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# Using Selected Chemical and Physical Factors to Cross-link a BioCo Polymer Binder - Mineral Matrix System

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## Abstract

This publication describes research on the course of the process of cross-linking new BioCo polymer binders - in the form of water-based polymer compositions of poly(acrylic acid) or poly(sodium acrylate)/modified polysaccharide - using selected physical and chemical factors. It has been shown that the type of cross-linking factor used influences the strength parameters of the moulding sand. The cross-linking factors selected during basic research make it possible to obtain sand strengths similar to those of samples of sands bonded with commercial binders. Microwave radiation turned out to be the most effective cross-linking factor in a binder-matrix system. It was proven that adsorption in the microwave radiation field leads to the formation of polymer lattices with hydrogen bonds which play a major role in maintaining the formed cross-linked structures in the binder-matrix system. As a result, the process improves the strength parameters of the sand, whereas the hardening process in a microwave field significantly shortens the setting time.

**Keywords:** Polymer binders, Moulding sands, Cross-linking, Hardening, Microwave radiation

## 1. Introduction

The utility of a given moulding or core sand in foundry technology is determined by its moulding ability and its behaviour in real conditions, i.e. at a high temperature when liquid metallic alloy is poured into the mould. The quality of castings produced in sand moulds usually depends on the composition of the moulding sand. For the majority of moulds produced of sands bonded with organic binders, the physical and chemical condition of moulding materials keeps changing throughout the hardening time. These changes are quick at the beginning, but as time passes, the state of the mould stabilises and chemical reactions stop. While the sand is hardening in the mould and then the mould is filled with a metallic alloy, organic binders containing sulphur, nitrogen, phosphorus atoms or phenyl groups in their structure may undergo physical and chemical transformations which cause environmental pollution and negatively impact the quality of castings. Contrast this with the fact that the final, expected result of the technology is a sound casting, very smooth, with the specified dimensional accuracy, free of internal defects, with the desired structure and mechanical properties. To meet these requirements, the process of producing castings must be considered in a comprehensive way [1, 2]. This publication describes a procedure which was to lead to an effective cross-linking, using selected chemical and physical factors, of new BioCo polymer binders in the form of water-based polymer

compositions of poly(acrylic acid) or poly(sodium acrylate)/modified polysaccharide in a binder-matrix system.

# 2. Research methods

In order to verify methods of cross-linking new BioCo polymer binders in moulding sand using both physical and chemical cross-linking factors, the binders were hardened in a binder-mineral matrix system.

## 2.1. Research material

The research concerned the following new polymer binders in the form of water-based polymer compositions of poly(acrylic acid) or poly(sodium acrylate)/modified polysaccharide were used [3]:

- BioCo1: poly(acrylic acid)/carboxymethyl starch (PAA/CMS);
- BioCo2: poly(acrylic acid)/dextrin (PAA/D);
- BioCo3: poly(sodium acrylate)/dextrin (PAANa/D).

The mineral matrix consisted of a moulding quartz sand from the Jaworzno Szczakowa mine (1K-0,2/0,16/0,32, PN-85/H-11001). 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.

## 2.2 Preparing sands

All moulding sands were prepared in the following way: 100 parts by weight of mineral matrix, namely the moulding quartz sand from the Jaworzno Szczakowa mine (1K-0,2/0,16/0,32, PN-85/H-11001) were fed into a paddle mixer (Ms-017A). Then, the specified amount of binder ranging from 1 to 3 parts by weight was added and the contents were mixed for 3 minutes. If chemical hardening was used, the following ingredients were fed in the following sequence: the matrix, a stoichiometrically determined quantity of $Ca(OH)_2$, then the components were mixed for 3 minutes, then the binder was added and another 3-minute mixing followed. 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.

## 2.3. Hardening sands

Moulding sand samples to be used for strength testing were hardened in accordance with the measurement parameters presented in Table 1. For chemically hardening sands using $Ca(OH)_2$ and $CO_2$, a system for blowing gas through compacted shapes was used. It consisted of: a blower supplying $CO_2$ and an electronic controller made by PRAXAIR which automatically closed the flow of gas after a programmed time.

