

K. MAJOR-GABRYŚ^{*,#}, A. BOBROWSKI^{*}, A. GRABARCZYK^{*}, ST.M. DOBOSZ^{*}**THE THERMAL AND STRUCTURAL ANALYSIS OF NEW BICOMPONENT BINDERS FOR MOULDING SANDS CONSISTING OF FURFURYL RESIN AND POLYCAPROLACTONE (PCL)**

The aim of the article is thermal and structural analysis of new two-component binders for foundry moulding sands. The previous research showed the possibility of using biodegradable materials as binders or parts of binders' compositions for foundry moulding and core sands. This paper is concentrated on estimating the influence of PCL on phenol-furfuryl resin thermal destruction (measured by derivatographic research) and its structure (measured by FTiR technology). The research proved that addition of new biodegradable additive PCL in the amount of 5-15% to the phenol-furfuryl resin doesn't change the resin thermal destruction course but it results in appearance of a new band in two-component binder structure. What's more there has been noticed a growth of intensity for band at wavenumber 1730 cm^{-1} (C = O) with the increasing addition of PCL.

Keywords: innovative foundry technologies and materials, moulding sands, furfuryl resin, polycaprolactone (PCL), spectroscopic studies (FTiR)

1. Introduction

According to the tendencies observed in recent years, moulding processes must meet high requirements connected to environmental protection.

One of scientific research directions is a gradual replacement of binding materials produced from petrochemical origin, with biopolymers coming from renewable resources. It is consistent with the conception of sustainable development, which is one of the priorities of the European Community policy. In the 90's the General Motors Co. elaborated a new binding system based on protein composition GMBOND [1]. The materials in the protein binder come from natural renewable resources and consist of polypeptide chains, which are non-toxic (safe) for the environment. K. Rusin's scientific group [2] tested possibilities of using biogenic binders based on proteins obtained from by-products of pharmacy industry production. The group tested water soluble not toxic polymers, including different polypeptide molecules with long amino acids chains. B. Grabowska [3-4] proposed use of aqueous biodegradable polymeric compositions consisting of acrylic derivatives and modified natural polymers as foundry moulding sands' binders (BioCo binders). Moulding sands with BioCo binders can be used in iron castings production [4].

The use of additives to the binders to improve moulding sands properties is the newest trend of global corporations in the production of foundry materials [5].

Literature data [6-8] shows that there is a possibility of using biodegradable materials as additives for petrochemical

materials to increase their biodegradability. For example poly(ϵ -caprolactone) (PCL) has a unique characteristic – 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 [6]. Primary studies of biodisintegrable polymer blends using PCL as a biodegradable component started with 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 [7]. Further advantages of using biodegradable polymers, such as PCL, as additives might include increase in flexibility of moulding sands with new two-component resins. The use of PCL as a plasticizer for plastics is not a new matter. From a technological point of view, the use of plasticizers for polymers is very important and widely used in various industries. In 1966 the use of PCL as a plasticizer for polyvinyl chloride (PVC) was patented. Polycaprolactone was used as a plasticizer in blends of: aliphatic polyesters, cellulose esters, aromatic polyesters, polycarbonates, polymers containing styrene (eg. Polystyrene), polyolefins, block copolymers, and in foundry resin type NOVOLAK [8-9].

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2. Own research

A broad analysis of literature data and own research led the authors to a new perspective on the production of moulding and core sands. The idea is based on partial replacement of synthetic foundry resins with biodegradable materials, to improve their properties [9]. This approach will reduce the technological costs in relation to approach which used only biodegradable material as moulding sand's binder. At the same time it will allow the modernization of well-known and widely used mould and core preparation technologies.

Preliminary research [10] has shown that the moulding sands with biodegradable materials as binders are not only lower in toxicity but they have a greater capacity to regenerate mechanically than traditional synthetic resin moulding sands. It can be concluded that the partial replacement of the petrochemical origin binder with biodegradable material will improve the quality of tested moulding sands [9-11]. In addition, the use of polycaprolactone as a component of the new binder can improve the resistance to deformation of the moulding sand at ambient temperature, known in the literature as flexibility/elasticity [12-13].

