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NEW BioCo BINDERS CONTAINING BIOPOLYMERS FOR FOUNDRY INDUSTRY

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Possibilities of cross-linking of new polymer binders from the BioCo group, their hardening in moulding sands at the application of cross-linking agents both physical and chemical are presented. Their thermal stability was determined. It was proved, that moulding sands bound by the BioCo binders are characterised by the compression strength (R_c^u) of an order of 2 MPa, and the bending strength (R_g^u) of 1 MPa, after 1 hour of a sample curing. The worked out BioCo binders are biodegradable and renewable in the part which was not completely burned. The investigated moulding sands with the BioCo binders are easily knocked out and have a good susceptibility for mechanical reclamation processes.

Key words: foundry, moulding sands, polymer binders, spheroidal cast iron, biodegradation

INTRODUCTION

Polymer binders applied in foundry practice contain synthetic or natural polymers dissolved in appropriately selected solvents [1, 2]. Among synthetic polymers are polysiloxanes, sodium polyacrylan and polyacrylic acid [3]. Papers dealing with the development of binding agents and processes using biopolymers and their derivatives can be also found [4-7].

Within the engineering of foundry processes increasing demands concerning technical, ecological and economic parameters of binding materials are presently observed. This fact supports the development of new technologies and utilising new binding agents as well as the explanation of accompanying cross-linking and degradation processes. This knowledge facilitates designing and control of the technological process and obtaining – at the final technological state – the sound castings of the required dimensions [1, 2].

The research concerning the application of new polymer binders for moulding sands are carried out in the Laboratory of Environment Protection, the Faculty of Foundry Engineering, AGH. Within these investigations the new, water soluble, binders containing biopolymers were worked out. These binders are polymer compositions in a form of water solutions of natural (polysaccharides) and synthetic (polyacrylanes) polymers. They are characterised by several desired physical, chemical and technological properties, due to which they can become a serious alternative of organic binders for moulding and core sands [8, 9]. Experimental tests performed in the foundry plant confirmed the laboratory results in the range of utilising the polymer compositions as moulding sands binders and the produced iron castings fulfilled all qualitative requirements [9].

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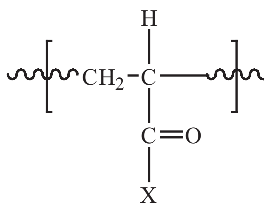
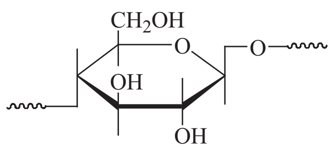
COMPOSITION OF THE BioCo BINDERS

The composition of the BioCo binders as a water polymer mixture was worked out with taking into consideration physical and chemical properties of initial polymer components, synthetic and natural (molecular mass, viscosity, pH, concentration) and their solubility in water (hydrophility) [10, 11]. The synthetic polymer belongs to polyacrylic group (formula I), while the biopolymer to polysaccharides (formula II).



Formula I



Formula II

CROSS-LINKING OF THE BioCo BINDERS

The appropriate selection of the cross-linking agent has a decisive influence on the bonding power of moulding sand matrix grains by a binder. For the BioCo binders the chemical cross-linking agents (glutaric aldehyde OHC-$(CH_2)_3$-CHO, $Ca(OH)_2 + CO_2$) as well as physical (temperature, microwave and UV radiation) were selected [8].

The structural FTIR examinations (spectrometer Digilab Excalibur FTS 3000 Mx with DTGS detector) proved, that the kind of the cross-linking agent applied is essential for the course of the cross-linking reaction of the polymer composition (Figure 1).

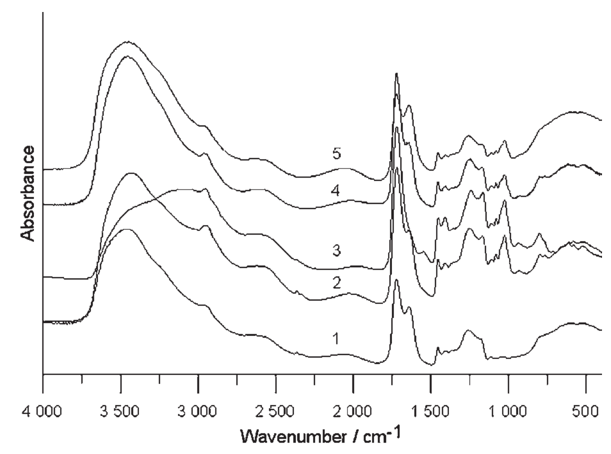


Figure 1 Examples of the FTIR spectra for the BioCo1 (1) binder cross-linked by various agents: (2) microwave, (3) UV, (4) aldehyde, (5) $Ca(OH)_2 + CO_2$

