

Use Thermal Analysis (TG/DTG/DSC) in the Study of Stability (Bio)Polymer Binder

B. Grabowska^{a*}, G. Grabowski^b, K. Kaczmarek^a

^aAGH - University of Science and Technology, Department of Casting Process Engineering, Faculty of Foundry Engineering, Reymonta 23 St, 30-059 Krakow, Poland

^bAGH - University of Science and Technology, Faculty of Material Engineering and Ceramics, 30 Mickiewicza St., Krakow, Poland

*Contact in writing: e-mail: beata.grabowska@agh.edu.pl

Received 22.10.2013; accepted in revised form 12.12.2013

Abstract

The fragment of investigations related to the thermal stability of new foundry polymer binders with biopolymer fractions is hereby presented. A sample of the foundry binding agent BioCo1, in a form of two-component polymer composition consisting of a modified biopolymer (polysaccharide) and a synthetic polymer (acrylic polymer), was subjected to the thermal analysis. Methods of thermal analyses (TG/DTG/DSC) were applied in investigations in order to perform the thermal degradation process of the tested BioCo1 binder sample by establishing thermal effects of transformations, structural changes and masses - occurring during its heating. Examinations were performed in the temperature range: -100 – 600 °C. It was found that the degradation process starts at a temperature app. 130 °C. The binding agent behaviour at increased temperatures is important in relation to the process of the moulding sand mould (with BioCo1 fraction) pouring with liquid metal.

Keywords: innovative foundry materials and technologies, polymer binders, foundry sands, thermal analysis, TG/DTG/DSC, thermal degradation.

1. Introduction

Heating polymer materials leads to their degradation, which consists in the macromolecule chains disintegrating into fragments. If the temperature is high enough, the intensive bond breaking process snowballs and causes the polymer to be destroyed. When macromolecules are heated, both reversible and irreversible changes can occur in their structure. Reversible changes result from phase transitions, the disaggregation of supra-molecular structures and the polymer transitioning into the plastic state.

At a temperature greater than the flow temperature (for amorphous polymers) or the melting point (for crystalline polymers), irreversible changes take place, and the majority of polymers are thermally degraded. The mechanism of the

degradation process depends on the structure of the macromolecule, the rate at which the sample is heated as well as exothermic and endothermic transformations [1-4].

The thermal analysis methods were applied for the determination of the (bio)polymer binder thermal stability, encompassing the determination of the destruction temperature and heat effects of transformations occurring during heating. The mechanism of thermal degradation process depends on the structure of the macromolecule, the rate at which the sample is heated as well as exothermic and endothermic transformations [1-7]. This publication presents the results of thermal examinations conducted to determine the course of the thermal degradation of a water-based (bio)polymer composition of synthetic polymer/modified biopolymer with a view to its use as a foundry binder for moulding and core sands (BioCo1). Thermal decomposition of the

BioCol binder is of essential meaning in relation to this binder behaviour at increased temperatures during the mould pouring with liquid metal as well as in relation to this used sand reclaimability. From the environmental point of view and work conditions, information concerning gaseous products of polymer decomposition, which can evolve into the atmosphere during the technological process, seems also important [8-13].

2. Experimental

2.1. Materials

New polymer binding agent BioCol in a form of two-component polymer composition formed by mixing in water a synthetic polymer (Fig.1a, poly(acrylic acid) of the BASF Company) and a modified biopolymer (Fig. 1b, modified starch of the Xenon Company) in the weight ratio 1:1 was used in the performed investigations.

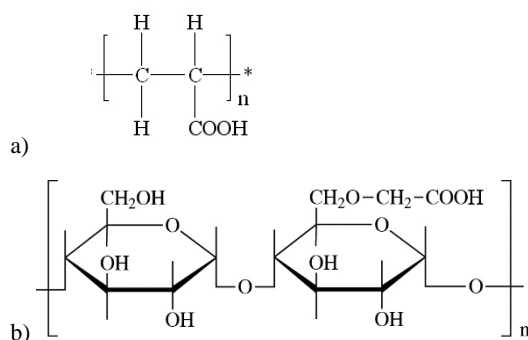


Fig. 1. Structure of: a) poly(acrylic acid), b) modified starch

Cross-linking of sample of the prepared composition was performed by means of $\text{Ca}(\text{OH})_2$ and CO_2 .

2.2. Thermal analysis methods

The thermal examinations were carried out by 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 measurement conditions, namely at the same rate of temperature increase (10 K/min), atmosphere and gas flow rate (40 ml/min). The measurements for the sample were taken in an anaerobic atmosphere.

