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Thermoanalytical Studies (TG-DSC, FTIR-DRS) of the Moulding Sand with the Polymer BioCo2 Binder

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Abstract

The publication presents the results of thermal examinations conducted to determine of the thermal degradation of the polymeric binder (BioCo2) in the moulding sand. Thermal degradation process was identified using literature data on the decomposition of the polymers materials and based on own research (TG-DSC, MIR-DRS). In order to determine the degradation temperature and the thermal effects of transformations occurring when the moulding sand were heated, two methods were used: the thermogravimetry (TG) and differential scanning calorimetry (DSC). In this paper the spectroscopic studies (MIR-DRS) were also performed in order to elucidate structural changes occurring in the BioCo2 binder under an influence of heating. Temperature spectra were made for the moulding sand sample in the temperature range: 25-400^{o}C (operation range of the temperature attachment of the IR spectrometer). The heating process was performed in a continuous way, and the spectra were recorded at a given temperature. On the bases of the performed thermal analysis of the moulding sand the temperature range required for the efficient thermal reclamation was indicated.

Keywords: Thermoanalytical methods, TG-DSC, FTIR-DRS, Polymeric binder, Moulding sands, Foundry

1. Introduction

Degradation of polymer materials covers all changes to the chemical structure and physical properties of polymers caused by external chemical or physical factors. Degradation is usually initiated by organic radicals that may form in polymers as a result of the action of such factors as temperature, mechanical stresses, light exposition or microorganisms. 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. If the temperature is high enough, the intensive bond breaking process snowballs and causes the polymer to be destroyed. 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 [1-3].

This publication presents the results of thermal examinations conducted to determine of the thermal degradation of the polymer binder (BioCo2) in the moulding sand [4]. Thermal degradation

process was identified using literature data on the decomposition of the polymers materials and based on own research (TG-DSC, FTIR-DRS) [5-9]. The thermoanalytical investigations (TG-DSC, FTIR-DRS) were applied as supplementary for the work on the optimisation of the thermal reclamation process [10, 11].

2. Experimental

2.1. Polymer binder BioCo2

The polymeric binder subjected to the thermal analysis was BioCo2 [4], a new polymer binder in the form of a water-based PAA/D polymer composition, namely a mixture of a synthetic polymer, poly(acrylic acid) (PAA by BASF) and a modified biopolymer: potato dextrin (D, by Fluka). The polymer composition contained 60% of water. The weight ratio of the PAA : D polymers was 7 : 8.

2.2. Preparing sand

Moulding sand (50 g) was prepared in the following with:

– mineral matrix, namely the moulding quartz sand BK D 0,16 - 0,32 MM from SIBELCO EUROPE - 2 (part by mass);
– polymeric binder BioCo2 - 1 (part by mass).

Moulding sand after 3 minutes of mixing in the rotor mixer was placed for 120 s in a microwave radiation with a power of 800 W in the microwave apparatus INOTEC MD 10940. The temperature in the microwave device was approx. 100 °C.

2.3. Thermal analysis TG-DSC

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 900°C.

2.4. FTIR-DRS

Structural analyses were carried out using an Excalibur FTIR spectrometer with a standard DTGS detector and the resolving power of 8 cm^{-1}. The research was carried using a DRS technique (diffuse reflectance spectroscopy). The use of high-DRS attachment allows the study of structural changes in the material in the temperature range up to 500°C. The DRS-attachment is coupled with a temperature controller. It has a water cooling system. The DRS technique is used in the study materials in the powders form, therefore the sample of moulding sand with BioCo2 binders was comminuted. The prepared sample was mixed in suitable proportions with KBr in order to obtain high quality spectra.

3. Results and discussion

3.1. Thermal analysis TG-DSC examinations

In an oxygen atmosphere (air), moulding sand with BioCo2 decomposes with three mass losses (Fig. 1, Tab. 1). On the DSC curve, at the temperature of 460°C exothermic effects are visible which may result from the combustion of the composition. In addition one endothermic effect are apparent on the DSC curve. The endothermic effect with a minimum in a temperature of 573 °C can be seen on the DSC curve of high-silica sand. It corresponds to the polymorphous transformation of quartz: (β)quartz→(α)quartz. The remaining part of the mass of the composition sample (some 85.16%) which has not decomposed up to the temperature of 900°C mainly contains mineral matrix.

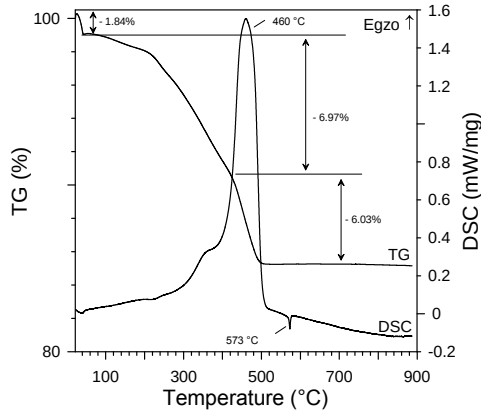

Fig. 1. TG-DSC curves of moulding sand with BioCo2 in an oxygen atmosphere

Key information obtained by analysing the TG-DSC curves for the moulding sand with BioCo2 is presented in Table 1.

