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Polymer Binder BioCo3 with Silicates and its Application to Microwave-Cured Moulding Sand

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Abstract

The effects of silica additive (Poraver) on selected properties of BioCo3 binder in form of an aqueous poly(sodium acrylate) and dextrin (PAANa/D) binder were determined. Based on the results of the thermoanalytical studies (TG-DTG, FTIR, Py-GC/MS), it was found that the silica additive results in the increase of the thermostability of the BioCo3 binder and its contribution does not affect the increase in the level of emissions of organic destruction products. Compounds from group of aromatic hydrocarbons are only generated in the third set temperature range (420-838°C). The addition of silicate into the moulding sand with BioCo3 causes also the formation of a hydrogen bonds network with its share in the microwave radiation field and they are mainly responsible for maintaining the cross-linked structures in the mineral matrix system. As a consequence, the microwave curing process in the presence of Poraver leads to improved strength properties of the moulding sand (R_m^u). The addition of Poraver's silica to moulding sand did not alter the permeability of the moulding sand samples, and consequently reduced their friability. Microstructure investigations (SEM) of microwave-cured samples have confirmed that heterogeneous sand grains are bonded to one another through a binder film (bridges).

Keywords: Polymer binder, Silica additive, Cross-link, Microwave radiation, Moulding sand

1. Introduction

In casting technology, not only resins but also synthetic or natural polymers are used as organic binding agents for foundry and core moulds [1–5]. From group of synthetic polymers are used, among others, polystyrene, poly(sodium acrylate) and polyurethanes, which are binders or are their constituents. At present, many research teams focus their research on the development of biopolymers or biomaterials [6]. Examples include the work of Patterson and Thiel in which the composition of new polyurethane binders was determined to replace polyhydric alcohols with naturally occurring materials (polysaccharides, humic acids) [7]. These binders, according to the authors, are an alternative to phenol-urethane or phenol-formaldehyde resins used in the no-bake and cold-box technologies. Known and used in the industry as an alternative to synthetic resins is the GMBOND (General Motors) protein binder in the form of a composition of polypeptides derived from natural sources. Binding of polypeptides in the moulding sand occurs as a result of the process of vaporization of physically bound water. One of the biggest advantages of GMBOND binder is its water solubility. The castings obtained in GMBOND technology meet the essential requirements for the proposed hot-box furan resin cores [8, 9]. Polysaccharides are also used in moulding sand technology. Starch and its derivatives are the most important material. In foundries, they are primarily used as additives for the green sands (with bentonite), to reduce their friability and as a bonding or stabilizing material for protective coatings. In recent years, a starch binder has been developed in Dalian University of Technology, China, which is a multi-constituent mixture of starch, kaolin, sodium silicate, dextrin, sodium hydrogen phosphate and water. The curing of the moulds is carried out thermally (heating at a temperature of 160-200°C) and the bonding process in the sand with bonding system takes place at elevated temperature. In addition, the ability to modify starch leads to new materials being used in many industries [10, 11], including in the foundry industry [12–14]. The carboxymethyl starch modified by the chemical modification is characterized by better solubility in cold water and better adhesion properties. This fact fosters the expansion of starch derivatives applications, including as binder for moulding and core moulds. In his work, X. Zhou and J. Yang have shown that thermally cured starch-based binders can replace furfuryl-based binders and that the quality of the inner surfaces of castings is very good at significantly reduced production costs. In addition, there are conducted tests to use polymers as auxiliary materials for use in the construction of foundry tools for drying and/or hardening of sand moulds and cores in the microwave field [15].

At the Faculty of Foundry Engineering AGH is also conducting the research on the use polymer in the foundry technology, including biopolymers and their derivatives [16, 17]. The attention was focused on aqueous polymer compositions with acrylic polymers (Fig. 1a) and modified biopolymer obtained from native starch (SN) as dextrin (Fig. 1b) or carboxymethyl starch (CMS-Na) with a degree of substitution (DS) in the range of 0.20-0.87 (a group of aqueous polymer binders BioCo).

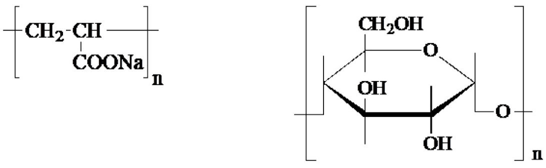

Fig.1. Structure: a) poly(sodium acrylate), b) dextrin [18]

BioCo polymer binders containing modified polysaccharides may be cured physically by microwave irradiation or chemically by calcium cations or glutaraldehyde (Fig. 2) [18].

