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# Studies on the Renewability of Polymeric Binders for Foundry

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## Abstract

In this paper the results of studies of polymeric binders on the example of the new BioCo2 binder, including the problem of its renewability, are presented. The results of structural studies (FT-IR) for the BioCo2 binder before and after crosslinking, and bending strength tests  $R_g^u$  fresh and renewed cured molding sands with BioCo2 binder are discussed. The cross-linking binder and curing of moulding sand was carried out by physical agents (microwave radiation, temperature). On the basis of obtained results was shown that it is possible to restore the initial properties of the adhesive of BioCo2 binder. The initial properties of moulding sand can be achieved, after the cross-linking binders and after curing in the moulding sands with bioCo2 binder, by supplementing the moulding sand composition by the appropriate amount of water.

**Key words:** Innovative foundry materials and technologies, Moulding sands, Polymeric binders, Crosslinking, Renewability.

## 1. Introduction

The prospect of tightening environmental regulations imposed on foundry industry leads to the introduction of new environmentally friendly binders, which are biodegradable under the influence of natural factors. Most of them are non-toxic green materials derived from renewable natural sources, which is associated with production costs reduction while maintaining good quality castings [1-10]. In different scientific publications, one can find data on the use of adhesives containing in its composition biopolymers (peptides, polysaccharides), which can be used as binders in the foundry industry.

In addition, an important issue is the recycling of used molding sands, so are highly valued binders, which are characterized by renewal of their binding properties after the appropriate treatment.

The alternative to the synthetic resin binders in the industry is the protein-based binder, which is a mixture of polypeptides derived from renewable natural sources, introduced by General Motors as GMBOND [8]. The molding sand binding process is the result of evaporation of physically bound water. There is no

chemical reaction during the process of curing moulding sand. One of the biggest advantages of a binder is its ability to dissolve in water, and bonding process of dehydrated binder can be reversed by re-introducing water into the moulding sand [8]. GMBOND is classified as the renewable binder.

The second example of eco-binders are biourethanes. Developed at the University of North Iowa in the U.S. biourethanes are formed by the reaction of polysaccharides or humic acid with an isocyanate. This binder can replace (as conventional phenolic - urethane binder) harmful compounds such as phenol, which in the presence of tertiary amines reacts with the isocyanate and produces polyurethane. The advantage of biourethane is the easy availability of the polymer components and lack of negative impact on the environment. Their thermal degradation already occurs at about 250°C, which facilitates shakeout of cores. The surface quality of castings obtained is comparable to that of conventional polyurethane cores [9].

In Dalian University of Technology in China was created a binder, which consists mainly of a modified polysaccharide: starch (CMS). CMS with varying degrees of substitution of the carboxyl groups are characterized by different properties such as

solubility in cold water, absorption of water. This gives a great hope for wider applications of starch as a binder.

Another study of the binders show that the core sand bonded carboxymethyl starch can successfully replace the core sand with furan resin. The quality of the internal surface of the cast is very good at significantly reduced costs of production [10].

The Laboratory of Environmental Protection (AGH University of Science and Technology) is also conducting research on the development of "environmentally friendly" polymeric binders, which include natural polymers from the group of polysaccharides and synthetic polymers from the group of polyacrylates [11-13].

The result of this research is a BioCo binder, which is a two-component aqueous polymer composition [11-13], which given the appropriate technological properties [14-15] and ready availability and low cost of obtaining the components as well as the susceptibility to biodegradation may be an interesting, environmentally friendly binder of the sand molds and core sands. The crosslinking of BioCo binders can be conducted either by physical factors (microwave radiation, UV) or chemical (glutaraldehyde  $\text{OHC}-(\text{CH}_2)_3-\text{CHO}$ ,  $\text{Ca}(\text{OH})_2 + \text{CO}_2$ ).

The physical crosslinking of the binder moulding sands is carried out mainly by the evaporation of physically bound water and also in the process of dehydration in a wet moulding sand, so in the reverse process - hydration - it is possible to recover the binder from non-burned moldings [11-13], which in industrial environments, can simplify the process of refreshing the moulding sands and reduce the cost of production molds or cores. By the renewability of the BioCo2 binder the ability of the binder to reproduce its original binding properties in the process of dissolution in water is meant.

