the running reaction), which is schematically shown in Fig. 7.

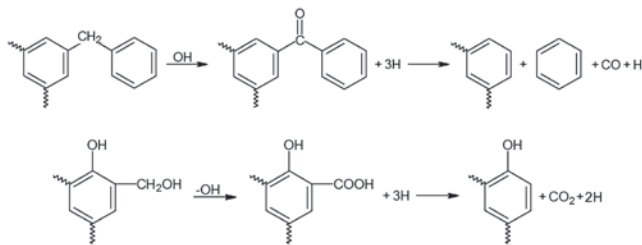
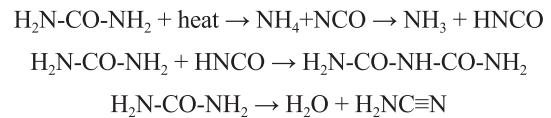


Fig. 7: Reaction of CO and CO₂ formation [8]

According to Ref. [40], the peak at 2,160 cm⁻¹ is attributed to CN triple bond and the -NCO groups. Their presence in the spectrum suggests that the binder contains urea, which undergoes thermal degradation by reaction [10]:



To complement the structural studies, the FTIR spectra for the phenolic binder were conducted. The samples of binder were heated continuously in an oven to the set temperature. The temperature points were the same as for the DRIFT technique. Figure 5 shows that, as a result of heating, the C-H bonds assigned to the range of 3,000–2,923 cm⁻¹ degraded while the O-H bonds remained. The outline of the band suggests, however, a partial evaporation of water. This can be also indicated by a marked reduction in the intensity of band at 1,663 cm⁻¹ and 1,570 cm⁻¹ (vibration bonds C=O and C=C) [8,9] in relation to the band at 1,410 cm⁻¹ (vibration C-H bonds). At 137 °C, the disappearance of vibration C-C bonds and C-O-O in the range of 1,272–1,152 cm⁻¹ is observed, which can affect the formation of the compounds in the gas phase (CO and CO₂). Similar to the results obtained using the DRIFT technique, it was found that the band at wavenumber 2,170 cm⁻¹ can be related to carbon monoxide formed in the thermal decomposition of the binder. It may be adsorbed on the surface of the sample and also take part in its structure or formation of CN triple bond and HCN groups. At 330 °C, the disappearance of the band at 1008 cm⁻¹, characteristic for the C-OH vibrations, is observed. Above 400 °C, a progressive decrease in the intensity of the band at 1,570 cm⁻¹ indicative of the presence of C=C aromatic ring, can be seen. The band intensity corresponding to the presence of C-H bond vibrations (1,410 cm⁻¹) is not visibly changed. Only a shift towards higher wavenumbers can be noticed. Table 2 shows the assigning of the chemical bonds to each band in the spectra.

Table 2: Assignment of bonds present in binder of phenolic resol type Estrofen [3,5,8,12,37]

Range of occurrence band (cm ⁻¹)	Assigned vibration bonding
3,600 – 3,400	OH
3,000 – 2,800	CH ₂
2,400 – 2,300	CO ₂
2,170 – 2,160	CO or C≡N
1,770 – 1,760	C=O
1,670 – 1,560	C=C, aromatic ring stretching
1,470 – 1,400	C-H aliphatic and C=C aromatic ring obscured by methylene ridges CH ₂
1,270 – 1,200	C-C-O assymetric stretch, an ether band, phenolic OH and CO stretching.
1,150 – 1,100	C-O stretch
1,050 – 1,000	Aliphatic hydroxyl eg. C-OH
880 – 800	C-H deformation
880 – 750	Phenol assymetric stretch C-C-OH or C-H out of the plane of the ring substituted

4 Conclusions

According to the results (TG/DTG/DTA, DRIFTS and FTIR – transmission technique) presented above, the following conclusions can be drawn:

(1) Within the temperature range of 20–500 °C, the binder phenolic resole, Estrofen type, used for the preparation of moulding sand applied in casting exhibits three exothermic thermal effects accompanying the thermal decomposition process. The first (at a temperature of 137 °C) can be associated with the loss of the residual water and unreacted phenol. Another two, recorded at temperatures of 412 °C and 440 °C, respectively, are probably related to the degradation of double bonds to form gaseous products of resin decomposition (CO and CO₂), as indicated by the disappearance of vibrations bonds C=O in the FTIR spectra. Vibrations in this wavenumber range may be associated with the formation of HCN groups and CN triple bond and suggest contamination of resin by urea.

(2) The low intensity endothermic effect shows on the DTA curve at a temperature of about 170 °C can be associated with reaching the boiling point of volatile substances in binder – probably a hardener residue.

(3) The results obtained by DRIFTS indicate that the introduction of the phenolic resin with a hardener from the group of esters has an impact on the stability of the structure around methylene bridges. They are not decomposed in the investigated temperature range. However, a clear weakening of vibrations is observed associated with bonds C=O at temperature of 330 °C.

