

Thermal analysis in foundry technology

Part 1. Study TG–DSC of the new class of polymer binders BioCo

Beata Grabowska¹ · Paweł Malinowski¹ · Michał Szucki¹ · Łukasz Byczyński²

Received: 17 October 2015 / Accepted: 30 March 2016 / Published online: 18 April 2016
© The Author(s) 2016. This article is published with open access at Springerlink.com

Abstract TG–DSC thermal analysis involved two new BioCo foundry binders in the form of a composition with poly(acrylic acid) and modified polysaccharides (dextrin, sodium salt of carboxymethyl starch). Thermal analysis was conducted to determine the effect of the thermal decomposition conditions and polymer structure on the progress of degradation in terms of processes occurring in the foundry sands, when they contact with liquid metal. Thermal analysis of the composition allowed for determining the temperature range where they do not undergo degradation, by which they do not lose their binding properties. It was evidenced that the course of thermal decomposition is complex (mixed degradation mechanism). With temperature increase, physical and chemical changes occur, related to evaporation of solvent water (20–100 °C) and next release of constitution water, while finally intermolecular dehydration (100–220 °C). In this temperature range, mainly reversible processes take place. Within the temperature range of 220–300 °C, polymer chains decompose, including decomposition of side chains and glycosidic bonds. Within the temperature range of 300–500 °C, polymer compositions decompose, and gas products of destruction are generated. A part of the compound that did not decompose at the temperature of approx 550 °C can contain carbonised coal. It was evidenced that

if the composition includes sodium atoms, inorganic compounds are formed which decompose at the temperature of approx 800 °C.

Keywords Polymer binders · Foundry sands · Thermal analysis · TG–DSC · Thermal degradation

Introduction

Sand casting is currently among the most developing fields of producing parts for machinery and equipment. It is a broad section of industry that uses the knowledge of many often separate fields of science, such as material engineering, metallurgy, chemistry, environmental protection, computer modelling, or mechanics. The key challenge in the foundry technology is the attainment of good quality large-sized castings, masses of which often reach several dozen tonnes. Cast parts of iron and steel are used in the energy, shipyard, and machine industries [1]. Due to large sizes, often complicated shapes, and single-time nature of the production, forging is a highly advanced field, which requires application of specialist tools and solutions, including the appropriate technological process supported with the results of computer simulations [2, 3]. Therefore, major challenges in the foundry processes include the development of new technologies using environment-friendly materials, as well as skilful planning of the foundry sands, the key component of which is the binder. The binder has the capacity of binding matrix particles and provides the bulk sand with a specific mechanical strength [4]. The binder in the compound is cross-linked with physical or chemical agents, so that the binding strength in the binder matrix system is sufficient to keep the predefined shape to the foundry sands (mould) when it is cast with

✉ Beata Grabowska
beata.grabowska@agh.edu.pl

¹ Faculty of Foundry Engineering, AGH - University of Science and Technology, Reymonta 23, 30 059 Kraków, Poland

² Faculty of Chemistry, Rzeszow University of Technology, Al. Powstańców Warszawy 6, 35 959 Rzeszow, Poland

liquid metal, and as a result to obtain a defect-free casting [5, 6].

The development of a new binder and its implementation in the fully operating industrial cycle requires, however, broad primary research. The research involves the preliminary development of the binder composition, its cross-linking mechanism, including the capacity of binding matrix particles [6]. The application of a new binder based on synthetic and natural polymers in the foundry technology undoubtedly brings along many benefits, yet raises a question as to its behaviour under the impact of a sudden temperature shock, while casting. Issues related to the determination of the degradation process and the accompanying thermal effect are particularly important here [7]. Moreover, significant issues include determination of the impact of gas products generated during thermal decomposition on the final cast quality and the environmental impact [8, 9]. Thermal analysis carried out within this study will, therefore, allow for determining the degradation process of the polymer binder (Part 1 of the publication) in order to better understand the phenomena occurring in the foundry sands bound with a polymer binder during the process of sand casting with liquid metal; this research area is the subject of Part 2 of this publication.

