ARCHIVES

of

FOUNDRY ENGINEERING

Effect of Silicate Modifier on the Emission of Harmful Compounds from Phenolic Resin used in Cold-Box Technology

S. Żymankowska-Kumon *, A. Bobrowski, D. Drożyński, B. Grabowska, K. Kaczmarska

AGH University of Science and Technology, Faculty of Foundry Engineering,
Reymonta 23, 30-059 Kraków, Poland
* Corresponding author. E-mail address: szk@agh.edu.pl

Abstract

In many foundries, the requirements placed on castings production have risen mainly over the few years. Further trends in recent years have been the ever increasing level of automation and introduction of new alloys, especially composites. On the other hand, the foundry environment has become increasingly difficult because is used many organic binders. Environmental regulations will be further tightened up. These processes are pursued at national, European and global level. Conformity with emission limits is becoming increasingly difficult. The problem is emission of aromatic hydrocarbons, phenol, odours and other harmful compounds to environment. The main purpose of many companies is reduction of this toxins. The new cold-box systems (based on phenolic resins) try to reduce the emission by introducing into the resin structure silicate modifiers. Research presented of this article evaluate the effectiveness of these methods. The results show comparison of two resins ("without" and "with" silicate modifier) for assessment of emission of harmful aromatic hydrocarbons and phenol.

Keywords: Environment protection, Resin, Aromatic hydrocarbons, Phenol, Emission, Cold-Box

1. Introduction

The cold box system was originally understood to be the phenolic/urethane/amine process, but now describes any core binder process that uses a gas or vaporized catalyst to cure resin coated sand while it is in contact with a room temperature pattern. The polyurethane cold-box process is based on the reaction of two components (Fig. 1):

- Part 1: a polyaddition of the phenol-formaldehyde resin;
- Part 2: the isocyanate, is initiated through basic catalysis, usually by means of gassing with a tertiary amine [1].

The cold box processes have eliminated the need for expensive, inconvenient heat curing. They offer advantages of dimensional accuracy, productivity and potentially higher quality than other core and mould systems. With the exception of the silicate/CO_2 process, all the cold box systems have the typical blow, gas, purging, strip core making sequence [2].
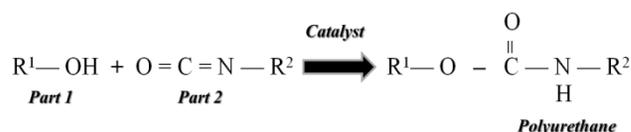

Fig. 1. Reaction of cold-box process

The cure cycle is relatively fast and can be completed within seconds. The most popular systems, which are all in this category are presented on Figure 2 [3].

Fig. 2. Cold-box systems

The cold box processes are exceptionally precise during the coremaking stages as: no thermally related expansion and contraction of the tooling takes place and core breakage is relatively low. The most popular advantages of this technology obtain [4]:

- no tooling heat required and cures at room temperature;
- cost effective to run in comparison to heat cured systems;
- low labor and energy cost;
- good dimensional accuracy;
- cores can be handled and cast almost immediately;
- long resin shelf life.

In addition to their process engineering strengths, modern cold box systems offer great potential for improvement of their environmental properties. Replacement of the solvents used in the resins and activators alone leads to a marked improvement in the pollutant balance (I and II generations). Aside from the problem of reducing pollutant emissions during production of castings, foundries are nowadays increasingly confronted with further types of emissions [5, 6]. The present geographic proximity of plants to residential areas, and the increased environmental awareness of the population have led to sensitization of nearby residents to the nuisance factors of noise and particularly odours. To preserve the social acceptance of the foundry, the foundry operator must become active in the question of odour emissions. Chronology of environmentally relevant evolution of new cold box generations includes four generations [7]:

- I – replacement of aromatic solvents by methyl esters of rapeseed fatty acids with consequent reduction of pollutant emissions[1], during core-making and after pouroff;
- II – use of modified methyl esters of fatty acids with the goal of reducing smoking during drying of cores and after pouroff compared to first-generation levels;
- III – reduction of the level of free phenol in the resin component with the goal of improving the disposability of used sand and further decreasing pollutant emissions;
- IV – use of silicate-based solvents with the goal of reducing odour emissions, smoking and condensate deposits after pouroff (Fig. 3).

