



Thermoanalytical tests (TG–DTG–DSC, Py-GC/MS) of foundry binders on the example of polymer composition of poly(acrylic acid)–sodium carboxymethylcellulose

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Abstract

The results of thermal analysis (TG–DTG–DSC) of a foundry binder from the BioCo group in the form of a polymer composition of poly(acrylic acid)–sodium carboxymethylcellulose (PAA/CMC-Na) are presented in this article. The range of temperature of degradation has been determined. It was found that as the temperature rises, physical and chemical changes take place in the binder as a result of evaporation of solvent water, release of constitutional water, intermolecular dehydration reactions and decomposition of polymer chains with the formation of gaseous decomposition products. Pyrolysis gas chromatography mass spectrometry method (Py-GC/MS) was used to identify PAA/CMC-Na binder degradation products in a predetermined temperature range based on the previously performed thermal analysis of TG–DTG–DSC. Py-GC/MS tests were also carried out to determine the emission level of gaseous products of the polymeric binder in the context of the processes occurring in the moulding (foundry) sand, in conditions of its contact with liquid metal. In addition, Py-GC/MS tests were carried out for two commonly used foundry binders based on alkaline phenolic resin cured with esters and based on urea-formaldehyde resin with furfuryl alcohol cured with sulphonic acids. The obtained Py-GC/MS results for commercial binders were referred to the results obtained for the new PAA/CMC-Na binder. It was found that the new polymer binder is characterized by the lowest emission level of gaseous products.

Keywords Polymer binders · Foundry sands · Thermal degradation · TG–DTG–DSC · Py-GC/MS

Introduction

At present, one of the largest groups of foundry sands used for the production of moulds and cores is the moulding sands based on the mineral matrix and bonded with organic binders in the form of synthetic resins. Resins are mixtures of synthetic monomers and polymers with a relatively small degree of polymerization, linear or

branched, in which the composition usually contains phenyl (aromatic) groups. The most commonly used foundry sands bonded with synthetic resins include moulding sands with organic resins, among others phenolic, furfuryl, phenol-formaldehyde (generally mixture of them) or alkyd resins [1, 2]. The process of cross-linking organic binders in moulding sand is usually carried out at room temperature. At the same time, this process is often aided by the blowing through the binder system of gaseous substances, including SO₂ or CO₂ and amines. This type of cross-linking has a positive effect on many moulding sand properties, including to increase the bonding rate in the binder matrix system, as well as to reduce energy consumption. On the other hand, the use of synthetic resins is associated with their negative impact on the environment like the presence of harmful organic compounds in their composition or using SO₂ or toxic amines in the curing process. In addition, during pouring the mould with a

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liquid metal, harmful products of thermal decomposition of binders are emitted to the atmosphere [2–9].

In foundry process, as organic binders for moulding sands and cores are mainly used polymer binders, which, unlike synthetic resins, contain only synthetic, natural or modified polymers dissolved in a suitably selected solvent. Among the synthetic polymers used in foundries are, among others, polystyrene, polyacrylates and polyurethanes. In the literature, one can find works focusing on the development of adhesives and casting processes using natural polymers, as well as polymers from the so-called renewable sources (including from biomass) [9–13].

At present, in the country and around the world, research is being carried out to obtain binders composed of materials derived from natural, often renewable sources, which is associated with a reduction in production costs, while maintaining good-quality castings. The activities are carried out to create new binders that are environmentally friendly in their original form and do not generate harmful substances in the technological process. It is important to minimize the emission of gaseous products of thermal decomposition during the pouring process of liquid metal [14–18].

Thermal degradation of polymeric materials is a complicated process running in a heterophasic system. Therefore, the choice of the analytical method and determination of measurement conditions is important in the context of the analysis of gaseous products generated during the thermal decomposition process. The control and identification of emissions of gaseous products is also important for environmental reasons, as harmful substances are released on an industrial scale, including CO, SO₂, H₂S, aromatic hydrocarbons or dioxins. In order to determine the emission level of gaseous products, numerous research works are carried out using thermoanalytical methods, including coupled methods that combine spectral (MS, IR, Raman) with thermal (TG-DSC) methods. Thermoanalytical techniques enable the combination of thermal analysis methods and analysis of evolved gaseous products using a mass spectrometer (MS) or an infrared spectrometer (IR) in a single measurement [19–23].

Synthetic resins, solvents and organic hardeners used in moulding sands and cores constitute the main source of harmful compounds emission. Emission may occur already at the stage of moulding sand preparation, while volatile organic components, mainly solvents, are released. However, the largest amount of gaseous substances is formed during the contact of the moulding sand with the liquid metal, when under the influence of high temperature thermal destruction of its organic components occurs [24].

The level of gas emissions from moulding sands becomes important in respect of maintaining the safety of work in the foundry, as well as having the final impact on

the quality of the casting. Foundry technologies using organic components containing phenyl, amine or sulphur groups in their structure are potentially harmful. The effect on the human body of released amines during the hardening of moulding sands or aromatic hydrocarbons generated during the destruction of the organic components is not indifferent. In addition, the technological and economic aspect should be taken into account, as the gases emitted during the destruction may enter undesirable reactions at the mould–cast interface, which is the reason for many defects of castings, including deterioration of the quality of their surface [25–29].