The basic measurement parameters are collected in Table 1.

Table 1. Measurement parameters

Parameters	BioCol
temperature range	RT – 500 °C
heating rate	10 K/min
atmosphere	nitrogen
flow rate	40 ml/min
crucible	Al_2O_3
sample mass	about 45 mg

3. Results and discussion

Figure 2 depicts the TG-DSC results for the sample BioCol (after cross-linking). At sub-ambient temperatures, no effects were observed. Three mass loss steps 8.1%, 25.5% and 41.7% were noticed, which were accompanied by endothermic effects visible in the DSC signal. Maxima in the rate of mass change occurred at 133 °C, 276 °C and 422 °C. In the temperature range -100-0 °C the polymorphous transformations were not found.

The pathway of thermal curves is complex since the degradation process occurs by stages, which results from the structure and physical and chemical properties of the two-component (bio)polymer composition. On the grounds of the thermal curves it can be stated that the degradation process starts at a temperature of app. 132 °C [9].

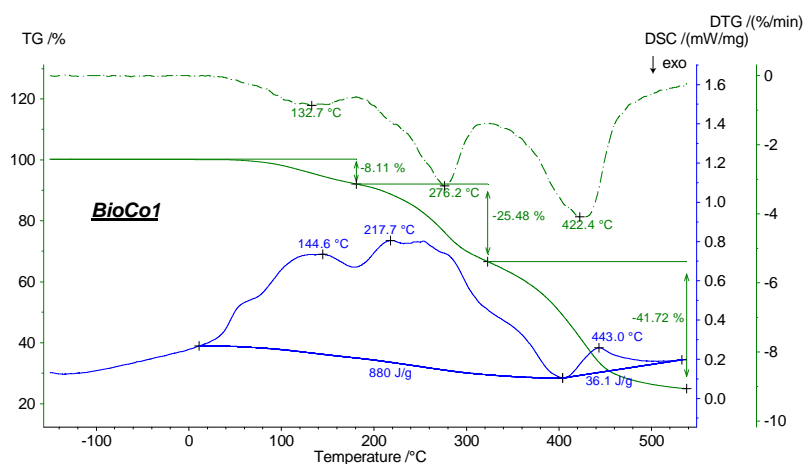


Fig. 2. Temperature-dependent mass change (TG), rate of mass change (DTG, dashed line) and heat flow rate (DSC) of the sample BioCol

At the first stage in bio-polymer binder pyrolysis, the weak C-O-C and C-C bonds in the glycoside bond are decomposed. At the temperature range of 133-324 °C, two exothermal effects due to the destruction of the organic part of the material are observed in sequence. Enthalpy value is estimated on 880 J/g. At 422 °C, the TG/DSC curve shows the last mass loss (42%) was accompanied by an exothermal effect (36 J/g). The remainder of the sample mass (approx. 24.7%) which has not decomposed up to the temperature of 600 °C probably contains organics and inorganics (eg. carbonised carbon) found in the binder cross-linking by means of Ca(OH)₂ and CO₂.

The results for investigated binder are summarized in Table 2.

Table 2. The characteristics of thermal derivatives

Nitrogen atmosphere				
Stage	Δm, %	Temperature range, °C	Maximum mass change speed at °C	DSC effect temperature, °C
I	-8,1	22-133	145	egzo-132
II	-25,5	133-177	218	egzo-276
III	-41,7	177-324	443	egzo-422
The remaining sample mass 24.7 %				

4. Conclusions

The fragment of investigations related to the thermal stability of new foundry polymer binders with biopolymer fractions is hereby presented. A sample of the foundry binding agent BioCo1, in a form of two-component polymer composition consisting of a modified biopolymer (modified starch) and a synthetic polymer (acrylic polymer), was subjected to the thermal analysis. The binding agent behaviour at increased temperatures is important in relation to the process of the sand mould (with BioCo1 fraction) pouring with liquid metal. Methods of thermal analyses (TG/DTG/DSC) were applied in investigations in order to perform the thermal degradation process of the tested BioCo1 binder sample by establishing thermal effects of transformations, structural and masses changes - occurring during its heating. Examinations were performed in the temperature range: -100 – 600 °C. It was found that the degradation process starts at a temperature app. 130 °C.

Acknowledgements

The work was supported by the Project AGH No 11.11.170.318/13.

