

TG-DTG-DSC, FTIR, DRIFT, and Py-GC-MS Studies of Thermal Decomposition for Poly(sodium acrylate)/Dextrin (PAANa/D) – New Binder BioCo3

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Abstract

TG-DTG-DSC, FTIR, DRIFT, and Py-GC-MS studies have been conducted to determine the effect of the thermal decomposition conditions and structure of foundry binder BioCo3 in the form of a composition poly(sodium acrylate)/dextrin (PAANa/D) on the progress of degradation in terms of processes occurring in foundry sands in contact with liquid metal. TG-DTG-DSC curves of the composition allowed us to determine the temperature range in which they do not undergo degradation, by which they do not lose their binding properties. With temperature increasing, physical and chemical changes occur that are related to the evaporation of solvent water (20–110°C), followed by the release of constitution water, and finally intermolecular dehydration (110–230°C). In this temperature range, processes that are mainly reversible take place. Within a temperature range of 450–826°C, polymer chains are decomposed, including the decomposition of side chains. Within a temperature range of 399–663°C, polymer composition decomposition can be observed (FTIR, DRIFT), and gas products are generated from this destruction (Py-GC-MS).

Keywords:

polymer binders, foundry sands, thermal analysis, TG-DTG-DSC, FTIR, Py-GC-MS, thermal degradation

1. INTRODUCTION

One of the most important challenges in casting processes engineering is skilfully planning the composition of molding sand, in which the binding material (binder) is the key component. The binder serves an important role in foundry technology; it not only has the ability to bind the sand grains and provide a specified mechanical strength to loose sand, but it also influences decides the technology influence with this binder on the environment [1]. The binder may be crosslinked in the molding sand by physical or chemical agents so that its bonding strength in the binder-sand system would be sufficient to maintain the desired shape of the molding sand (form) while pouring it with liquid metal; as a result, it could be possible to receive a cast without any defects [2, 3]. Chemical cross-linking agents supplement the mixture of molding sand, but their presence often intensifies the negative impact of technology on the environment [4, 5]. For this reason, using new binders based on synthetic and natural polymers in the technology of foundry clearly brings a lot of benefits. However, there is a question as to how it behaves under the influence of sudden increases in temperature during the production of castings. Particularly

important are the issues associated with determining the process of degradation and destruction [6, 7]. In addition, another important issue is the determination of the influence of gas products created during thermal destruction on the quality of the final cast as well as on the environment [8, 9].

After thermal analysis, polymer binder BioCo3 belongs to a new group of binding materials that are ternary polymer compositions containing water and a synthetic polymer that comes from an acrylic polymers group (poly (acrylic acid) – PAA or poly(sodium acrylate) – PAANa) and modified polysaccharide (sodium salt carboxymethyl – CMS, dextrin – D) [10, 11]. The polymer compositions that are being considered are complex systems, and analysis of thermal degradation requires extensive knowledge within the scope of the literature related to the thermal properties of initial polymer components [12–16].

On the basis of literature data, it can be concluded that the thermal degradation of acrylic polymers often proceeds specific cross-linking reactions, which is revealed in the occurrence of endothermic effects within a temperature range of 120–180°C on the DSC curves. These effects are related to dehydration and the formation of short

polymer chains [12, 13]. In the case of polysaccharides within a temperature range of 300–450°C, weak bonds of C-O-C and C-C in the glycoside ring can fall apart. Then, as the temperature rises, it starts a reaction of detaching the side groups that, in conjunction with the breaking of C-O bonds, leads to the depolymerization of the chain. The final effect (at approximately 500°C) comes with the total destruction of the dehydrated polymer and the forming of volatile products and charred material [14–16].

2. EXPERIMENTAL

2.1. Material

Thermal analysis involving the BioCo3 binder as polymer composition of poly(acrylic acid) and dextrin (PAANA/D, Fig. 1) cross-linked with microwave radiation.

Characterization and cross-linking conditions of PAANA/D are provided in Table 1.

