The Influence of Biomaterial in a Binder Composition on Biodegradation of Waste from Furan Moulding Sands

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Abstract

Due to the observed increase in the amount of waste in landfills, there has been an increase in the demand for products made of biomaterials and the composition of biomaterials with petroleum-derived materials. The problem of waste disposal/management also applies to waste from the casting production process with the use of disposable casting moulds made with the use of organic binders (resins), as well as residues from the process of regeneration of moulding sands. A perspective solution is to add a biodegradable component to the moulding/core sand. The authors proposed the use of polycaprolactone (PCL), a polymer from the group of aliphatic polyesters, as an additive to a casting resin commonly used in practice. As part of this study, the effect of PCL addition on the (bio) degradation of dust obtained after the process of mechanical regeneration of moulding sands with organic binders was determined. The (bio) degradation process was studied in the environment reflecting the actual environmental conditions. As part of the article, dust samples before and after the duration of the (bio) degradation process were tested for weight loss by thermogravimetry (TG) and for losses on ignition (LOI).

Keywords: Moulding Sand, Organic Binder, Biodegradable PCL additive, Biodegradation process

1. Introduction

The growing production resulting from the growing demand for products causes a sharp increase in post-production waste and used products stored in landfills.

The foundry industry generates waste mainly from moulding and core sands used for casting production. Currently, most of the binding materials used in foundry practise for the production of disposable moulds are not decomposable. The remains of materials left over from the production of castings and the regeneration process are resistant to naturally decomposing environmental factors. They are not damaged by water, air, sunlight, or the action of microorganisms.

In recent years, the growing problems related to the amount of collected waste resulted in an increased interest in photodegradable materials and biomaterials with a controlled lifetime. The degradation of these materials begins after their use. According to the definition, degradation is an irreversible process leading to changes in the chemical structure of the material. This process causes the loss of material's functional properties. The degradation can be caused by various factors in the environment.

- Abiotic degradation - degradation due to electromagnetic radiation, mechanical forces, heat or active chemical compounds.
- Biotic degradation - degradation caused by the action of biological factors which are mainly enzymes produced by various microorganisms such as bacteria or fungi. This type of degradation is called biodegradation or biological degradation.

There is specific biodegradability and total biodegradability of materials. Specific biodegradability is the potential of a material to biodegrade. It is determined on the basis of appropriate laboratory tests carried out under strictly defined, controlled conditions. Total biodegradability is the total degradation of a material by microorganisms. The process takes place in the presence of oxygen to CO_2, H_2O and mineral salts with the formation of new biomass (aerobic biodegradation) or under anaerobic conditions to CO_2, CH_4, inorganic salts and biomass (anaerobic biodegradation, biomethanization) [1-4]. Therefore, the current direction of research and development is the possibility of obtaining biodegradable, environmentally friendly materials [3]. It is consistent with one of the priorities of the European Community policy which is the conception of sustainable development.

The trend is also observed in foundry technologies development [5-9].

The author's idea [9-10] is the use of biodegradable additives to the binders to improve moulding sands properties and it seems to be a solution that will be of interest. It consists in modernizing a well-known and widely used technology without the need to change the production profile and it may solve the problem of the environmental impact of used but thermally undegraded moulding / core sand [11-15].

Literature data [16-17] proves the possibility of using biomaterials as additives for petroleum-derived materials to increase their biodegradability.

There are numerous methods to determine the degree of degradation and biodegradation. Their main target is to determine the time of the decomposition process and the type and quantity of formed products. Fig. 1 shows the classification of test methods for the biodegradation process [4].

As part of this study, the effect of PCL addition on the (bio) degradation of dust obtained after the process of mechanical regeneration of moulding sands with organic binders was determined. Dust samples before and after the duration of the (bio) degradation process were tested for weight loss by thermogravimetry (TG) and for loss on ignition (LOI).
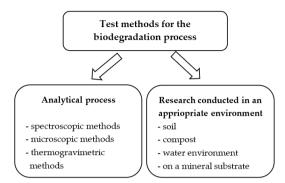

Fig. 1. Test methods for the biodegradation process [4, 18]

2. Research Methodology

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

- Furan resin, without nitrogen and the free formaldehyde in the range of 0.05 - 0.15 %; the amount of furfuryl alcohol 78 %.
- Hardener - an aqueous solution of paratoluenesulfonic acid.
- Polycaprolactone (PCL) - a biodegradable additive and plasticizer; a biodegradable polymer in solid form with an end of the hydroxyl group. PCL was dissolved in furan resin without the need of using an additional solvent.

As part of this work, samples from two different moulding sands were subjected to the biodegradation tests. The samples were dusts obtained after mechanical regeneration of no-bake moulding sands with furfuryl resin with and without biodegradable additive. The background and the composition of the furan moulding mixtures are presented in Table 1.

