

# Studies of the Thermal Degradation of the BioCo3 Polymer Binder

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## Abstract

The basic research included a thermal analysis of the BioCo3 polymer binder in the form of a water-based poly(sodium acrylate)/dextrin composition to determine the temperature range in which this binder does not degrade and hence does not lose its binding properties in the binder/matrix system. The thermal decomposition was proven to be complex and to occur in multiple stages. It was found that as the temperature rises, physical and chemical changes take place in the binder as a result of the solvent water (20-100 °C) and then of the structural water evaporating, and finally of intermolecular dehydration reactions (100-220 °C) Mainly reversible processes occur within this temperature range. Within the temperature range of 220-300 °C, polymer chains decompose, which includes the disintegration of side groups and glycoside bonds. Between 300 and 500 °C, the polymer composition decomposes producing with gaseous destruction products, including mainly small-molecule inorganic compounds (CO<sub>2</sub>, H<sub>2</sub>O, CO) and organic ones (hydrocarbons). The part of the mass which has not decomposed at the temperature of about 550°C may contain carbonised carbon.

**Keywords:** Polymer binders, Foundry sands, Thermal analysis, TG-DSC, Thermal degradation

## 1. Introduction

In general, the term “polymer degradation” covers all changes to the chemical structure and physical properties of polymers caused by external chemical or physical factors. The modification of the structure by breaking polymer chains leads to the loss of elastic properties and an increase in the degree of crystallinity. Degradation is usually initiated by organic radicals that may form in polymers as a result of the action of such physical and chemical factors as temperature, mechanical stresses, light exposition or microorganisms [1, 2].

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].

This publication presents the results of thermal examinations conducted to determine the course of the thermal degradation of a water-based polymer composition of poly (sodium acrylate)/dextrin with a view to its use as a foundry binder of moulding and

core sands [5]. The course of thermal degradation was identified using literature data on the decomposition of the acrylic acid and polysaccharides [6-9] and based on own research (TG-DSC, TG-FTIR) [10,11]. In order to determine the degradation temperature and the thermal effects of transformations occurring when samples of the composition were heated, the following thermal analysis (TA) methods were used: the thermogravimetry (TG) and differential scanning calorimetry (DSC). In addition, an attempt was made to determine the mechanism of the thermal decomposition process of the PAANa/D composition. For this purpose, volatile decomposition products were analysed using the combined TG-FTIR technique, i.e. the thermogravimetric method coupled on-line with Fourier Transform Infrared Spectroscopy (FTIR).

## 2. Research methods

### 2.1. Research material

The binder subjected to the thermal analysis was BioCo3, a new polymer binder in the form of a water-based PAANa/D polymer composition, namely a mixture of a synthetic polymer, poly(sodium acrylate) (PAANa by BASF) and a modified biopolymer: potato dextrin (D, by Fluka). The polymer composition contained 60% of water. The weight ratio of the PAANa : D polymers was 9 : 8. The apparent viscosity of the composition amounted to 30 mPa.s.

### 2.2 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 measurement conditions, namely at/in the same temperature increase rate (10°C/min), atmosphere and gas flow rate (40 ml/min). The measurements for the sample were taken in an oxygen atmosphere (air) and an oxygen-free one (argon). The sample undergoing the TG-DSC thermal analysis weighed approximately 15 mg. Platinum crucibles were used, as they allowed measurements up to 1000°C. In order to more fully analyse the course of the thermal degradation process, including by attempting to identify gaseous decomposition products, examinations were carried out using TG method coupled online with infrared spectrometry (IR), employing the following equipment: a thermal analyser - NETZSCH TG 209 F1 Iris®, and a Fourier-transform infrared spectrometer - BRUKER Optics FTIR TENSOR™. The measurements for the sample were taken in an oxygen-free atmosphere (nitrogen). The sample undergoing the TG-FTIR thermal analysis weighed approximately 24 mg. Aluminium crucibles were used for measurements.

## 3. TG-DSC thermal analysis

In an oxygen atmosphere, PAANa/D decomposes with five mass losses (Fig. 1, Tab. 1). On the DSC curve, at the temperatures of 301°C, 347°C, 452°C, 552°C and 497°C, four

exothermic effects are visible which may result from the combustion of the composition. In addition, two endothermic effects are apparent on the DSC curve. The last effect, occurring at 826°C, is due to the decomposition of an inorganic compound, probably sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), which may originate from the decomposition of PAANa, i.e. the carboxylate group containing sodium atoms (-COONa). The remaining part of the mass of the composition sample (some 28.6%) which has not decomposed up to the temperature of 1000°C, probably mainly contains carbonised carbon.