2.1. The materials investigated as components of a new two-component binder

The following materials were selected as components for the new binders:

- Phenol-furfuryl resin from Hüttenes-Albertus Company under the name of Kaltharz XA20. The study used furan resin that did not contain nitrogen, and the free formaldehyde content was in the range of 0.05 - 0.15%. The amount of furfuryl alcohol was 78%.
- Hardener from Hüttenes-Albertus Company under the name of Aktivator 100T3. An aqueous solution of paratoluene-sulfonic acid.
- Polycaprolactone (PCL) from Polysciences, Inc. was used as a biodegradable additive and plasticizer in powdered form. It is a biodegradable polymer having an end hydroxyl group.

Selection of these materials is primarily based on the fact that PCL can be dissolved in the Kaltharz XA20 resin. There is therefore no need for an additional solvent to dissolve the biodegradable polymer.

2.2. Measurements and discussion

The influence of PCL on thermal degradation of phenol-furfuryl resin was tested by derivatographic research. The tests were carried out on the Iota derivatograph in the following measurement conditions: heating temperature range 20–1000°C, heating rate 10°C/min. The measurement was conducted in oxygen atmosphere. Figures 1-2 show the derivatographic measurement results

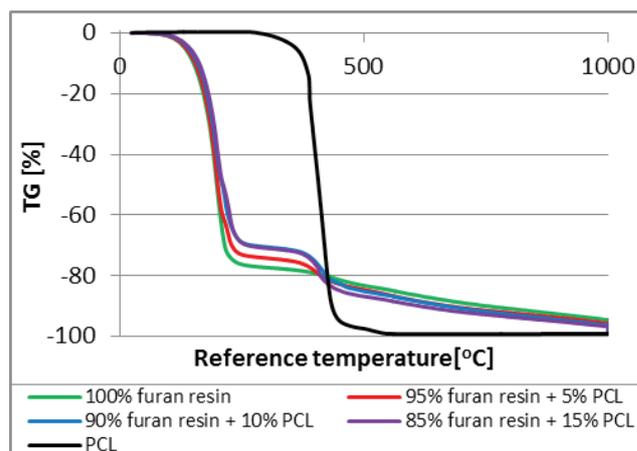


Fig. 1. TG curves of applied resins [9]

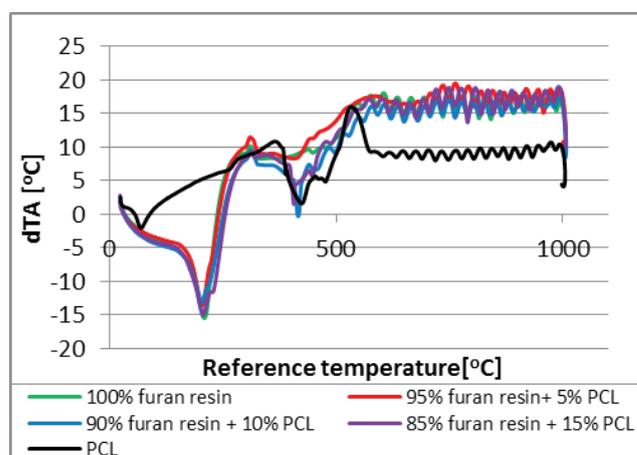


Fig. 2. DTA curves of applied resins [9]

The study showed that the phenol-furfuryl resin has a lower temperature of the beginning of thermal destruction (temperature approx. 120°C). The violent process ends at a temperature of approx. 230°C and transitions into slow decay to approx. 820°C. Thermal destruction of the biodegradable material (PCL) is very intense – starting at a temperature of approx. 370°C and ending at a temperature of approx. 450°C. This means that the loss of PCL specimen weight begins much later than in commonly used moulding sand foundry resins and is more violent [9]. The thermal destruction of two-component adhesives process is similar to the TG curve of pure furfuryl resin (Fig. 1). It can be noted, however, that the destruction changes its course towards somewhat higher temperatures (Fig. 2). The changes are adequate to the percentage of the PCL material in the binder [9].