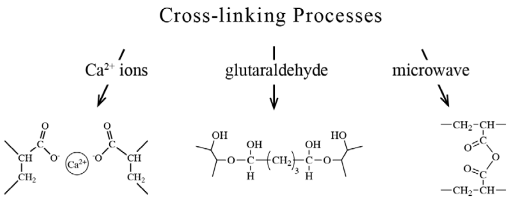

Fig. 2. BioCo binder cross-linking methods [18]

Microwave radiation is a physical factor leading to the activation of silanol groups (Si-OH) present on the surface of the mineral matrix (quartz sand). In the case of BioCo polymer binders, the formation of inter- and intramolecular cross-linking hydrogen bonds, mainly Si-OH···OH and Si-OH···O=C in the quartz -binder system (Fig. 3), is an effect of microwave radiation. These further results in the creation of a hydrogen bonding network in the considered system. Cross-linking bonds are formed within the active moieties between the adjacent polymer chains and between the polymer chains and the mineral matrix surface [19–22].

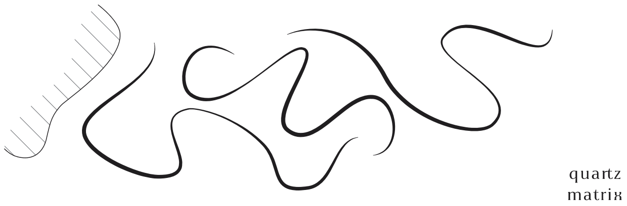

Fig. 3. Cross-linking bonds in the quartz matrix system-BioCo polymer binder formed in the microwave field [20]

Chemical bonding results in the formation of cross-linking chemical bonds (calcium or ether cationic bonds) between polymeric chains. The results of the studies have also proved that CMS-Na can be used as an main binder, and the essence of the modification is the introduction of the hydrophilic group (-CH_2COONa) into the ring of SN by its etherification. This process is carried out to stabilize the aqueous solutions of the starch and to reduce the tendency to retrogradation it at low temperature [23, 24]. Technological researches of moulding sand bonded with BioCo binders have shown their applicability. The obtained results of technological tests are on the similar level obtained for moulding sands with water-glass. In addition, it has been proven during the work carried out that, as the increases of degree of substitution of the CMS-Na, the higher strength and friability resistance of the cured moulding sands can be observed.

From an environmental point of view, the advantage of BioCo binders is their total biodegradability in the aqueous environment and in the soil, and its biodegradation products do not pose a threat to the environment. However, environmental planning should not be omitted from the thermal analysis of binders, including the determination of the level of gaseous emissions generated during the process of pouring liquid metal in moulds [25, 26]. In this field, extensive research is carried out to quantitatively and qualitatively analyse of the volatile products released under the conditions of high temperatures from moulding sand with organic binders [27–31]. In addition, the knowledge of the thermal stability of the binder is also important in terms of the possibility of thermal regeneration of the spent sands [32, 33].

In this work, results of TG-DTG, DRIFT and Py-GC/MS investigations for microwave cross-linked BioCo3 polymer binder, aqueous acrylic acid and dextrin (PAANa/D) with silica materials are presented. In addition, bonded silica-bonded BioCo3 was prepared, followed by a strength test for microwave-cured normative specimens. This work was aimed at determining the effect of silicate additive on the thermal properties of BioCo3 binder, including on the course of thermal destruction, and identification of degradation products. It was also important in the work to determine the effect of silica additive on the bonding ability of BioCo3 to the selected technological properties.

2. Methodology

2.1. Materials

The following materials were used in the study:

- Polymer binder BioCo3 (Table 1),
- Silica additive from Dennert Poraver GMBH (Poraver, Constituent: SiO_2 70-75%, Na_2O 10-15%, CaO 7-11%, Al_2O_3 0.5-5%, MgO 0-5%, K_2O 0-4%, loss o iginition 0.2%),
- Mineral matrix, silica grain sand Sibelco Poland, main fraction: 0,20/0,16/ 0,32 mm (PN-85/H-11001).

Characteristic of polymer binder BioCo3 with Poraver cross-linked with microwave radiation are presented in Table 1.

