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MODIFIED POLYSACCHARIDES AS ALTERNATIVE BINDERS FOR FOUNDRY INDUSTRY

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Polysaccharides constitute a wide group of important polymers with many commercial applications, for example food packaging, fibres, coatings, adhesives etc. This review is devoted to the presentation of polysaccharide application in foundry industry. In this paper the selected properties of foundry moulding sand and core sand containing modified polysaccharides as binders are presented according to foreign literature data. Also, author's own research about effect of using moulding sand binder consisting of modified polysaccharide (modified starch) or its composition with non-toxic synthetic polymers are discussed. Based on technologies taken under consideration in this paper, it could be concluded that polysaccharides are suitable as an alternative for use as binder in foundry moulding applications.

Key words: foundry, moulding sand, binder, polymer, modified

INTRODUCTION

The trend towards introducing some new or replacing existing harmful substances by alternative biodegradable raw materials is present in many industries, including the foundry [1 – 6]. This is due to, among other things, an increase of the environmental awareness of entrepreneurs and vision of future exhaustion of the world's non-renewable resources. Currently used foundry synthetic adhesives generally provide good properties of moulds and cores and, consequently, good quality of castings. However, they can have a destructive impact on the environment [7, 8].

The alternative binders include materials produced from natural substance (e.g. vegetable, animal, bacterial) [1], including a very broad group of polysaccharides.

Polysaccharides are the polymers commonly found in nature. They can be divided into natural and modified ones. Polysaccharides of economic importance are, above all, cellulose, starch, pectin, and hemicelluloses [8, 9]. Among the polysaccharides in native or modified form, starch has captured the greatest attention in the newly establishing moulding technologies [2 – 6], and therefore this paper is focused particularly on starch polysaccharides foundry applications.

NATIVE STARCH

Starch is a polysaccharide of vegetable origin, composed of two fractions: amylose and amylopectin. Amylose molecules consist of long linear chains of anhydroglucose rings interconnected by **α**-1,4-glycosidic bonds. The branched chains of amylopectin anhydroglucose rings are also connected by **α**-1,6-glycosidic linkage (Figure 1) [10].

The content and ratio of the two sugars to a large extent determines the properties of the starch. For example, in starch obtained in the process using a mechanical grindometer, after washing and refining, potato tubers are poorly soluble in cold water. Starch adhesives, which are colloidal systems with low mechanical stability [11], can be obtained by heating the solution.

So far, natural starch in the form of colloid constituted an auxiliary additive factor that improves the hardness and strength of the green sands. The addition of native starch in the form of a solution also prevents casting defects associated with expansion, as the binder firing process allows the deformation to occur without deformations of the sand form. However, the starch may reduce the flowability of the moulding and deteriorates resistance to erosion and penetration of liquid metal into the mould [7].

So far, native starch was hardly considered to be an effective self-adhesive. However, in recent years, the

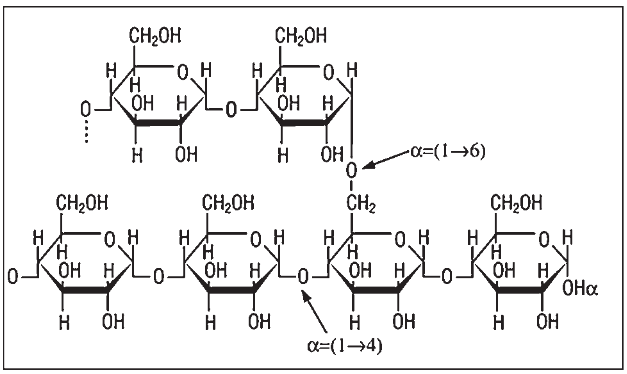

Figure 1 Structure of starch fraction – amylopectin [10]

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literature on this subject included information about new research on the development of moulding technologies involving adhesives mostly based on unmodified starch locally occurring in Africa starch from tubers of plants such as yam or cassava [3,6]. In these technologies, it is an interesting trend to use starch as a cheaper substitute for difficult to reach moulding materials, e.g. bentonite [3].