The research team has been carrying out analytical work for several years, including qualitative and quantitative analysis of gaseous products emitted during the technological process, including the process of pouring the mould with a liquid metal. The measurement method developed in this area using spectral techniques allows to determine the quantity and kinetics of emission of gases emitted, as well as qualitative and quantitative analysis of aromatic hydrocarbons: benzene, toluene, ethylbenzene and xylenes (BTEX) during the pouring process [30]. The research also uses a pyrolysis gas chromatography coupled with mass spectrometry (Py-GC/MS) method to determine the emission level of gaseous substances released in the technological process [31–34].

This paper presents the results of a thermoanalytical cycle research using the thermal methods (TG–DTG–DSC) and pyrolysis gas chromatography coupled with mass spectrometry (Py-GC/MS). The research was aimed at completing the knowledge of the thermal degradation process of a new group of BioCo polymer binders in a given temperature range and at the same time determine the emission level of gaseous substances released during the destruction process. A new polymeric binder from the BioCo group [13, 34–38] was tested, which contained two dissolved in water polymers: poly(acrylic acid) and sodium carboxymethylcellulose. In addition, Py-GC/MS tests were carried out for two popular and commercial binders used in the foundry industry based on alkaline phenolic resin cured with esters and urea-formaldehyde resin with furfuryl alcohol cured with sulphonic acids. Before the binders were sent for testing, they were subjected to a hardening process, because in their hardened form they are degraded in real conditions, i.e. in contact with liquid metal.

Experimental

Materials

For the research were used three different binders used in foundry process (with one of innovative and

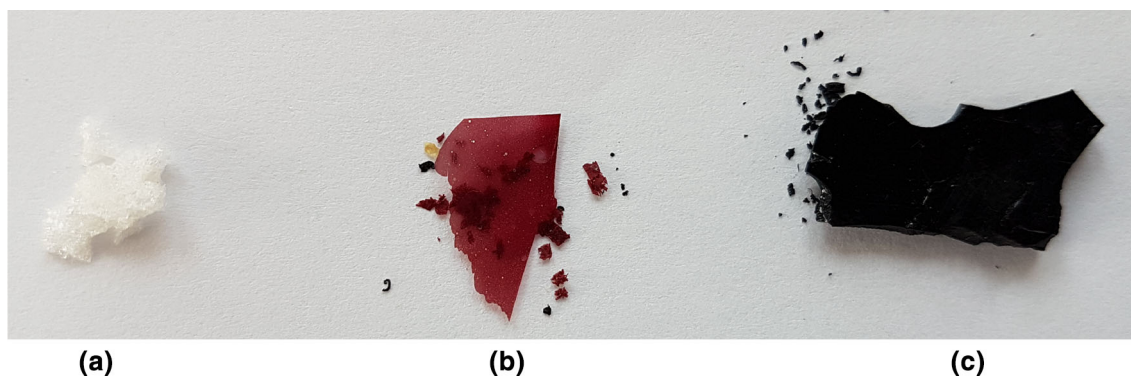


Fig. 1 Samples used in this study: **a** PAA/CMC-Na, **b** ARR, **c** UFR

Table 1 Characteristics of compositions and their cross-linking parameters

| Composition components | Hardening conditions |
|--|--|
| 60% aqueous solution of poly(acrylic acid) (PAA, 100 000 g mol ⁻¹ , BASF) and cellulose (CMC-Na, modified cellulose), in a mass ratio 7:8, pH 2 | Microwave device: RM 2001 Pc, Plazmatronica Microwave power of 800 W Frequency of 2.45 GHz Microwave action time: 60 s Temperature inside the device: 100 °C |

environmentally friendly). The samples were prepared in accordance with the manufacturer/inventor's guidelines and according to the appropriate proportions:

1. Polymer composition of poly(acrylic acid)–sodium carboxymethylcellulose (PAA/CMC-Na) (Fig. 1a). Their characterization and cross-linking condition PAA/CMC-Na is provided in Table 1.
2. Alkaline resol resin (ARR)—alkaline resol type phenolic resin “R” (33–50% of phenol), liquid binder cured with esters; hardener (activator) “H”—mixture of organic esters, liquid with a slight characteristic odour and medium curing time (Fig. 1b); proportion of mixture H:R = 1:5.
3. Urea-formaldehyde resin (UFR)—urea-formaldehyde resin “R” modified by furfuryl alcohol (content of a furfuryl alcohol is about 80%); hardened by mixture of sulphonic acid and inorganic acid (Fig. 1c); proportion of mixture H:R = 1:2.

The most important parameters of binders alkaline resol resin and urea-formaldehyde resin are presented in Table 2.