Table 1.
Characteristics of polymer binder BioCo3 with Poraver and their cross-linking parameters

Polymer binder BioCo3 with Poraver	Cross-linking conditions
- 10 parts by weight BioCo3 - 40% aqueous solution of poly(sodium acrylate) (PAANa, BASF) and dextrin (D, modified potato starch, Fluka), in a weight ratio 9:8, pH 8.5; - 1 part by weight Poraver (grain sizes 0.04-0.125 mm, bulk density 530 kg/m^3, particle density 1400 kg/m^3).	Microwave device: Samsung MS23F301TAS Microwave power: 800 W Frequency: 2.45 GHz Curing time: 60 s

The polymer binder BioCo3 with Poraver after cross-linking in the microwaves field was sent to the thermoanalytical research (TG-DTG, Py-GC/MS). In addition, some structural tests have been done (FTIR) for BioCo3 conducted to the process of heating in the temperature range of 20-420ºC.

2.2. Preparing and hardening moulding sand

All moulding sands were prepared in the following way: 100 parts by weight of silica sand, 3 parts by weight of polymer binder BioCo and 0.3 parts by weight of Poraver. The components of each system were mixed for 3 minutes using an R-1 mechanical agitator (DANLAB, 1,000 rpm) in order to precisely spread the binder between the matrix grains. The compacting system consisted in a LUZ-1 vibrator produced by WADAP (Wadowice). The device was fitted with a control module allowing the amplitude and duration of vibration to be set while the frequency was constant at 50 Hz, and a production module allowing the maximum of 9 standard shapes compacted to the same degree to be produced.

Normative samples of moulding sands for flexural strength and compressive strength studies were cured in the microwave radiation field (2.45 GHz, 800W) into the reaction chamber of the Samsung MS23F301TAS microwave oven with a series of samples of approximately 350 g total weight. Moulding sand samples were cured for 180 s.

2.3. Examinations

Thermal analysis
The thermal examinations (thermogravimetry TG-DTG) were performed by using Thermal Analyzer produced by Jota. The temperature range of test was 20-1000°C and a heating rate was of 10°C/min in oxygen atmosphere.

Fourier transform infrared spectroscopy
The research was conducted by Fourier transform infrared spectroscopy (FTIR) with the use of the spectrometer Digilab Excalibur FTS 3000 Mx. Potassium bromide mixture (about 200 mg) with the selection of the researched sample was pressed into pellet. The study of FTIR-DRS with DRIFT method was made by using snap-in high-temperature, cooled by water, with the possibility of heating the sample to a temperature of 500°C, coupled to the temperature controller. Registration of the spectrum was carried out in the range of 4000-600 cm^{-1}, with the ability to dash 8 cm^{-1}. The time of receiving the set temperature was respectively:

- 20-116 °C – 35 seconds,
- 116-293 °C – 115 seconds,
- 293-420 °C – 220 seconds.

The total measurement time was 6 minutes 10 seconds.

Additionally, there were conducted investigations by transmission FTIR technique to verification of phenomena occurs in mounding sand after 1 h, 4 h and 24 h of storage time after curing by microwave radiation.

Pyrolysis gas-chromatography/mass spectrometry
The pyrolysis gas-chromatography/mass spectrometry (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 heating of a sample to any temperature within the range 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 heating rate 20 °C/min was maintained for 3 min. Helium carrier gas at 1 mL/min, sample split ratio 1:30. The separated compounds are analysed in a mass spectrometer "MS" (ISQ Thermo Scientific) in the full range m/z. Electron ionisation (70 eV) at a temperature of 250°C was applied.

Permeability, friability and strength testing of moulding sands
Microwave-cured normative samples of moulding sands were sent to strength testing. The tensil strength (R_m^u) was regularly measured after certain time intervals (the sample maturing time) – 1 h, 4 h and 24 h - using the LRu-2e device for testing the strength of moulding sands in accordance with the standard PN-83H-11073/EN. The strength values obtained after a setting time were calculated as the averages of at least 6 measured results.

The permeability of the moulding sands was performed by fast method in electrical apparatus type LPiR1. The permeability values are expressed in the SI unit 10^{-8} m^2/Pa·s. The permeability was determined for uncured cylindrical samples and for microwave-cured samples after 1 h and 24 hours of the storage (PN–80/H–11072).

The friability resistance was determined by means of the special apparatus (Huta Stalowa Wola production) according to the accepted procedure [34]. Friability was examined after 1 h and 24 hours storage.

During all activities to produce the moulding sand - prepare a series of moulding sand samples for strength testing and perform the strength tests - the temperature in the laboratory was kept at 20°C (± 2°C), and the relative air humidity ranged from 45% to 50%.

