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The Compositions: Biodegradable Material - Typical Resin, as Moulding Sands' Binders

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Abstract

The paper presents possibility of using biodegradable materials as parts of moulding sands' binders based on commonly used in foundry practice resins. The authors focus on thermal destruction of binding materials and thermal deformation of moulding sands with tested materials. All the research is conducted for the biodegradable material and two typical resins separately. The point of the article is to show if tested materials are compatible from thermal destruction and thermal deformation points of view. It was proved that tested materials characterized with similar thermal destruction but thermal deformation of moulding sands with those binders was different.

Keywords: Moulding sand's binder, Biodegradable material, Resin, Thermal destruction, Thermal deformation

1. Introduction

Foundry is an area of science, in which there will never be a situation that there will be available only one technology of preparing moulding sands and one technology of preparing core sands. The variety of materials that castings are made of (types of alloys and their casting temperature) will always put before foundry men the requirements for obtaining moulds and cores having high technological properties. Moreover in accordance with the tendencies observed in recent years, technologies of foundry moulds and cores manufacturing must also meet high requirements connected to environmental protection.

Group of binders, which are predominant in the production of foundry moulds and cores of synthetic (petrochemical) resins used in the processes of loose self-hardening moulding sands (no-bake technology), the cold-box technologies and the hot-box technologies. Particularly phenol, urea and furfuryl resins are used. Phenol-formaldehyde resins are classified as phenoplasts resulting from condensation polymerization reaction of phenol or

its derivatives with aldehydes [1]. These processes lead to the formation of macromolecular phenol-formaldehyde resins. They are called resols. Based on microscopic studies, it is assumed that the hardened resins may be treated as a collection of interconnected by chemical bonds micelles. The dimensions of the micelle is 40 - 60nm [2]. Urea-formaldehyde resins are classified as aminoplastics resulting from the reaction of formaldehyde with urea [2]. Furfuryl resins are resulting from the condensation polymerization reaction of furfuryl alcohol with phenol, or furfuryl alcohol with formaldehyde, urea, phenol and other compounds [1]. The resins are cross-linked by heating or by chemical factors.

Increasing requirements connected to environmental protection cause leading changes in foundry practice. There are noticed the following modernizations:

- The reduction of furfuryl alcohol in resins.
- Solvents based on PAHs used in cold-box technology (ensuring moulding sands' bending strength $R_g^u = 5-6\text{MPa}$) have been replaced with mineral solvents (ensuring moulding sands' bending strength $R_g^u = 3-3,5\text{MPa}$). There are also

noticed in cold-box technology the tendencies of replacement the organic solvents with ecological solvents, in which carbon atoms are replaced with silicon atom [3].

In the face of the changes it seems necessary to replace petroleum binders with other environmentally friendly materials. A significant group of such binders are inorganic binders. The most important group of moulding sands with inorganic binders are moulding sands with hydrated sodium silicate popularly called water glass. These moulding sands are very popular due to their environmentally friendly nature. Unfortunately, inorganic binder, which is the water glass, causes low knock-out properties and low ability to mechanical reclamation. The paper's author has for many years been successfully conducted research aimed at improving self-hardening moulding sands with water glass knock-out properties and improving the quality of reclaim from the tested moulding sands. Glassex additive was used to improve moulding sands with water glass knock-out properties [4-6] and new ester hardeners were applied to provide better quality of reclaim from tested moulding sands [5, 7-8].

There are also alternative solutions using inorganic binders to produce the moulding sands. An example of such a solution is moulding sand with a geopolymer binder [9-10]. Geopolymers belong to alkaline aluminosilicates. These are materials containing silicon, aluminium and an alkali metal such as sodium or potassium. In nature there exist similar materials, such as zeolite. Geopolymers are not created as a result of geological process, they are produced synthetically. They are called geopolymers due to the fact that their composition is similar to the composition of natural minerals. Geopolymers are in the centre of attention of many branches of industry. The materials can also be interesting for the foundry practise [11].

Another scientific research direction is gradually replacement of the binding materials produced from petrochemical stocks, with biopolymers coming from renewable resources. It is consistent with the conception of sustainable development, which is one of the policy priorities of the European Community.

