

Biodegradation of New Polymer Foundry Binders for the Example of the Composition Polyacrylic Acid/Starch

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Received 11.04.2011; Approved for print on: 26.04.2011

Abstract

The investigations on the biodegradation process pathway of the new polymer binders for the example of water soluble composition polyacrylic acid/starch are presented in the hereby paper. Degradation was carried out in water environment and in a soil. The determination of the total oxidation biodegradation in water environment was performed under laboratory conditions in accordance with the static water test system (Zahn-Wellens method), in which the mixture undergoing biodecomposition contained inorganic nutrient, activated sludge and the polymer composition, as the only carbon and energy source. The biodecomposition progress of the polymer composition sample in water environment was estimated on the basis of the chemical oxygen demand (COD) measurements and the determination the biodegradation degree, R_t , during the test. These investigations indicated that the composition polyacrylic acid/starch constitutes the fully biodegradable material in water environment. The biodegradation degree R_t , determined in the last 29th day of the test duration achieved 65%, which means that the investigated polymer composition can be considered to be fully biodegradable.

During the 6 months biodegradation process of the cross-linked sample of the polymer composition in a garden soil several analysis of surface and structural changes, resulting from the sample decomposition, were performed. Those were: thermal analyses (TG-DSC), structural analyses (Raman spectroscopy) and microscopic analyses (optical microscopy, AFM).

Key words: polymer binders, polymer composition, moulding sands, biodegradation, biodecomposition

1. Introduction

One of the main directions of science and technique development in the field of material engineering is obtaining biodegradable 'environment friendly' materials which after being spent would be fast decomposed [1-5]. This fact is a result of

more and more demanding environmental requirements due to negative environment influences of processing wastes.

Polymer materials during processing as well as during being in use and in storage are undergoing the influence of several physical (mechanical stresses, temperature, sun radiation, ultrasounds), chemical (air, oxygen) and biological (bacteria, fungi, enzymes) factors. As the result of these factors influence the destruction of the polymers chemical structure

occurs (degradation, cross-linking) by recombination of free radicals, formation of branched structures, change of bond numbers and location [5, 6].

The polymers biodegradation process [5, 6] is based on its decomposition in an environment, after a certain time of the end of its using. This occurs under an influence of microorganisms such as bacteria, funguses or algae under favourable for their growth conditions, in the presence of oxygen, moistness, mineral nutrients, at a suitable temperature and pH. The polymers biodegradation is a complex process. The chemical constitution of macroparticles is the main factor deciding whether the biodecomposition is possible at all. Biodegradable compounds contain in their structures polar functional groups, such as hydroxylic, carboxylic, ester, ether or amide. The final products of the biodecomposition process is formation of a biomass (waste organic mater) with an evolution of water and gases such as: carbon dioxide, methane and ammonia.

The environmental problem in the foundry industry is mainly related to the storage of spent moulding sands. Therefore the selection of the proper binder for the matrix sand grain binding is essential. The properly selected binding material should not only meet the technical standard requirements but should not be hazardous for the environment, during the technological process of moulding sands preparation, casting mould production, liquid metal pouring into moulds (making casting), as well as at the last stage when spent sands are stored.

Investigations of using polymers, including biopolymers, as ecological binders for moulding sands have been carried out for some years already in the Environment Protection Group in the Department of Foundry Engineering under Prof. M. Holtzer direction. New polymer binding materials were developed together with a way of their cross-linking in moulding sands and tests of their utilization in the foundry technology performed [7-9].

However, in the domain of foundry engineering processes the knowledge of a biological degradation of a polymer foundry binder is still quite negligible, thus the aim of the presented investigations was to broaden this field of knowledge for the example of the biodegradation process of the new polymer binder: composition of polyacrylic acid/starch.

2. Investigation methodology

2.1. Biodegradation examinations in water environment

Biodegradation examinations in water environment were carried out on the basis of the static test (Zahn-Wellens method) [10]. Susceptibility of non-volatile, water soluble organic substances for the final biodegradation occurring due to microorganisms operations (of a concentration in the range of 50 - 400 mg/dm³ during the static testing) are estimated in this method.