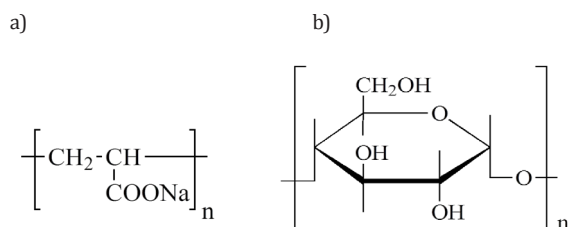


Fig. 1. Structural formula of a) poly(sodium acrylate) and b) dextrin

Table 1
Characteristics of compositions and their cross-linking parameters

BioCo3 – composition PAANA/D	Hardening conditions
40% aqueous solution of poly(sodium acrylate) (PAANA, BASF) and dextrin (D, modified potato starch, Fluka), at a weight ratio of 9:8, pH 8.5.	Microwave device: Samsung MG23H3125NK
	Microwave power of 800 W
	Frequency of 2.45 GHz
	Microwave action time: 60 s Temperature inside the device: 100°C

Polymer composition PAANA/D after cross-linking in the microwaves field was used for the thermo-analytical research (TG-DTG-DSC, Py-GC-MS). In addition, structural tests (FTIR) were conducted on a sample heated to a temperature range of 20–826°C. The heating of PAANA/D was carried out in a SNOL 7.2/1300 oven with a velocity of heating of about 10°C/min. The total time of the heating process of the sample in the oven was 80 min.

2.2. Examinations

TG-DTG-DSC

The thermal examinations were carried out using a NETZSCH STA 449 F3 Jupiter® thermal analyzer, which supports simultaneous TG and DSC measurements (thus

providing two independent signals recorded in the same measurement conditions; namely, at the same temperature increase rate (10°C/min), atmosphere and gas flow rate (40 ml/min). Measurements for the sample were taken in both oxidizing (air) and oxygen-free (argon) atmospheres. The sample submitted to the TG-DSC thermal analysis weighed approximately 15 mg. Platinum crucibles were used, as they allowed for measurements up to 1000°C.

FTIR and DRIFT

The research was conducted by using the transmission technique (with KBr pellets) and DRIFT with the use of a Digilab Excalibur FTS 3000 Mx spectrometer. A potassium bromide mixture (about 200 mg) with an adequate amount of the researched sample was pressed in a hydraulic press in a special matrix. The spectrum was recorded by the Resolution Pro program, with an infrared radiation range of 4000–400 cm⁻¹ with a power of resolution of 4 cm⁻¹. The preparation of samples involved heating continuously at a set temperature in a Snol Lab 7.2/1300 oven with a rate of heating of about 10°C/min. The time for achieving the highest temperature point (826°C) was 80 min. The study of FTIR-DRS with the DRIFT method was made by using a water-cooled high-temperature attachment coupled with a temperature controller, with the possibility of heating the sample to a temperature of 500°C. Registration of the spectra was carried out within a range of 4000–600 cm⁻¹, with the ability to dash 8 cm⁻¹. The time of receiving the set temperature was as follows (respectively):

- 20–148°C (45 s),
- 148–298°C (105 s),
- 298–450°C (240 s),
- 450–495°C (900 s).

The total measurement time was 21 min and 30 s.

Py-GC-MS

The pyrolysis gas chromatography (Py-GC/MS) method is based on transforming a solid sample (2–3 mg) into gas by heating in an atmosphere of inert gas (helium) in a pyrolyzer “Py” Pyroprobe 5000 (CDS Analytical Inc.), which is accompanied by thermal decomposition. It has a platinum ribbon, which enables the heating of a sample to any temperature within a range of 240–1300°C. The obtained mixture of compounds (pyrolysate) is separated on a chromatographic column in a chromatograph “GC” (Focus GC, Thermo Scientific). A temperature program was applied: an initial temperature of 40°C was held for 3 min; ramped 3°C/min up to 100°C and held for 3 min, and then 250°C with a heating rate of 20°C/min was maintained for 3 min (helium carrier gas at 1 ml/min, sample split ratio 1:30). The separated compounds are analyzed in a mass spectrometer “MS” (ISQ Thermo Scientific) in the full range mass number/

charge number (m/z). Electron ionisation (70 eV) at a temperature of 250°C was applied.