Despite many advantages, the market for biopolymers and biocomposites, is currently quite small in comparison to the market for petrochemical materials. It is being forecast however, within the next few years, the biodegradable polymers will cover 10% of the world's market of polyolefines used in agriculture and for packaging. The increase in production of polymers of natural descent will be possible thanks to improvement in production processes and the accompanying decrease of biopolymer prices [12].

2. Biodegradable polymers

According to ASTM standard D-5488-94d, biodegradable means capable of undergoing decomposition into carbon dioxide, methane, water, inorganic compounds, or biomass in which the predominant mechanisms is the enzymatic action of microorganisms that can be measured by standard tests, over a specific period of time, reflecting available disposal conditions. There are different media (liquid, inert or compost medium) to analyze biodegradability. Compostability is material biodegradability using compost medium [13-15]. The ASTM D6400 standard defines compostable plastics as materials that undergo degradation by biological processes during composting to yield carbon dioxide, water, inorganic compounds, and biomass at a rate consistent with other known compostable materials and that leave no visible distinguishable or toxic residue [16].

Biodegradation is the degradation of an organic material caused by biological activity - mainly microorganisms' enzymatic action. This leads to a significant change in the material chemical structure. The end-products are carbon dioxide, new biomass and water (in the presence of oxygen: aerobia) or methane (oxygen absent: anaerobia), as defined in the European Standard EN 13432:2000 [13].

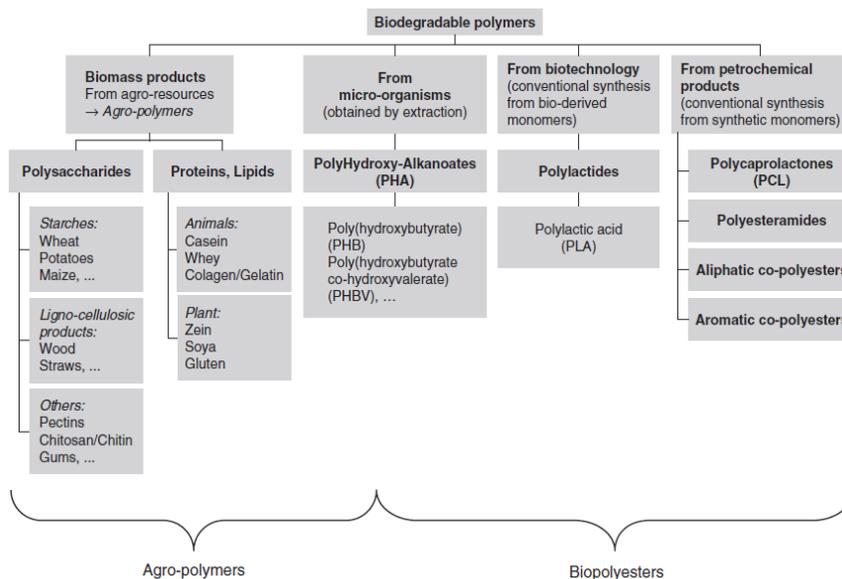


Fig. 1. Classification of the biodegradable polymers [13-14]

Polymers from renewable resources have still an insignificant share in the market for polymeric materials, but their world production is growing very rapidly (11 to 19% annually), making it one of the fastest developing branches of the agrochemical industry in countries in the Americas, Europe and Japan [12, 17].

3. Biodegradable polymers as additives for petrochemical polymers

All kinds of synthetic resins can be fragmented and biologically assimilated, however mostly these processes can take tens or even hundreds of years. According to literature data [18] one of the solutions of this problem is replacing typical resins with oxy-biodegradable polymers characterizing with short decomposition time. Oxy-biodegradation is possible thanks to special additives for polymers which – added in appropriate moment of polymer production – cause dissociation of binding between carbon atoms. Thanks to this the molecular weight of the plastic is lower. Microorganisms have better access to carbon and hydrogen which causes material's biodegradation – conversion the material into water, carbon dioxide and biomass by bacteria and fungi [18].

Literature data [16, 19] shows that there is possibility of using biodegradable materials as additives for petrochemical materials to cause their biodegradability.