The next stage was spectroscopic studies (FTIR) of new binders. The aim of these studies was to determine the effect of used biodegradable material on the structure of the new two-component binder. Structural analyses were carried out using an Excalibur FTIR spectrometer with a standard DTGS detector and the resolving power of 4 cm⁻¹. The spectra of samples were obtained at room temperature using the transmission technique (KBr pellet). A small amount of liquid binder was smeared onto a KBr pellet (prepared by pressing KBr powder under force of

$8 \cdot 10^3$ kg). The number of scans was constant for all samples. The results were registered for wave numbers from 4000 to 400 cm^{-1} with resolution 4 cm^{-1} as shown in Figs. 3-4 and Tables 1-2.

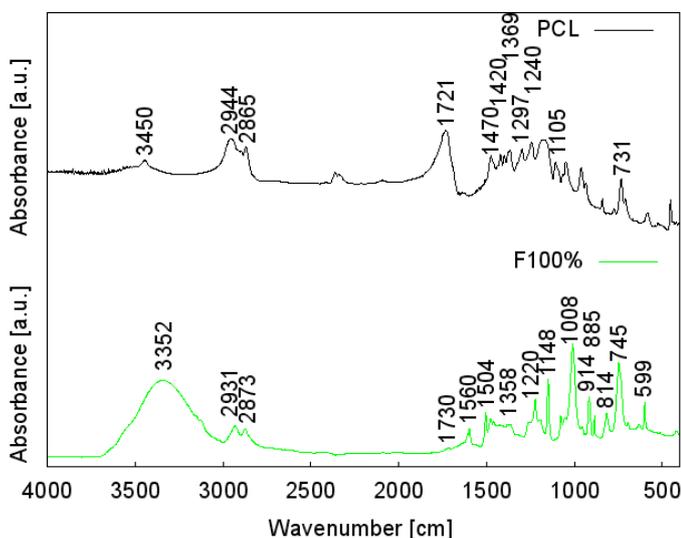


Fig. 3. FTIR spectrum of PCL and 100% furfuryl resin

Characteristic vibrations of the O-H stretching bonds at wavenumber 3450 cm^{-1} can be identified in the PCL spectrum (Fig. 3, Table 1) [14]. Asymmetrical vibration of CH₂-O were registered at 2944 cm^{-1} and balanced vibration of methylene groups CH₂ at 2865 cm^{-1} [15-16]. The intense band characteristic of the carbonyl group is observed at a wavenumber 1721 cm^{-1} and is associated with the vibration of the C = O aliphatic ester in PCL [15-16]. Band at 1470 cm^{-1} refers to the asymmetrical vibration of C-H of a methylene group [15]. The remaining bands in the 1470-1369 cm^{-1} and 1105-730 cm^{-1} are also in the vibration characteristic of C-H bond [15,17-19]. In the wave number range 1297-1160 oscillation of C-O bonds occurs [15-18].

TABLE 1

Chosen wavenumbers with vibration descriptions for PCL

PCL		
Wave-number [cm ⁻¹]	Description of vibrations	Source
3450	(-OH) peak	[14]
2944	(CH ₂ -O) asymmetric elongation/stretching	[15,16]
2865	(CH ₂ -) symmetric elongation/stretching	[15,16]
1721	(CO ₂ -) stretching of carbonyl belonging to an aliphatic ester	[15,16]
1470	(C-H) asymmetric elongation in methylene	[15]
1420	δ (CH ₂ - CH ₃)	[17]
1369	δ (CH ₂)	[18-19]
1297	ν_{cr} (C-O) and ν_{cr} (C-C) stretching in the crystalline phase	[16-18]
1240	ν_{as} (C-O-C) asymmetric stretching	[15-17]
1160	C-O	[20]
1105	CH ₂	[18-19]
730	p(CH ₂ -) asymmetric elongation of long CH ₂ - chains corresponding with the 1470 methylene group	[15]

