New Materials in the Production of Moulding and Core Sands

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Received 28.04.2015; accepted in revised form 15.07.2015

Abstract

The article shows the influence of environment requirements on changes in different foundry moulding sands technologies such as cold box, self-hardening moulding sands and green sands. The aim of the article is to show the possibility of using the biodegradable materials as binders (or parts of binders’ compositions) for foundry moulding and core sands. The authors concentrated on the possibility of preparing new binders consisting of typical synthetic resins - commonly used in foundry practice - and biodegradable materials. According to own research it is presumed that using biodegradable materials as a part of new binders’ compositions may cause not only lower toxicity and better ability to reclaim, but may also accelerate the biodegradation rate of used binders. What’s more, using some kinds of biodegradable materials may improve flexibility of moulding sands with polymeric binder. The conducted research was introductory and took into account bending strength and thermal properties of furan moulding sands with biodegradable material (PCL). The research proved that new biodegradable additive did not decrease the tested properties.

Keywords: Environment protection, Innovative foundry technologies and materials, Moulding sand, Binder, Biodegradable material

1. Introduction

Modern economy requires the production process to meet the highest quality criteria. To this branch we can include the production of most responsible castings, which are used in automotive, constructive and steel industry, also in cement industry and energetic, or other branches like art and jewellery industry. In the case of polish economy castings production is a very important branch. There are more than 240 registered foundries in Poland, with a varied production profile. What is important, polish casting industry exports more than 50% of its’ products, which places it in the lead of national exporters. The vast majority of castings is produced in disposable ceramic moulds made out of moulding and core sand mixtures. Moulding and core sands should provide castings with set mechanical properties, high dimensional accuracy and high surface smoothness. As far as the first requirement goes, the mechanical properties of the casting depend solely on the type of the alloy, more precisely on its grain structure. The other two properties are the ones that depend on the quality of the foundry moulds and cores. Moulding sands are also required to be highly economical in production and to be of low hazard for the environment. The economics of the process is not only the cost of the ingredients, it’s also the moulding process efficiency, bounding speed, ease of making the moulds and cores, good knock-out properties, and recuperation of used moulding sand.
2. Ecological factors

Further development of production technologies for moulding and core sands is very limited by strict environmental protection laws. Those tendencies are growing to such a degree, that technologies used for decades in the industry have to be replaced by more ecological processes. Liquid moulding sands with ethyl silicate used in lost wax technology are a good example of such technology. The process of silicate hydrolysis used in this technology is realized with organic solvents, which use should be minimized. That is why precision casting is shifting towards water based colloidal silica binders [1]. Combustible protective coatings widely used in industry can be another example. Protective coatings have been used in the industry widely and for a long time. Previously used coatings were mainly based on organic solvents, mainly IPA. Latest requirements of the European Union demand the elimination of organic solvents use in the industry. The protective coatings used so far were lit after covering the mould and cores with them, the solvent then evaporated and a durable protective coating was left on the surface. As you can see the basis of such a decision in European Union is organic solvents’ harmful influence on the environment. It is therefore enforced by environmental conditions to produce new generation of coatings. It compels the coating producers to find new solutions based on new water based solvents so-called water dilutable, ones that contain such low amount of water that they do not require drying in heating chambers [2-3].

With the date of 1st December 2010 the Regulation of the European Parliament and Council Regulation (EC) (no. 1272/2008 from 16th December 2008 regarding classification, labelling and packaging substances and mixtures) entered into force, it classifies furfural resins with more than 25% of free furfuryl alcohol as toxic. Furfural resins which contain lower amount of free furfuryl alcohol and treated as harmful. In addition, technological processes that emit harmful substances from the group of BTX-s, especially with polycyclic aromatic hydrocarbons (PAHs), should be limited, and these are emitted from the currently used technology of furfuryl resin moulding sands. This will cause the self hardening sands with furfural resin (so-called furan moulding sands) [4], which are dominant on the global foundry market, to lose their importance, due to the deterioration of the technological properties which will follow the reduction of the levels of free furfuryl alcohol in the moulding sands [5-6].

Cold-box process, which is a top achievement of foundry industry in terms of mass production of foundry cores, is another example of stimulating the technical progress by the requirements of environmental protection. Over the years, the process of cold-box has changed very significantly in terms of environmental aspects. In the primary solution in this method, used as solvents for the two component binder (resin and activator) were high boiling aromatic hydrocarbons (BTX fraction - benzene, toluene, xylene, higher alkylbenzenes) characterized by a major toxicity. This technology, however, gave very high strength properties of the moulding sands which predestined them to be used for the production of most complex cores. In the next generation of technologies BTX fraction was replaced with methyl esters of fatty acids, thus reducing the amount of gas generated during curing and pouring processes.

Currently widespread resins for the cold-box process contain ester solvents and silicate esters in their composition [7-8]. In these solutions there are used both ester solvents and alkyl orthosilicates, which have a high boiling point and low toxicity (their compounds are not classified as harmful, carcinogenic or mutagenic). These and other physico-chemical properties of silicate esters significantly reduce the emission of harmful gases and effectively reduce the unpleasant smell. However, due to the high price, resins containing this ingredient are used only by few and large foundries cooperating mainly to car manufacturers. Still, the basic problem of the use of the new generation of solvents is a significant decrease in the strength of the moulding sands.