This paper presents TG–DSC analysis in oxygen and oxygen-free conditions for two polymer compositions, as the actual degradation and destruction process of the cross-linked polymer binder inside the mould occurs with limited oxygen access, under the impact of high temperature of casting with a liquid metal alloy. When casting the mould, due to strong stresses at the liquid metal/mould interface phases and the spreading heat wave, one can also expect oxidative degradation. Furthermore, hardened mould is a non-uniform system, which can include blocked air bubbles, by which the oxygen presence may cause thermal decomposition according to oxidative degradation. New polymer binders BioCo subjected to thermal analysis are three-component aqueous polymer compositions containing water and poly(acrylic acid) (PAA) and modified polysaccharide (sodium salt of carboxymethyl starch—CMS, dextrin—D). The analysed PAA/CMS and PAA/D systems are thus complex, and the determination of the course of their thermal degradation requires the literature research in the area of input polymer components [10–14]. The literature indicates that poly(acrylic acid) heated to the temperature of approx 140 °C begins to lose (solvent and constitution) water, while dehydration to anhydride—as a result of intramolecular reaction of forming a six-membered ring—occurs at the temperature of approx 250 °C. An intermolecular reaction is also possible, which can result in cross-linked structure formation. Further quick PAA decomposition takes place at the temperature of approx 400 °C. Moreover, thermal degradation of acrylic

polymers often occurs with characteristic cross-linking reactions, hence endothermic effects visible on DSC curves (in the range 123–183 °C) related to the aforementioned dehydration, formation of short polymer chains, carbon dioxide release, whereas monomer is released in small quantities—approximately 0.3 % of input compound [12, 13]. In the case of polysaccharides, within the temperature range of 300–450 °C, weak C–O–C and C–C bonds in the glycoside ring decompose. Next, with temperature increase, side chains fall apart, which together with C–O bond cracking leads to depolymerisation of the sugar chain. Finally, at the temperature of approx 500 °C, dehydrated polymer undergoes complete destruction, whereas gas products and carbonised material are formed [14, 15].

Considering the literature data presented above, and accounting for the presence of aqueous polymer compositions: PAA, CMS, and D, an attempt was made to determine the course of their thermal degradation. The knowledge obtained from TG–DSC thermal analysis on thermal stability of the polymer binders analysed will allow for passing onto the next phase of research on determining their thermal properties in the binder-mineral matrix (foundry sands) system. Thermal analyses (TG–DSC, TG–MS, and TG–IR) to determine the course of thermal degradation process in respect of new binders in the foundry sands, including thermal effects accompanying the process and the impact of gases generated during thermal destruction of moulds on the quality of the final casts, as well as environmental impact, will be the subject of Part 2 of the publication. Results of the study will also prove helpful to verify physical and chemical properties in order to create a database of materials used in foundry technology of products. Information contained in the database will make it easier to search for materials by their physical and chemical properties (search criteria). The material database can be one of the modules of a technological knowledge management system [16].

Experimental

Materials

Thermal analysis involved two polymer compositions cross-linked with microwave radiation. Their characterisation and cross-linking conditions are provided in Table 1.

Thermal examinations

The thermal examinations were carried out using a NETZSCH STA 449 F3 Jupiter® thermal analyser which supports simultaneous TG and DSC measurements, thus providing two independent signals recorded in the same

Table 1 Characteristics of compositions and their cross-linking parameters

Polymer	Composition	Hardening conditions
PAA/ CMS	80 % aqueous solution of poly(acrylic acid) (PAA, 100,000 g mol ⁻¹ , BASF) and sodium salt of carboxymethyl starch (CMS, modified starch with potato, DS 0.2, Xenon), in a mass ratio 4:1, pH 2.5	Microwave device: RM 2001 Pc, Plazmatronica Microwave power of 800 W
PAA/D	62 % aqueous solution of poly(acrylic acid) (PAA, 100,000 g mol ⁻¹ , BASF) and dextrin (D, modified starch with potato, Fluka), in a mass ratio 7:8, pH 1.5	Frequency of 2.45 GHz Microwave action time: 60 s Temperature inside the device: 100 °C

measurement conditions, namely at/in the same heating rate (10 °C min⁻¹), atmosphere, and gas flow rate (40 mL min⁻¹). The measurements for the sample were taken in an oxidising atmosphere (air) and an oxygen-free one (argon). The sample submitted to the TG–DSC thermal analysis weighed approximately 15 mg. Platinum crucibles were used, as they allowed measurements up to 1000 °C.