For example poly(ϵ -caprolactone) (PCL) has a unique characteristic - its compatibility with various other polymers. PCL is semi-compatible or mechanically compatible with some polymers such as PVAc (polyvinyl acetate), PS (polystyrene), polycarbonate, etc. Moreover, PCL is compatible with other polymers such as PVC (polyvinyl chloride), SAN (styrene acrylonitrile copolymer), poly(hydroxy ether), etc. This characteristic of PCL enables the formation of various biodisintegrable blends using it as a biodegradable component [20].

The primarily studied biodisintegrable polymer blends using PCL as a biodegradable component have been the PCL/polyolefin blend systems based on polyolefins such as LDPE (low density polyethylene) and PP (polypropylene). More detailed studies on the biodegradability of PCL/polyolefin blend including the relationship between the biodegradability and the phase structure were performed by Iwamoto and Tokiwa [21]. Since PCL/polyolefin blend is only mechanically compatible, it generally has a larger phase domain than that of the compatible blend, and thus generates larger non-degradable residues [21]. Generated particles with a large size can give rise to secondary pollution in the natural environment. In contrast, it is expected that a compatible biodisintegrable blend with a small domain size will generate particles small enough to be harmless for the natural eco-system and thus could make a contribution to the more effective reduction of the pollution problem caused by plastic waste [19].

PCL belongs to biopolyesters group. In foundry practice from group of unsaturated polyester resins there are used alkyd resins [22].

Inserting biodegradable materials to petrochemical binders could be led in the following ways:

- During the binder synthesis;
- Inserting into petrochemical binders prepared earlier nanoparticles of biodegradable materials in appropriate (for the used resin) solvent suspension.

According to literature data [23-25], there are some methods of preparing nanoparticles. The selection of appropriate method for the preparation of nanoparticles depends on the physicochemical character of the polymer. The primary manufacturing methods of nanoparticles from preformed polymer includes:

- *Emulsion-Solvent Evaporation Method;*
- *Double Emulsion and Evaporation Method;*
- *Salting Out Method;*
- *Emulsions- Diffusion Method;*
- *Solvent Displacement / Precipitation method.*

This method has been applied to various polymeric materials such as PLA, PLGA, PCL, and poly(methyl vinyl ether-comaleic anhydride) (PVM/MA) [24].

- Inserting biodegradable material to moulding sand as a component of two-component composition in appropriate solvent suspension – biodegradable material earlier dissolved in an organic solvent and then introducing second solvent into solution (e.g. water or another appropriate for resin solvent).

4. Polymers thermal degradation

Heating of the polymer leads to its degradation, which involves the disintegration of the macromolecule chain into fragments. At a sufficiently high temperature process of intensive cracking of bindings snowballs and leads to the destruction of the polymer. During the heating of macromolecules there can occur reversible and irreversible changes in their structure. Reversible changes occur as a result of phase transformations, disaggregation of supermolecules' structures and the transition of the polymer in the plastic state (conversion of first and second order). At a temperature higher than the flowing point (amorphous polymers) or a melting temperature (crystalline polymers) irreversible changes occur, and for most polymers thermal degradation occurs. The mechanism of degradation process depends on the construction of a macromolecule, the heating rate of the sample and occurring of changes both exothermic and endothermic [25]. Each polymer material, however, has a specific thermal stability (thermal stability), which is important in terms of their processing and usage. The thermostability at elevated temperature is one of the most crucial factors determining the application usefulness of the polymer [25]. Thermo-stability measurements are carried out using thermoanalytical methods: thermogravimetry (TG), differential scanning calorimetry (DSC). You can also use the method coupled using a variety of instrumental analysis techniques [26]. In this case, the test sample is subjected to several techniques at the same time. Methods coupled are most commonly used in the development of the mechanism of thermal decomposition.