## 2. Experimental

### 2.1. Materials

- polymer BioCo2 binder -- polymer composition of poly (acrylic acid) and dextrin in aqueous solution [13];
- sand grains - silica sand of grain size 0.2 / 0.16 / 0.32 from "Szczańska" mine.

### 2.2. The cross-linking of binder samples were carried out with physical agents:

- microwave radiation power of 800 W. The process of cross-linking was carried out in a microwave device INOTEC MD 10 940 with adjustable power and time action of microwaves. radiation time of binder samples was 60 s at 100 ° C;
- temperature. Crosslinking process was conducted in a laboratory dryer SUP-65 for 1 h at 100°C.

### 2.3. Preparation of molding sand

Silica sand was put to the ribbon mixer (LM-R1), and then the polymer BioCo2 binder was added in an amount of 3 wt%. and stirred for 3 minutes.

In studies on the renewability of the BioCo2 binder the same method of preparation molding sand with the same ratio of binder to the sand grains (3: 100 parts by weight) was used. Preparations of molding sands were carried out at 25.5% relative humidity and ambient temperature of 19 ° C.

The molding sand with the BioCo2 binder was used for preparation of standard samples designed to test the bending strength of molding sand  $R_g^u$ .

### 2.4. Curing of the moulding sand

Samples prepared with moulding sand were cured by radiating them with microwaves or subjected to a temperature in the same way as for crosslinking the binder and using the same facilities.

### 2.5. Structural investigations

Structural investigations were performed using Excalibur FTIR spectrometer with a standard detector DTG and the resolving power of  $4 \text{ cm}^{-1}$ . Spectra of samples were performed by transmission technique at ambient temperature (with KBr pellets).

### 2.6. Bending strength tests of the cured moulding sands

The bending strength of cured moulding sands were rated with the universal camera LRU-2e, manufactured by Multiserw Morek, with a measuring range  $0-870 \text{ N/cm}^2$ . A series of measurements of the bending strength were done for  $R_g^u$  standard samples prepared from fresh sand and renewed after 1 h and 24 h of storage in a desiccator.

### 2.7. Microscopic studies

Observations of microstructures of cured molding sand with the BioCo2 binder were performed using the optical microscope Nikon Eclipse LV 100 with software NIS-Elements AR 2.10

## 3. The results and discussion

### 3.1. FTIR investigation of the structural changes

In the first stage of the research the structural analysis of the BioCo2 binder before and after crosslinking by physical factors (microwave radiation and temperature) was carried out using infrared spectroscopy FTIR. To determine the possibility of renewing the properties of the binder after crosslinking (carried

out by physical means); the binder was subjected successively to operations: dissolving in water and physical crosslinking. For each of the binder samples before and after crosslinking a series of FT-IR spectra (Fig. 1 and 2) was performed.

Figure 1 shows the FTIR spectra for the samples of the BioCo2 binder subjected to subsequent processes: microwave-linking and dissolving in water.

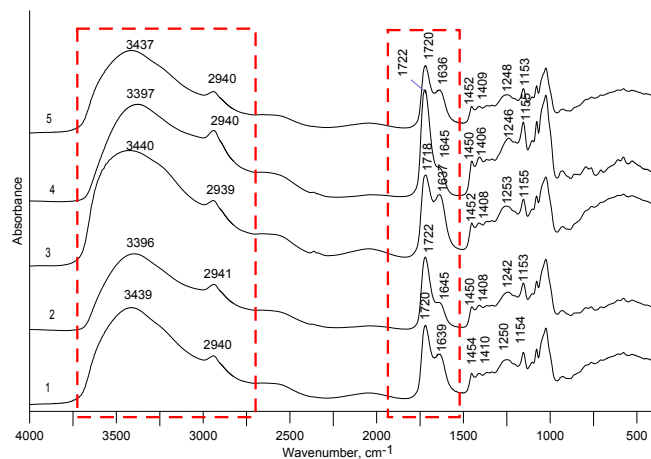


Fig. 1. IR spectra of the BioCo2 binder - microwave curing: 1-sample of non-crosslinked binder, 2-sample of crosslinked binder, 3- crosslinked sample of the binder dissolved in water, 4-crosslinked sample after the binder dissolving in water, 5 - sample of cross-linked binder after re-dissolving in water

Table 1 presents the analysis of the characteristic absorption bands for the obtained FT-IR spectra for the BioCo2 binder.