Results and discussion

TG–DSC thermal analysis

In an air atmosphere, decomposition of cross-linked PAA/CMS polymer composition occurs with five mass losses (Fig. 1a). Within the temperature range of 20–100 °C, the remains of solvent water evaporate, followed by constitution water. Next, within the temperature range of 100–220 °C, 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 thermal degradation process starts at the temperature of

approx 220 °C. Next, polymer chains decompose, including decomposition of side chains and glycosidic bonds (temperature range of ~220–300 °C). Further on, progressive decomposition takes place with intensive generation of gas products of destruction, including in the combustion reactions in an oxygen atmosphere (temperature range of ~300–500 °C). At the DSC curve, at the temperature of 424 and 497 °C, there are two exothermic effects visible, which may be a result of composition combustion process (Fig. 1a). Moreover, at the DSC curve, one can notice three endothermic effects (due to the adopted scale, they are invisible in the figure). A sample of the PAA/CMS composition actually completely decomposes at the temperature of 1000 °C (remaining sample mass 2.9 %).

In the oxygen-free atmosphere, PAA/CMS decomposition is different (Fig. 1b). At the TG curve of the composition, five mass losses can be observed, while at the DSC curve, six endothermic effects and one exothermic effect are visible. The last small mass loss (5.0 %) at the temperature of maximum rate loss of 748 °C, not accompanied by any thermal effects, is most probably related to further transformations of compounds containing sodium atoms,

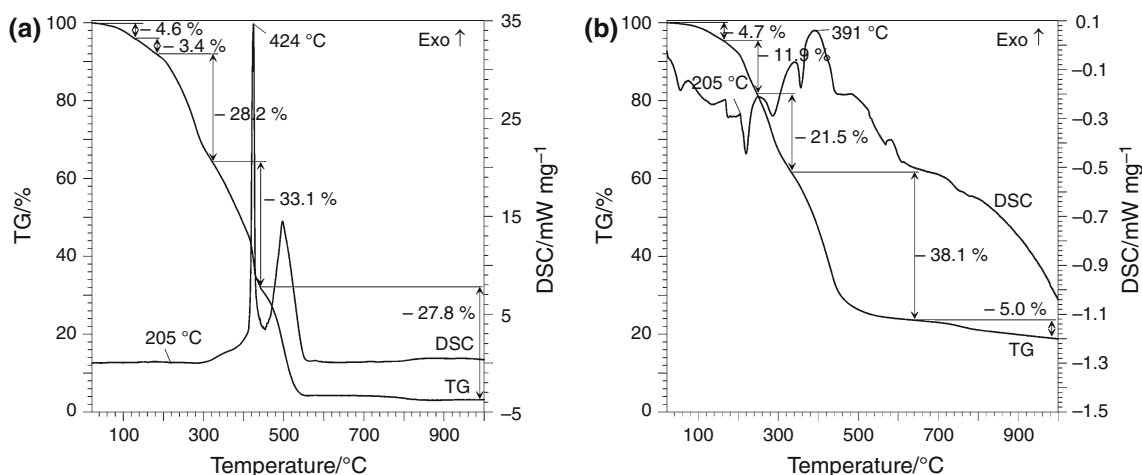
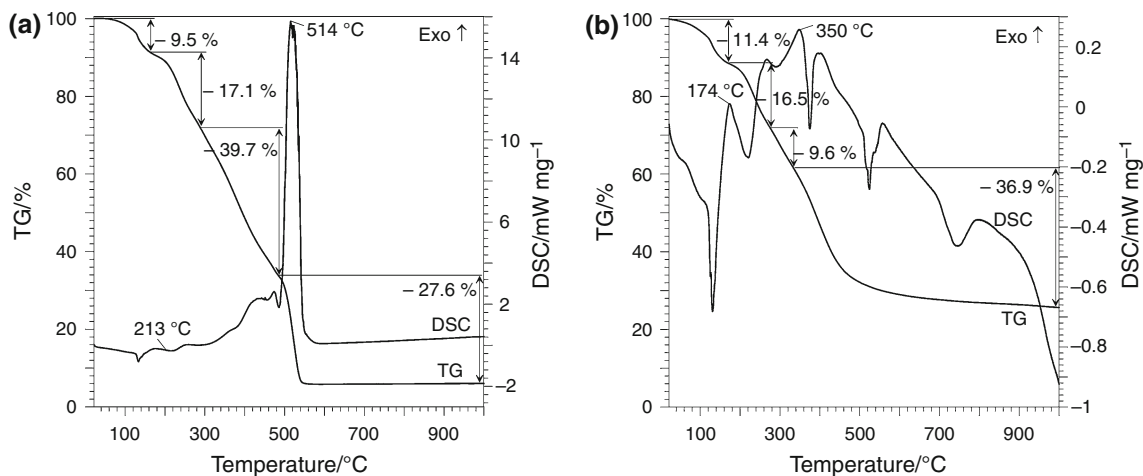