Thermal degradation of polymer may have aerobic (oxidation) or anaerobic course. It is important from the point of view of real

foundry mould where both kinds of degradation occur. Kind of degradation process depends on the distance of analyzed moulding sand's layer to alloy-mould contact area. The influence of oxygen on thermal degradation of polymer is very different and depends on kind of polymer and its structure. In high temperature polymers in oxygen atmosphere react with oxygen which may cause thermal oxidation process and there may be formed low molecular weight organic compounds such as alkenes, alcohols, ketones, aldehydes or carboxylic acids. Wherein there haven't been so far defined the oxygen share in the mechanism of degradation [25]. On the other hand there are polymers for which influence of oxygen on thermo-oxidation degradation is minimal and their thermal curves are the same regardless of measurement conditions. The phenomena is connected to forming the carbonized layer that prevents the process of oxidation gradation. Moreover the resistance on oxygen action reinforces the presence in polymers structure the not oxidizable groups. In case of polymers having oxygen in structure, including copolymers with branched side chains and polymer composites, the destruction process occurs by mixed mechanisms (aerobic and anaerobic course). During this process there is isolated a fairly large amount of low molecular weight degradation products of the polymer [25].

5. Own research

The aim of the paper was comparing thermal degradation of biodegradable material PCL (used as a binder) to thermal degradation of typical foundry moulding sands' binders – alkyd and phenol-furfuryl resins.

The thermal degradation was measured by derivatographic research and by hot-distortion research.

5.1. Derivatographic research

The samples of analysed resins were subjected to thermal analysis. There were used the Iota derivatograph in the following measurement conditions : heating temperature range 20 - 1000°C, heating rate 10°C/min. The research was conducted in oxygen atmosphere.

The results of the measurements are shown in Figures 2-3.

In Figure 2 there are shown the TG curves of phenol-furfuryl and alkyd resins. The phenol-furfuryl resin characterizes with the lowest beginning temperature of thermal destruction process (temperature of about 120°C). The rapid process ends in temperature of about 230°C and then goes into slow decomposition in temperature of about 820°C. The alkyd resin characterizes with much complex process of destruction with intensive decomposition in temperature range 320-450°C. the final decomposition of the binder ends in temperature of about 670°C. In figure 3 there is shown the TG curve for biodegradable material PCL. Its thermal destruction is very intensive. It begins in temperature of about 370°C and ends in temperature of about 450°C. That means that mass loss of the PCL sample begins much later than mass loss of typical resins and is more rapid.

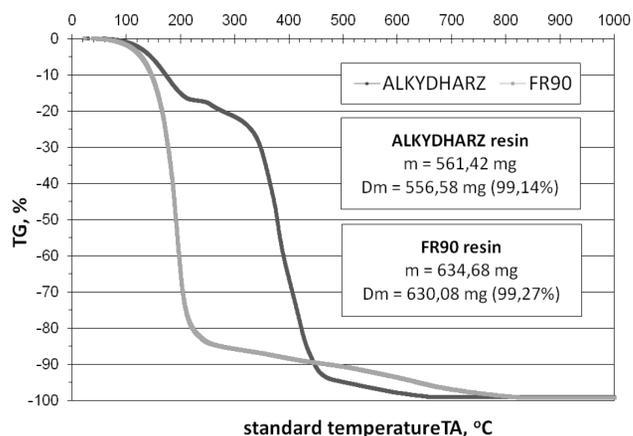


Fig. 2. The TG curves of ALKYDHARZ (alkyd resin) and FR90 (phenol-furfuryl resin)

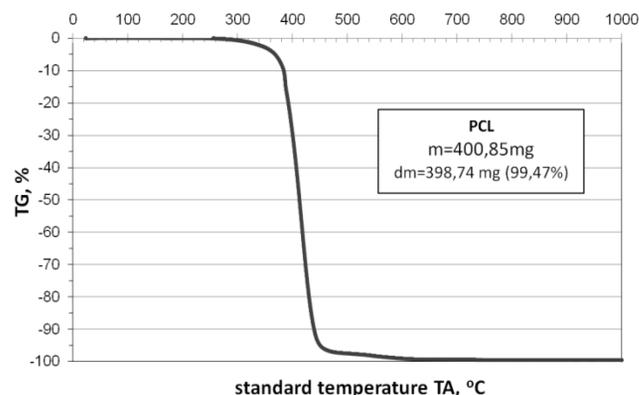


Fig. 3. The TG curve of PCL (polycaprolactone)

5.2. Hot-distortion research

In the next stage of the research there were studied moulding sands' tendency to thermal deformation by determining the hot distortion parameter. A detailed description of the method has been presented in previous publications of the authors [27].