Scanning electron microscope

Observations of microstructure of cured moulding sand samples were carried out by scanning electron microscopy (SEM) using ultrasonic scannable electron microscope NOVA NANO SEM 200 (FEI EUROPE COMPANY manufacturer) cooperating with EDA analyzer EDSX.

3. Results and discussion

3.1. Thermoanalytical studies of TG-DTG, DRIFT and Py-GC/MS polymer binder BioCo3 with silica additive

In an oxidizing atmosphere, decomposition of cross-linked polymer binder BioCo3 with silica additive Poraver occurs with four weight losses (Fig. 4). In total, four mass loss steps of 11.6%, 21.1%, 23.2% and 14.4% were observed. The maximal mass loss rates were observed at the temperatures 116°C, 293°C, 420°C and 838°C which can be seen from the DTG signal.

Within temperature range of 20-116°C, the remains of solvent water evaporate, followed by constitution water. Next, within temperature range of 116-293°C, intermolecular dehydration reaction takes place. In this temperature range, mainly reversible processes occur: physical transformations and reversible reactions [35]. On the basis of TG curves, it can be stated that thermal degradation process starts at the temperature of approx. 293°C.

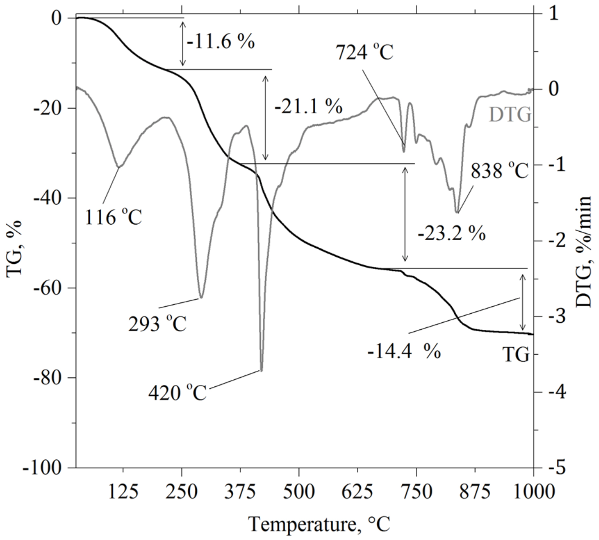

Fig. 4. TG-DTG curves of polymer binder BioCo3 with Poraver in an oxidizing atmosphere

Next, including decomposition of side chains and glyosidic bonds in dextrin (temperature range of ~293-420°C). Further on, the progressive decomposition takes place with intensive generation of gas products of destruction, including in the combustion reactions in an oxygen atmosphere [36]. A sample of the BioCo3 actually completely decomposes to the temperature of 1000°C (remaining sample mass 29.7%). Information obtained by analysing the TG-DSC curves for the BioCo3 with Poraver is presented in Table 2.

Table 2.
The analysis of TG-DTG curves

Stage	Δm, %		Temp. of maximum rate of weight loss, °C	
	BioCo3[27]	BioCo3 with Poraver	BioCo3[27]	BioCo3 with Poraver
I	12.9	11.6	110	116
II	23.1	21.1	300	293
III	16.7	23.2	450	420
IV	12.8	14.4	552	838
V	5.9	-	822	-

The thermal analysis showed that the silicate addition positively influenced the thermal stability of the BioCo3 binder. The thermal decomposition process is four steps, not five, as is the case with the original BioCo3 binder. Figure 5 presents IR spectra for cross-linked polymer binder BioCo3 with Poraver obtained at temperature 20ºC (spectrum a), 116ºC (spectrum b), 293ºC (spectrum c) and 420ºC (spectrum d).

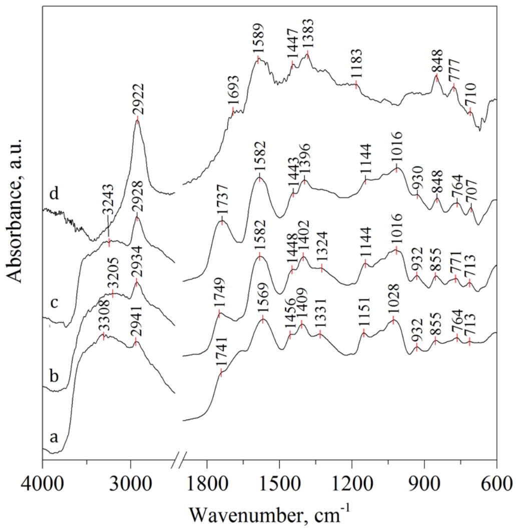

Fig. 5. IR spectra of polymer binder BioCo3 with Poraver: a) 20ºC, b) 116ºC, c) 293ºC, d) 420ºC