Table 1.
Dust samples tested in biodegradation tests.

Sample no.	Sample background		Moulding sand's composition	
1	after initial regeneration	**Moulding sand no. 1**	silica sand furan resin hardener	100 p.b.w. 1.1 p.b.w. 0.55 p.b.w.
2	after mechanical regeneration: 5 minutes			
3	after mechanical regeneration: 10 minutes			
4	after mechanical regeneration: 15 minutes			
5	after initial regeneration	**Moulding sand no. 2**	silica sand furan resin PCL hardener	100 p.b.w. 1.045 p.b.w. (95% of binder) 0.055 p.b.w. (5% of binder) 0.55 p.b.w.
6	after mechanical regeneration: 5 minutes			
7	after mechanical regeneration: 10 minutes			
8	after mechanical regeneration: 15 minutes			

The regeneration process was carried out in an RD-6 rotor regenerator with a closed dust chamber. Firstly, the used moulding sand was initially regenerated by crushing and dedusting in a cascade classifier (samples no. 1 & 5 were taken). After initial regeneration, the regeneration process was carried out for 5, 10 and 15 minutes. The obtained reclaims were dedusted in a cascade classifier (samples no. 2-4 & 6-8 were taken) [19].

The first stage of presented research was studying the degree of biodegradation of tested dust samples. The tests were carried out in the natural environment which was water from the Vistula River taken in the Kościuszko barrage in Krakow. The water was collected on 07/06/2020 by the employees of WATERWORKS Kraków and it was a cloudy solution. 100 ml of water was added to each polypropylene vessel with 3 g sample of tested dust. The closed vessels were stored at ambient temperature for 3 months. After biodegradation process, the samples were drained and dried to constant weight in a laboratory dryer. The weight loss was calculated according to equation 1:

$$\Delta m = \frac{m_p - m_{sp}}{m_p} \cdot 100, \%, \qquad (1)$$

where:
Δm – percentage of weight loss, %,
m_p – starting weight, g,
m_{sp} – mass of solid residue, g.

The next stage of own research was thermogravimetry (TG) tests. The aim of the research was primarily to determine the percentage of weight loss (TWL - the total weight loss), including the assessment of the impact of the biodegradation process on its size. TG measurements were carried out using a STA 449 F3 Jupiter® thermal analyzer from Netzsch. Measurement of the mass change TG (mg) as a function of temperature was determined with the Netzsch Proteus Thermal Analysis 6.1.0 software. The measurement consisted in placing the crucible with the specified mass of the sample in the sample carrier (weighing pan), which is surrounded by an electric heater. This position of the carrier allows the sample to be slowly heated and thus evenly transported heat to the inside of the tested material. Changes in sample weight are transferred with a balance rod and measured with a sensor. The result of the measurement is the total mass value which is the sum of the mass of the sample, the crucible and the support. The tests were carried out in the temperature range of 25-600ºC.

The study also carried out tests aimed at determining the ignition losses (LOI) of dust samples before and after the biodegradation process. A weight of about 1 g of the sample was placed in a calcined porcelain crucible, and then the pot with the sample was calcined at the temperature of 900°C for 2 h.

3. Results of examinations and discussion

3.1. Results of the biodegradation tests

At the first stage of the research, the residues of the binding material in the form of post-regeneration dust were subjected to biodegradability tests. The residues were separated from the matrix grains. 8 samples of post-regeneration dust from moulding sands with and without additive in the binder composition were tested. Samples of the material (dust) obtained from the moulding sands before the process of mechanical regeneration and after 5-, 10- and 15-minute cycles of mechanical regeneration were tested. Fig. 2 shows the percentage weight loss determined after the biodegradation process [20]. In the case of samples 1 – 4 a slight weight loss was noted, amounting to approx. 3%. Greater weight loss of up to 9% was recorded for samples 5 to 8, i.e. dust samples after the regeneration process of moulding sand with furan resin and the addition of biomaterial [20].
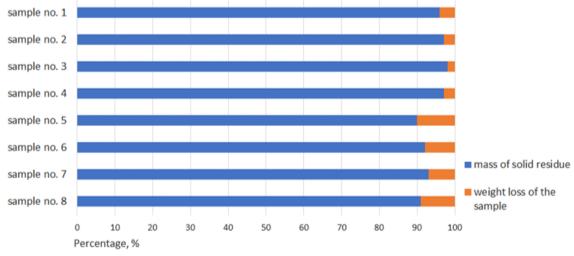

Fig. 2. Percentage loss of weight and residue materials after the biodegradation process [20]

The research proved the greater weight loss of the samples with the addition of the biomaterial [20].

