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ST.M. DOBOSZ*, D. DROŻYŃSKI*, J. JAKUBSKI*, K. MAJOR-GABRYŚ*

THE INFLUENCE OF THE CONTENT OF FURFURYL ALCOHOL MONOMER ON THE PROCESS OF MOULDING SAND'S THERMAL DESTRUCTION

WPŁYW ZAWARTOŚCI MONOMERU ALKOHOLU FURFURYLOWEGO NA PROCES DESTRUKCJI CIEPLNEJ MAS FORMIERSKICH

The article discusses the issue of the influence of furfuryl alcohol content in resin binders on properties of moulding sand at elevated temperature. Reducing the share of this component - due to the requirements of the European Union regarding its toxicity - may cause a decrease in temperature of moulding sands' destruction and, consequently, the thermal deformation of moulds and the creation of many casting defects. The study examined the impact of the furfuryl alcohol content of the thermal destruction processes and on the strength of the moulding sand at an ambient temperature and the tendency to thermal deformation.

Keywords: moulding sand, thermal destruction, bending strength, hot-distortion

W artykule omówiono zagadnienie wpływu zawartości alkoholu furfurylowego w spoiwach żywicznych na właściwości mas formierskich w podwyższonej temperaturze. Zmniejszenie udziału tego składnika – spowodowane wymaganiami Unii Europejskiej odnośnie jego toksyczności – może powodować obniżenie temperatur destrukcji masy, a w konsekwencji deformację cieplną form i powstanie wielu wad odlewniczych. W pracy przebadano wpływ zawartości alkoholu furfurylowego na procesy cieplnej destrukcji spoiwa a także na wytrzymałość masy w temperaturze otoczenia oraz skłonność do deformacji cieplnej.

1. Introduction

In the last period in the structure of the European foundry industry there have appeared some significant changes. There has been a rapid development of the production of cast iron with compact graphite, and lightweight alloys, mostly at the expense of reducing steel castings.

This has created a significant gap in the production of heavy castings for the steel, cement and energy industries. These are castings of a high weight exceeding even 30 Mg. The first problem required to solve the production of heavy steel castings is to prepare a large amount of metal and have developed techniques to keeping it in liquid form over a period of several hours, in which the device will be re-heated, with continuous quality control of its parameters

Another problem is the technology of mould for such heavy castings. Their time of solidification and cooling amounts to a few days. Moulding material is exposed to prolonged thermal and mechanical load. Foundries for steel castings currently use mostly moulding sands bonded with synthetic resins. Production of this type of casting has been dominated by the loose self-hardening moulding sands bonded with furfuryl resin, commonly called the furan moulding sands.

The reason for this is:

- ► Obtaining castings of high dimensional precision,
- ► The possibility to produce complicated moulds,
- ► Bonding at ambient temperature,
- ► Easy process of making moulds and knocking-out castings,
- ► Low binder content,
- ► Good knocking out properties and ability to mechanical reclamation.

The disadvantages of this technology may include a relatively long bonding time, and a short service life and high harmfulness of emitted gases [1]. These masses are suited for the production of small and medium-sized castings, but for heavy castings they may require substantial modification. This is particularly important because of the ecological requirements of the EU legislation in the field of content of furfuryl alcohol in resins.

On 1 December 2010, entered into force a Regulation of the European Parliament and of the Council (EC) (No 1272/2008 of 16 December 2008 on classification, labeling and packaging of substances and mixtures), which classifies furfuryl resins containing more than 25% of the free furfuryl alcohol as toxic. Furfuryl resins, which contain a lower level of free furfuryl alcohol are regarded as harmful.

Reducing the amount of free furfuryl alcohol can lower the onset temperature and the temperature range of thermal

* AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, FACULTY OF FOUNDRY ENGINEERING, DEPARTMENT OF MOULDING MATERIALS, MOULD TECHNOLOGY AND FOUNDRY OF NON-FERROUS METALS, AL. A. MICKIEWICZA 30, 30-059 KRAKÓW, POLAND

destruction of the binder, and durability of moulding sand at high temperatures and thus increase the tendency of the mould cavity to deform during the pouring. Reduction of free furfuryl alcohol may promote the formation of a number of casting defects. They are caused by a possible thermo - mechanical deformation of mould and transition of the components of weight into the structure of the casting.