The wide wavenumbers range of 3800-3000 cm^{-1} corresponds to vibrations of the free hydroxyl group (spectrum a) derived from water and results from the presence of hydrogen bonds (spectra a-d). Hydrogen bonds form a cross-linked structure with the characteristic groups (C=O, -OH) contained in the polymer binder BioCo3, as well as silanol groups (Si-OH) present on the surface of the quartz matrix as well as Poraver silica material (band in the region 3200-3300 cm^{-1}, 855-848 cm^{-1}). Above the temperature of 100°C, the intensity of the bands in the range of 3200-3300 cm^{-1} is related to the evaporation of solvent water (spectra b-c), and at about 420°C their total destruction (spectrum d). In contrast, the bands in the 855-848 cm^{-1} region present in IR spectra recorded at 293°C (spectrum c) and 420°C (spectrum d) increase in intensity. This demonstrates the presence in the silanol group's silicon-based interaction system. The wavenumber corresponding to the 1737 cm^{-1} was assigned to the C=O vibrations in the carboxyl group [37]. As the temperature rises, it is shifted and at 420°C it disappears. On the other hand, a new 1662 cm^{-1} band appears. In addition, a band shift of 1569-1589 cm^{-1} is observed at the set temperature range. These changes are related to structural degradation in the carboxylate (COO^-), glycosidic (C-O-C) and hydroxyl (-OH) groups. At 293°C, a 932 cm^{-1} loss was observed. This fact is related to the degradation of polymer chains within the dextrin glycosidic bonds.

It is noteworthy that the Poraver silicate additive participates in the high temperature bonding process. This is evidenced by the change in the position of the bands with wavenumbers in the range 3300 cm^{-1}, 1150 cm^{-1} and 830 cm^{-1}.

Above 420°C there is a progressive destruction of the polymeric binder, the characteristic bands disappear, hence the IR spectrum is not recorded in the higher temperature range [27].

Table 3 summarizes the results of detailed identification of characteristic absorption bands for the IR spectra obtained by using literature data [38–40].

Table 3.
Characteristic bands in the IR spectra of polymer binder BioCo3 with Poraver

20°C	116°C	293°C	420°C	Assignment/ Remarks
Wavenumber, cm^{-1}				
3308	3205	3243	---	Hydrogen bonds: ν-OH O-H···O-H O-H···O=C Si–O–H···O–H Si–O–H···O=C
2941	2934	2928	2922	ν-C-H Stretching vibrations asymmetric and symmetric
1741 ---	1749 ---	1737 ---	--- 1693	ν_s-C=O Stretching vibrations of carbonyl group
1569	1582	1582	1589	ν_{as}-COO^- Stretching asymmetric vibration
1456	1448	1443	1447	$\delta(CH_2)_n$ Shearing symmetric vibrations
1409	1402	1396	1383	δ(C–OH) δ(CH) bending $\delta(CH_2)$ scissors
1151	1144	1144	1183	Si-O-Si Stretching vibrations
1028	1016	1016	---	$C\text{-}CH_2$ Stretching vibrations
932	932	930	---	Skeletal vibration of the glycosidic bond (C–O–C)
855	855	848	848	Si(OH)
764	771	764	777	ν(C–C) glucopyranose ring
713	713	707	710	

Qualitative analysis of gaseous products generated at the set temperature (293°C, 420°C and 838°C) during the destruction of the BioCo3 with Poraver polymer binder was performed using Pyro GC/MS (Pyrolysis Gas Mass Spectrometry). Temperature values at which the polymer binder BioCo3 with silica addition was determined, followed by GC/MS measurements based on the TG-DTG curve analysis (Fig.4) and recorded IR spectra (Fig. 5). Three temperature ranges were taken into account:

I range: 20-293°C – physical transformations and reversible reactions,

II range: 293-420°C – thermal degradation and decomposition process,

III range: 420-838°C – completely destruction.

Figure 6 shows the GC/MS chromatograms recorded for the polymer binder BioCo3 with Poraver submitted for pyrolysis at 293°C, 420°C and 838°C.