TABLE 2

Chosen wavenumbers with vibration descriptions for furfuryl resin

100% Furfuryl resin		
Wave-number [cm ⁻¹]	Description of vibrations	Source
3352	(O-H)	[21,22-23]
2931	(C-H)	[22-25]
2873	(C-H)	[22-25]
1730	(C = O)	[26]
1560	(C = C)	[27]
1358	(OH) vibrations of the furan ring or of the OH phenolic deforming the bond along the plane	[22-23]
1220, 1148, 1008	Band recognized in cured resin	[22]
914, 885, 814	(C-H) deforming vibrations of the furan ring	[21]
745	skeleton vibrations coming from bonds found in furfuryl alcohol	[21]
599	vibrations of the entire furan ring	[21]

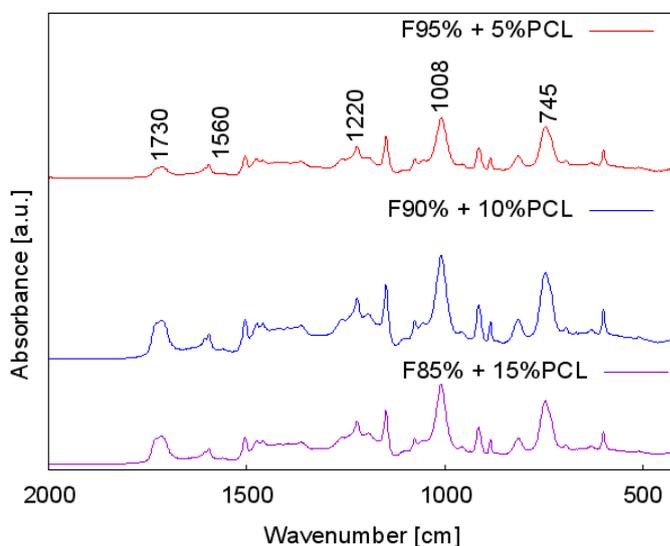


Fig. 4. FTIR spectrum of two-component binders

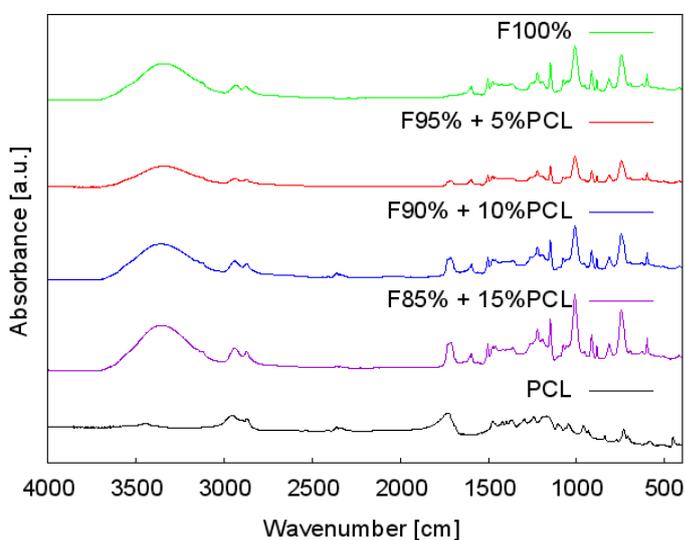


Fig. 5. FTIR curves for chosen resins and PCL

PCL addition in the amount of 5-15% to the furan resin (Figs. 4-5) results in the appearance of a band at a wavenumber of 1105 cm^{-1} derived from the vibration of CH_2 in PCL (Tables 1-2) [18-19]. There has also been a growth of intensity for band at wavenumber 1730 cm^{-1} caused by vibration of extending carbonyl bond $\text{C}=\text{O}$ with the increasing addition of PCL [26]. Other bands in the spectrum of the resin do not change with the increasing addition of PCL (Fig. 4-5).

3. Conclusions

Analysis of literature data and the author's own research yield the following conclusions:

- The biodegradable additive PCL in the amount of 5-15% to the phenol-furan resin does not significantly affect the thermal degradation of phenol-furfuryl resin (TG, dTA curves). However this impact of PCL increases with its quantity.
- PCL addition in the amount of 5-15% to the phenol-furan resin results in the appearance of a new band at a wavenumber of 1105 cm^{-1} and a growth of intensity for band at wavenumber 1730 cm^{-1} in two-component binders. It is possible that PCL came into the phenol-furfuryl resin structure but such a claim must be proved by different type of research.

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