There should be emphasized the importance of researches leading to the development of moulding sands adapted to transfer the long-term heat loads and mechanical stress resulting from slow cooling, which is the result of large module of clotting. Global companies producing binders for foundry industry are already proposing a new solutions in this field. And so the company Hüttenes - Albertus proposes resins of type Kaltharz series 8616 and 8700, containing less than 25% of free furfuryl alcohol [2]. However this results in an increase in water content, a slight increase in density but mostly rapid increase in viscosity. Also ASK Chemicals company [3] developed a new resin with a content of furfuryl alcohol monomer less than 25% named MAGNASET TM. Unfortunately, there are no data on the thermal resistance of the moulding sands with these binders. Factor in the accomplishment of these tasks are physicochemical tests on new organic binders with favorable characteristics of high temperature. It is about the ability to retain the stable dimensions of the mould, dependent on the conditions of high temperature destruction.

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 [4-6].

Each polymer material, however, has a specific thermal stability (thermal stability), which is important in terms of their processing and usage. The thermo stability at elevated temperature is one of the most crucial factor determining the application usefulness of the polymer [7]. 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 [3]. 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.

An important research goal is therefore to determine the course of thermal degradation of various resins in the context of their use as binders in foundry practice. Recognition of the mechanism of thermal degradation was made on the basis of the results of author's own research. To determine the degradation temperature and thermal effects of changes taking place during the heating of the tested resins, will be used methods of derivatography analysis and new methods of measurement - the author's method of measuring the tendency of the moulding sands to the thermal deformation heat – measurement of the hot distortion parameter.

2. Own researches

During tests, there were elaborated loose self-hardening moulding sands with the same quantitative composition, differing in the type of resin and hardener. The composition by weight was as follows:

- quartz sand – 100 pcs. the masses, resin – 1.0 part the masses, hardener – 0.5 part the masses,
- applied urea- formaldehyde furfuryl alcohol content: 1, 45, 75 and 90 % and produced based hardeners sulfonic acids.

2.1. Derivatographic researches

The test samples of analysed moulding sands were subjected to thermal analysis, using the Iota derivatograph in the following measurement conditions: heating temperature range 20-1000°C, heating rate 10°C/min. The results of the measurements are shown in Figures 1-3.

Derivatographic data analysis has shown that for moulding sands bonded with the resin with an alcohol content 1,75 and 90% there appears a very similar course of changes along with the increase of temperature. In the initial stage of heating there is a slow loss of weight, and when the temperature exceeds approximately 300°C this process becomes intense and lasts up to a temperature of approximately 550°C. The maximum rate of decomposition of the binder is present at about 470°C. One can observe a lower intensity of weight loss of sample bonded with resin with the lowest alcohol content in the initial warm-up period (up to a temperature of approximately 300°C). The total weight loss of the samples is associated with an alcohol content in the resin – the greater alcohol content generates increased weight loss.

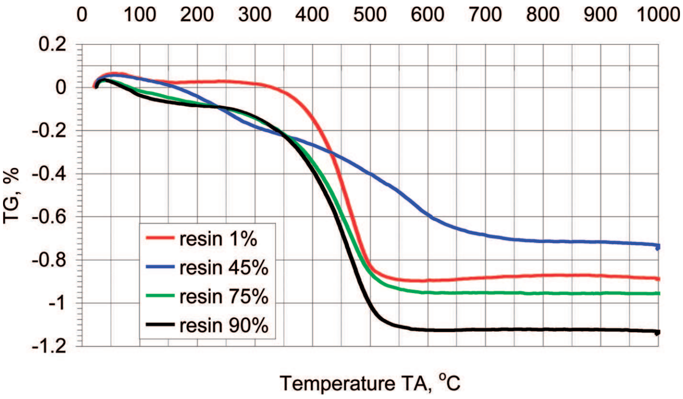

Fig. 1. TG curves for different resin – bonded moulding sands. Sample masses: mass bound to the resin 1% – 951.43 mg, the weight of the resin bound 45% – 1177.17 mg, the weight of the resin bound 75% – 1233.53 mg, the weight of the resin bound 90% – 1136.32 mg

