Strength properties of moulding sands with chosen biopolymer binders

St.M. Dobosz*, K. Major-Gabryś
Department of Moulding Materials, Mould Technology and Foundry of Non-ferrous Metals, Faculty of Foundry Engineering, AGH University of Science and Technology, ul. Reymonta 23, 30-059 Kraków, Poland
*Corresponding author. E-mail address: dobosz@agh.edu.pl, katmg@agh.edu.pl

Received 30.04.2010; accepted in revised form 01.07.2010

Abstract

The article presents the results of primary researches of the IV generation moulding sands, in which as the binders are used different biodegradable materials. The bending and the tensile strength of the moulding sands with polylactide, poly(lactic-co-glycolic acid), polycaprolactone, polyhydroxybutyrate and cellulose acetate as binders were measured. The researches show that the best strength properties have the moulding sands with polylactide as binder. It was proved that the tested moulding sands’ strength properties are good enough for foundry practice.

Keywords: moulding sand, binder, biodegradable, biopolymer

1. Introduction

In the 90-ties the General Motors Co. elaborated the new binding system based on the protein composition GMBOND [1]. The materials in the protein binder comes from natural renewable resources and are the compound of polypeptide chains, being not toxic (save) for environment. The binder is well soluable in water and the binding process begins during the dehydration reaction of wet moulding sand. The hydration reaction (the opposite reaction) can tend to get some binder back. The technological experiments with using the protein binder showed high enough castings properties (high dimension precision, no thermoplastic deformations, perfect casting surface) though the binder quantity was reduced of 45% to the furfuryl resin binder quantity used to core production by hot-box technology. The sand grains’ kind, temperature and humidity have no influence on the moulding sand physicochemical and technological properties. The binder was tended to the foundry practice in 1996.

On the other hand new technologies must have good knock-out properties and good reclamation ability, having good enough mechanical properties. The base to obtain such binders are proteins which are water soluble and their hardening process is coming in quite low temperature (70 – 120°C). The hardening process can be leaded by blowing hot air through the core box, in the hot core box or by microwave hardening. The hardening process has the following form:

\[
\begin{align*}
\text{HN—H} & \quad \text{HO} \\
\text{CH}_2 & \quad \text{C} = \text{O} \\
\text{CH}_2 & \quad \text{O} = \text{C} \\
\text{OH} & \quad \text{H—NH}
\end{align*}
\]

The moulding sand with 0,5 – 1,0 parts per weight of the binder has the bending strength equal 3 – 6 MPa. The technology is especially used in aluminum alloys foundry.

K. Rusin’s scientific group [2] tested possibilities of using biogenic binders based on proteins coming as by-products from
pharmacy industry production. The group tested water soluble not toxic polymers including different polypeptide molecules with long amino acids chains. The quartz sand was added to the solution and the moulding sand was densified in core box and dried in the temperature of 70°C through 2 hours. After cooling down the sample was stored in the desiccator. There was 0,25 – 2,0% of the binder added to the moulding sand. The compound of the biopolymer materials can be prepared earlier and dried before usage. Its low humidity (>4%) fastens cores drying process and no organic solvents are needed in the moulding sand.

There is no chemical reaction in the process, only the reaction of dehydration during the heating process. It’s recommended to use the sand having circular grains. The tensile strength depends on the quantity of the binder in the moulding sand and can be verified in about 1,0MPa. The samples’ surface is good and has good wear resistance. The protein binder good thermal disintegration gives possibilities for easy moulding sand reclamation with getting not used binder back (as the binder is water soluble). This kind of moulding sand can be used for not heavy aluminum alloys castings.

2. Own researches

2.1. The materials used in the researches

As a result of looking for polymer binders, the following materials were taken into elaboration:

**PLA** - poly lactic acid or polylactide is a biodegradable, thermoplastic, aliphatic polymer derived from renewable resources, such as corn starch or sugarcanes. PLA has been known for more than a century, but in light of its biodegradability, it has become popular in recent years. The biggest PLA manufacturer in the world is the Nature Works LLC Co. from USA. In Europe it is produced by PURAC Company. PLA is usually available in the form of cylindrical granule and in that form PLA was used in the researches.

![Fig. 1. Ring-opening polymerization of lactide to polylactide](image)

**Usage:**
- short life products,
- thermofomed products,
- injection molded products,
- agricultural products,
- packaging.

The complete biodegradability and other functional properties enable to convert to advance in production areas, which could not be reached with traditional thermoplastic materials.

**PLA1** – modified PLA (BIOPLAST GS 2189) – plasticizer-free thermoplastic material from BIOTEC Co. in the form of cylindrical granule. Products made of BIOPLAST GS 2189 are completely biodegradable and depending on their thickness, compostable. The material is registered by DIN as biodegradable (according to DIN EN 13432) and non-toxic for the composting process.

**PLA2** – Bio-Flex F 6510 from FKuR Kuststoff GmbH in the form of cylindrical granules - biodegradable polymer–blend based on polylactic acid (PLA) contains a copolyester and additives.

**Usage:**
- films,
- injection moulded parts,
- approved for food contact.

Bio-Flex F 6510 is almost odourless, its melting temperature is 150-170°C, it is water-insoluble.

**PLGA** - poly(lactic-co-glycolic acid) is a biodegradable copolymer. PLGA is synthesized by means of random ring-opening co-polymerization of two different monomers, the cyclic dimers (1,4-dioxane-2,5-diones) of glycolic acid and lactic acid. Common catalysts used in the preparation of this polymer include tin(II) 2-ethylhexanoate, tin(II) alkoxides, or aluminum isopropoxide. During polymerization, successive monomeric units (of glycolic or lactic acid) are linked together in PLGA by ester linkages, thus yielding a linear, aliphatic polyester as a product.