The wide band corresponding to the vibrations of the free group - OH (H<sub>2</sub>O) and hydrogen bonds does not disappear after crosslinking in the range of wave number 3800 - 3000 cm<sup>-1</sup> (spectrum 2). There is a visible reduction in the maximum intensity and a shift to lower wave numbers.

Occurrence of this band is due to the presence of bound water in the crosslinked BioCo2 binder.

An adsorption band corresponding to vibrations of C = O (1720 cm<sup>-1</sup>) remains unchanged before and after crosslinking, while slight shifts of wave numbers are within the limits of the measurement error (+ / - 4 cm<sup>-1</sup>).

Band of a wave number 1639 cm<sup>-1</sup> (vibrations of C-OH) decreases in intensity.

In addition after crosslinking a shape change in the band 1250 cm<sup>-1</sup> and its shift to lower wave numbers is visible. Structural changes in this area are related to the participation of the groups C-OH and C = O in the process of cross-linking. The bands related to vibrations of CH (-CH<sub>2</sub> group and-CH) remain the same.

After re-dissolution of the crosslinked BioCo2 binder in the appropriate stoichiometric amount of water another FTIR spectrum (Fig. 1, spectrum 3) was recorded. By comparing the spectra of 1 and 3 it can be stated that the BioCo2 binder retains its initial structure.

Table 1. The characteristic absorption bands in FT-IR spectra of non-crosslinked and microwave cross-linked polymeric BioCo2 binder

Wavenumber [ cm <sup>-1</sup> ]					Ascripti on	Characteri stic
Spectr um 1	Spectr um 2	Spectr um 3	Spectr um 4	Spectr um 5		
3439	3396	3440	3397	3437	v-OH O-H...O- H O- H...O=H	band of free groups - OH (water) hydrogen bonds
2940	2941	2939	2939	2940	v-C-H	symmetric and asymmetric stretching vibrations
1720	1722	1718	1722	1720	v <sub>s</sub> -C=O	stretching vibrations of carboxyl group in carboxylic acids
1639	1645	1637	1645	1636	δ-C-OH C=O	deforming vibrations, stretching vibration of carboxyl group
1454	1450	1452	1450	1454	δ(CH <sub>2</sub> ) <sub>n</sub>	symmetric and scissor vibration
1409	1408	1408	1406	1409		
1250	1242	1253	1236	1248	C-O C-OH	stretching vibrations deforming vibrations
1154	1153	1155	1155	1153	C-CH <sub>2</sub>	deforming torsional vibrations

Repeated exposure to microwaves radiation of the BioCo2 binder samples leads to the occurrence of changes in the structure analogous to the spectrum 2 (Fig. 2, spectrum 2 and 4).

Figure 2 presents the FT-IR spectra for samples with the BioCo2 binder subjected to the following processes: thermal cross-linking and dissolving in water.

Table 2 presents the analysis of the characteristic absorption bands for the obtained FT-IR spectra for the BioCo2 binder.

Just as for the binder crosslinked by microwave, so after thermal crosslinking in the range of wave numbers 3800 - 2900 cm<sup>-1</sup> a decrease in absorbance band corresponding to the stretching vibrations of OH-groups is visible (Fig. 2, spectrum 2). The changes are a consequence of the evaporation of water during treatment the BioCo2 binder to a temperature in the laboratory dryer. Band 1720 cm<sup>-1</sup>, which corresponds to the vibrations of -C = O (shifts of wave numbers are within the limits of sensitivity of the method), occurs in all FT-IR spectra of thermal crosslinked samples, but under the influence of crosslinking agent there is a noticeable reduction in its intensity. Band in the wave number 1639 cm<sup>-1</sup> corresponding to the vibration -COH after crosslinking almost completely disappears (Fig. 2, spectrum 2). In the wave number 1250 cm<sup>-1</sup> a decrease in absorbance bandwidth and shifting maximum of band to lower wave numbers is visible.