Fig. 1 TG–DSC curves of PAA/CMS composition: **a** in an oxidising atmosphere, **b** in oxygen-free atmosphere

Table 2 Analysis of TG–DSC curves of PAA/CMS composition in an oxidising and argon atmosphere

Stage	Oxidising atmosphere				Oxygen-free atmosphere			
	Mass loss/%	Range of temperature/°C	Temp. of maximum rate of mass loss/°C	DSC effect temperature/°C	Mass loss/%	Range of temperature/°C	Temp. of maximum rate of mass loss/°C	DSC effect temperature/°C
I	4.6	22–133	113	endo-46	4.7	22–166	148	endo-56 endo-133
II	3.4	133–177	163	endo-161	11.9	166–240	219	endo-220
III	28.2	177–324	279	endo-217	21.5	240–331	281	endo-286
IV	33.1	324–449	422	exo-424	38.1	331–625	427	endo-357 exo-390 endo-569
V	27.8	449–1000	496	exo-497	5.0	625–1000	748	–
	Remaining sample mass 2.9 %				Remaining sample mass 18.8 %			

**Fig. 2** TG–DSC curves of PAA/D composition: **a** in an oxygen atmosphere, **b** in oxygen-free atmosphere**Table 3** Analysis of TG–DSC curves of PAA/D composition in an oxidising and argon atmosphere

Stage	Oxidising atmosphere				Oxygen-free atmosphere			
	Mass loss/%	Range of temperature/°C	Temp. of maximum rate of mass loss/°C	DSC effect temperature/°C	Mass loss/%	Range of temperature/°C	Temp. of maximum rate of mass loss/°C	DSC effect temperature/°C
I	9.5	22–179	131	endo-133	11.4	22–173	129	endo-131
II	17.1	179–281	240	endo-215	16.5	173–274	237	endo-221
III	39.7	281–486	382	exo-422 exo-474	9.6	274–329	301	endo-291
IV	27.6	486–1000	511	exo-514	36.9	329–1000	393	exo-348 endo-375 endo-525 endo-746
	Remaining sample mass 6.1 %				Remaining sample mass 25.6 %			

formed during CMS decomposition. The remaining part of the composition sample mass (approx 18.9 %) which did not decompose at the temperature of 1000 °C probably contains carbonised coal and low molecular weight compounds containing sodium atoms.

Key information obtained by analysing the TG–DSC curves for the PAA/CMS composition is presented in Table 2.

The course of TG–DSC curves indicates that the process of thermal decomposition of cross-linked PAA/D composition must also be analysed while considering degradation of both polymer components (Fig. 2), as in the case of PAA/CMS. Together with the temperature increase, degradation in the air occurs gradually (Fig. 2a). Four phases of decomposition can be identified. Within the temperature range of 22–215 °C, one can notice two endothermic effects, probably related to the process of solvent water evaporation (up to 100 °C), followed by dehydration. The temperature of 215 °C can be considered as the beginning of polymer chain decomposition. Within the temperature range of 422–515 °C, three exothermic effects are visible, which may be a result of combustion process, whereas the last one is the strongest. At the temperature of approx 500 °C, PAA/D undergoes complete destruction (strong exothermic effect is observed).

In the oxygen-free atmosphere, PAA/D decomposition occurs with four mass losses (TG curve, Fig. 2b). DSC curve shows six endothermic effects and one exothermic effect accompanying pyrolysis. The remaining part of the sample mass (approx 25.6 %) which did not decompose at the temperature of 1000 °C probably contains carbonised coal.

Key information obtained by analysing the TG–DSC curves for the PAA/D composition is presented in Table 3.

Conclusions

On the basis of the obtained results of TG–DSC, it can be stated that the course of decomposition is complex (mixed degradation mechanism), which is a result of the structure, as well as physical and chemical properties of polymer compositions analysed. At the same time, it depends on the conditions in which decomposition occurs. With temperature increase, physical and chemical changes occur in the analysed samples of PAA/CMS and PAA/D polymer compositions.

Within the temperature range of 20–100 °C, evaporation of physically bound water occurs, followed by constitution water, and above the temperature of 100 °C, intermolecular dehydration reaction takes place with formation of intermolecular anhydride bonds among carboxyl groups of neighbouring polymer chains (cross-linking), which is a

characteristic of thermal decomposition of poly(acrylic acid). On the basis of TG curves, it can be stated that thermal degradation process starts at the temperature of approx 220 °C. Degradation of modified starch begins with decomposition of weak C–O–C bonds in the glycoside bond (polysaccharides)—temperature range: ~220–300 °C. In this temperature range, polyacrylic chains also get fragmented. Furthermore, side chains can break off, and bonds may crack in the poly(acrylic acid) chain in the –COOH group or in carboxymethyl starch within the –CH₂O–CH₂O–CH₂–COONa group.