Table 1.
The analysis TG-DSC curves of moulding sand with BioCo2 in an oxygen atmosphere

Stage	Oxygen atmosphere		
	Δm, %	Range of temperature, °C	DSC effect temperature, °C
I	-1.84	22-232	-
II	-6.97	232-430	-
III	-6.03	430-900	egzo-460 endo-573
	Remaining sample mass 85.16 %		

In an oxygen-free atmosphere (argon), the decomposition of moulding sand with BioCo2 follows a different course. The TG

curve of the composition shows three mass losses (Fig. 2 and Table 2). On the DSC curve, five effects are visible. The endothermic effect with a minimum in a temperature of 573 °C can be seen on the DSC curve of high-silica sand (transformation: β quartz →α quartz). The remaining part of the composition sample mass (some 89.36%) which has not decomposed up to the temperature of 900°C mainly contains mineral matrix and probably carbonised carbon.

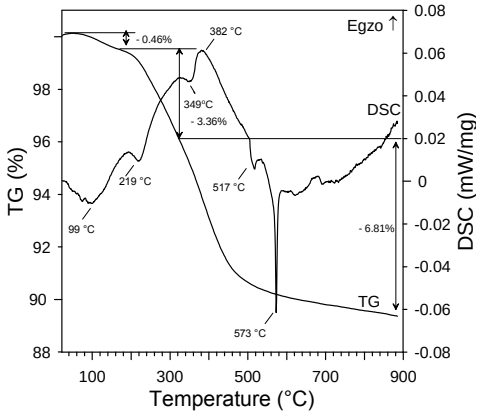

Fig. 2. TG-DSC curves of moulding sand with BioCo2 in a argon atmosphere

Key information obtained by analysing the TG-DSC curves for the moulding sand with BioCo2 composition is presented in Table 2.

Table 2.
The analysis TG-DSC curves of moulding sand with BioCo2 composition in an argon atmosphere

Stage	Oxygen-free atmosphere		
	Δm, %	Range of temperature, °C	DSC effect temperature, °C
I	-0.46	22-210	endo-99
II	-3.36	210-326	endo-219
III	-6.81	326-900	endo-349 egzo-382 endo-517 endo-573
	Remaining sample mass 89.36%		

3.2. FTIR-DRS examinations and their analysis

In the temperature range: 25-400°C in the IR spectra (Fig. 3), within wave numbers 3700-3000 cm^{-1}, the wide band – corresponding to stretching vibrations of the hydroxyl group (band of a free -OH group from water and hydrogen bonds: -O-H···O=C-) - occurs.

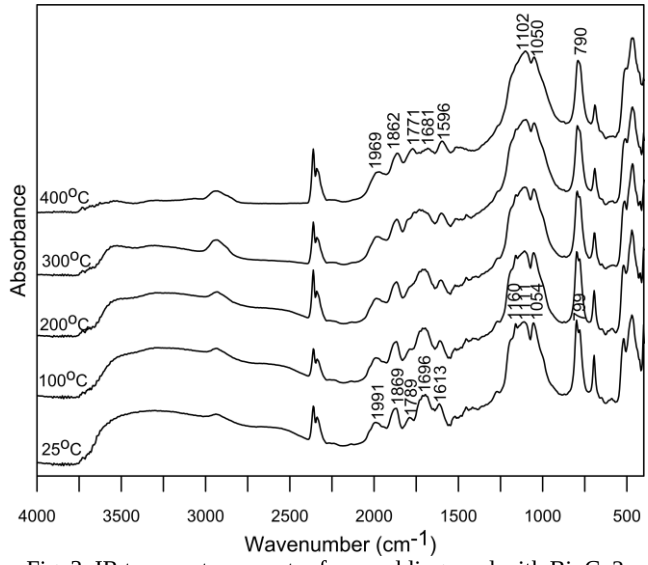

Fig. 3. IR temperature spectra for moulding sand with BioCo2

Gradually with the temperature increase the intensity of this band decreases, which is related to the solvent water evaporation and constitutional water release during heating. In the range of wave numbers 1900-1500cm^{-1} bands corresponding successively to vibrations of the carbonyl group (C=O vibrations), asymmetric carboxyl group (ν_{as}-COO^- vibrations) and hydroxyl groups (C-OH vibrations) are seen. The band characteristic for carboxyl groups gradually decays and at a temperature of 300°C. The changes is related to the progressing degradation process in polymer chains. Bands present in the range: 1900-1600 cm^{-1} shift in the directionof smaller wave numbers, when the temperature increases. The intensity of the bands decreased. At a temperature of 400°C the appearance of new bands, being the result of the progressing degradation process, can be noticed in the range 1900-1600 cm^{-1}. In the characteristic wave number range 1100-1050 cm^{-1} are seen (stretching ν_{as}Si-O-Si vibrations), while in the lower wave numbers the binary band: 799 cm^{-1} (25°C) and 790 cm^{-1} (400°C) - stretching ν_sSi-O-Si and δSi-OH vibrations. In addition, the newly formed band in the range 2300 cm^{-1} is related to the evolution of CO_2.

4. Conclusions

The cycle of investigations in which thermoanalytical methods (TG-DSC, FTIR-DRS) were applied as supplementary ones for the works on the optimisation of the thermal reclamation process is presented in the hereby paper. Physical and chemical changes take place in the moulding sands as a result of the evaporation of the solvent water, 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 220-400°C, polymer chains decompose, including the disintegration of side groups and glycoside bonds. It was found that in the temperature range of 400-500°C a gradual degradation of polymer manifests, followed - above 500°C - by its total destruction (last mass loss, Fig.1 and Fig. 2).

The thermoanalytical investigations allowed to determine the temperature range within which a degradation followed by destruction of an organic binder in a moulding sand occurs. Having such information and using properly constructed devices, it is possible to create individual processes, which will be efficient, in removal of thermal degradation remaining products and binder left-overs from the grain matrix (in the temperature range of 500-600^{o}C), as well as economical due to limiting the energy consumed in its realisation.

Acknowledgements

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