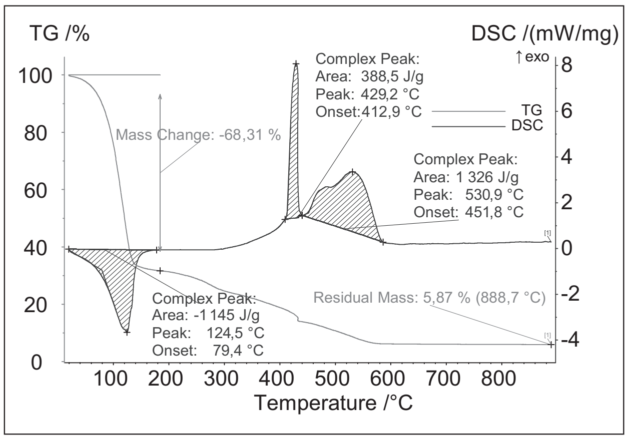


Figure 2 Examples of the mass change (TG) and the DSC curves dependence on the temperature for the BioCo1 binder

Glutaric aldehyde as a two-functional compound has a possibility of cross-linking polymer chains of neighbouring carboxylic and hydroxylic groups. In the cross-linking process performed by means of $Ca(OH)_2$ + CO_2, two-positive Ca^{2+} cations are built into polymer chains. This is a ionic reaction and no significant changes in the absorption bands positions in the IR and Raman spectra - before and after the cross-linking – are observed. Only intensity changes of individual bands can be noticed. The cross-linking process of composition samples: poly(acrylic acid)/carboxymethylstarch by microwaves and UV radiation occurs with new bonds formation with the participation of carbonyl group –C=O. During the microwaves operation probably also occurs the dehydration reaction in between two carboxylic groups either within one polymer chain or between groups belonging to the neighbouring chains. Hydrogen bonds are essential in the cross-linking process being done by microwaves. In the case of the cross-linking process performed by the UV radiation the radical course of reaction is probable. Such reaction occurs with the formation of active radicals in polymer particles. These radicals can react with each other and in consequence the reaction leads to forming the cross-linked product of a highly branched structure.

THERMAL STABILITY OF THE BioCo BINDERS

The thermal analysis methods (NETZSCH model STA 449 ***F3*** *Jupiter*®) were applied in order to determine the thermal stability of the BioCo binders by means of establishing their destruction temperatures and thermal effects occurring during heating.

On the basis of the obtained results (DSC-TG) and their analysis it can be stated (Figure 2), that the thermal degradation of the BioCo binders occurs in two stages, in accordance with the general mechanism of the radical disintegration [12, 13]. The degradation is preceded by the dehydration process, which occurs at a temperature of app. 130 ^{o}C and consists of the loss of the solving water followed by the loss of the constitutional water. The dehydration process can be accompanied by the formation of intramolecular anhydride rings. The real thermal degradation process starts at the initiation stage, during which free macroradicals are formed due to cracking the interatomic bond in the main chain of the macromolecule. Above a temperature of 300 ^{o}C an intensive cracking of chemical bonds occurs in macromolecules. This process grows rapidly with a monomer emission followed by gaseous products of the organic substances decomposition, which finally leads to the sample destruction. In addition, on the basis of the analysis of these volatile decomposition products, carried out by means of the thermo-gravimetric (TG) method coupled on-line with the mass spectrometry (MS), it was found that quite considerable amount of small-molecule decomposition products evolve: carbon dioxide (IV), water and methane.

MOULDING SANDS BOUND BY THE BioCo BINDER

Moulding sands with the BioCo binders, containing biopolymers, hardened by microwaves are characterised by the compression strength (R_c^u) of an order of 2 MPa and the bending strength (R_g^u) of an order of 1 MPa, after 1 hour of a sample maturing. The weight ratio of the binder and sand grains in moulding sands is usually maintained in proportion: 3 to 100 [6-8].

The prepared moulds made of a moulding sand with the BioCo2 binder thermally hardened was poured with liquid cast iron. A temperature of pouring was app. 1 400 °C. The obtained cast iron had the following chemical composition:
C – 3,71 %; Si – 2,69 %; Mn – 0,44 %; P – 0,05 %;
S – 0,010 %; Cr – 0,04 %; Mg – 0,042 %; Cu – 0,02 %.

The microstructure of the spheroidal cast iron in the boundary: casting/mould - is shown in Figure 3. Metallographic investigations were performed by the optical microscope Leica MEF-4M. The microstructure was estimated at magnifications of 25 and 100 x.