Thermal examinations

The thermal examinations were carried out using a Netzsch STA 449 F3 Jupiter[®] thermal analyser which supports

Table 2 Characterization of components of binders alkaline resol resin and urea-formaldehyde resin

| Parameters | ARR | UFR |
|-------------------------------------|-----------|-----------|
| <i>R</i> | | |
| Density in 20 °C/g cm ⁻³ | 1.55–1.65 | 1.20–1.30 |
| Viscosity/CST | 15–25 | 50–150 |
| Formaldehyde/% | 0.12–0.14 | < 0.2 |
| Nitrogen/% | 3–4 | – |
| Gelation time in 20 °C/min | 7–12 | 11–14 |
| <i>H</i> | | |
| Density in 20 °C/g cm ⁻³ | 1.22–1.24 | 1.09–1.28 |

simultaneous TG and DSC measurements, thus providing two independent signals recorded in the same measurement conditions, namely at/in the same temperature increase rate (10 °C min⁻¹) and atmosphere and gas flow rate (50 mL min⁻¹). The measurements for the sample were taken in an oxygen-free one (nitrogen). The sample submitted to the TG-DSC thermal analysis weighed approximately 15 mg. Crucibles with Al₂O₃ were used, as they allowed measurements up to 1000 °C.

Pyrolysis gas chromatography coupled with mass spectrometry

The pyrolysis gas chromatography mass spectrometry (Py-GC/MS) method is based on transforming a solid sample (4 mg) into gas by heating in an atmosphere of inert gas (helium) in a pyrolyzer “Py” (Pyroprobe 5000, CDS Analytical Inc., USA), which is accompanied by thermal decomposition. It has a platinum ribbon, which enables heating of a sample to any temperature within the range 240–1300 °C at a rate of up to 10,000 °C s⁻¹. The obtained mixture of compounds (pyrolysate) is separated on a chromatographic column (Rxi-5Sil MS columns, fused silica with low-polarity phase: Crossbond 1,4-bis(dimethylsiloxy)phenylene dimethyl polysiloxane,

Restek Corporation, USA) in a chromatograph “GC” (Focus GC, Thermo Scientific, USA). A temperature programme was applied: an initial temperature of 40 °C was held for 3 min; ramped 3 °C min⁻¹ up to 100 °C and held for 3 min, and then 250 °C with heating rate 20 °C min⁻¹ was maintained for 3 min. Carrier gas (helium) flow rate was 1 mL min⁻¹ and sample split ratio was 1:30. The separated compounds are analysed in a mass spectrometer “MS” (ISQ Thermo Scientific, USA) in the full range m/z. Electron ionization (70 eV) at a temperature of 250 °C was applied [36].

Results and discussion

TG–DTG–DSC analysis

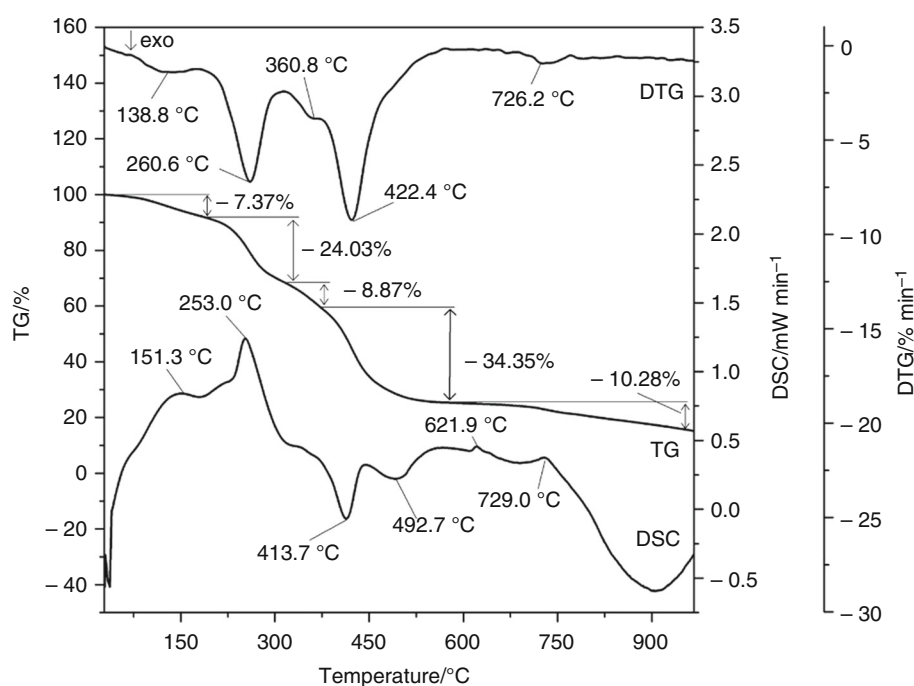
Figure 2 depicts the temperature-dependent mass change (TG), rate of mass change (DTG) and heat flow rate (DSC) of the polymer mixture PAA/CMC-Na. In total, five mass loss steps of 7.37%, 24.03%, 8.87%, 34.35% and 10.28% were observed. The maximal mass loss rates were obtained for the temperatures 138.8 °C, 260.6 °C, 360.8 °C, 422.4 °C and 726.2 °C which can be seen from the DTG signal. In correlation with the mass loss steps, different energetic effects occurred in the DSC signal. Three overlapping endothermic effects with peak temperatures of 151.3 °C, 253.0 °C, 621.9 °C and 729 °C occurred. The fourth mass loss step correlated with an exothermic peak at 413.7 °C and 492.7 °C.