3. RESULTS AND DISCUSSION

TG-DTG-DSC

In an oxidizing atmosphere (air), decomposition of the cross-linked PAANA/D polymer composition occurs with five weight losses (Fig. 2).

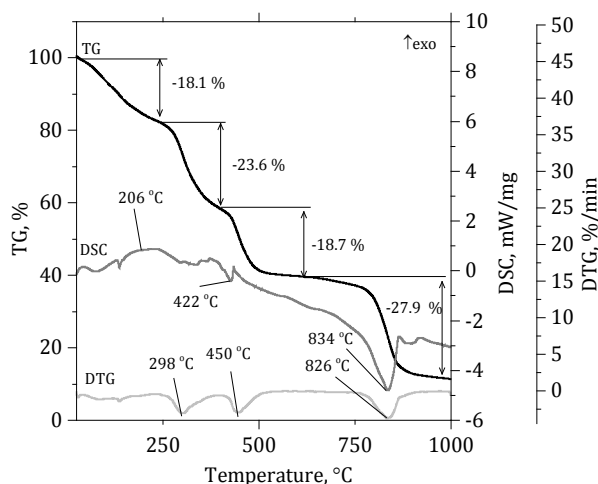


Fig. 2. TG-DTG-DSC curves of composition PAANA/D in oxidizing atmosphere

Within a temperature range of 20–110°C, the remains of the solvent water evaporate, followed by the constitution water. Next, within a temperature range of 110–230°C, the intermolecular dehydration reaction takes place. In this temperature range, mainly reversible processes occur: physical transformations and reversible reactions. On the basis of TG curves, it can be stated that the thermal degradation process starts at a temperature of approx. 230°C. Next, polymer chains decompose, including the decomposition of side chains and glycosidic bonds. Further on, progressive decomposition takes place with the intensive generation of gas products of destruction, including combustion reactions in an oxygen atmosphere. At the DSC curve at temperature of 452°, 552°, and 822°C, there are three exothermic effects visible (which may be the result of the PAANA/D combustion process). Moreover, three peaks can be noticed at the DTG curve: 300°C, 450°C, and 522°C. A sample of the composition PAANA/D almost completely decomposes to a temperature of 1000°C (residual sample mass – 28.6 %).

In the oxygen-free atmosphere (argon), the PAANA/D decomposition process is different (Fig. 3). At the TG curve of the composition, four weight losses (Δm) can be observed, while three endothermic effects are visible at the DSC curve. At the DTG curve, one can notice three peaks: 298°C, 450°C and 826°C. The residual part of the composition sample mass (approx. 11.7 %) probably contains carbonized carbon and low-molecular-weight compounds with sodium atoms, which means that BioCo3 did not decompose at a temperature of 1000°C.