## 2.4. Strength testing

After the sands were hardened using physical and chemical methods, their flexural strength ($R_g^u$) and compressive strength ($R_c^u$) were regularly measured after certain time intervals (the sample maturing time) - 1h, 2h, 3h and 24h - using the LRu-2e device for testing the strength of moulding sands and in accordance with the standard PN-83H-11073/EN. The strength values obtained after a certain time were calculated as the averages of at least 6 measured results.

During all activities to produce the 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%.

Table 1.
Methods used to harden samples of moulding sands

| Hardening method | Device | Hardening conditions |
|---|---|---|
| $Ca(OH)_2$ and $CO_2$ | blower supplying $CO_2$ | distributing the cross-linking substance<br>$CO_2$ blowing time: 60s |
| heat | laboratory oven SNOL 82/1100 | holding temperature 100-150°C<br>holding time 1h |
| microwaves | microwave device: RM 2001 Pc, Plazmatronica | microwave power 800 W<br>microwave action time 60s<br>temperature inside the device 100°C |

## 2.4. Structural examinations of sands

Structural examinations were carried out by Fourier Transform Infrared Spectroscopy (FTIR) using a Digilab Excalibur FTS 3000 Mx spectrometer with an electrically cooled DTGS detector.

# 3. Strength test of sands bonded with BioCo binders hardened using selected chemical and physical factors

The results of flexural strength tests of samples of sands hardened with $Ca(OH)_2$ and blown with $CO_2$ show that the BioCo1 binder exhibits the greatest binding strength in this system (Fig. 1).

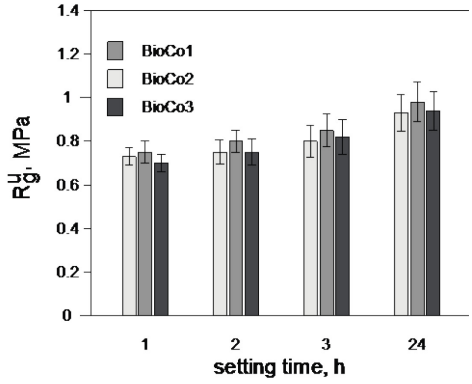


Fig. 1. Flexural strength measurement results for samples of sands bonded with BioCo binders hardened with $Ca(OH)_2$ and $CO_2$

It is also apparent that flexural strength rises gradually over 24 hours. This proves that the setting process occurs during this time (Fig. 2).

Two functional groups are involved in the cross-linking reaction: carboxyl (-COOH, found in PAA) and carboxylate (-COONa, found in CMS) [3].

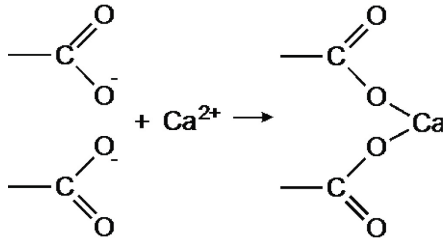


Fig. 2. An ion reaction network of chemical cross-linking with $Ca(OH)_2$

The results of flexural strength tests of sand samples hardened with microwave radiation show that sands bonded with the BioCo2 binder exhibited the highest binding strength in this system after only 1h of sand sample maturing (Fig. 3). It should also be noted that after 24 hours, the flexural strength values of sand samples stayed the same (differences within the statistical error range). This supports the conclusion that the full strength (level of hardening) is achieved after just 1 hour of sand samples maturing and the time of sample maturing causes practically no change in the strength value.

If samples of moulding sands are traditionally, thermally hardened by baking, they reach lower flexural strengths than those hardened with microwaves. This suggests that the way heat propagates in moulding sand impacts the course of the cross-linking reaction, and hence also the strength characteristics of the sand. The BioCo2 binder exhibits the greatest binding strength in this system after just 1h of maturing (Fig. 4). It can also be seen that, just as in the case of microwave radiation hardening, the flexural strength values of sand samples hardened traditionally (by baking) stay practically the same over 24 hours. In this case the time of sample maturing does not cause any strength change either.