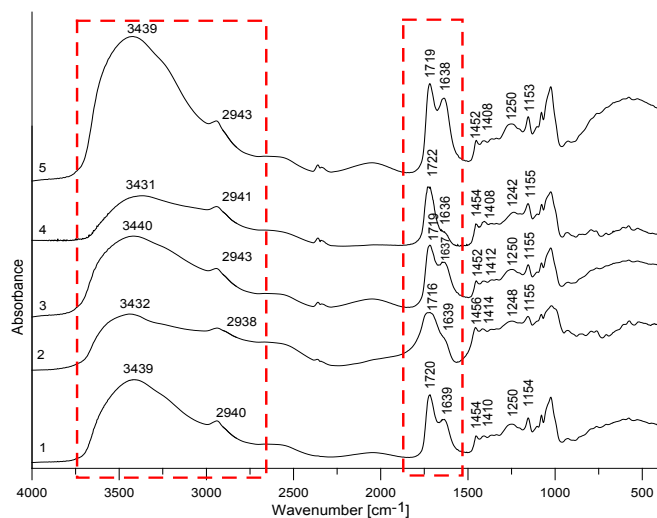


Fig. 2. FT-IR spectra of the BioCo<sub>2</sub> binder - thermal curing: 1-sample of non-crosslinked binder, 2-sample of crosslinked binder, 3-crosslinked sample of the binder dissolved in water, 4-crosslinked sample after dissolving the binder in water, 5 - sample of cross-linked binder after re-dissolving in water

The effect of conversion of the polymer structure (compared to baseline - Figure 2, spectrum 1) is observed during the crosslinking of each sample dissolved in water (Fig. 2, spectra 2 and 4), but after re-dissolved cross-linked binder in water, the course of the spectrum baseline returns to its state before crosslinking (Fig. 2, spectra 3 and 5).

### 3.2. The study of bending strength of molding sand bonded BioCo<sub>2</sub>

The bending strength test ( $R_g^u$ ) for fresh and renewed after molding sand was carried out after the storage period of 1 h and 24 h, taking into account the type of crosslinking agent (microwaves, temperature).

The term "renewed molding sand" was used in the work for the determination of the cured sand, which was supplemented with appropriate amount of water to dissolve the BioCo<sub>2</sub> binder and to restore its original properties.

The results of bending strength of fresh and rebonded moulding sand BioCo<sub>2</sub> are presented in Figure 3.

These values of bending strength as real values were estimated on the basis of calculating the arithmetic  $\bar{x}$  mean for the six samples from each batch.

This shows that the curing process occurs reversibly by physical means (dehydration), and after re-introduction of water the BioCo<sub>2</sub> binder keeps its binding properties [11-13].

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Table 2. The characteristic absorption bands in FT-IR spectra of non-crosslinked and thermal cross-linked polymeric BioCo<sub>2</sub> binder.

Wavenumber [cm <sup>-1</sup> ]					Ascription	Characteristic
Spectrum 1	Spectrum 2	Spectrum 3	Spectrum 4	Spectrum 5		
3439	3432	3440	3431	3439	v-OH O-H...O-H O-H...O=H	band of free groups - OH (water) hydrogen bonds
2940	2938	2943	2941	2943	v-C-H	symmetric and asymmetric stretching vibrations
1720	1716	1719	1722	1719	v <sub>s</sub> -C=O	stretching vibrations of carboxyl group in carboxylic acids
1639	1639	1637	1636	1638	δ-C-OH C=O	deforming vibrations, stretching vibration of carboxyl group
1454	1456	1452	1454	1452	δ(CH <sub>2</sub> ) <sub>n</sub>	symmetric and scissor vibration
1410	1414	1412	1408	1408		
1250	1248	1250	1242	1250	C-O C-OH	stretching vibrations deforming vibrations
1154	1155	1155	1155	1153	C-CH <sub>2</sub>	deforming torsional vibrations

Therefore, the BioCo<sub>2</sub> binder can be classified, in a similar fashion as the GMBOND binder [8], to a group of renewable binders. In the later stage of research the possibility of renewability of binders in the moulding sand after curing will be investigated.