As the temperature rises, physical and chemical changes occur due to evaporation of the solvent water (20–100 °C) and then of the structural water, and then intermolecular dehydration reactions (100–260 °C). Within this temperature range, mainly reversible processes occur. In the temperature range of 260–360 °C, polymer chains decompose, including the disintegration of side groups and glycoside bonds (from CMC-Na). In the temperature range of 360–700 °C, the polymer compositions decompose with the formation of gaseous products of destruction. The part of moulding sand which has not decomposed to about 900 °C may contain carbonized carbon. Based on the thermal analysis of TG–DTG–DSC for PAA/CMC-Na, the temperature range (450 °C, 700 °C, 800 °C) for Py-GC/MS method was determined for all tested binders.

Py-GC/MS analysis

Compounds found after pyrolytic decomposition for all studied samples: PAA/CMS-Na, ARR and UFR, are summarized in Tables 3–5. The comparison of the measured mass spectra to the National Institute of Standards Technology database (NIST MS Search 2.0) and own patterns (e.g. benzene, toluene) gave possible types for the released compounds. For some peaks, structural similar compounds (e.g. structural isomers) were found with high quality of probability. Some pyrolysis products which occupy large peak areas in the Py-GC/MS chromatograms (pyrogram, replaceable name) cannot be identified clearly because of the low matching quality in mass library. Resulting products are not decomposed under mild conditions of pyrolysis

Fig. 2 TG–DTG–DSC curves of PAA/CMC-Na composition



(from 250 to about 400 °C); therefore, exemplary chromatograms (pyrograms) in the selected temperature range: 450 °C, 700 °C and 800 °C, are shown in Figs. 3–5.

The strongest signal in the pyrogram of all tested samples is that corresponding to carbon dioxide emission (full range of temperature, Figs. 3–5). Sample ARR at 700 °C

Table 3 Compounds in the pyrogram of sample PAA/CMC-Na for selected temperature points/areas

| Peak no. | Name of compound | No. CAS | Mass weight/u | Retention time R_T /min | | | |
|----------|------------------|----------|---------------|---------------------------|--------|--------|--------|
| | | | | 250–650 °C | 700 °C | 750 °C | 800 °C |
| 1. | Carbon dioxide | 124-38-9 | 44 | 2–5 | 2.13 | 2.14 | 2.14 |
| 2. | 3-Methylfuran | 930-27-8 | 82 | – | – | 3.50 | 3.46 |
| 3. | Butan-2-one | 78-93-3 | 72 | – | 3.81 | 3.83 | 3.75 |
| 4. | Benzene | 71-43-2 | 78 | – | – | 4.60 | 4.60 |
| 5. | Toluene | 108-88-3 | 92 | – | – | 7.53 | 7.46 |

Table 4 Compounds in the pyrogram of sample ARR for selected temperature points/areas

| Peak no. | Name of compound | No. CAS | Mass weight/u | Retention time R_T /min | | | | |
|----------|----------------------------|----------|---------------|---------------------------|------------|------------|--------|--------|
| | | | | 250–450 °C | 500–600 °C | 650–700 °C | 750 °C | 800 °C |
| 1. | Carbon dioxide | 124-38-9 | 44 | 1.7–2.14 | 2.10 | 2.09 | 2.11 | 2.10 |
| 2. | 2-Methylfuran | 534-22-5 | 82 | – | – | 3.38 | 3.38 | 3.34 |
| 3. | Benzene | 71-43-2 | 78 | – | 4.55 | 4.55 | 4.52 | – |
| 4. | Toluene | 108-88-3 | 92 | – | 7.46 | 7.40 | 7.43 | 7.32 |
| 5. | Ethylbenzene | 100-41-4 | 106 | – | 11.49 | 11.49 | 11.49 | – |
| 6. | <i>m</i> -Xylene | 108-38-3 | 106 | – | 11.63 | 11.66 | 11.64 | – |
| 7. | Phenol | 108-95-2 | 94 | – | 13.45 | 13.51 | 13.51 | – |
| 8. | Styrene | 100-42-5 | 104 | – | 13.62 | 13.68 | 13.66 | – |
| 9. | Indene | 95-13-6 | 116 | – | 22.53 | 22.60 | – | – |
| 10. | Naphthalene | 91-20-3 | 128 | – | 28.99 | 29.03 | – | – |
| 11. | Benzo[<i>c</i>]thiophene | 270-82-6 | 134 | – | 29.42 | 29.45 | – | – |