3.2. Results of the thermogravimetric analysis

The aim of the thermogravimetric analysis was primarily the determination of the percentage of weight loss, including the assessment of the impact of the biodegradation process on its size. Figures 3-10 show exemplary TG/DTG curves of tested samples taking from the material before biodegradation process. The analysis of the process of degradation of dust samples after the mechanical regeneration of standard moulding sands (samples of moulding sand no. 1) and dust samples after the sand regeneration process with the addition of a biodegradable component (samples of moulding sand no. 2) showed that the decomposition process begins at a temperature of approximately 80°C and has three stages.

The first stage ends at a temperature of about 160°C - 180°C, in which the weight loss was 1% and was mainly related to the evaporation of water. The second stage ends at a temperature of about 420°C, in which the recorded weight loss amounted to: for sample 1 -M1 Dust after initial regeneration 1.89%; for sample 2 - MS1 Reg 5 min 1.44 %; for sample 3 - MS1 Reg 10 min 1.14 %; for sample 4 - MS1 Reg 15 min 0.96%. On the other hand, for the MS2 series samples, the recorded weight loss amounted to 5 - MS2 Dust after initial regeneration 2.01%; for sample 6 - MS2 Reg 5 min 1.53%; for sample 7 - MS2 Reg 10 min 1.11%; for sample 8 - MS2 Reg 15 min 0.74%. The test was completed at a temperature of 600°C, after which the total weight loss was determined, the results are summarized in Table 2.
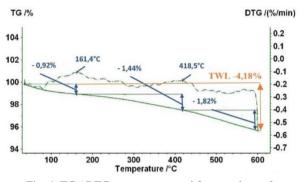

Fig. 3. TG / DTG curve measured for sample no. 1

Fig. 4. TG / DTG curves measured for sample no. 2

Fig. 5. TG / DTG curves measured for sample no. 3
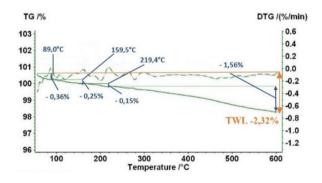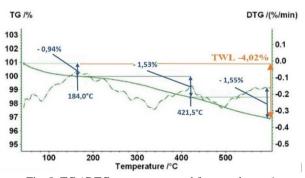

Fig. 6. TG / DTG curves measured for sample no. 4

Fig. 7. TG / DTG curves measured for sample no. 5

Fig. 8. TG / DTG curves measured for sample no. 6

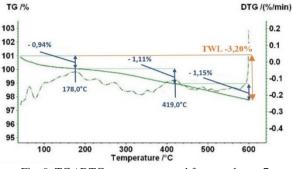Fig. 9. TG / DTG curves measured for sample no. 7

Fig. 10. TG / DTG curves measured for sample no. 8

The weight of loss was also measured for dust samples after the biodegradation process. The TG/DTG curves for selected samples are shown in Fig. 11-18. The analysis of these curves obtained for the dust samples after the biodegradation process showed that the decomposition pr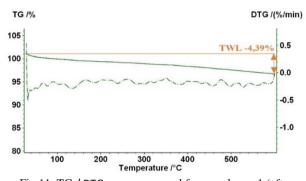ocess of the samples takes place in one stage, unlike the decomposition process taking place under the influence of the temperature determined for the dust samples before this process. The decomposition process, as shown by the results, starts at about 80°C. Table 2 presents a summary of the percentage weight loss determined using the thermogravimetric method.

Fig.11. TG / DTG curve measured for sample no. 1.(after biodegradation process)

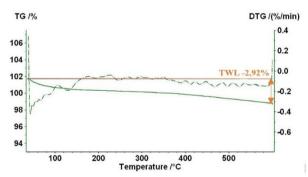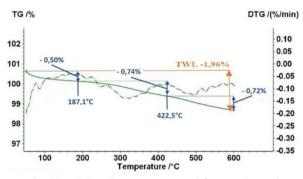Fig.12. TG / DTG curve measured for sample no. 2 (after biodegradation process)

Fig.13. TG / DTG curve measured for sample no. 3 (after biodegradation process)

Fig.14. TG / DTG curve measured for sample no. 4 (after biodegradation process)
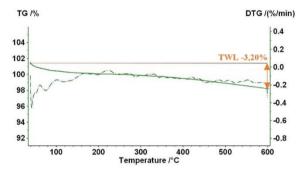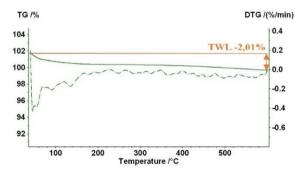
Fig.15. TG / DTG curve measured for sample no. 5 (after biodegradation process)
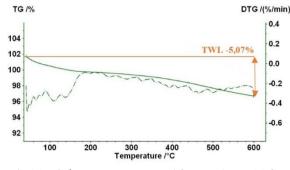