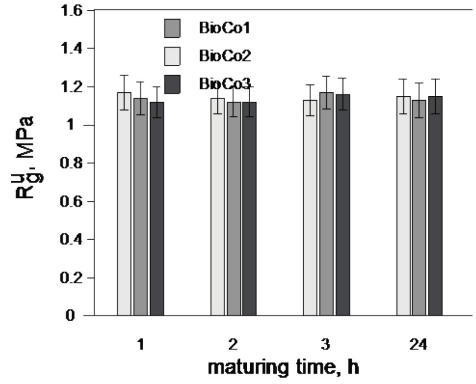


Fig. 3. Results of flexural strength measurements of sand samples bonded with BioCo binders hardened with microwave radiation

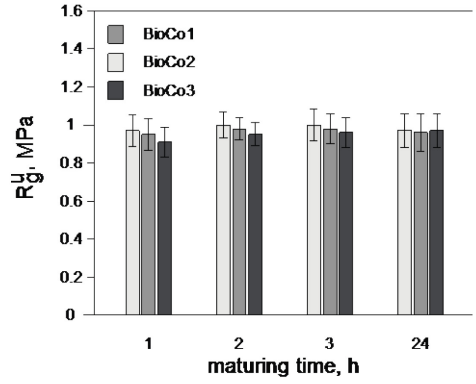


Fig. 4. Results of flexural strength measurements of sand samples bonded with BioCo binders hardened thermally

In addition, compressive strength tests of sand samples bonded with BioCo polymer binders maturing for 1 hour yielded values of around 2 MPa for thermally hardened samples and 2.3 MPa for those hardened with microwaves. The maturing time did not cause a change in the compressive strength. Also in the case of compressive strength sands thermally hardened by baking exhibited slightly lower values than those hardened with microwaves. Moulding sands containing polymer binders hardened with calcium hydroxide and $CO_2$ were characterised by lower compressive strength of approximately 1.5 MPa after 1h of maturing.

The selected methods of physically hardening moulding sands bonded with BioCo polymer binders make it possible to achieve strengths similar to those of sands bonded with commercial organic and inorganic binders [4-8]. The flexural strength results obtained for sand samples bonded with new BioCo polymer binders are comparable to those of sand samples bonded with water-glass or with a phenol resol resin hardened with $CO_2$ (for instance Hüttenes-Albertus CARBOPHEN 6240). However, the strength values achieved are much lower than those of sands bonded with furfuryl resins (e.g. Hüttenes-Albertus Kaltharz U404). For this reason, at the current stage of work, sands bonded

with the new BioCo binders can only be used to produce moulds for producing simple castings.
Among the methods used to harden sand samples bonded with BioCo binders, the best strength characteristics were obtained for moulding sands hardened with microwave radiation. Consequently, further work focused on finding the reason for this phenomenon.

# 4. The cross-linking process in the microwave field

At the first stage of moulding sand preparation, physical adsorption occurs as a result of binder molecules collecting on the surface of the matrix due to van der Waals intermolecular interactions, dispersion or electrostatic forces. However, the energy of these interactions is low. Only as a result of the hardening process are strong cross-linking bonds created in the binder-matrix system, and these lead to the strength of the sand increasing [8-11]. Electromagnetic radiation in the microwave range causes temperature to rise because a part of the microwave energy is converted into heat and the resonance excites groups within polymer chains making them rotate, thus contributing to the formation of cross-linked structures. In the complex system of the considered moulding sand, microwave radiation can activate both polymer molecules and the surface of quartz crystals. An analysis of literature data indicates that chemical adsorption is usually activated thermally [12, 13]. In addition, the research carried out on adsorption phenomena in sands bonded with a polyacrylate binder also indicates that the adsorption process plays an important role in the hardening of the sand in a microwave radiation field [3, 8]. In the case of adsorption in the analysed binder-matrix system, the temperature conducive to adsorption ranges from 100°C to 200°C. Below this range, the process speed is too slow, while above it, the equilibrium state can shift towards desorption and then degradation [3, 8, 12]. Microwave radiation may activate the binder-matrix system, leading to chemical adsorption and the formation of C-O-Si bonds. However, the growth of the bonding power of a binder-matrix system in a microwave field is mainly caused by physical adsorption, as strongly cross-linked structures are formed with intermolecular hydrogen bridges.