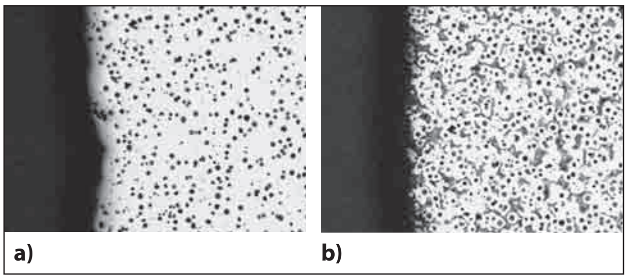


Figure 3 Microstructure of castings obtained in moulds containing the new generation of polymer BioCo2 binders: a) Polished section not etched, b) Etched polished sections

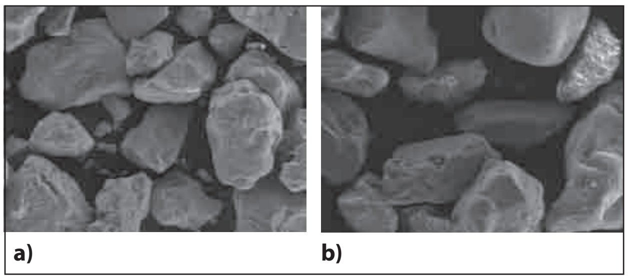


Figure 4 Surface morphology: a) Spent sand, b) Reclaim

The metallographic tests (Figure 3 a), b) indicate, that graphite nodules are uniformly distributed within the whole casting cross-section.

Defects related to the moulding sand influencing the casting surface and the microstructure were not seen in the castings. Castings were without such defects as: pittings, surface deformations, gaseous porosities or graphite deformation in the near surface layer.

RECLAIMABILITY OF SPENT SANDS WITH THE BioCo BINDER

Investigations of the reclamation process were carried out by means of the device operating on the basis of the rotor reclaimer. On the grounds of the obtained reclaimability results of the investigated spent sand with the BioCo binder, it can be stated that it is characterised by a good susceptibility for the mechanical reclamation processes. The obtained indices of the degree of liberating sand grains from binding materials after 15 minutes of the reclamation process were from 12,95 % to 49,95 % (this is a very high level – much higher than obtainable for sands with furfuryl resin) respectively, for the process performed with the slowest and highest rotational speed of the testing device rotor.

The reclamation process performed even at a very intensive reclamation influence (rotational speed of 1 760 rpm) does not cause unfavourable crushing of a matrix, which enables obtaining so high degree of cleaning the spent sands.

The morphology of the spent sand with the BioCo2 binder and the reclaim is presented in Figure 4 a), b).

RENEWABILITY AND BIODEGRADATION OF THE BioCo BINDERS

The BioCo binders in moulding sands are renewable in this part, which was not totally burned and the spent sand was easily knocked out, enabling its recycling. The possibility of the reclaimability of the BioCo binders in sands constituted a point of departure for the trials of rebounding the spent moulding sand bound by the BioCo binders. It was found, that the composition of the reclaimed sand depends on the burning degree of the spent sand bound with the BioCo2 binder. Therefore, from the economic point of view. a relatively fast casting knocking out from the mould – after pouring it with liquid metal – is essential to prevent the binder carbonization in a significant mould volume. A separation of the burned part from the spent part is also important, since the part without the binder decreases the overall sand resistance.

Investigations of the biodegradation of the BioCo binders allow to state, that there is a possibility of using the static test (Zahn Wellens) as a method testing the biodegradability of water soluble foundry binders. After 28 days of the test duration the biodegradation degree exceeds 60 %, which means that the BioCo binders can be considered as fully biodegradable in the water-solution. In addition, the biodegradation investigations (the results of structural and microscopic investigations and thermal analysis) of the tested polymer composition performed in the soil indicated that this material undergoes a gradual biodegradation under an influence of moisture and substances contained in the soil. This means that the BioCo binders are suitable for the biodestruction under conditions being close to the ones usually existing in dumping grounds.

CONCLUSIONS

The development direction of the moulding sands production and at the same time the possibility of using synthetic resins is related to several technological as well as economic and ecological aspects. Widely applied – in the foundry industry - synthetic resins as binding agents of moulding sands must meet several requirements demanded by the foundry plants and by the clients for whom the final castings are intended. Quite often these final products are harmful for the environment and of high production costs resulting from prices of the applied resins and additions.

New polymer compositions containing biopolimers characterised by several desired physical and chemical as well as technological properties can constitute a serious alternative of moulding and core sands binding agents. The presented hereby investigations related to working out the new BioCo binders seems promising in respect of technology (suitable sands properties), ecology (non-toxicity, biodegradability, renewability) and economy (relatively low price of a binder). A modified starch from polysaccharides group deserves the special attention, since this is easily obtainable, biodegradable and the cheapest biopolymer. At a current low price of this polymer, as well as possibilities of using agricultural wastes for its production, the problem of the starch application in the foundry industry can become really significant.

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Note: The responsible translator for English language: "ANGOS" Translation Office, Kraków, Poland