References

- [1] Singh, B., Sharma, N. (2008). *Mechanistic implications of plastic degradation*. Polymer Degradation and Stability, 93, p. 561-584.
- [2] Pielichowski, J., Pielichowski, K., (1995), *Application of thermal analysis for the investigation of polymer degradation process*, Journal of Thermal Analysis, vol. 43, p. 505-508.
- [3] Pielichowski, K., Njuguna, J. (2005). *Thermal degradation of polymeric materials*, Rapra Technology, United Kingdom,
- [4] Lattimer, R.P. (2003). *Pyrolysis mass spectrometry of acrylic acid polymers*, Journal Analytical Applied Pyrolysis, 68-69, p. 3-14.
- [5] Jandura, P., Riedl, B. & Kockt, B.V. a, (2000). *Thermal degradation behavior of cellulose fibers partially esterified with some long chain organic acids*. Polymer Degradation and Stability Volume 70 (3), 387–394
- [6] Vallés, Lluch, 1A. Martínez, Felipe, 1A. Ribes, Greus, 1A. Cadenato, X., Ramis, J.M., Salla, J.M. Morancho *Thermal Analysis Characterization of the Degradation of Biodegradable Starch Blends in Soil*, DOI 10.1002/app.21428
- [7] Hirokazu, Morita. (1956). *Characterization of Starch and Related Polysaccharides by Differential Thermal Analysis*, Anal. Chem., 28 (1), 64–67. DOI: 10.1021/ac60109a019
- [8] Grabowska, B., Holtzer, M., Górný, M., Dańko, R., Grabowski, G. (2011). *Microstructure and properties of test casting of cast iron made in moulding sands with the BioCo2 binder*, Archives of Foundry Engineering, 11, p. 47–50.
- [9] Grabowska, B., Holtzer, M., Eichholz, S., Hodor, K., Bobrowski, A. (2011). *Thermal analysis of a sodium salt of the maleic acid-acrylic acid copolymer used as a polymeric binder*, Polimery, t. 56, no. 2, p. 62–66.
- [10] Grabowska, B. (2010). *Examining the thermal degradation of polymer binders using FTIR spectroscopy*, Archives of Foundry Engineering, 10 (4), 43–46.
- [11] Grabowska, B. (2013). *New polymer binders in form of aqueous compositions with poly(acrylic acid) or his salts and modified biopolymer for foundry practice applications*. Kraków: Wydawnictwo Naukowe AKAPIT (in Polish).
- [12] Grabowska, B., Holtzer, M., Eichholz, S., Hodor, K., Olejnik E. (2012). *Thermal Analysis of the Composition of Poly(Acrylic Acidy/Carboxymethylstarch Used as a Polymeric Binder*, Supplemental Proceedings: Materials Processing and Interfaces, TMS, 1, 231–238. DOI: 10.1002/9781118356074.ch31
- [13] Grabowska, B., Pilch-Pitera, B., Kaczmarek, K., Trzebicka, B., Mendrek, B. (2013). *Studies on the stability of new binder for foundry on the example of water soluble composition of poly (acrylic acid)/sodium carboxymethyl starch „Chemia – tradycja i nowe wyzwania”*, 56. zjazd naukowy Polskiego Towarzystwa Chemicznego i Stowarzyszenia Inżynierów i Techników Przemysłu Chemicznego, Siedlce, 16–20 września 2013 / Warszawa: PTCh, 481.(in Polish).

Analiza termiczna (TG/DTG/DSC) w badaniach stabilności spoiw (bio)polimerowych

Streszczenie

Przedstawiono wycinek badań związanych z określeniem termicznej stabilności nowych odlewniczych spoiw polimerowych z udziałem biopolimerów. Poddano analizie termicznej próbkę spoiwa odlewniczego BioCo1 w postaci dwuskładnikowej kompozycji polimerowej złożonej z modyfikowanego biopolimeru (polisacharydu) i polimeru syntetycznego (polimeru akrylowego). W badaniach wykorzystano metody analizy termicznej (TG/DTG/DSC) w celu przeprowadzenia procesu degradacji termicznej badanej próbki spoiwa BioCo1 poprzez ustalenie efektów cieplnych przemian zachodzących podczas jego ogrzewania, zmian strukturalnych oraz masy. Badania prowadzono w zakresie temperatury -100 – 600 °C. Ustalono, że proces degradacji rozpoczyna się od temperatury 130 °C. Przeprowadzona analiza termiczna spoiwa ma istotne znaczenie w odniesieniu do procesu zalewania ciekłym metalem formy z masy odlewniczej wiązanej spoiwem BioCo1.