Figure 5 shows example FTIR spectra obtained for the BioCo1 binder (the PAA/CMS polymer composition) in the binder-matrix system after microwave hardening (60 s, 800 W). Between the 3,700 $cm^{-1}$ and 2900 $cm^{-1}$ wave numbers, there is a broad absorption band corresponding to stretching vibrations of –OH groups (hydrogen bonds). Ultimately, after the binder has cross-linked in the system, the shape of this band changes: it significantly broadens. This change may be due to the creation of new intermolecular hydrogen bonds between polymer chains and of new hydrogen bonds resulting from the interaction between the Si-O-H silanol groups and carboxyl (-COOH) or carbonyl groups (>C=O) of the following types: Si-O-H···O-H and Si-O-H···O=C. After the cross-linking, in the 2000-600 $cm^{-1}$ wave number range, the absorption band around the 1635 $cm^{-1}$ wave number (spectrum 2, C-OH deformation vibrations) disappears (spectrum 3), while the band around 1718 $cm^{-1}$ (spectra 1 and 2) becomes significantly more intensive (spectrum 3), but the shift that occurs does not exceed the sensitivity limits of this method. These changes may result from the superimposition of vibrations associated with the formation of new bonds involving the carbonyl group –C=O (of an ester or an anhydride type) during the cross-linking reaction.

Within the 1080-700 $cm^{-1}$ range of wave numbers, there are absorption bands that can be associated with the asymmetrical and symmetrical stretching vibrations $\nu_{as}$Si-O-Si and $\nu_s$ Si-O-Si (1081 $cm^{-1}$, spectra 3 and 4). Within the analysed range, slight differences can be observed in the spectra of samples containing quartz sand. In addition, the 796 $cm^{-1}$ band (spectrum 4) shifts towards a higher wave number of 801 $cm^{-1}$, which may also be associated with the formation of a small number of C-O-Si bonds or the presence of the vibrations $\nu_s$ Si-O-Si.

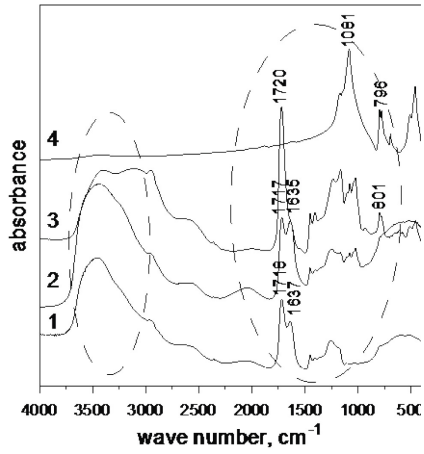


Fig. 5. Example FTIR spectra of the samples: 1. BioCo1 binder, 2. BioCo1 binder-matrix system, 3. BioCo1 binder-matrix system, microwaves, 4. Matrix

During the cross-linking in a microwave field, the binder-matrix system undergoes chemical changes (dehydration-hydration) and physical changes, including reversible processes (solvent evaporation, the formation of hydrogen bonds) [3]. Thus the process of BioCo polymer binder setting under the influence of microwaves has a physical and chemical character, with reversible intermolecular lattices forming (Fig. 6).