(4) The appearance of a single band at 2160–2170 cm⁻¹ and the change of intensity of the band at 2,360 cm⁻¹ were recorded at a temperature of 330 °C, in the spectra obtained by both FTIR and DRIFTS. It can therefore be assumed that as a result of the thermal degradation of the binder, the volatile decomposition products (CO and CO₂) are formed and adsorbed on the surface of the sample. The investigation results allow an explanation of disappearance of the band C-C-O, C-O and C-OH in the binder structure.

(5) The results obtained by the FTIR method suggest, however, that at a temperature of 330 °C, the hydroxymethylene band C-O (1,006 cm⁻¹) degrades and the C-H bonds in a substituted aromatic ring (703 cm⁻¹) desintegrate. It is also observed that with an increase in temperature, the intensity of vibration bonds in the aromatic ring is gradually weakened.

(6) Thermoanalytical studies results suggest that the thermal reclamation process of spent moulding sand with phenolic resin at temperatures below 500 °C can be carried out. At such a temperature, the grain of the quartz matrix should be free of the used binder.

References

- [1] Hardrict S N. Novel novolac-phthalonitrile and siloxane-phthalonitrile resins cured with low melting novolac oligomers for flame retardant structural thermostets. Thesis of Master of Science in Chemistry. Blacksburg: Virginia Polytechnic Institute and State University, 2003.
- [2] Movahed F S, Cheng G C, Venkatachari B S, et al. Atomistic simulation of thermal decomposition of crosslinked and non-crosslinked phenolic resin chains. In: 42nd AIAA Thermophysics Conference, 2011: 1–13.
- [3] Poljanšek I, Krajnc M. Characterization of Phenol-Formaldehyde Prepolymer Resins by In Line FT-IR Spectroscopy. Acta Chim. Slov., 2005, 52: 238–244.
- [4] De-en Jiang, van Duin A C T, Goddard III W A, et al. Simulating the Initial Stage of Phenolic Resin Carbonization via the ReaxFF Reactive Force Field. J. Phys. Chem. A, 2009, 113: 6891–6894.
- [5] Alonso M V, Oliet M, Dominguez J C, et al. Thermal degradation of lignin-phenol-formaldehyde and phenol-formaldehyde resole resins. Journal of Thermal Analysis and Calorimetry, 2011, 105: 349–356.
- [6] Desai T G, Lawson J W, Keblinski P. Modeling initial stage of phenolic pyrolysis: Graphitic precursor formation and interfacial effects. Polymer, 2011, 52: 577–585.
- [7] Reghunadhan Nair C P, Bindu R L, Ninan K N. Addition curable phenolic resins based on ethynyl phenyl azo functional novolac. Polymer, 2002, 43: 2609–2617.
- [8] Chen Z, Chen Y, Liu H. Pyrolysis of phenolic resin by TG-MS and FTIR analysis. Advanced Materials Research, 2013, 631-632: 104–109.
- [9] Yangfei Ch, Zhiqin Ch, Shaoyi X, et al. A novel thermal degradation mechanism of phenol-formaldehyde type resins. Thermochimica Acta, 2008, 476: 39–43.
- [10] Zhao Y, Yan N, Feng M W. Thermal degradation characteristic of phenol – formaldehyde resins derived from beetle infested pine barks. Thermochimica Acta, 2013, 555: 46–52.
- [11] Jiang H, Wang J, Wu S, et al. The pyrolysis mechanism of phenol formaldehyde resin. Polymer Degradation and Stability, 2012, 97: 1527–1533.
- [12] Poljanšek I, Šebenik U, Krajnc M. Characterization of phenol-urea-formaldehyde resin by inline FTIR Spectroscopy. Journal of Applied Polymer Science, 2006, 99: 2016–2028.
- [13] Costa L, di Montelera L R, Camino G C, et al. Structure-charring relationship on phenol-formaldehyde type resins. Polymer Degradation and Stability, 1997, 56: 23–35.
- [14] Bates C E, Scott W D. The decomposition of resin binders and relationship between gases formed and the casting surface quality, part 2 – gray iron. AFS Transactions, 1980, 76: 793–804.
- [15] Winardi L, Griffin R D, Littleton H E, et al. Variables Affecting Gas Evolution Rates and Volumes from Cores in Contact with Molten Metal. AFS Transactions, 2007, 116: 505–521.
- [16] McKinley M D, Lytle C A, Bertsch W. Pyrolysis of core resins used in metalcasting. AFS Transactions, 2007, 407–412.
- [17] Holtzer M, Bobrowski A, Daňko R, et al. Emission of polycyclic aromatic hydrocarbons (PAHs) and benzene, toluene, ethylbenzene and xylene (BTEX) from the furan moulding sands with addition of the reclaim. Metalurgija, 2014, 53 (4): 451–54.
- [18] Bobrowski A, Holtzer M, Żymankowska-Kumon S, et al. Harmfulness assessment of moulding sands with a geopolymer binder and a new hardener, in an aspect of the emission of substances from the BTEX group. Archives of Metallurgy and Materials, 2015, 60 (1): 341–344.
- [19] Bobrowski A, Holtzer M, Daňko R, et al. Analysis of gases emitted during a thermal decomposition of the selected phenolic binders. Metalurgia International, 2013, 18 (7): 259–261.
- [20] Holtzer M, Bobrowski A, Daňko R, et al. Influence of a liquid metal temperature on a thermal decomposition of a phenolic resin. Archives of Foundry Engineering, 2013, 13 (2): 35–38.
- [21] Grabowska B, Holtzer M, Eichholz S, et al. Thermal analysis of a sodium salt of the maleic acid-acrylic acid copolymer used as a polymeric binder. Polimery, 2011, 56 (2): 62–66.
- [22] Kaczmarek K, Grabowska B, Drożyński D, et al. Modified polysaccharides as alternative binders for foundry industry.