The aim of this work was the influence of silicate modifier on the emission of harmful substances (especial hydrocarbons) from phenolic resin used in cold-box technology. For many years, the assessment of the harmfulness of foundry resins has been the subject of research in Faculty od Foundry Engineering in AGH University of Science and Technology in Cracow [8-10].

$$4R—OH + Si(OC_2H_5)_4 = \begin{array}{c} R \quad\quad R \\ \backslash \quad\quad / \\ O \quad O \\ \backslash \; / \\ Si \\ / \; \backslash \\ O \quad O \\ / \quad\quad \backslash \\ R \quad\quad R \end{array} + 4C_2H_5OH$$

Fig. 3. Reaction schemes from alkyl (ethyl) orthosilicate [11]

2. Tested materials

The research were conducted phenolic resins used in cold-box technology, mainly to cores production. Resin R1 is synthetic phenolic resin dissolved in plant solvents and resin R2 is synthetic phenolic resin dissolved in an anhydride based on alkyl orthosilicate. Table 1 presented short characteristic of the tested materials.

Table 1.
Characteristic of the tested resins

Parameters	Resin R1	Resin R2
Density (20°C)	1.111 g /cm^3	1.115
Viscosity (20°C)	0.60-0.70 Pa·s	0.13-0.16 Pa·s
Harmful substances	Phenol Aromatic hydrocarbons	Phenol Aromatic hydrocarbons Ethyl silicate

3. Research methodology

The aim of research was to check how silicate modifier influences on the emission of harmful substances (especial hydrocarbons) from phenolic resin used in cold-box technology. The article obtained three type of research:

- thermal analysis – to check the differences between the tested resins and to select the temperature range for chromatographic analysis;
- structural studies by FTIR transmission technique – also to check the differences between the tested resins, especially detection of silicate modifier and its impact on structural changes;
- chromatographic analysis by pyrolysis gas chromatography mass spectrometry (Py-GCMS) method – to check the impact of silicate modifier to emission of aromatic hydrocarbons and phenol.

4. Results and discussion

---

[1] mainly BTEX group – benzene, toluene, ethylbenzene and xylenes

The TG/DTG thermograms for resins R1 and R2 as a function of temperature at the heating rate of 10°C /min are given in Figs. 4 and 5. Curves were recorded in the temperature range of 20-1000°C, in the air atmosphere.
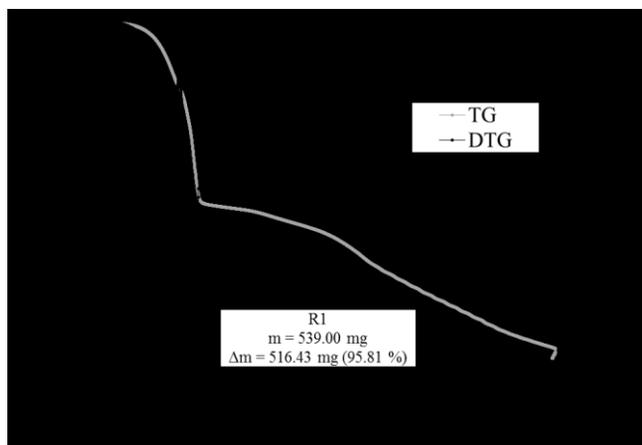

Fig. 4. Thermogram TG/DTG of resin R1

The process of R1 can be subdivided into three stages based on the DTG profile. The first stage shows a mass loss of 19.66 % for drying the sample between 25 and 170°C (small endothermic effect); surface moisture and inherent moisture are emitted in this stage [12, 13]. The second stage is fast thermal decomposition between 180 and 450°C; the maximum mass loss (about 41.12 wt.% of the total weight) occurs in this stage. The third stage shows 32.65 wt.% of the total mass loss due to further decomposition of resin R1. This last stage has a wide temperature range, from 500°C to the end of this experiment (1000°C) – second small endothermic effect. During the process, there are three peaks of the DTG curve (mass loss rate) at 152.92, 195.95 and 562.52°C in first, second and last stage degradation, respectively. The maximum mass loss rate of 11.5 %/min occurred at 195.94°C.
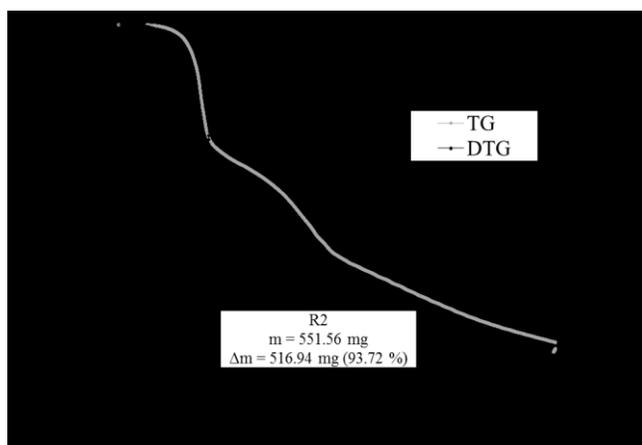
Fig. 5. Thermogram TG/DTG of resin R2