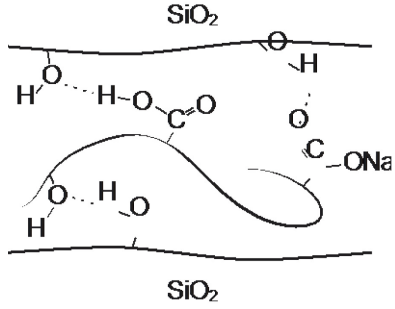


Fig. 6. A diagram of the formation of polymer lattices, including the formation of intermolecular hydrogen bonds

Thus BioCo binders, just like the protein GMBOND binder produced by General Motors, can be classified to the group of so-called renewable binders [14, 15]. However, BioCo binders are fully renewable only up to the temperature of approximately 220°C, as above ~250°C, irreversible changes may occur in the binder structure (thermal degradation). Still, as BioCo binders are renewable within a certain temperature range, there are reasons to start work on a process of rebonding recycled sands bonded with BioCo binders.

During the structural examinations, vibrations corresponding to the formation of cross-linking hydrogen bonds in the binder-matrix system were observed for the whole group of BioCo binders [3].

# 5. Summary

BioCo binders in a moulding sand can be hardened chemically, by feeding $Ca(OH)_2$ as a crosslinking agent to the sand and blowing it with $CO_2$. This method is known and used, for instance, in the technology of sands in which the binder consists of water-glass or synthetic resins like CARBOPHEN (Hüttenes Albertus). In addition, sands bonded with BioCo polymer binders can be hardened physically (with microwaves, temperature). Methods of hardening by thermal drying (baking) or hot-box technologies are also used in the foundry industry. One example is the phenol resin called RESITAL B (Hüttenes Albertus) which bonds at a higher temperature. Another hardening method is microwave radiation, which is also used in foundry practice, e.g. for water-glass and organic binders. Thus the presented method of hardening (both physical and chemical) would not require adding extra equipment into the technological processes. It has been found that the highest flexural strength was achieved by sands hardened in the microwave field.

In the process of hardening sands with electromagnetic radiation, the main role is played by the process of physical and chemical adsorption activated by microwaves. The microwaves used activate both the polymer molecules and the surface of quartz crystals and cause temperature to rise quickly in the analysed system. This contributes to physical/chemical adsorption and the formation of chemical bonds (ester, anhydride) as well as intermolecular hydrogen bridges (polymer lattices in the binder-matrix system), making the strength properties of the sand grow, whereas if the hardening process is conducted in a microwave field, this significantly cuts the setting time. In addition, it should be noted that the process of setting under the influence of microwaves is a result of the formation of reversible polymer lattices with hydrogen bonds.

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# Zastosowanie wybranych czynników chemicznych i fizycznych w procesie sieciowania układu spoiwo polimerowe BioCo – osnowa mineralna


## Streszczenie

W pracy przedstawiono badania nad przebiegiem procesu sieciowania wybranymi czynnikami fizycznymi i chemicznymi nowych spoiw polimerowych BioCo w postaci wodnych kompozycji polimerowych poli(kwas akrylowy) lub poli(akrylan sodu)/modyfikowany polisacharyd. Wykazano, że rodzaj zastosowanego czynnika sieciującego ma wpływ na właściwości wytrzymałościowe masy formierskiej. Przy czym wytypowane podczas badań podstawowych czynniki sieciujące dają możliwość uzyskania wytrzymałości mas zbliżonych do osiąganych przez próbki mas wiązanych spoiwami komercyjnymi. Promieniowanie mikrofalowe okazało się najefektywniejszym czynnikiem sieciującym w układzie spoiwo-osnowa. Udowodniono, że w polu promieniowania mikrofalowego na drodze adsorpcji zachodzi proces tworzenia się sieci polimerowych z udziałem wiązań wodorowych i to one są głównie odpowiedzialne za utrzymanie powstałych usieciowanych struktur w układzie spoiwo-osnowa. W konsekwencji proces ten prowadzi do poprawy właściwości wytrzymałościowych masy, przy czym prowadzenie procesu utwardzania w polu mikrofal znacznie skraca czas wiązania.