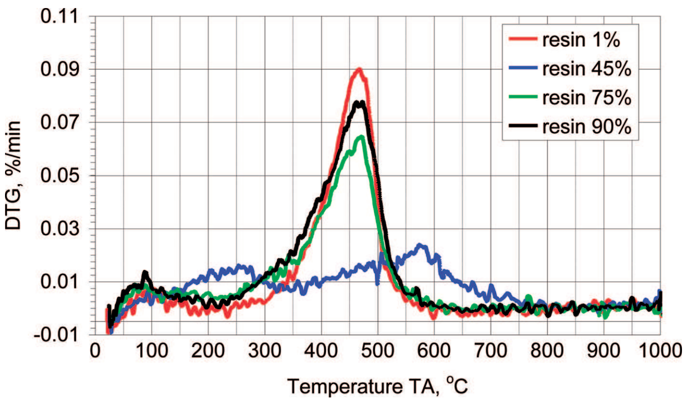

Fig. 2. DTG curves for different resin – bonded sand. Sample masses: mass bound to the resin 1% – 951.43 mg, the weight of the resin bound 45% – 1177.17 mg, the weight of the resin bound 75% – 1233.53 mg, the weight of the resin bound 90% – 1136.32 mg

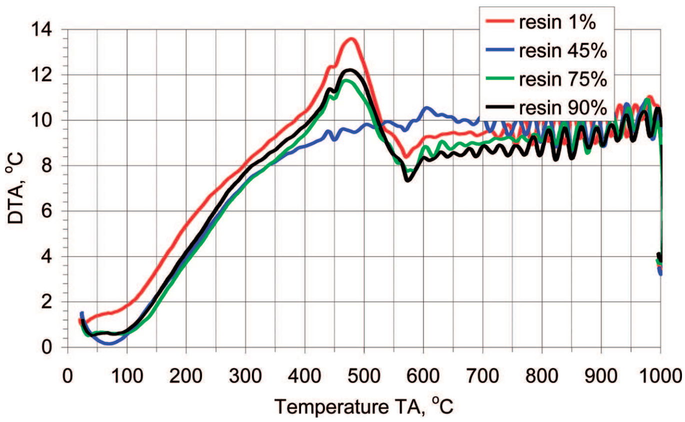

Fig. 3. DTA curves for different resin – bonded sand. Sample masses: mass bound to the resin 1% – 951.43 mg, the weight of the resin bound 45% – 1177.17 mg, the weight of the resin bound 75% – 1233.53 mg, the weight of the resin bound 90% – 1136.32 mg

In the case of moulding sand bonded with a resin having an alcohol content of 45%, there occur two stages of the increased intensity of degradation of the binder. First in the range of 120 – 320°C with lower intensity with a maximum obtained at about 260°C. The second in the range of about 400-800°C of greater intensity, with a maximum obtained at temperature of about 580°C.

The difference between the resins with an alcohol content of 1%, 75% and 90%, and a resin with content of 45% alcohol can be caused by the another way of preparing the resin, derived from another supplier. Generally it can be said that the change of content of furfuryl alcohol in resin only slightly changes the kinetics of the binder's decomposition.

2.2. Hot- distortion researches

In the next stage of the researches for moulding sands with the same compositions, there were studies of a moulding sand's tendency to thermal deformation – during flooding – by determining the hot distortion parameter. A detailed description of the method has been presented in previous publications of the authors [8]. Carried out strength tests at ambient temperature and tests of a tendency to thermal deformation, expressed by the value of parameter hot- distortion did not show the existence of a logical relationship. Changing the content of furfuryl alcohol in resin caused a slight increase in strength – especially for the contents of 90%. (Fig. 4). It has been shown, however, that the increase in strength does not reduce the thermal deformation (Fig. 5).

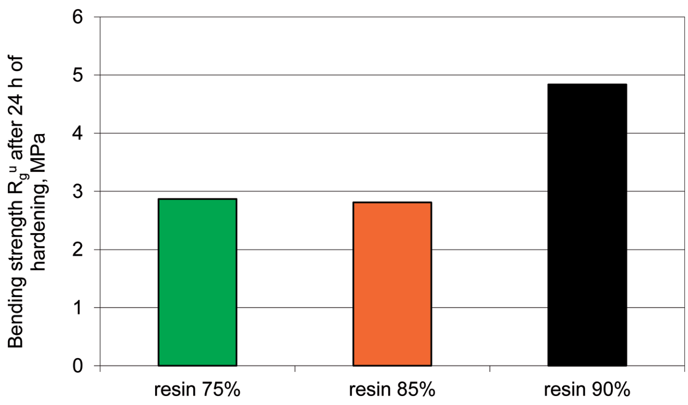

Fig. 4. Effect of furfuryl alcohol's content in the binder on strength at ambient temperature