The thermogram of R2 is little different. The first stage shows a maximum of mass loss of 39.93% for drying the sample between 25 and 250°C (fast thermal decomposition). The second and third

stage are small endothermic effects: I – from 350 to 450°C (14.17 wt.% of the total weight) and II – from 460 to 500°C (6.59 wt.% of the total weight). There are three peaks of the DTG curve (mass loss rate) one in the first and two in the second stage. The maximum mass loss rate occurred at 210.45°C (9.33 %/min).

The IR spectra for resins R1 (a) and R2 (b) are given in Figs. 6 and 7.
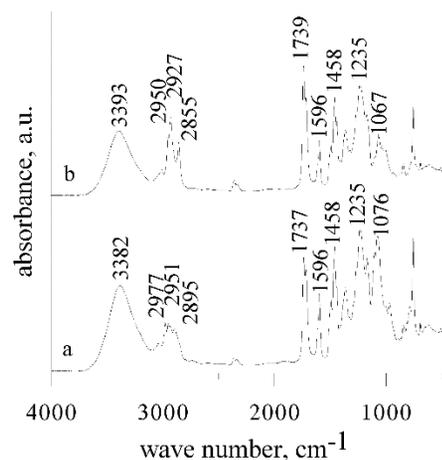
Fig. 6. IR spectra of the resins R1 (a) and R2 (b) in the range of wave number 4000-1100 cm^{-1}

The bands at the wave number 3393 and 3382 cm^{-1} corresponds to the O-H stretching vibrations (Fig. 6). In the range of 3000-2850 cm^{-1} the vibrations attributed to C-H bonds (both CH_2 and CH_3) are recorded. Appearance of the bands in the range of wave number between 1750-1700 cm^{-1} indicates the occurrence of vibrations of C=O bonds [14].
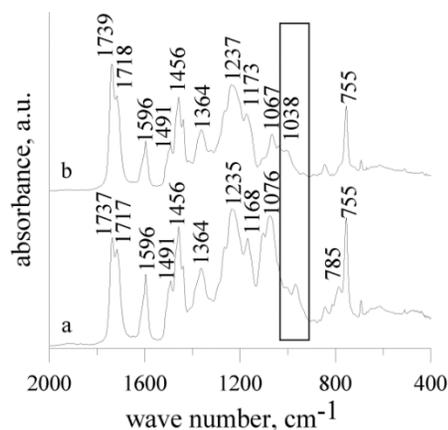
Fig. 7. IR spectra of the resins R1 (a) and R2 (b) in the range of wave number 2000-400 cm^{-1}

The bands at the wave number 1596 and 1491 cm^{-1} are associated with C=C bonding in the aromatic ring. Appearance of the band at the wave number 1364 cm^{-1} is attributed to O-H phenol vibrations in the plane [15, 16]. Band at the wave number 1235 cm^{-1} is assigned as asymmetric C-C-O stretching bonds, while at 1168 cm^{-1} as deformation vibrations of C-H bond in the plane [17]. Within the range of 1080-1016 cm^{-1} there are bands that can be attributed

to single C-O bonds associated with the -C-OH stretching groups [18]. At the wave number 755 cm^{-1} recorded the band of vibrations beyond the plane of C-H bond (Fig. 7).

The chemical structure of both samples of phenolic resins observed on FTIR spectra in the range of wave number 4000-1100 cm^{-1} is very similar. Appearance differences in the modified resin (R2) are observed in the range of wave number 1080-1000 cm^{-1}. A band at wave number 1038 cm^{-1} appears, which indicates the addition of a silicate modifier (Fig. 7, spectrum b). This band is characteristic of Si-O stretching vibrations [19-23].