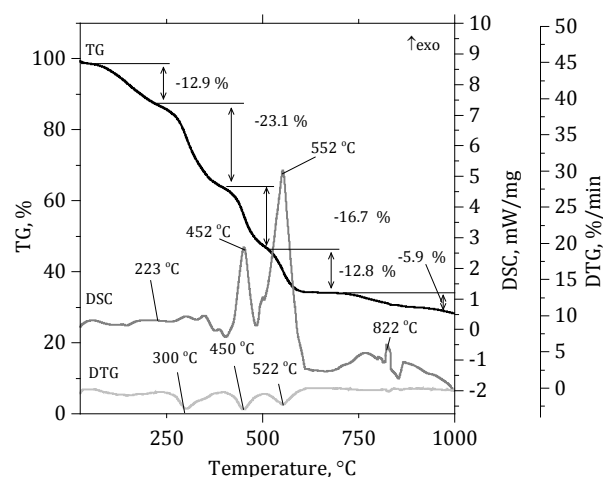


Fig. 3. TG-DTG-DSC curves of PAANA/D composition in argon atmosphere

FTIR and DRIFT

Figures 4 and 5 show the IR spectra for the PAANA/D recorded at a temperature range of 20–826°C. The PAANA/D composition was heated in the oven, and its sample used for the FTIR tests was collected at specific temperatures. Spectroscopic studies in infrared were carried out with the FTIR method (Fig. 4) and DRIFT method (Fig. 5). The temperature values in which the IR spectrum was recorded were 298°C, 450°C, 552°C, 826°C. The temperature was determined on the basis of observed mass losses and the thermal effects on the course of TG-DTG-DSC curves. The PAANA/D sample was heated in the oven to the set temperature; then, the next spectrum was recorded.

On the IR spectra obtained by the FTIR and DRIFT methods (Figs. 4 and 5, respectively), a wide band within a range of wavenumbers 3800–3000 cm^{-1} corresponds to the vibration of a free group (OH) from water and from the existence of hydrogen bonds. At a temperature of 298°C, a lower intensity of this band can be observed; this is connected with the solvent and evaporation of constitutional water. In addition, a change in band shape at around 1570 cm^{-1} and the forming of a new band (1735 cm^{-1}) shows a progressive reaction caused by the higher temperature (Fig. 4).

The band corresponding to the wavenumbers at around 1735 cm^{-1} (FTIR – Fig. 4) and 1740 cm^{-1} (DRIFT – Fig. 5) indicates the presence of carbonyl groups (C=O), which corresponds to the following chemical changes associated with the formation of new compounds in the thermal degradation process. This temperature range also creates a reaction of dehydration with the formation of the anhydride groups – for this reason, some changes in the spectrum can be observed. Two bands at around 1456 cm^{-1} and 1408 cm^{-1} are assigned to the symmetric stretching vibration of C–H bonds that occurs in the structure of PAANA/D (Fig. 4). At a temperature of 450°C, a new band is formed in the same range with wavenumber 1430 cm^{-1} , and then it moves towards higher numbers (1437 cm^{-1}).

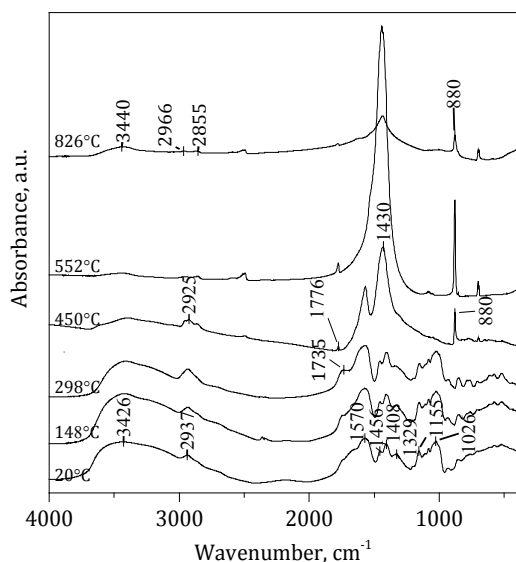


Fig. 4. IR spectra of PAANa/D obtained by FTIR method

These changes indicate chemical changes within the carbon skeleton (-C-C-C-) related to the breaking of hydrocarbon chains. Also, the change of the position of band $2937\text{ cm}^{-1} \rightarrow 2925\text{ cm}^{-1}$ indicates changes in the hydrocarbon chain. The band with its peak near wavenumber 1329 cm^{-1} is assigned to the O-H group stretching vibration (IR spectrum recorded at a temperature of 20°C). At a temperature of 450°C , this band is lost; this is associated with degradation of the hydroxyl groups. In addition, the appearance of two new bands is noticed on the IR spectrum obtained by the DRIFT method for the PAANa/D sample heated at 450°C (Fig. 5); one at 2463 cm^{-1} , and an intensive band at 2360 cm^{-1} . These bands can also be attributed to the new hydrocarbon systems.