These tendencies also apply to the classic molding sands with bentonite, so far considered completely environmentally friendly. The reason is the widespread use of coal dust additives in these moulding sands or other additives which lead to carbon formation. After taking into account the high emissions of benzo-a-pyrene (PAHs) they are one of the major risk factors in the foundry. In terms of reducing the emission of harmful substances into the environment different technologies of moulding sands with bentonite are used. This can be achieved by introducing into the moulding sands a coal dust replacement, characterized with reduced emission, it can be applied with technologies of advanced oxidation of emerging harmful substances (so-called Advanced Oxidation Process AOP also known as Blackwater) [9-11] or by introducing an additional substances which substantially neutralize harmful compounds in the moulding sands. Technologies which use traditional bonding materials as synthetic resins will have to be limited and use of inorganic materials including silicate binders will increase their importance. Their low impact on the environment, however, combines with technological problems, such as poor knock-out properties or small ability to recuperate. Yet other interesting solutions can also be sands bonded with geopolymers, biopolymers, phosphates or salts.

3. Moulding sands with organic binders based on petrochemical and biodegradable polymers

An interesting solution may be a concept of partial replacement in the composition of oil-based resin binder with biopolymers. While all kinds of synthetic resins may be fragmentated and biologically assimilated, in most cases, these processes can take tens or even hundreds of years. As Professor Scott says [12], one of possible solutions to this problem is to replace conventional synthetic resin with oxy-biodegradable polymers which are characterized by short time of decomposition. Oxo-biodegradation is possible thanks to special additives in polymers. Introduction of the additives to the production process at the appropriate time causes dissociation between carbon atoms and thus the molecular weight of the polymer is lowered. This allows the microorganisms to have better access to carbon and hydrogen, and thus there the biodegradable material is converting into water, carbon dioxide and biomass by processed by bacteria and fungi [12]. As we can find in the literature [13-14], it is also possible to use biodegradable materials as additives to oil-based materials to cause their biodegradation. Thus, the additive can
improve the properties of the moulding sands with oil-based resins and enable the degradation of reclamation products. Some of biodegradable materials (e.g. PCL) are used as plasticizers for many not flexible enough polymeric materials [15]. The problem of low flexibility of moulds and cores prepared in different technologies of moulding sands is very important from practical point of view and will be the object of authors next research.

The advantages of biodegradable PCL encouraged the authors of the paper to use this ecological material as an additive to typically used moulding sand [16-17].

The first stage of own research there were performed thermogravimetric. The test sample was subjected to thermal analysis, using manual derivatograph produced by Jota s.c. The measurements went under the following conditions: heating temperature range 20 - 1000 °C, heating rate 10 °C / min.

Figure no.1 shows TG curves for furfuryl resin and biodegradable material PCL – polycaprolactone. Process of thermal destruction of the furfuryl resin starts at approx. 120 °C. Its rapid progress continues to about 200 °C, and then goes into slow decay ending at about 760 °C. Figure 1 shows the TG curve of the biopolymer PCL. Its thermal decomposition is also very intense, but starts only at about 370 °C and ends at 450 °C. Thus, the sample mass loss starts much later than the oil-based resins and is more rapid.

![Thermogravimetric research of furfuryl resin and PCL](image)

In the next stage of the research for the moulding sands with these binders - the same composition as for the thermogravimetric research - the tendency of the moulding sands to undergo thermal deformation has been studied - during pouring - by determining the parameter hot distortion (Figure 2). A detailed description of the method is presented in earlier publications of the authors [18].

![Hot distortion research of moulding sand containing furfuryl resin (moulding sand no.1) and moulding sand containing PCL (moulding sand no.2) as a binder](image)

The thermal deformation of the moulding sand with furfuryl resin has a typical course, characterized by continuous and intensive growth of the deformation and a rapid break of the moulder, when the temperature exceeds 400 °C. However, deformation behaviour in case of the moulding sand with the biopolymer PCL is substantially different. Even at low temperatures (approx. 70 °C) the moulding sand enters a determined state of plasticity. This feature of the moulding sand can change the effective compensation for thermal expansion of the core surface. Despite the lower strength this moulding mixture can effectively reduce the formation of defects generated by the thermal expansion of the quartz matrix and further improve knock-out properties of the moulding sand and reduce the emission of harmful gases.

The next stage of the experiments included technological research of furfuryl resin moulding sands and moulding sands in which part of the furfuryl resin was replaced with a variable contribution of PCL biodegradable material. These studies were focused on bending strength as a function of curing time. Sample comparison is shown in Figure 3.

As you can see the addition of a biodegradable material PCL 5-15% weight does not compromise strength and even with the participation of 10% significantly increases it. Only with the participation of 15% by weight shows much lower strength than the moulding sand without the addition of PCL.
4. Conclusions

Comments presented in this article do not cover all the conditions for the development course of the molding and core sands. They are only intended to signal the needs and opportunities for further research in this area. The results confirm that one of the possible solutions can be the usage of biodegradable materials as additives to oil-based molding resins.

Acknowledgements

Scientific research financed from AGH, No 11.11.170.318 - 3

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