The chromatograms for resins R1 and R2 are given in Figs. 8 and 9. The temperature range was coherent to obtained data from TG/DTG curves. The pyrolysis gas chromatography (Py-GC/MS) method is based on transforming a solid sample (about 5 mg) into gas by heating in an atmosphere of inert gas (e.g. helium) in a pyrolyzer, which is accompanied by thermal decomposition [24]. The temperature range of work of pyrolyzer is 240–1300°C. The obtained mixture of compounds is separated on a chromatographic column in a chromatograph coupled with mass spectrometer. A temperature program was applied: an initial temperature of 40°C was held for 3 min; ramped 3°C/min up to 100°C and held for 3 min, and then 250°C with a heating rate of 20°C/min was maintained for 3 min (helium carrier gas at 1 ml/min, sample split ratio 1:30) [25]. Conditions of mass spectrometer: the full range mass number/charge number (m/z); electron ionisation (70 eV) at a temperature of 250°C [26].
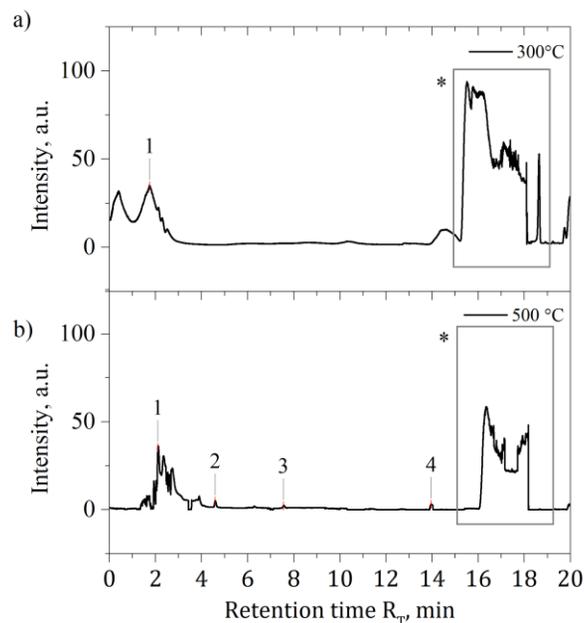
Fig. 8. Chromatogram for resin R1

Attention was focused to the emission of aromatic hydrocarbons and phenol. The list of obtained compounds was shown in Tables 2.
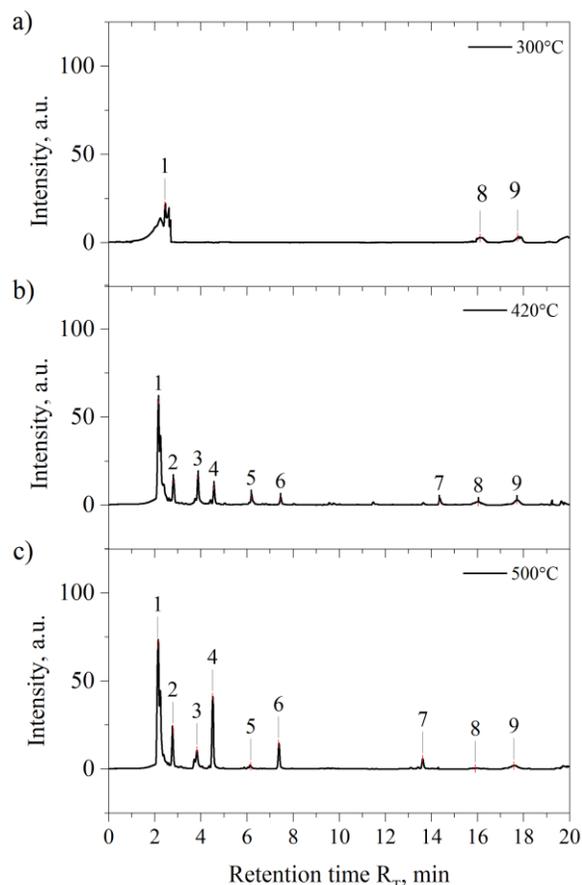

Fig. 9. Chromatogram for resin R2

Table 2.
Results of the qualitative analysis of Py-GC/MS research

No.	Compound	Retention time R_T, min	
		300°C	500°C
R1			
1	Carbon dioxide	2.01	2.12
2	Benzene	n.a.	4.53
3	Toluene	n.a.	7.67
4	Styrene	n.a.	14.05
*	thermal degradation products of plant solvents and phenol	15-19.00	16-18.00

No.	Compound	Retention time R_T, min		
		300°C	420°C	500°C
R2				
1	Carbon dioxide	2.03	2.09	2.05
2	Cyclopentadiene	n.a.	2.76	2.79
3	Formamide	n.a.	3.92	3.96
4	Benzene	n.a.	4.55	4.56
5	Glycolic acid	n.a.	6.12	6.18
6	Toluene	n.a.	7.65	7.69
7	Styrene	n.a.	13.98	13.93
8	Phenol	16.32	16.36	16.39
9	m-Cresol	17.89	17.95	17.94

At 300°C carbon dioxide, thermal degradation products of plant solvents (resin R1) and phenol (both resins) were found. For resin R2 the temperatures 420°C and 500°C gave the similar products of thermal degradation. At 500°C some marks of benzene, toluene and strynene decomposition were found in the products of both resins.