A characteristic feature of these technologies is the large share of starch-binder in a mass - coming up to 30 % [3]. Unfortunately, high binder content deteriorates permeability, generating surface defects and internal defects crude castings (porosity) with no positive effect on the strength properties of the mass after drying (compressive strength approx. 0,10 – 0,25 MPa), and makes it an uneconomical technology. A limitation of the use of this type of moulding sand bonded by starch is also caused by the fact that, as a consequence of drainage and curing, the mould is deteriorated and the dimensional accuracy of the mould is affected, which causes defects in shape [7].

To improve the solubility of starch in water, a modification can be carried out. According to Polish Standard PN-87/A-74820, modified starch is a natural starch in which, by suitable treatment, one or more of its initial physical or chemical properties were changed. Modifying the starch has an aim to improve its functional properties or give it new features.

WATER-SOLUBLE MODIFIED STARCH BINDER – WMSB

An example of application of starch after treatment is the water-soluble modified starch binder (WMSB), probably obtained by acid hydrolysis. The WMSB composition, as a mixture of potato starch, formaldehyde, phosphoric acid, urea, poly (vinyl alcohol), and water, is used to prepare the core sand. The WMSB binder can be used in the technology of moulding in steel, iron, and non-ferrous alloys casting [5].

Core curing can take place in ambient conditions (self-hardening mass), but in order to optimize its properties, additional annealing at 150 °C is conducted. Experiments have proved that the tensile strength in the cured state with the participation of the binder in the range of 4 – 7 wt %. changes the proportion from 0,8 to approx. 2,5 MPa [5].

The mass with the water-soluble binder based on the modified starch can be characterized by low resistance to moisture absorbed from the environment, so that in conditions of high humidity in the foundry, cores could absorb water, which may contribute to the formation of casting defects [7]. The hygroscopicity of WMSB binder in the cured moulds makes them difficult to store, but undesirable amount of water absorbed during storage can be evaporated again by placing the cores in the preheated oven. Also, the unused mixture can be re-used in forming after crushing as well as the addition of water to the mixture suitable portion. An advantage of moulding sand WMSB is also lower gas emission compared to the core sand based on oils or furan resin [5]. Harmfulness of WMSB bonded moulds is certainly lower than other commercial binders. However, due to the remaining components in the form of formaldehyde, urea, and phosphoric acid, it is difficult to include binder WMSB in the group of fully ecological binders.

ETHERIFIED STARCH

A binder based on carboxymethyl starch (CMS) seems to be one of more environmentally friendly solutions. This is a cold water-soluble product of starch etherification, which, depending on the operating conditions of the synthesis reaction, may be characterized by varying in the molecular weight, degree of substitution, and solution viscosity [11, 12]. The modification of starch was carried out by etherification of starch slurry in ethanol monochloroacetic acid in the Williamson synthesis [11, 12].

When compared to the native starch, CMS has better binding capacity of the matrix grains in core sand, which is associated with increased viscosity, cold water solubility, or adhesiveness of the bonding material. The changes in the molecular structure of starch are determined by the degree of substitution (DS), defined as an average number of substituted hydroxyl groups on each anhydroglucose ring. Viscosity, the ability of swelling in cold water, and the stability of CMS increase in proportion to the degree of substitution [11, 12]. Suitable parameters for a core sand binder are up to 2,5 weight parts. CMS and bentonite, phosphates, have been already achieved with a degree of substitution in the range of 0,3 – 0,5. An adhesive with a degree of substitution ensures the best resistance to humidity and also high bending strength, i.e. 2,0 MPa [4]. The obtained mechanical properties are more favourable when compared to the moulding sand with furan resin, and that is why, in the future, CMS may be an alternative for commercial organic resins. Furthermore, the implementation of this technology requires no additional special equipment and because of the availability of starting materials, the cost of making the cores is significantly lower in relation to the cost of furan resins core production technology [4].