Table 5 Compounds in the pyrogram of sample UFR for selected temperature points/areas

| Peak no. | Name of compound | No. CAS | Mass weight/u | Retention time R_T /min | | | | | |
|----------|----------------------------|-----------|---------------|---------------------------|--------|------------|------------|--------|--------|
| | | | | 250–400 °C | 450 °C | 500–600 °C | 650–700 °C | 750 °C | 800 °C |
| 1. | Carbon dioxide | 124-38-9 | 44 | 1.5–2.5 | 2.11 | 2.10 | 2.10 | 2.09 | 2.11 |
| 2. | Hydrogen sulphide | 7783-06-4 | 34 | – | – | 2.19 | 2.17 | 2.18 | – |
| 3. | Carbon disulphide | 75-15-0 | 76 | – | – | 2.89 | 2.90 | 2.92 | – |
| 4. | 2-Methylfuran | 534-22-5 | 82 | – | 3.39 | 3.38 | 3.38 | 3.38 | 3.34 |
| 5. | Benzene | 71-43-2 | 78 | – | – | 4.55 | 4.54 | 4.52 | – |
| 6. | Toluene | 108-88-3 | 92 | – | 7.41 | 7.45 | 7.44 | 7.43 | 7.32 |
| 7. | Ethylbenzene | 100-41-4 | 106 | – | – | 11.46 | 11.50 | 11.49 | – |
| 8. | <i>m</i> -Xylene | 108-38-3 | 106 | – | – | 11.63 | 11.65 | 11.64 | 11.59 |
| 9. | Phenylethyne | 536-74-3 | 102 | – | – | 13.45 | 13.52 | – | – |
| 10. | Styrene | 100-42-5 | 104 | – | – | 13.61 | 13.67 | 13.64 | – |
| 11. | Indene | 95-13-6 | 116 | – | – | 22.53 | 22.60 | – | – |
| 12. | Naphthalene | 91-20-3 | 128 | – | – | 28.98 | 29.05 | – | – |
| 13. | Benzo[<i>c</i>]thiophene | 270-82-6 | 134 | – | – | 29.42 | 29.45 | – | – |
| 14. | Biphenyl | 92-52-4 | 154 | – | – | 31.60 | – | – | – |
| 15. | Acenaphthylene | 208-96-8 | 152 | – | – | 32.47 | – | – | – |
| 16. | Bibenzyl | 103-29-7 | 182 | – | – | – | 32.70 | 32.69 | – |