Additionally, three new bands appear at 826°C (IR spectrum obtained by the FTIR method): 3400 cm^{-1} , 2966 cm^{-1} , and 2855 cm^{-1} are associated with the aromatic C-H out-of-plane bending vibrations. The occurrence of these bands indicates the progressive formation of aromatic compounds. In addition, the band at 880 cm^{-1} that were observed on the spectra also shows the formation of some new aromatic compounds.

Py-GC-MS

In order to obtain further information regarding the thermal decomposition of PAANa/D in the context of the impact on the environment of molding sand bonded by the BioCo3 binder, a coupled analytical technique was used in these studies: pyrolytic gas chromatography coupled with mass spectroscopy (Py-GC-MS). Application of the Py-GC-MS method made it possible to submit gaseous products formed in the process of PAANa/D destruction for qualitative analysis. The temperature values in which decomposition has been carried out (as in the case of the IR measurements) were selected on the basis of thermal analysis TG-DTG-DSC curves. Figure 6 shows the chromatograms recorded for the PAANa/D sample submitted for pyrolysis at 298°C , 450°C , 552°C and 826°C .

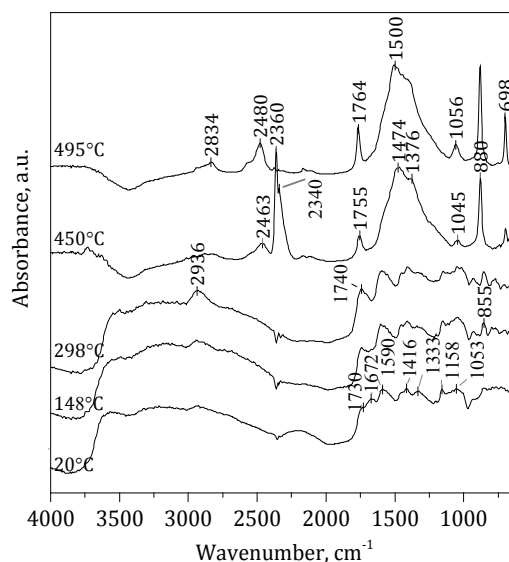


Fig. 5. IR spectra of PAANa/D obtained by DRIFT method

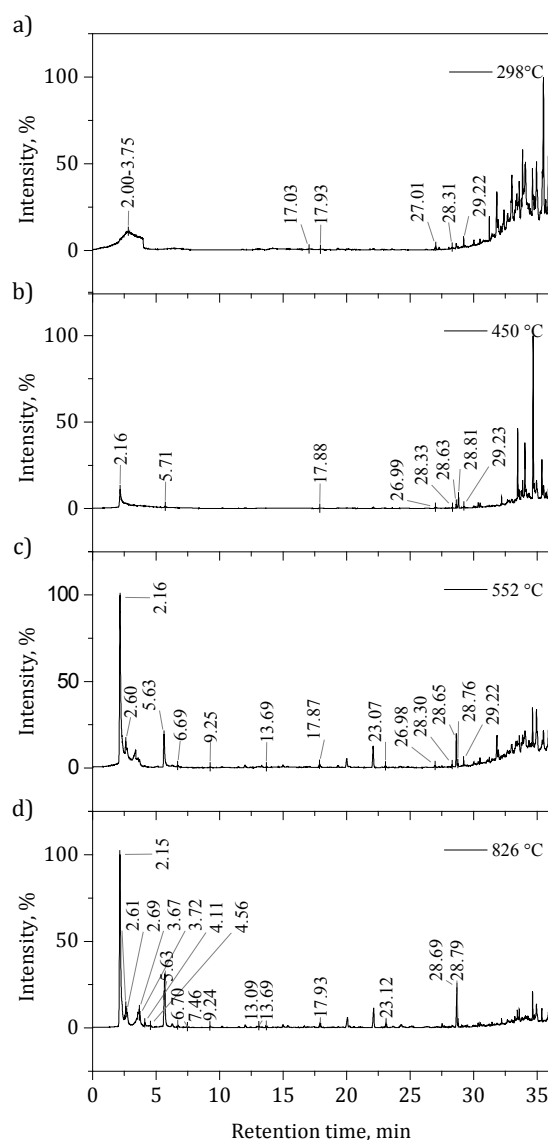


Fig. 6. Chromatograms obtained for PAANa/D samples at the following temperature: a) 298°C ; b) 450°C ; c) 552°C ; d) 826°C

Table 2 depicts the results of the qualitative analysis. Qualitative analysis was carried out with the use of the 2.2 Xcalibur (NIST MS Search 2.0) program.