![Fig. 2. Structure of poly(lactic-co-glycolic acid).](image)

Depending on the ratio of lactic to glycolide used for the polymerization, different forms of PLGA can be obtained. All PLGAs are amorphous rather than crystalline and show a glass transition temperature in the range of 40-60°C. Unlike the homopolymers of lactic acid (polylactide) and glycolic acid (polyglycolide) which show poor solubilities, PLGA can be dissolved by a wide range of common solvents, including chlorinated solvents, tetrahydrofuran, acetone or ethyl acetate.

PLGA degrades by hydrolysis of its ester linkages in the presence of water. It has been shown that the time required for degradation
of PLGA is related to the monomers' ratio used in production: the higher the content of glycolide units, the lower the time required for degradation. An exception to this rule is the copolymer with 50:50 monomers' ratio which exhibits the faster degradation (about two months). In addition, polymers that are end-capped with esters (as opposed to the free carboxylic acid) demonstrate longer degradation half-lives. PLGA has been successful as a biodegradable polymer because it undergoes hydrolysis in the body to produce the original monomers, lactic acid and glycolic acid. These two monomers under normal physiological conditions, are by-products of various metabolic pathways in the body [6].

**PCL** - polycaprolactone is a biodegradable polyester with a low melting point of around 60°C and a glass transition temperature of about −60°C. PCL is prepared by ring-opening polymerization of ε-caprolactone using a catalyst such as stannous octanoate [3].

![Fig. 3. Ring-opening polymerization of ε-caprolactone to polycaprolactone [3]](image)

The most common use of polycaprolactone is in the manufacture of specialty polyurethanes. Polycaprolactones impart good water, oil, solvent and chlorine resistance to the polyurethane produced. It also finds some application based on its biodegradable character in domains such as controlled release of drugs, soft compostable packaging etc.
PCL is often used as an additive for resins to improve their processing characteristics and their end use properties (e.g. impact resistance). Being compatible with a range of other materials, PCL can be mixed with starch to lower its cost and increase biodegradability or it can be added as a polymeric plasticizer to PVC [3].

**PHB** – polyhydroxybutyrate belongs to the polyesters class that was first isolated and characterized in 1925 by French microbiologist Maurice Lemoigne. PHB is an isotactic, absolutely linear, thermoplastic homopolyester built of 3-hydroxy butyric acid [7].

![Fig. 4. Chemical structure of PHB (P3HB) [7]](image)

PHB is produced by micro-organisms (like Alcaligenes eutrophus or Bacillus megaterium) apparently in response to conditions of physiological stress. The polymer is primarily a product of carbon assimilation (from glucose or starch) and is employed by micro-organisms as a form of energy storage molecule to be metabolized when other common energy sources are not available. PHB serves as nutrient only, when phosphates, nitrogen, salts, humidity, and heat allow the microorganisms to grow [7].

Microbial biosynthesis of PHB starts with the condensation of two molecules of acetyl-CoA to give acetooacetyl-CoA which is subsequently reduced to hydroxybutyril-CoA. This latter compound is then used as a monomer to polymerize PHB.

PHB is free from even traces of catalysts. PHB is waterproof and is highly crystalline (60 to 70%), providing excellent resistance to solvents. It is not toxic and it is completely biodegradable. Its melting point is 175°C and glass transition temperature is 15°C. PHB has good oxygen permeability and good ultra-violet permeability. PHB has poor resistance to acids and bases [7].

**CA** - cellulose acetate is an amorphous thermoplastic material belonging to the cellulose resin family. It is obtained by introducing the acetyl radical of acetic acid into cellulose (as cotton or wood fibres) to produce a tough plastic material [8].

![Cellulose acetate](image)

Cellulose acetate is used for transparent, translucent and opaque objects (e.g. typewriter keys, switches, car wheel coverings). Furthermore, it is especially suitable for coatings applications requiring high melting point, toughness, clarity, and good resistance to ultraviolet light, chemicals, oils, and greases [8].

### 2.2. The researches

Moulding sands with the following composition were taken into elaboration:

- Quartz sand - 100 parts by weight
- PCL, PLA, PGLA - 1,67 parts by weight
- PLA1, PLA2 - 2 – 4 parts by weight
- Solvent (CH2Cl2, acetone) - to the biopolymers complete dissolvation.

According to the low solvents boiling points, moulding sands were mixed by hands and the samples were densified by hand pressure. The strength properties of the moulding sands were tested after their complete hardening (after the solvents vaporization).

The researches results of the tested moulding sands’ bending and tensile strength are shown on the figures 6 – 9.

The figures 6 and 7 show the comparison of bending and tensile strength of moulding sands with biodegradable materials: synthetic biopolymers CA and PCL, and natural biopolymers PHB, PLA, PGLA as binders. The figures show that the moulding sands with the natural biopolymers PLA and PLGA have better bending and tensile strength than the moulding sands with synthetic biopolymers CA and PCL. The researches prove that the moulding sands’ with PLA and PLGA as binders strength properties are good enough for foundry practice.
The figures 6 and 7 show the comparison of bending and tensile strength of moulding sands with PHB, CA, PCL, PLGA, PLGA. The researches proved that the moulding sand with PLA2 as binder strength properties are good enough for foundry practice.

3. Conclusions

The applied researches of strength properties of the moulding sands with biopolymer binders proved that this ecological materials are useful for foundry practice. It seems appropriate to continue the researches with the biodegradable binders in technological aspects.

In the future researches also biopolymers degradation process in aspect of moulding sands reclamation will be considered.

Acknowledgements

Scientific researches finance from Ministry of Science and Higher Education project no NN 508 391 435.

References