Above the temperature of 300 °C, intensive cracking of chemical bonds occurs, which results in breaking of most bonds (temperature range III ~300–500 °C). The process becomes massive, which has an effect of releasing volatile low molecular weight inorganic and organic compounds and finally leads to complete destruction of a sample. At the temperature of approx 550 °C, only carbonised form remains, which can contain carbonised coal, whereas if sodium atoms form part of the composition, low molecular weight compounds are formed containing sodium atoms.

Acknowledgements The authors acknowledge the financial support from The National Centre for Research and Development through Grant No. PBS2/A5/39/2013.

Open Access This article is distributed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

References

- Górny M, Tyrała E. Effect of cooling rate on microstructure and mechanical properties of thin-walled ductile iron castings. *J Mater Eng Perform*. 2013. doi:10.1007/s11665-012-0233-0.
- Wang J, Sun X, Guan Y, Wang P, Li H, Bai L, Sun X. Numerical simulation and process optimization for producing large-sized castings. *China Foundry*. 2008;5:179–85.
- Cholewa M, Szuter T. Thermo-insulating moulding sand for thin walled castings. *Arch Metall Mater*. 2014. doi:10.2478/amm-2014-0184.
- Zhou X, Yang J, Sua D, Qu G. The high-temperature resistant mechanism of starch composite binder for foundry. *J Mater Process Technol*. 2009. doi:10.1016/j.jmatprotec.2009.04.010.
- Popoola API, Abdulwahab M, Fayomi OSI. Synergetic performance of palm oil (*Elaeis guineensis*) and pine oil (*Pinus sylvestris*) as binders on foundry core strength. *Int J Phys Sci*. 2012. doi:10.5897/IJPS12.347.
- Grabowska B, Sitarz M, Olejnik E, Kaczmarska K, Tyliczszak B. FT-IR and FT-Raman studies of cross-linking processes with Ca²⁺ ions, glutaraldehyde and microwave radiation for polymer composition of poly(acrylic acid)/sodium salt of carboxymethyl starch, Pt. 1. *Spectrochim Acta A*. 2015. doi:10.1016/j.saa.2015.06.084.

7. Svidr6 JT, Di6szegi A, T6th J. The novel application of thermal analysis in foundry technologies. *J Therm Anal Calorim.* 2014;115:331–8.
8. Zhang H, Zhao H, Zheng K, Li X, Liu G, Wang Y. Diminishing hazardous air pollutant emissions from pyrolysis of furan no-bake binders using methanesulfonic acid as the binder catalyst. *J Therm Anal Calorim.* 2014;116:373–81.
9. Grabowska B, Szucki M, Suchy JS, Eichholz S, Hodor K. Thermal degradation behavior of cellulose-based material for gating systems in iron casting production. *Polimery.* 2013. doi:10.14314/polimery.2013.039.
10. Grabowska B, Holtzer M, Da6nko R, G6rny M, Bobrowski A, Olejnik E. New BioCo binders containing biopolymers for foundry industry. *Metalurgija.* 2013;52:47–50.
11. Pielichowski J, Pielichowski K. Application of thermal analysis for the investigation of polymer degradation process. *J Therm Anal.* 1995;43:505–8.
12. Kader MA, Bhowmick AK. Thermal ageing, degradation and swelling of acrylate rubber, fluororubber and their blends containing polyfunctional acrylates. *Polym Degrad Stab.* 2003;79:283–95.
13. Lattimer RP. Pyrolysis mass spectrometry of acrylic acid polymers. *J Anal Appl Pyrolysis.* 2003;68–69:3–14.
14. Lawal OS, Lechner MD, Kulicke WM. The synthesis conditions, characterizations and thermal degradation studies of etherified starch an unconventional source. *Polym Degrad Stab.* 2008;93:1520–8.
15. Llu6 AV, Felipe AM, Greus AR, Cadenato A, Ramis X, Salla JM. Thermal analysis characterization of the degradation of biodegradable starch blends in soil. *J Appl Polym Sci.* 2005;96:358–71.
16. Malinowski P, Suchy JS, Jakubski J. Technological knowledge management system for foundry industry. *Arch Metall Mater.* 2013;58:965–8.