Table 2
Results of Py-GC-MS investigations

Compounds	M _w *	Retention time RT, min			
		298°C	450°C	552°C	826°C
Carbon dioxide	44	2-3,75	2,16	2,16	2,15
Isopropyl alcohol	60	-	-	-	2,61
Ethanoic acid	60	-	-	-	3,67
Glycolaldehyde	60	-	-	-	3,72
Hydroxymethyl-cyclopropane	72	-	28,63	28,65	28,69
Methoxyacetaldehyde	74	-	-	2,60	4,11
Acetol	74	-	5,71	5,63	5,63
Benzene	78	-	-	-	4,56
Cyclopentenone	82	-	-	13,69	13,69
2-butanone	88	-	-	6,69	6,70
1-hydroxy-2-butanone	88	-	-	9,25	9,24
2-Propanone	88	-	-	-	2,69
Toluene	92	-	-	-	7,46
2-Hydroxycyclopent-2-en-1-one	98	17,93	17,88	17,87	17,93
2-Cyclopenten-1-one	112	-	-	23,07	23,12
Hexanoic acid	116	17,03	-	-	-
Levoglucosenone	126	-	28,81	28,76	28,79
Octanoic acid	144	27,01	26,99	26,98	-
Nonanoic acid	158	29,22	29,23	29,22	-
Dodecanoic acid	216	28,31	28,33	28,30	-

*M_w - molecular weight, u

At 298°C, carbon dioxide, 2-hydroxycyclopent-2-en-1-one, and carboxylic acids were found. At 450°C, hydroxymethylcyclopropane, acetol, and levoglucosenone were also formed. At 552°C (with the aforementioned, methoxyacetaldehyde, cyclopentenone, and 2-butanone), 1-hydroxy-2-butanone and 2-cyclopenten-1-one are also created. Based on the compiled results, it can be concluded that the compounds from the aromatic hydrocarbon group are only generated at 826°C. At this temperature, some marks of benzene, toluene, ethyl benzene, xylene, and naphthalene decomposition were found in the products. There was no sign of the existence of carboxylic acids.

4. CONCLUSIONS

On the basis of the obtained results of TG-DTG-DSC, FTIR, DRIFT, and Py-GC-MS, it can be stated that the course of decomposition is a complex process, which is a result of the structure as well as the physical and chemical properties of the analyzed BioCo3 binders in form composition of PAANA/D. With a temperature increase, physical and chemical changes occur in the analyzed sample of the polymer PAANA/D composition.

Within the temperature range of 20–110°C, the

evaporation of physically bound water occurs, followed by constitution water; and above a temperature of 110°C, an intermolecular dehydration reaction takes place with the formation of intermolecular anhydride bonds, which is characteristic of the thermal decomposition of poly(acrylic acid). Above a temperature of 450°C, intensive cracking of the chemical bonds occurs, which results in the breaking of most bonds. The process becomes massive, which has an effect of releasing volatile low-molecular-weight inorganic (CO₂) and organic compounds, and finally leads to the complete degradation of BioCo3.

Knowledge about the thermal stability of BioCo3 obtained from the studies of the TG-DTG-DSC, FTIR, and Py-GC-MS thermal analysis methods has allowed us to identify the process of PAANA/D degradation in the context of its use as a binder in molding sand. This allows us to better understand the phenomena that constantly occur in molding sand bonded by polymer binder BioCo3 during the process of pouring the mold with liquid metal.

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