This method is applied when the organic substances used in the test:

1. Dissolve in water under experimental conditions,
2. Do not hamper bacteria growth,

3. Exhibit very low vapour pressure under experimental conditions,
4. Are adsorbed in the testing system only in a limited range.

The biodegradation process was performed in vessels of a capacity of 1dm³ equipped with a device for mixing and aerating. Mixtures containing: activated sludge (microorganisms), nutrient components (basic solution for bacteria) as well as water solutions of samples undergoing biodegradation as the sole carbon source were placed in such vessels [Fig. 1]. Concentration of samples was within a range of 50 - 400 mg/dm³.

The incubation process was carried out for 28 days, according to recommendations of the test in the dark, maintaining an ambient temperature: 20 – 25 °C, at the mixture aeration degree of app. 8 mg/l.

The following samples were subjected to the biodegradation:

- Ethylene glycol (GE) as a standard (reference value of the biodegradation degree > 90%), POCH,
- Polymer of a natural origin: modified starch (S), XENON,
- Synthetic polymer: polyacrylic acid (PA), BASF,
- Polymer composition: polyacrylic acid/starch (PA/S).
- Reference sample (O) containing only activated sludge and nutrient components (blank test).

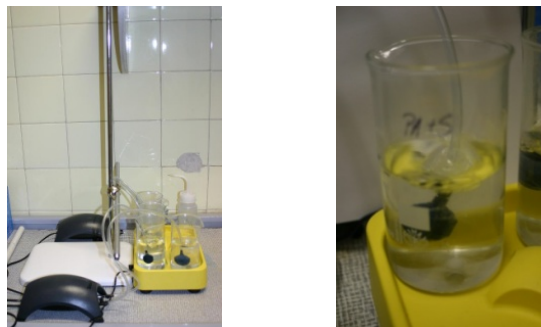


Fig.1. Measuring stand for the biodegradation process investigations in water environment

Microorganisms (activated sludge) supplied by the Central Laboratory of the Water Supply and Sewage Municipal System from Kraków were used in experiments.

Microscopic photographs of microorganisms examples present in the activated sludge (after 2 days from sampling) are presented in Figure 2.

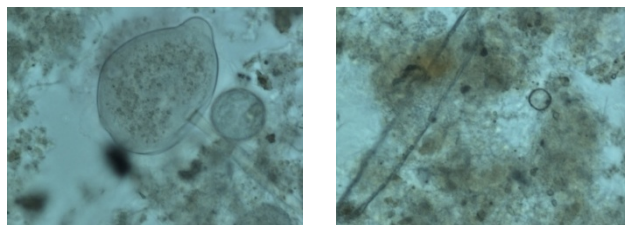


Fig.2. Examples of microscopic photographs of microorganisms

2.2. Measurements of the Chemical Oxygen Demand (COD)

The biodecomposition process was monitored within the determined time intervals for 28 days by performing the spectrophotometric determination of the chemical oxygen demand (COD), according to recommendations of the standard concerning the chemical oxygen demand [11].

Changes of the biodegradation degree (R_t) of samples were estimated on the basis of the chemical oxygen demand acc. to the Zahn-Wellens method during the samples biodegradation process in water environment. The ratio of the chemical oxygen demand value (being lower after each interval) determined at the beginning of the experiment, to the value determined after 3 hours, was used for the determination of the biodecomposition R_t after this time [10].

2.3. Investigations of the biodegradation in a soil

The sample of polymer composition cross-linked by microwaves was placed in a garden soil in such a way that a part of the sample was under the soil surface at a depth of 2 cm and another part above the surface. The biodegradation was carried out under conditions resembling the natural ones, under which the majority of foundry waste is degraded (waste dumping ground), at a room temperature and a moderate soil moistness (app. 25%). The biodegradation process in a soil was carried out for 6 months, after which the sample underwent structural and thermal analysis.

2.4. Microscopic examinations

Atomic Force Microscope (AFM)

Atomic Force Microscope (AFM) (Picoforce, Veeco, USA) working in a tapping mode was used to characterize surfaces in the air. Standard silicon cantilevers (Veeco) with a nominal spring constant 40 N/m and the tip radius <10 nm were used for all measurements.