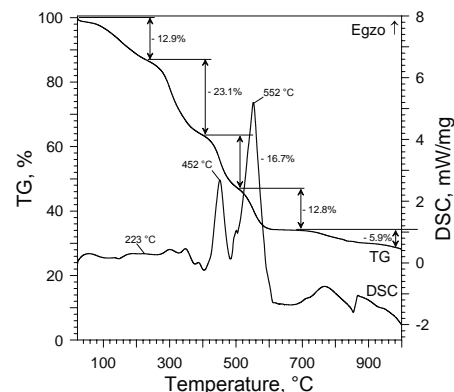


Fig. 1. TG-DSC curves of PAANa/D composition in an oxygen atmosphere

Key information obtained by analysing the TG-DSC curves for the PAANa/D composition is presented in Table 1.

Table 1. The analysis TG-DSC curves of PAANa/D composition in an oxygen atmosphere

Stage	Oxygen atmosphere			
	$\Delta m$ , %	Temperature range, °C	Maximum mass change speed at °C	DSC effect temperature, °C
I	-12.9	22-232	148	endo-147
II	-23.1	232-399	298	exo-301 exo-347
III	-16.7	399-507	450	exo-452
IV	-12.8	507-663	552	exo-552
V	-5.9	663-1000	826	endo-854
Remaining sample mass 28.6%				

In an oxygen-free atmosphere, the decomposition of PAANa/D follows a different course. The TG curve of the composition shows five mass losses. On the DSC curve, five effects are visible (Fig. 2 and Table 2). The last mass loss (28.1%) with the maximum speed at 833°C, is probably due to the decomposition of the sodium carbonate formed, when PAANa is decomposing. The remaining part of the composition sample mass (some 11.3%) which has not decomposed up to the temperature of 1000°C probably mainly contains carbonised carbon. Key information obtained by analysing the TG-DSC curves for the PAANa/D composition is presented in Table 2.

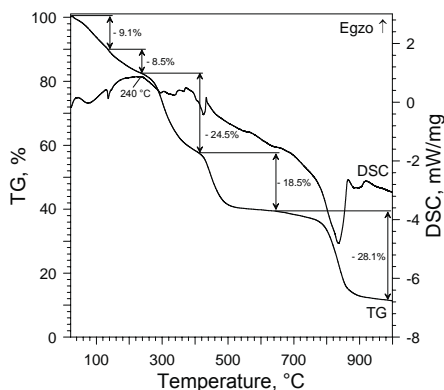


Fig. 2. TG-DSC curves of PAANa/D composition in a argon atmosphere

Table 2.

The analysis TG-DSC curves of PAANa/D composition in an argon atmosphere

Stage	Atmosfera beztlenowa			
	$\Delta m$ , %	Temperature range, °C	Maximum mass change speed at °C	DSC effect temperature, °C
I	-9.1	22-127	89	endo-74
II	-8.5	127-238	136	endo-136
III	-24.5	238-406	301	endo-335
IV	-18.5	406-634	445	endo-425
V	-28.1	634-1000	833	endo-835
Remaining sample mass 11.3%				

## 4. Thermoanalytical examinations

From the point of view of basic research, the thermal degradation of polymer materials is a complicated process running in a hetero-phase system. This is why the correct interpretation of thermal examination results should include the analysis of gas products formed during the thermal decomposition. The control and identification of gaseous products is also important for environmental reasons, as on the industrial scale, harmful substances such as CO, SO<sub>2</sub>, H<sub>2</sub>S, aromatic hydrocarbons or dioxins are emitted. For a more complete thermal analysis and a more accurate identification of the course of the thermal degradation of polymer compositions, thermoanalytical examinations were carried out using the following thermoanalytical method: thermogravimetry coupled online with infrared spectrometry (TG-FTIR). These examinations made it possible to determine the probable structure of decomposition products and to identify them by reference to standard spectra. IR temperature spectra at the maximums appearing on the obtained TG-DSC curve (Fig. 3) were extracted from the set of IR spectra within the 100°C-500°C temperature range, and then these IR temperature spectra were compared to standard spectra found in the spectrum catalogue. At the temperature of 143°C and the wave number of 3300 cm<sup>-1</sup>, vibrations were detected that could come from water (ν-OH, O-H···O-H vibrations), and the IR spectrum recorded at 275°C shows that CO<sub>2</sub> is emitted (the band

in the vicinity of the 1750 cm<sup>-1</sup> wave number, the ν<sub>s</sub>-C=O vibration).

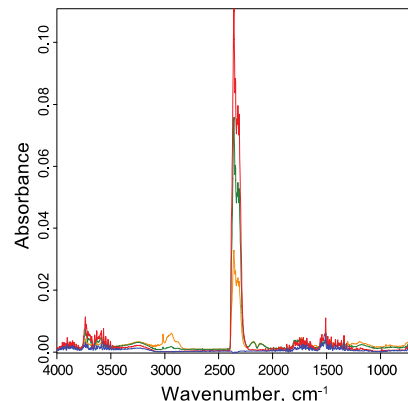


Fig. 3. Extracted IR spectra of the specimen at 143°C (blue), 275°C (red), 390°C (green) and 441°C (orange)

At the temperature of 390°C, one can observe bands characteristic for asymmetrical and symmetrical stretching vibrations ν-C-H (the 2940 cm<sup>-1</sup> band), stretching vibrations of the carbonyl group (the band around the 1750 cm<sup>-1</sup> wave number, vibration ν<sub>s</sub>-C=O), stretching vibrations of C-O and out-of-plane deforming vibrations of C-O-H (the 1170 cm<sup>-1</sup> band). The spectrum obtained was compared to standard spectra for the following compounds: CO, CO<sub>2</sub> and CH<sub>4</sub>.