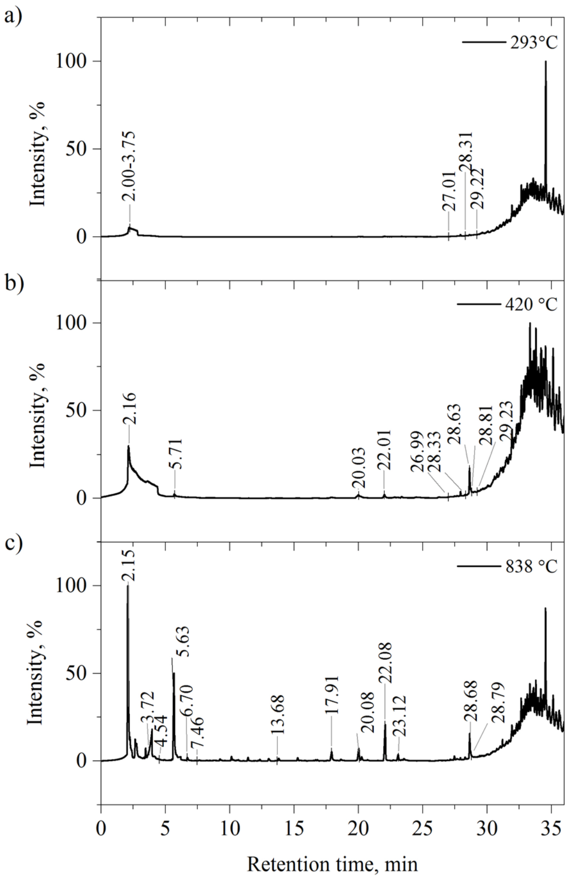

Fig. 6. Chromatograms GC/MS obtained for artwork polymer binder BioCo3 with Poraver treated with temperature: a) 293ºC, b) 420ºC, c) 838ºC

Table 4 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.

Based on the obtained results (Fig. 6 and Table 4) it can be stated that compounds from the aromatic hydrocarbon group during the degradation of the Praver silica BioCo binder are generated only in the third temperature range. Above 293°C, the increase in the presence of signals (retention time, R_T) can be observed, which indicates the progressive distribution of the binder sample in question. At a lower temperature range, only the release of carbon dioxide and organic compounds from the carboxylic acid group (chromatogram a) are released. It was only at 838°C that benzene and toluene were found in decomposition products. In addition, aliphatic and cyclic ketones were identified at 838°C. A high signal at 838°C, attributed to carbon dioxide, indicates a progressive process of destruction. In order to confirm the identification of gaseous products emitted at the set temperature, the recorded spectra of electron ion masses (EI) were analyzed. Figure 7 shows the mass spectra of benzene EI at 838°C. The most abundant peak in the spectrum (m/z = 78, 100% intrinsic) was determined from the depicted relationship of mass to charge (m/z) of positively molten fragments and their relative concentrations. The base peak at m/z = 78 was attributed to the benzene molecule. For all obtained mass spectra of EI, the analysis was carried out and the emission of the compounds of Table 3 was confirmed.

Table 4.
The results of the measurements Py-GC/MS of polymer binder BioCo3 with Poraver

Compounds	M_W*, u	Retention time R_T, min		
		293°C	420°C	838°C
Carbon dioxide	44	2.00-3.75	2.16	2.15
Glycolaldehyde	60	-	-	3.72
Hydroxymethylcyclopropane	72	-	28.63	28.68
Acetol	74	-	5.71	5.63
Benzene	78	-	-	4.54
Cyclopentenone	82	-	-	13.68
gamma-Butyrolakton	86	-	20.03	20.08
2-butanone	88	-	-	6.70
Toluene	92	-	-	7.46
2-Hydroxycyclopent-2-en-1-one	98	-	-	17.91
2-Cyclopenten-1-one	112	-	-	23.12
Pyroterebic acid	114	-	22.01	22.08
Levoglucosenone	126	-	28.81	28.79
Octanoic acid	144	27.01	26.99	-
Nonanoic acid	158	29.22	29.23	-
Dodecanoic acid	216	28.31	28.33	-