Thermal degradation products of chromatographic column

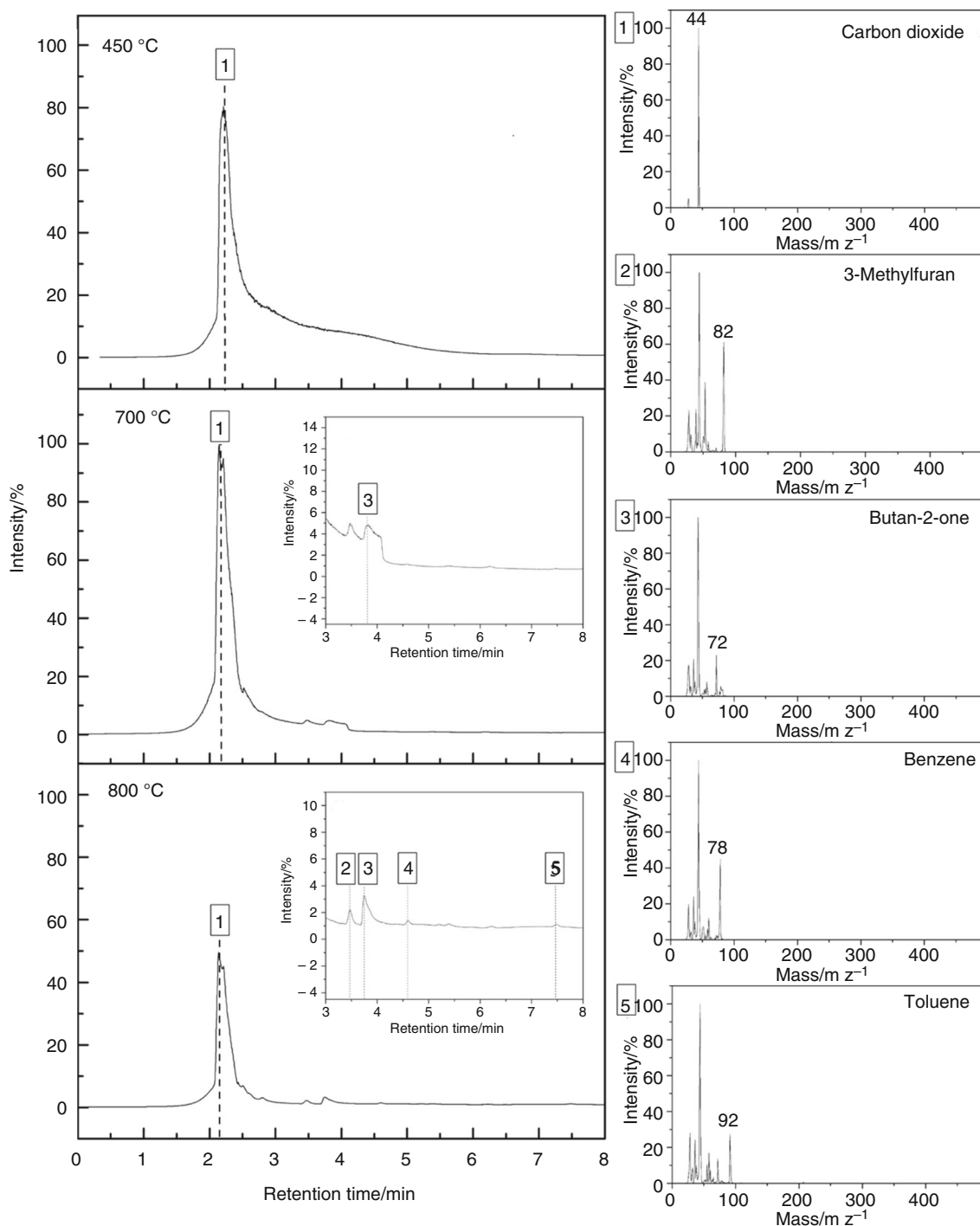


Fig. 3 Pyrograms of sample PAA/CMC-Na in full range of temperature: 450 °C, 700 °C, 800 °C

observed new small signal from butan-2-one. At the temperature range of 750–800 °C, other new signals correspond to 3-methylfuran, benzene and toluene (Fig. 3). Observed signals (except carbon dioxide) are quite weak, and as a result of pyrolysis, very few compounds are released from the sample (Table 3).

In the pyrograms (Figs. 4, 5) of samples, ARR and UFR are more expanded. Among those identified pyrolysis compounds of samples ARR and UFR, the main signals correspond to large group of aromatic hydrocarbons from groups BTEX and PAH (polycyclic aromatic hydrocarbons).