## 5. Identification of the decomposition mechanism of the BioCo3 polymer binder

The course of the decomposition of the BioCo3 polymer binder is complex and consists of multiple stages, which is due to the structure and the physical/chemical properties of this dual component water-based polymer composition: PAANa/D. The TG-DSC thermal analysis of the binder justifies the statement that as the temperature rises, physical and chemical changes occur, which are probably due to:

- The evaporation of the solvent water (20-100°C), then of the structural water, and then intermolecular dehydration reactions (100-220°C). Within this temperature range, mainly the following reversible processes occur: physical transformations and reversible reactions (cross-linking through dehydration);
- The decomposition (disintegration) of polymer chains, including of side groups and glycoside bonds. In addition, the shapes of TG thermal curves suggest that the thermal degradation process starts at the temperature of approximately 220°C;
- The progressive decomposition and the intense formation of gaseous destruction products, *inter alia* during the reaction of combustion in an oxygen atmosphere or pyrolysis in an oxygen-free one.

The degradation of polymer compositions probably starts with the disintegration of weak C-O-C bonds in the glycoside bond (dextrin) and the formation of oligomeric radicals, which decompose further to form radicals with even shorter chains – range II (Fig. 4). Probably polyacrylic chains are also

fragmenting. In addition, side groups may be separated and bonds may break in the poly(sodium acrylate), in the  $-\text{COONa}$  group.

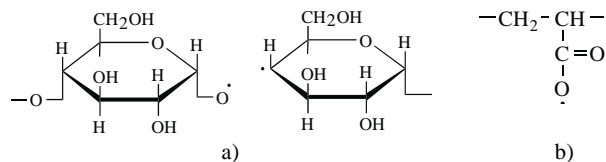


Fig. 4. Example formulas of the radicals produced: a) in the D chain, b) in the PAANa chain

All that is left at the temperature of approximately 550°C is a carbonised form which may contain carbonised carbon, and as the composition contains sodium atoms, inorganic compounds (probably sodium carbonate) are formed, and then decompose at the temperature of about 800°C. The confrontation of the obtained FTIR spectra with standard spectra shows that during the thermal degradation of the composition in the 143°C-390°C temperature range, small-molecule compounds are probably emitted (water, carbon oxide (IV), carbon oxide (II) and methane).

## 6. Summary

The course of the thermal decomposition of the BioCo3 binder, i.e. a PAANa/D polymer composition, has been shown to be complex and multi-stage. It was found that as the temperature rises, physical and chemical changes take place in the material as a result of the evaporation of the solvent water (20-100°C), then of the structural water, and finally as a result of intermolecular dehydration reactions (100-220°C). Mainly reversible processes occur within this temperature range. Between 220°C and 300°C, polymer chains decompose, including the disintegration of side groups and glycoside bonds. Within the 300°C-500°C temperature range, polymer compositions decompose producing gaseous destruction products, including mainly small-molecule inorganic compounds ( $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$ ) and organic ones (methane). The part of the mass which has not decomposed at the temperature of about 550°C may contain carbonised carbon.

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## Badania degradacji termicznej spoiwa polimerowego BioCo3

### Streszczenie

Badania podstawowe obejmowały analizę termiczną spoiwa polimerowego BioCo3 w postaci wodnej kompozycji poli(akrylan sodu)/dekstryna, która umożliwiła ustalenie zakresu temperatury, w jakim nie ulega ono degradacji, przez co nie traci swoich właściwości wiążących w układzie spoiwo-osnowa. Wykazano, że przebieg termicznego rozkładu jest złożony i wieloetapowy. Stwierdzono, że wraz ze wzrostem temperatury w spoiwie dochodzi do zmian fizycznych i chemicznych związanych z odparowywaniem wody rozpuszczalnikowej (20-100°C), następnie wody konstytucyjnej i wreszcie z reakcjami dehydratacji intermolekularnej (100-220°C). W tym zakresie temperatury zachodzą głównie procesy odwracalne. W zakresie temperatury 220-300°C dochodzi do dekompozycji łańcuchów polimerowych, w tym rozpadu grup bocznych i wiązań glikozydowych. W zakresie temperatury 300-500°C następuje rozkład kompozycji polimerowej z powstawaniem gazowych produktów destrukcji, w tym przede wszystkim małych cząsteczkowych związków nieorganicznych ( $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$ ) i organicznych (węglowodory). Część masy, która nie uległa rozkładowi w temperaturze około 550°C może zawierać skarbonizowany węgiel.

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