*M_W - molecular weight

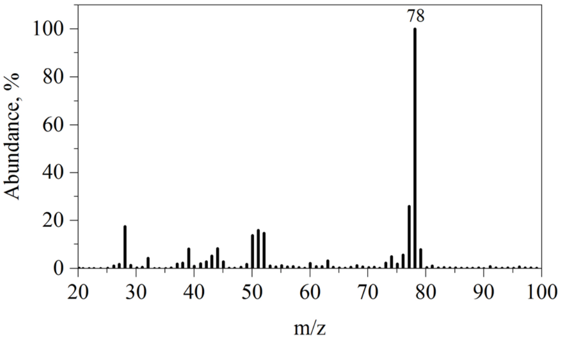

Fig. 7. Mass spectrum of benzene EI

3.2. Effect of silicate additive on selected properties of BioCo3 bonded binder in microwave field

The results of tensile strength tests (R_m^u) of sand samples hardened with microwave radiation show that sands bonded with the BioCo3 with silica additive Poraver exhibited the highest binding strength in this system after only 24 h of sand sample storage time (Fig. 8). This supports the conclusion that the full strength (level of hardening) is achieved after just 24 hours of

sand samples storage time and the longer time of sample storage causes change in the strength value.
It has been observed that moulding sands permeability after the microwave curing not significantly increased due to the evaporation of water contained in the binder solvent.
The permeability (determined after 1 h and 24 h storage) of microwave-cured moulding sand with BioCo3 binder without and with Poraver silica additive was in the range of 340×10^{-8} m^2/Pa·s. The introduction of Poraver silicate additive did not alter the moulding sand permeability.
The positive effect of Poraver's additive on the reduction of friability of the moulding sand was found, however.
The measurements carried out after 1 h and 24 hours of the storage showed friability of the moulding sand with the BioCo3 being 14.70 (± 0.92) %, while the moulding sand with the BioCo3 with the Poraver was characterized by a much lower parameter, being 11.26 (± 0.24) %.

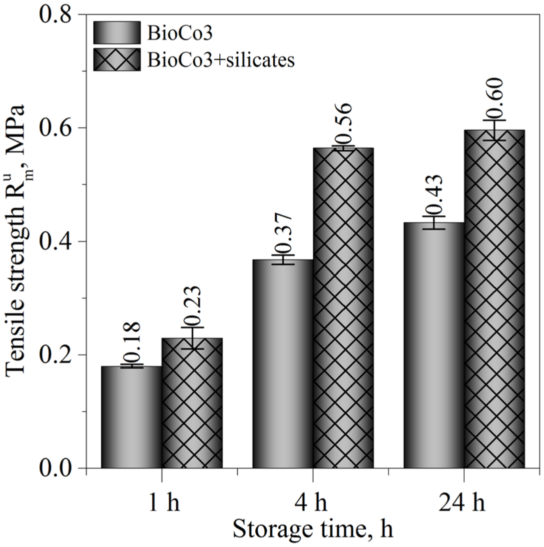

Fig. 8. Results of tensile strength measurements of microwave-cured moulding sand contains polymer binder BioCo3 without and with Poraver

Figure 9 shows an example of an SEM image of the morphology of a BioCo3 with Poraver bonded polymer binder. In SEM images, non-homogeneous quartz grains may be seen adjacent to each other, and a bonding film bonded to the matrix grains between them. Visible binders of silica sand grains are a result of cross-linking the structure formed by the intermolecular bonding of hydrogen bonds between polar moieties and silanol groups present on the surface of the mineral matrix (quartz grains).

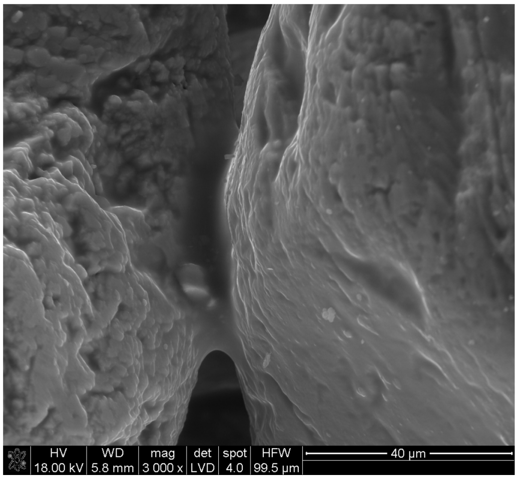

Fig. 9. SEM of microwave-cured moulding sand with polymer binder BioCo3 with Poraver