- Metalurgija, 2016, 55 (4): 839–842.
- [23] Grabowska B, Bobrowski A, Grabowski G, et al. Thermoanalytical studies (TG-DSC, FTIR-DRS) of the moulding sand with the polymer BioCO₂ binder. *Archives of Foundry Engineering*, 2015, 15 (1): 27–30.
- [24] Bobrowski A, Grabowska B. The impact of temperature on furan resin and binder structure. *Metallurgy and Foundry Engineering*, 2012, 38 (1): 73–80.
- [25] Conley R T, Bieron J F. A kinetic study of the oxidative degradation of phenol-formaldehyde polycondensates using infrared spectroscopy. *Journal of Applied Polymer Science*, 1963, 7: 103–117.
- [26] Lochte H W, Strauss E L, Conley R T. The thermo-oxidative degradation of phenol-formaldehyde polycondensates: Thermogravimetric and elemental composition studies of char formation. *Journal of Applied Polymer Science*, 1965, 9: 2799–2810.
- [27] Jackson W M, Conley R T. High temperature oxidative degradation of phenol-formaldehyde polycondensates. *Journal of Applied Polymer Science*, 1964, 8: 2163–2193.
- [28] Chang Ch, Tackett J R. Characterization of phenolic resins with thermogravimetry-mass spectrometry. *Thermochimica Acta*, 1991, 192: 181–190.
- [29] Chen Y, Chen Z, Xiao S, et al. A novel thermal degradation mechanism of phenol-formaldehyde type resins. *Thermochimica Acta*, 2008, 476 (1–2): 39–43.
- [30] Alonso M V, Oliet M, Dominguez J C, et al. Thermal degradation of lignin-phenol-formaldehyde and phenol-formaldehyde resol resins. *Therm Anal Calorim*, 2011, 105: 349–356.
- [31] Chen Y, Fan D, Qin T, et al. Thermal degradation and stability of accelerated-curing phenol-formaldehyde resin. *BioResources*, 2014, 9 (3): 4063–4075.
- [32] Jiang H, Wang J, Wu S, et al. The pyrolysis mechanism of phenol formaldehyde resin. *Polymer Degradation and Stability*, 2012, 97: 1527–1533.
- [33] Bobrowski A. Analysis of gases from BTEX group by Fourier Transform Infrared Spectroscopy (FTIR). *Archives of Foundry Engineering*, 2014, 14 (4): 17–20.
- [34] Żymankowska-Kumon S, Bobrowski A, Grabowska B. Comparison of the emission of aromatic hydrocarbons from moulding sands with furfural resin with the low content of furfuryl alcohol and different activators. *Archives of Foundry Engineering*, 2016, 16 (4): 187–190.
- [35] Holtzer M, Daňko R, Żymankowska-Kumon S, et al. Assessment of the harmfulness of moulding sands with alkyd resin subjected to the high temperature influence. *Archives of Metallurgy and Materials*, 2016, 61 (4): 2171–2176.
- [36] Šupová M, Svitilová J, Chlup Z, et al. Relation between mechanical properties and pyrolysis temperature of phenol formaldehyde resin for gas separation membranes. *Ceramics – Siilikáty*, 2012, 56 (1): 40–49.
- [37] Manocha S M, Patel K, Manocha L M. Development of carbon foam from phenolic resin via template route. *Indian Journal of Engineering & Materials Science*, 2010, 17: 388–342.
- [38] Ma T F, Wang X F, Yang F L. Effect of Carbonization Temperature on the Elastic Modulus of Resin Carbon. *Advanced Materials Research*, 2015, 1079–1080: 83–87.
- [39] Gerakines P A, Schutte W A, Greenberg J M, et al. The infrared band strengths of H₂O, CO and CO₂ in laboratory simulations of astrophysical ice mixtures. *Astronomy and Astrophysics*, 1995, 296: 810–818.
- [40] Schaber P M, Calson J, Higgins S, et al. Thermal decomposition (pyrolysis) of urea in an open reaction vessel. *Thermochimica Acta*, 2004, 424: 131–142.