The results of earlier research strength in the weight of the binders based on polyacrylate [11-13] have shown that the measurement conditions have a significant effect on strength properties. In addition, the parameters of samples thermal curing of moulding sands (microwaves, temperature) have influenced on the values of bending strength. The  $R_g^u$  value for samples from the fresh moulding sand after thermally cured amounted to about 2.6 MPa, and after microwave curing  $R_g^u$  reached a value of approximately 1.5 MPa. Irradiation time of samples of the moulding sands was 90s is allowed to obtain a value sufficient to prepare the  $R_g^u$  correct form. The prolonged action of microwaves during curing sample of moulding sand wasn't significantly influenced on the value of their bending strength.

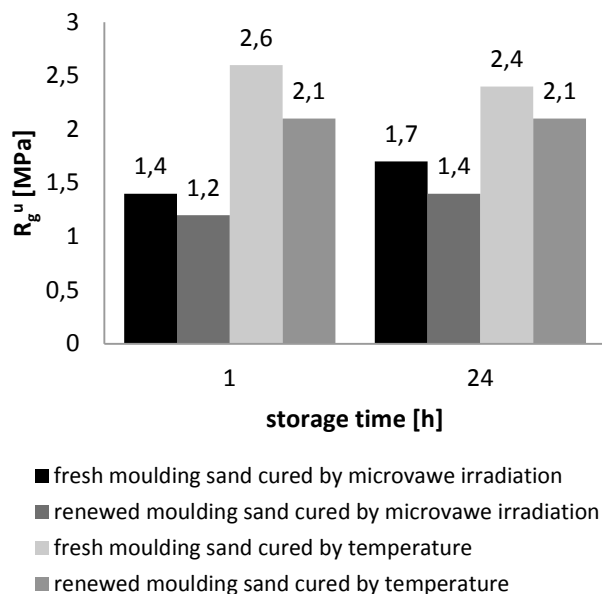


Fig. 3. The bending strength of fresh and renewed moulding sand microwave and thermally cured (25.5% relative humidity, ambient temperature 19 °C)

The bending strength of the renewed moulding sand remained at 2.1 MPa after thermal curing, and about 1.4 MPa after microwaves curing. The difference in the obtained values of strength  $R_g^u$  between cured fresh and renewed moulding sand; (regardless of the crosslinking agent) was within the error limits of the measuring device for testing of bending strength of the mouldings. So we can conclude that after the renewal of a binder BioCo2, its not lost binding power.

### 3.3. Morphology of the molding sand bonded BioCo2

The aim of this test was to determine the microscopic morphology and the method of binding surface of sand grains.

Figure 4 shows the morphology of cured molding sand bonded BioCo2 drawn up on a silica sand. The grains of sand adjacent to each other, surrounded by a layer of binder, which formed webbing binding the sand grains are visible in the figure.

## 4. Summary

Structural studies confirm the renewability of the BioCo2 binder. The results of spectroscopic investigations indicate that crosslinking of the BioCo2 binder by physical factors is a reversible process, and the dissolution of cross-linked binder in water leads to a reversal of changes in the binder structure, which occurred as a result of water evaporation.

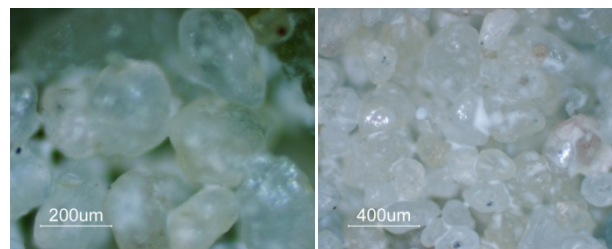


Fig. 4. The morphology of the cured molding sand with a BioCo2 binder and silica sand

The type of crosslinking agent (microwaves, temperature), the course and the process conditions have a significant effect on the bending strength of cured molding sand with the BioCo2 binder. Although the type of crosslinking agent (microwaves, temperature), the course and process conditions affect the bending strength of the cement hardened mass BioCo2.

From the results obtained the testing bending strength  $R_g^u$  has been determined efficiency of physically cross-linking agents BioCo2 binder in moulding sand. Renewed moulding sand has comparable bending strength to the fresh cured moulding sand, from a technological point of view of the results obtained for the renewed moulding sand  $R_g^u$  are sufficient for the proper execution of form.

Included in the article results of research related to the renewable BioCo2 binder constitute the starting point for further experiments on moulding sands with polymeric BioCo binders.

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