Into hot distortion measurement there was taken the following moulding sands:

- typical self-hardening moulding sand with furfuryl resin with the composition of: 100 parts by weight of quartz sand and 1,1 part by weight of phenol-furfuryl resin hardened with 0,55 part by weight of aqueous solution of PTS acid;
- typical self-hardening moulding sand with alkyd resin with the composition of: 100 parts by weight of quartz sand and 1,0 part by weight of alkyd resin hardened with 0,25 part by weight of activator;
- moulding sand with the composition of: 100 parts by weight of quartz sand and 2 parts by weight of biodegradable PCL and organic solvent; hardening of the moulding sands followed by solvent evaporation. *The problem here is the toxicity of organic solvents. It seems reasonable to check whether there is a possibility of inserting biodegradable material into the sand after being earlier dissolved in an*

organic water soluble solvent and then inserting water (as a second solvent) into solution. In that case moulding sand would be made of sand grains and thermoplastic binder's particles in water suspension.

The results of the measurements are shown in Figures 4-5.

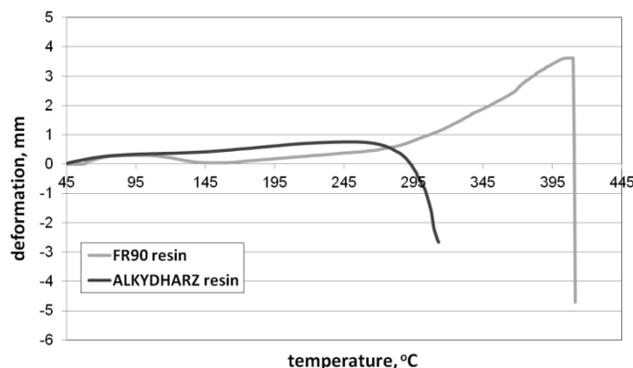


Fig. 4. Thermal deformation of ALKYDHARZ (alkyd resin) and FR90 (phenol-furfuryl resin)

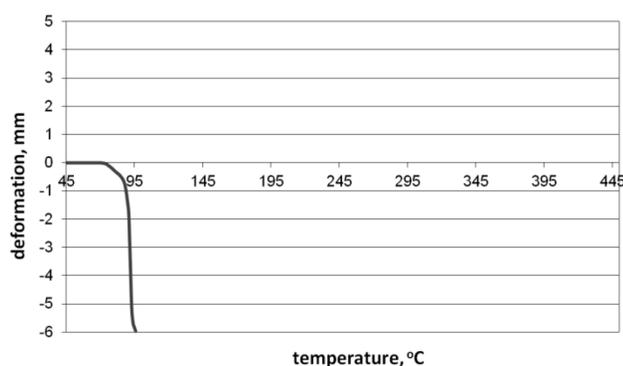


Fig. 5. Thermal deformation of PCL (polycaprolactone)

Despite very similar temperature range of complete thermal destruction of petrochemical resins, thermal deformation resistance of moulding sands with them as binders is different (Fig. 4). Moulding sand with phenol-furfuryl resin has typical course of deformation with continuous intensive growth and then rapid sample collapse when the temperature exceed 400°C. moulding sand with alkyd resin characterizes with little deformation with smooth transition in the plastic state. Completely different is deformation course of moulding sand with PCL (Fig. 5). Even at low temperature (about 70°C) moulding sand moves in a definitely plastic state. Such a property of moulding sand may affect the effective compensation of thermal expansion of cores' surface.

6. Conclusions

All the considerations and own research presented in the article were to prove usefulness of adding the biodegradable material to typical resin commonly used in foundry practice. The role of creation the composition: typical resin – biodegradable material as a binary binder is to improve moulding sands' with

synthetic resins quality. Keeping high strength properties of moulding sands caused by usage of typical synthetic resins and low environmental harmfulness caused by usage of biodegradable materials, the authors aim to create new binder for moulding sands.

Own research presented in the paper showed that typical resins and chosen biodegradable material have similar thermal destruction.

Thermal deformation research showed different deformation courses of moulding sands with all the tested binders. The connection of binders biodegradable material – synthetic resin) may positively affect the properties of moulding sands.

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