Sample of microwave-cured moulding sand bonded BioCo3 binder with Poraver was characterized by a lower friability value compared to the result obtained for the moulding sand without Poraver additive. The obtained result can be explained by the formation of crosslinked hydrogen bonds during the time of storage (e.g. 24 h) on the surface of the sample (bonds between the polar carboxyl groups –COOH and -OH in the binder and Si-OH silane groups in the mineral matrix (Fig. 10, spectrum b; ~945 cm^{-1}). On the obtained FT-IR spectra a characteristic absorption bands at the wavenumber ~1559 cm^{-1} and ~1327 cm^{-1} are typical for salts of carboxylic acids (symmetrical stretching vibrations of carboxyl anions –COO$^-$) (spectrum a and d). Negligible differences in the shape of this band – before and after the microwave cross-linking – are the result of -OH groups participation in hydrogen bonds. Band of a free OH group from water (~1645 cm^{-1}) disappear after cross-linking Fig. 10, spectra d-e).

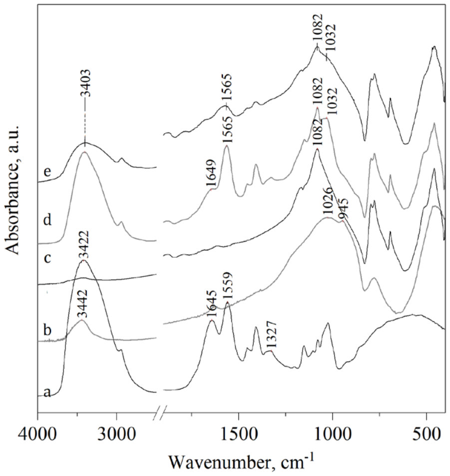

Fig. 10. IR spectra: a) BioCo3, b) Poraver, c) silica sand and moulding sand with BioCo3+Poraver system: d) before and e) after microwave curing

In addition, during the storage time on the surface of the moulding sand, moisture adsorption occurs, so that additional hydrogen bonding networks can be formed with adsorbed water (Fig.11, compare spectrum a with spectra a b-c, range 4000-3000 cm^{-1}). Poraver also contains compounds capable of binding to water (adsorption). As a result of the physicochemical phenomena described above, a layer of densely packed hydrogen bonding network is formed, which is why the increase in the stability of the surface layer of the moulding sample and the friability decrease in the sample with Poraver additive has been observed.

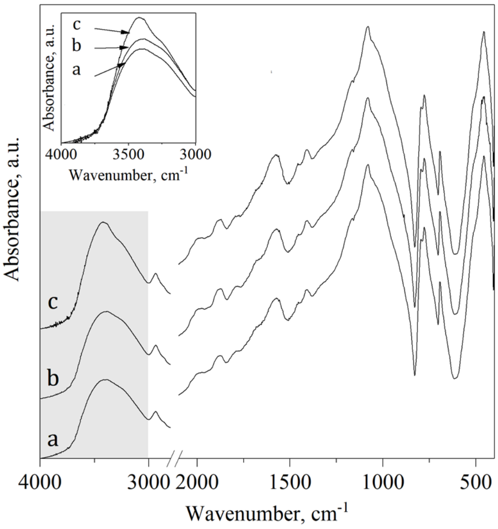

Fig. 11. IR spectra: of microwave-cured moulding sand containing polymer binder BioCo3 with Poraver after: a) 1 h, b) 4 h and c) 24 h storage time

4. Conclusions

The publication describes the effect of silica additive (Poraver) on selected properties of BioCo3 binder an aqueous poly (sodium acrylate) and dextrin (PAANa/D) binder. Based on the results of the thermoanalytical studies (TG-DTG, DRIFT, Py-GC-MS), it was found that the silica additive increases the thermostability of the BioCo3 binder and its contribution does not increase the emission of organic destruction products. It has been shown that compounds from the aromatic hydrocarbon group during the degradation of the silica additive Poraver with BioCo binder system are only generated in the third temperature range (420-838°C). At 838°C benzene and toluene were found among degradation products.

The addition of silicate into the moulding sand of BioCo3 also causes the formation of a hydrogen bonding network with its share in the microwave radiation field, and they are mainly responsible for maintaining the cross-linked structures in the mineral matrix. Consequently, the microwave cure process in the presence of Poraver leads to improved strength properties of the mass (R_m^u). The addition of Poraver silicate material to the moulding sand does not alter the permeability of the moulding sand samples, and has therefore reduced their friability. Microstructure investigations (SEM) of microwave-cured moulding sand samples have confirmed that heterogeneous sand grains are bonded to one another through the binder film.

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