For the resin R1 the chromatograms have much more signals than for resin R2. The characteristic area for resin R1 within a retention time (R_T) range of about 15-19 min includes a number of signals that derived from the decomposition of plant solvents and phenol. As the temperature of decomposition increases, these compounds will be more pronounced in the chromatograms.

Chromatogram for the resin R2 has much less singals than for R1. In the products of thermal degradation were identified some hydrocarbons (benzene, toluene and stryrene), phenol and its derivatives (e.g. m-cresol). At temperature 420°C and 500°C also were founded cyclopentadiene (reagents in organic synthesis), formamide (solvent for resins and plasticizers), glycolic acid (useful intermediate for organic synthesis, in a range of reactions including e.g. esterification or long chain polymerization).

5. Conclusions

Based on the obtained results, the following conclusions can be drawn:

- the thermal analysis of tested resins R1 and R2 allows the indicate of characteristic temperature points accompanied by a loss of weight. The first one was probably related to the loss of solvent (main component of resin), the next one to the decomposition of C-H bonds and phenol;
- the FTIR studies confirm occurrence of silicate modifier in resin R2;
- the Py-GC/MS analysis showed that silicate modifier reduces emission of some hydrocarbons and products of phenol (planning quantitative analysis will be confirm the difference between tested resins - mainly decrease amount of emission of benzene);
- the addition of silicate modifier also affects the reduction on plant solvents, so resin R2 in more friendly for environment;

Because of the limits of the Py-GC/MS apparatus (fused silica column), it is impossible to delineate the silicate products in the tested samples (mainly resin R2).

Acknowledgements

References

[1] Li, C. et al. (2016). Silicone-modified phenolic resin: Relationships between molecular structure and curing behavior. *Thermochemical Acta*. 639, 53-65. DOI: 10.1016/j.tca.2016.07.011.

[2] http:// www.mancusochemicals.com, 2017-08-01, 18:52.

[3] Żymankowska-Kumon, S., Kolczyk, J. (2016). Chromatographic analysis of selected products of thermal decomposition of core sands made in cold-box technology. *Transactions of the Foundry Research Institute*. 16(4), 369-378. DOI: 10.7356/iod.2016.25.

[4] Reduction of foundry odor emissions by use of new generations of organic binders, materials from Hüttenes-Albertus.

[5] Fabbri, D. & Vassura, I. (2006). Evaluating emission levels of polycyclic aromatic hydrocarbons from organic materials by analytical pyrolysis. *Journal of Analysis and Applied Pyrolysis*. 75, 150-158. DOI: 10.1016/j.jaap.2005.05.003.

[6] Fox, J.R., Adamovits, M. & Henry, C. (2002). Strategies for Reducing Foundry Emissions. *AFS Transactions*. 110, 1299-1309.

[7] Fang, S. et al. (2015). Preparation and curing behavior of silicone-modified phenolic resin. *Applied Mechanics and Materials*. 713-715, 2798-2803. DOI: 10.4028/www.scientific.net/AMM.713-715.2798.

[8] Holtzer, M., Dańko, R., Dańko, J., Kubecki, M., Żymankowska-Kumon, S., Bobrowski, A., Spiewok, W. (2013). *The assesment of harmfulness of binding materials used for a new generation of core and molding sands*. Kraków: Akapit.

[9] Kubecki, M., Holtzer. M. & Żymankowska-Kumon, S. (2013). Investigations of the temperature influence on formation of compounds from the BTEX group during the thermal decomposition of furan resin. *Archives of Foundry Engineering*. 13(2), 85-90.

[10] Żymankowska-Kumon, S., Bobrowski, A. & Grabowska, B. (2016). Comparison of the emission of aromatic hydrocarbons from moulding sands with furfural resin with the low content of furfuryl alcohol and different activators. *Archives of Foundry Engineering*. 16(4), 187-190.