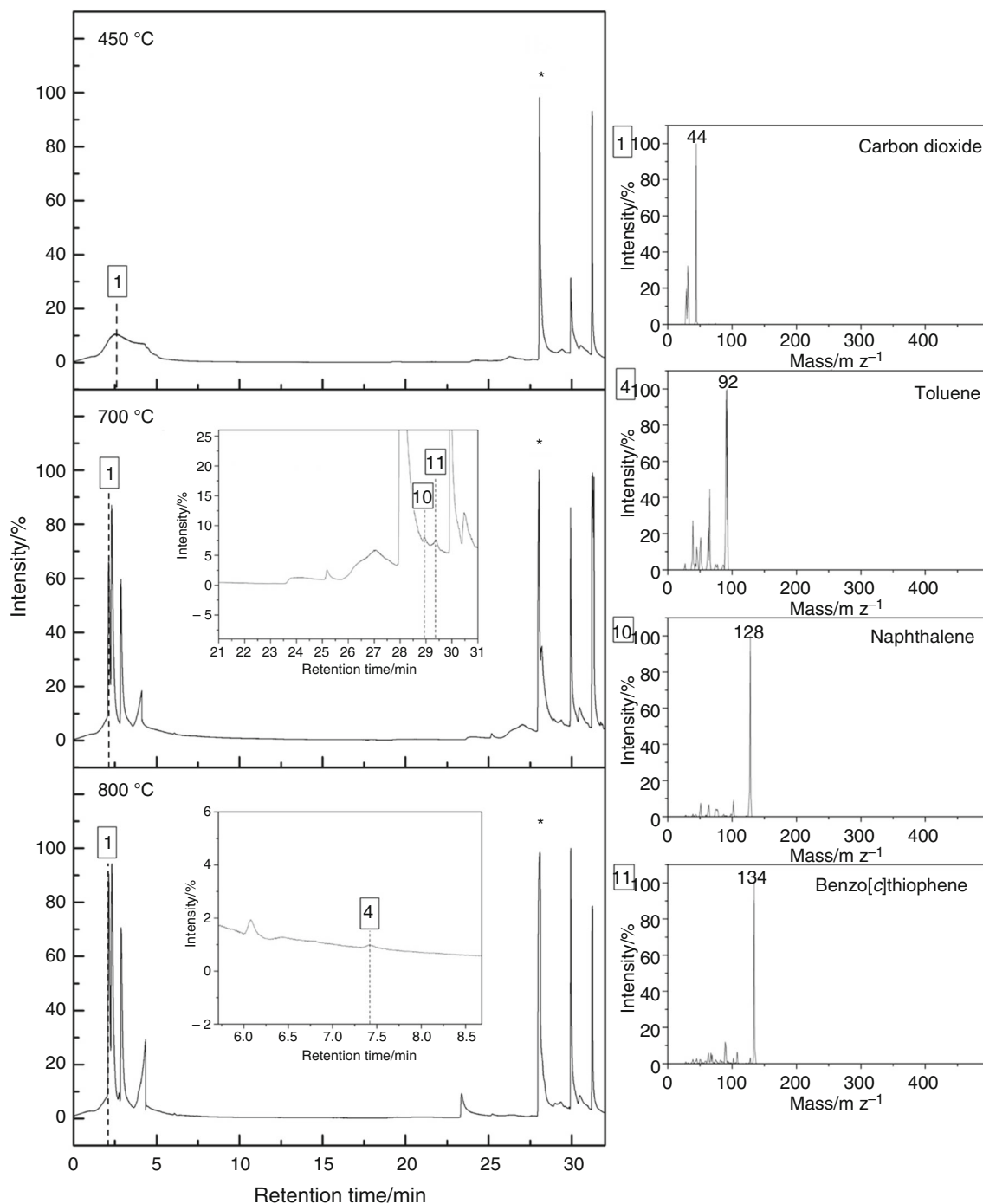


Fig. 4 Pyrograms of sample ARR in full range of temperature: 450 °C, 700 °C, 800 °C

The decomposition of sample ARR released mainly aromatic hydrocarbons like benzene, phenol and their derivatives and the low-volatile compounds (Table 4). In the temperature range from 250 to 450 °C, no significant changes are observed. The temperature range 500–700 °C observed a lot of signals from aromatic hydrocarbons group (Fig. 4). The highest signal is from benzene and toluene. Other signals correspond to 2-methylfuran, ethylbenzene,

m-xylene, phenol (main compound of sample ARR), styrene, indene, naphthalene and benzo[*c*]thiophene. At 800 °C, most of signals disappeared. (It may be related to their total degradation.) The compounds identified in this sample are connected to chemical composition of thermal decomposition of resole resin [32].

The comparison of the pyrograms samples ARR and UFR did not give significant difference in aromatic

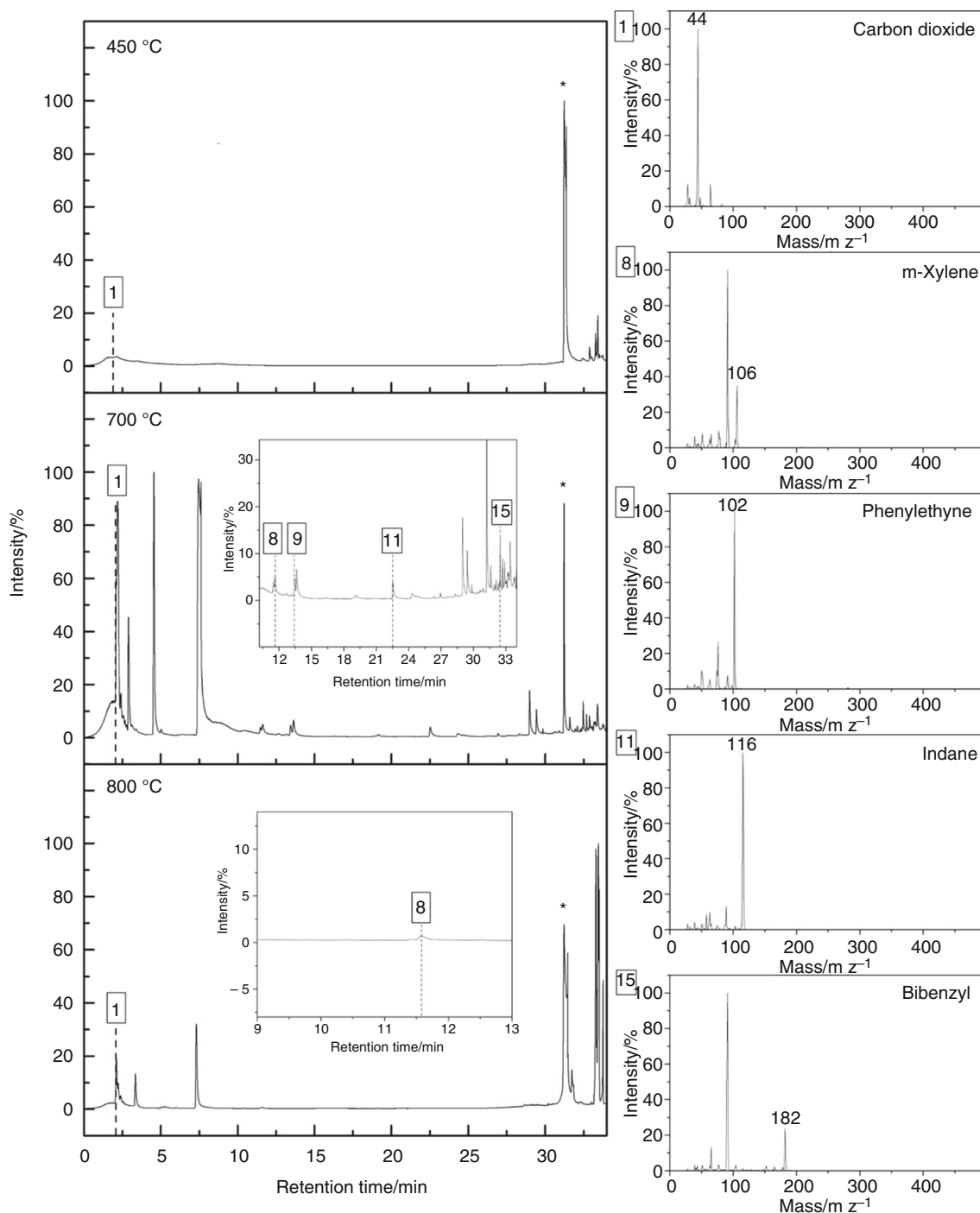


Fig. 5 Pyrograms of sample UFR in full range of temperature: 450 °C, 700 °C, 800 °C