A similar study was performed for the moulding sands with resins with different, lower contents of free furfuryl alcohol (Fig. 6). The characteristics of deformation curves obtained for all the moulding sands correspond to behavior of moulding sands bonded with a furfuryl binder specified in the earlier studies of the authors [9-11]. We observe the deformation from the heat source associated with the difference of expansion between the lower and the upper surface of the sample. This type of deformation lasts until the moment, when as a result of the loss of moulding sand's strength caused by the thermal destruction of the binder, follows the breakage of tested fitting. On the graph it corresponds to a sudden collapse of the curve in the form of a vertical line.

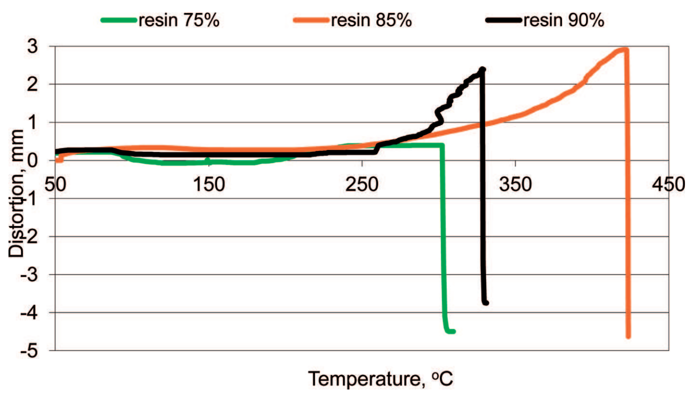

Fig. 5. Effect of furfuryl alcohol's content in the binder on the propensity to thermal deformation

Among the binders which contain more than 45% of furfuryl alcohol all have a similar thermal deformation resistance (between 410 and 430°C). Slightly larger differences are seen in the degree of thermal deformation (the maximum strain of the initial position). Moulding sand with 90% resin has the highest deformation of up to 4 mm, moulding sand with resin 75% reached a deformation of 3.4 mm, whereas in case of a moulding sand bonded with resin 45% the deformation was less than 3 mm. For a moulding sand with a resin containing 1% of furfuryl alcohol deformation resistance is much lower, but the sample (fitting) is destroyed even at a temperature of about 330°C and the maximum degree of deformation is 1.37 mm.

Thus, with a significant reduction of furfuryl alcohol, lowers the resistance to thermal deformation of moulding sand, despite the fact that it can not be assessed by measuring the resistance at ambient temperature.

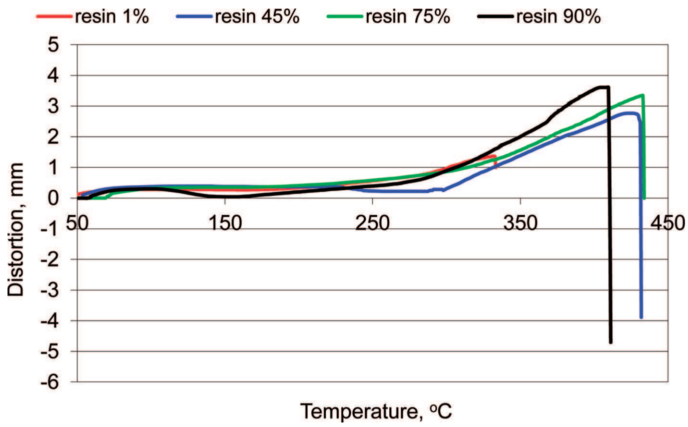

Fig. 6. Hot- distortion curves for the tested moulding sands

3. Conclusion

– Conducted thermo-gravimetric researches showed a little influence of the furfuryl alcohol content – with its high contents – on the process of thermal destruction of binder.

– Study of the influence of furfuryl alcohol's content on the strength of the moulding sands at ambient temperature showed a slight increase in strength,

– Reduction of furfuryl alcohol's content in the binder from 90% to about 4 % does not impair strongly the quality of the moulding sand, while reducing its content to 1% drastically increases the tendency to deformation, expressed by hot-distortion parameter. This tendency can not be predicted on the basis of the strength measurements.

– Included in the article studies were focused on the content of free furfuryl alcohol in the binder. Further works should include testing the moulding sands with a binder containing furfuryl alcohol in the form of free and bound, which is currently the usual practice.

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