[11] Nason, H.K. (1939). Silicon modified phenolic resins and process for producing same. Patent US 2182208 A.

[12] Ahamad, T. & Alshehri, S.M. (2014). Thermal degradation and evolved gas analysis: A polymeric blend of urea formaldehyde (UF) and epoxy (DGEBA) resin. *Arabian Journal of Chemistry*. 7, 1140–1147, DOI: 10.1016/j.arabjc.2013.04.013.

[13] Jingai, S., Rong, Y., Hanping, C., Baowen, W., Dong, H.L. & David, T.L. (2008). Pyrolysis characteristics and kinetics of sewage sludge by thermogravimetry Fourier transform infrared analysis. *Energy Fuels*. 22, 38-45. DOI: 10.1021/ef700287p.

[14] Costa, L. et al. (1997). Structure-charring relationship on phenol-formaldehyde type resins. *Polymer Degradation and Stability*. 56, 23-35. DOI: 10.1016/S0141-3910(96)00171-1.

[15] Yangfei, C., Zhiqin, C., Shaoyi, X. & Hangbo, L. (2008). A novel thermal degradation mechanism of phenol-formaldehyde type resins. *Thermochimica Acta*. 476(1-2), 39-43. DOI: 10.1016/j.tca.2008.04.013.

[16] Jiang, H. & Wang, J. et al. (2012). The pyrolysis mechanism of phenol formaldehyde resin. *Polymer Degradation and Stability*. 97(8), 1527-1533. DOI: 10.1016/j.polymdegradstab.2012.04.016.

[17] Poljanšek, I., Šebenik, U. & Krajnc, M. (2006). Characterization of phenol-urea-formaldehyde resin by inline FTIR Spectroscopy. *Journal of Applied Polimer Science*. 99, 2016-2028. DOI: 10.1002/app.22161.

[18] Zhao, Y., Yan, N. & Feng, M.W. (2013). Thermal degradation characteristic of phenol-formaldehyde resins derived from beetle infested pine barks. *Thermochimica Acta* 555, 46-52. DOI: 10.1016/j.tca.2012.12.002.

[19] Jiang, D. et al. (2009). Simulating the initial stage of phenolic resin carbonization via the reaxff reactive force field. *Journal of Physical Chemistry A*. 113(25), 6891-6894. DOI: 10.1021/jp902986u.

[20] Poljanšek, I. & Krajnc, M. (2005). Characterization of phenol-formaldehyde prepolymer resins by in line FT-IR Spectroscopy. *Acta Chimica Slovenica*. 52, 238-244.

[21] Alonso, M.V. et al. (2011). Thermal degradation of lignin–phenol-formaldehyde and phenol-formaldehyde resol resins. *Journal of Thermal Analysis and Calorimetry*. 105(1), 349-356. DOI: 10.1007/s10973-011-1405-0.

[22] Chen, Z., Chen, Y. & Liu, H. (2013). Pyrolysis of phenolic resin by TG-MS and FTIR analysis. *Advanced Materials Research*. 631-632, 104-109. DOI: 10.4028/www.scientific.net/AMR.631-632.104.

[23] Costa, L. et al. (1997). Structure-charring relationship on phenol-formaldehyde type resins. *Polymer Degradation and Stability*. 56, 23-35. DOI: 10.1016/S0141-3910(96)00171-1.

[24] Żymankowska-Kumon, S., Kolczyk, J. (2016). Chromatographic analysis of selected products of thermal decomposition of core sands made in cold-box technology. Transactions of the Foundry Research Institute 16(4), 369-378. DOI: 10.7356/iod.2016.25.

[25] Grabowska, B., Kaczmarska, K., Bobrowski, A., Żymankowska-Kumon, S. & Kurleto-Kozioł, Ż. (2017). TG-DTG-DSC, FTIR, DRIFT, and Py-GC-MS Studies of Thermal Decomposition for Poly(sodium acrylate)/Dextrin (PAANa/D) – New Binder BioCo3. *Journal of Casting & Materials Engineering*. 1(1), 27-32. DOI: 10.7494/jcme.2017.1.1.27.

[26] Fabbri, D. & Vassura, I. (2006). Evaluating emission levels of polycyclic aromatic hydrocarbons from organic materials by analytical pyrolysis. *Journal of Analysis and Applied Pyrolysis*. 75, 150-158. DOI: 10.1016/j.jaap.2005.05.003.