hydrocarbons area, probably only in concentration of released compound (Table 5). The temperature range 500–700 °C observed a lot of signals from aromatic hydrocarbons group (Fig. 5) and also compounds like hydrogen sulphide carbon disulphide (component of sample UFR, hardener for resin). The highest signal is from benzene and toluene like in sample ARR. Other signals correspond to similar compounds from sample ARR

2-methylfuran, ethylbenzene, *m*-xylene, styrene, indene, naphthalene and benzo[*c*]thiophene. A few new ones are also identified—phenylethyne, biphenyl, acenaphthylene and bibenzyl. At 750 °C and 800 °C, most of signals disappeared. Only toluene, 2-methylfuran, *m*-xylene are visible.

Py-GC/MS was found to be appropriate method for assessment of changes taking place during pyrolysis of

tested samples of foundry binders. Results indicate that during the pyrolysis process only one of these samples is friendly to environment (PAA/CMC-Na). The changes in type and emission of these compounds in samples ARR and UFR are small. The presented results of the Py-GC/MS measurements show that the applied analytic methods are feasible to perform only a qualitative characterization of the binder samples (due to the construction of pyrolyzer). In the temperature range up to 450–500 °C, mainly carbon dioxide emissions are observed, related to the decomposition of carbonates (components of tested samples). At the temperature above 500 °C, secreted compounds are mainly volatile aromatics from BTEX and PAH groups or phenol (component of sample ARR). Most of these compounds belongs to group of high risk and pose a threat to humans and the environment. The highest concentration of hazardous and dangerous substances in gas form occurs during the mould pouring with liquid metal (mainly cast iron). Gases emitted to the atmosphere should be neutralized (e.g. scrubbers, filters with active carbon). In addition, it can be concluded that the PAA/CMC-Na polymeric binder is characterized by the lowest emission level of gaseous products in a given temperature range.

Conclusions

The sample of a foundry binder in the form of a poly(-acrylic acid)-sodium carboxymethylcellulose polymer composition has been subjected to thermal analysis of TG–DTG–DSC in order to determine the course of its thermal destruction taking into account temperature ranges in which mass losses and gaseous decomposition products occur. It was found that with the temperature rise, there are physical and chemical changes associated with the evaporation of solvent water, release of constitutional water, intermolecular dehydration, and then decomposition of polymer chains with the formation of gaseous products of destruction. On the basis of the thermal analysis for the PAA/CMC-Na polymer composition, the temperature ranges (450 °C, 700 °C, 800 °C) in which the pyrolysis gas chromatography with mass spectrometry will be performed. In addition, commercial samples of two foundry binders (alkaline resol resin and urea-formaldehyde resin) were included in the study, which allowed to compare their emission levels and the type of gaseous decomposition products.

It was found that the course of degradation with the release of gaseous hydrocarbon products, including BTEX and their derivatives for commercial binders based on ARR and UFR resins, is similar in a given temperature range, with the most signals on pyrograms observed in the 500–700 °C temperature range. The highest signal comes

from benzene and toluene for the ARR sample. In the temperature range of 750–800 °C, most of the signals disappear; however, the signal from toluene, 2-methylfuran and *m*-xylene is still visible.

Based on the conducted research, it can be concluded that pyrolysis gas chromatography mass spectrometry method is suitable for assessing the changes occurring during the pyrolysis of foundry binders. In combination with thermal analysis, TG–DTG–DSC gives the possibility of full assessment of emission levels and gaseous products released.

The results obtained indicate that only one of these samples is environmentally friendly during the pyrolysis process. It is a sample of a new polymer binder from the BioCo group (PAA/CMC-Na). The type and emission of gaseous products is small compared to the observed emission level in ARR and UFR samples. The presented results of Py-GC/MS measurements confirm that the applied analytical methods are only able to perform the qualitative characteristics of binder samples. In the lower temperature range of 250–500 °C, mainly CO₂ emissions are observed. Above 500 °C, the observed compounds are mainly volatile aromatics from the BTEX and PAH groups, and phenol, which is the main component of the ARR sample.

It is important to note that most of the emitted compounds belong to the high-risk group and pose a threat to people and the environment, with the highest concentration of hazardous and dangerous gaseous substances occurring during casting process. In this context, the obtained knowledge can be the basis for undertaking work on reducing and optimizing the process of neutralizing the gases emitted during casting process, when the mould has the contact with liquid metal.

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