Fig.16. TG / DTG curve measured for sample no. 6 (after biodegradation process)

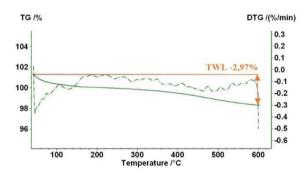Fig.17. TG / DTG curves measured for sample no. 7 (after biodegradation process)

Fig.18. TG / DTG curve measured for sample no. 8 (after biodegradation process)

The results of the tests determined by the thermogravimetric method showed that the greatest percentage weight loss of the sample was recorded for the dust samples collected after the initial regeneration stage and collected after 5 minutes of the regeneration process. It was 4.92% for samples MS1 and MS2 before and after the biodegradation process; 5.01%; 4.39% and 5.07%, and for samples taken after 5 minutes of the regeneration process, 4.18%, respectively; 4.02%; 3.20%; 4.00%. In the case of dust samples after the biodegradation process, slightly greater weight losses were found in relation to the values determined for the corresponding weight losses for the dust samples before the biodegradation process. The lowest values of the percentage weight loss at the level of 2% were recorded for all dust samples collected after 15 minutes of the regeneration process.

The conducted tests do not show any significant influence of the conducted biodegradation on the weight losses of the samples.
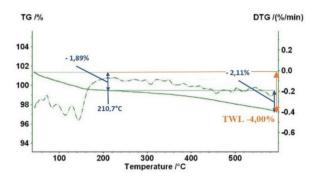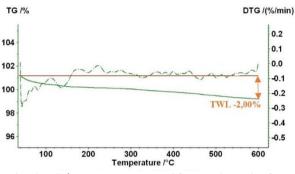
Table 2.
Percentage weight loss determined using the thermogravimetric method.

Sample no.	Weight loss at 600°C, %	
	Before biodegradation process	After biodegradation process
1	4.92	4.39
2	4.18	3,20
3	3.60	2.92
4	2,32	2.01
5	5,01	5.07
6	4.02	4.00
7	3,20	2.97
8	1.96	2.00

3.3. Results of the loss ignition tests (LOI)

The results of the measurement of loss on ignition (LOI) are presented in Table 3. The data show that greater weight losses were recorded for the dust samples obtained after the initial regeneration process of the moulding sand with the addition of a biodegradable component (moulding sand no. 2). The initial sample was 12.89%, and in the case of the dust sample after the biodegradation process, 10.67%. Additionally, the addition of a biodegradable component to the dust resulted in a greater and easier decomposition of organic substances compared to the results determined for dust without the

addition of PCL, as evidenced by higher percentages of loss on ignition.

In contrast to thermogravimetric tests, in the case of ignition loss tests, the influence of the biodegradation process on the recorded weight losses is observed.

Table 3.
The results of the measurement of loss on ignition (LOI).

Sample no.	Weight loss at 900ºC, %	
	Before biodegradation process	After biodegradation process
1	9.30	4.15
2	7.69	4.24
3	4.76	1.90
4	4.48	2.54
5	12.89	10.67
6	8.69	6.58
7	6.49	4.28
8	4.84	3.10

The TG analysis and LOI research showed that most of the organic substances that were burnt out was in the dust from the sand after the initial regeneration. Along with the extension of the regeneration time, the percentage of organic material in the tested samples decreases. After a 15-minute regeneration process, the amount of burnt substances (TG tests) is reduced by approx. 56% for the dust from moulding sand no. 1 and by approx. 60% for the dust form moulding sand no. 2. The purpose of the regeneration process is to remove residual binding material from the matrix grains. In the case of sands with resins, it is an organic binding material. After the regeneration process, the material is removed from the matrix (its presence in the regenerate is reduced) and appears in the dust. The obtained results may indicate that the tested moulding sands are characterized by a very high ability to mechanically regenerate and are already well regenerated after the initial regeneration process. Extending the regeneration time may reduce the percentage of organic substances in the dust, and there is more inorganic substance in the dust from damaged / worn matrix grains. These observations will be confirmed by additional studies.

4. Conclusions

The analysis of the results of the carried-out research allowed to formulate the following conclusions:
• Biodegradation tests proved that furan moulding sand with biomaterial in binder composition is characterized by about three times better biodegradability than standard furan sand.
• The thermogravimetry tests do not show any significant influence of the conducted biodegradation on the mass losses of the samples.
• The ignition loss tests proved the influence of the biodegradation process on the recorded weight losses. Higher ignition losses for the samples from moulding sand with biomaterial in binder composition may indicate a higher efficiency of the mechanical regression process.

The presented results are part of complex research and will be continued, especially in the field of biodegradability of moulding sands with new binders.

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