The authors of this publication also decided to use the starch in the modified form of starch ethers as the main ingredient of binder [2] and a supplement to the green sands with bentonite. The material is water-soluble etherified starch as a sodium, so substituted groups in the polymer chains include sodium carboxymethyl group [12].

Preliminary performed technological tests presented in [2] concerning the aqueous solution of CMS-Na as a binder for curing moulding under microwave irradiation showed that the material of CMS-Na is the potential binding material. For example, the strength of the moulding of binder based on the solution of CMS-Na (the ratio of the binder to matrix: 3 to 100) with a high degree of substitution (DS 0,9) is approx. 0,5 MPa. However, a significant limitation of the use of colloidal solutions CMS-Na is marked with a large abrasion of cured mouldings, approx. 30 % for CMS-Na with DS 0,9 [4].

Continuation of research in the use of sodium carboxymethyl starch proved that the introduction of this powdery modified polysaccharide to the moulding sand of a quantity of 1,5 – 2,5 weight parts of CMS-Na and supplement during mixing by 5 weight parts of solvent water allows to obtain the tensile strength of the order of 0,5 – 2,0 MPa for CMS-Na with DS 0,2 and 1,5 – 3,8 MPa for CMS-Na with DS of 0,9 after curing in microwave field. This is a satisfactory result compared to the moulding sand with commercial starch binder or water glass hardened by the same method [13]. At the same time, the moulding sand has a very good resistance to mechanical damage, i.e. abrasion of cured samples was obtained at a level of 1,5 % CMS-Na with DS 0,2 and about 0,3 % of CMS-Na DS of 0,9.

THE BioCo BINDERS

Great potential use of modified polysaccharides can be also created by the preparation of polymer compositions that combine the properties of a synthetic polymer and a natural modified one.

Such compositions include the group of BioCo binders developed at the Department of Foundry Engineering (Patent PL 218966 B1). They are biodegradable water-soluble binders which include modified biopolymers – dextrin or CMS-Na – and polyacrylates. Moulding sands with participation of BioCo can be cured using both chemical agents such as glutaraldehyde, $Ca(OH)_2 + CO_2$ as well as physical – by conventional heating or exposure to microwave radiation [8]. An example of the strength of the microwave cured moulds containing 3 weight parts, the binder addition approx. 2,0 MPa, binding properties of the binders BioCo in moulding sand are reversible, i.e. in physical cured but unburned part of moulding, sand can restore the binding capacity of the matrix grains after the introduction of the appropriate amount of water. It is noted also that after pouring the molten metal into moulds the binder is burned off easily, resulting in a good knock-out properties of moulding sand [8].

CONCLUSIONS

On the basis of literature data it may be noted that in recent years starch polysaccharides are of great interest as a binder or auxiliary new establishing in moulding sand technology.

Relatively low strength, strong demand on the bonding material in the moulding sands are the reasons why natural starch doesn't appear to be competitive enough to commercial binders and synthetic resins. However, the polysaccharides starch derivatives in the form of e.g. WMSB, CMS, CMS-Na, dextrin, or polymer compositions such as BioCo seem to be promising materials as a replacement for toxic adhesives used in the foundry industry. The process of modifying starch provides opportunities for the application of this biopolymer not only as an excipient for moulding bentonite, but also as main binder for moulding. This fact has also been confirmed in studies conducted by the authors of this publication.

The obtained strength and technological properties are comparable, and often superior to the moulding sands with furan, furfuryl resins, or water glass. Modified starch properties affect the good quality of the moulding in the technological (corresponding properties of the moulding), environmental (water solubility, non-toxicity, biodegradability, renewability of binder, and reclamation of used sands), and economic aspect (relatively low price of the binder).

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