Optical microscope:

Nikon Eclipse LV 100, equipped with: NIS-elements AR 2.10.

2.5. Raman spectroscopy

Measurements were made on the Fourier Transform Spectroscopy, FTS 6000 of the American Bio-Rad Company with FT – Raman attachment.

Measuring parameters:

- laser power on a sample 120 mW,
- resolution 4 cm^{-1} ,
- measuring range 4000–80 cm^{-1} .

2.6. Thermal examinations

Thermal analysis was performed by means of the thermal analyser NETZSCH STA 449 F3 Jupiter® allowing for a simultaneous performance of TG and DSC measurements, which warranted obtaining independent signals recorded at the same measuring conditions, it means at the same heating rate, atmosphere and pressure. Such method of analysis ensured better effectiveness and allowed to obtain complex information concerning thermal characteristics of the investigated sample.

The basis measurement parameters are shown in Table 1.

Table 1 TG-DSC measurement parameters

temperature range	23 – 920°C
heating rate	10 °/min
atmosphere	nitrogen
flow rate	40 ml/min
crucible	Pt
sample mass	about 10 mg

3. Biodegradation investigations in water environment

The biodecomposition process was monitored everyday by checking pH changes, temperature and deaeration degree of the investigated samples. During the whole period of the test the required conditions were maintained (ambient temperature: 20 – 25 °C, aeration degree app. 8 mg/l).

In accordance with the test requirements the COD value was estimated in the selected time intervals. The COD results (decreasing after each interval), versus the value determined after 3 hours from the moment of the test beginning provides the percentage biodegradation value (Table 2).

Tabela 2 The obtained COD results

Sample	GE	S	PA/S
Day	COD [mg/IO_2]		
3h	1251	985	865
1	1160	907	820
2	1110	793	790
3	997	561	744
4	985	432	723
5	743	458	690
6	588	441	667
7	236	415	620
8	212	387	603
9	215	325	498
10	214	318	478

On the basis of the obtained COD results the biodecomposition percentage value (R_t) was found at the experiment end for the investigated samples:

$$R_t(\%) = \left[1 - \frac{(C_T - C_B)}{(C_A - C_{BA})} \right] \times 100 \quad (1)$$

where:

- R_t - Biodegradation % in time (days),
- C_A - COD values in the tested mixture determined 3hours after the investigation beginning (mg/dm^3),
- C_T - COD values in a mixture during sampling (mg/dm^3),
- C_B - COD values in a blank test during sampling (mg/dm^3),
- C_{BA} - COD values in a blank test, determined 3hours after the beginning of the experiment (mg/dm^3).

The percentage decomposition value is determined as the percentage decay of the COD indicator.

The calculated R_t values are presented in the graph as a function of the biodegradation time, obtaining the biodegradation curve (Fig. 3).

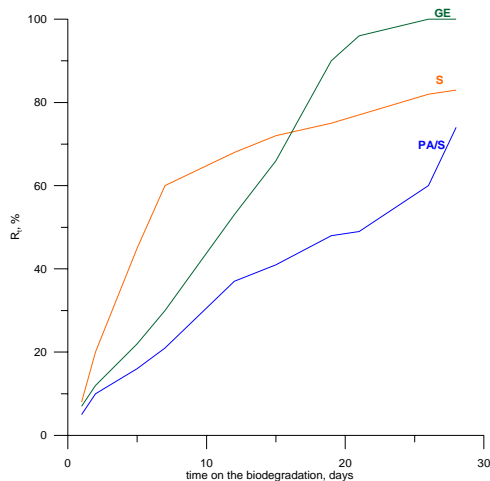


Fig.3. Biodegradation curves

A polymer is considered to be biodegradable when its biodegradation degree after 28 days of a cycle obtains at least 60% [11]. This condition was satisfied by samples: S ($R_t = 80\%$, Fig.1) and PA/S ($R_t = 74\%$, Fig.1). Synthetic polymer polyacrylic acid contained in the PA/S sample rendered difficult its biodecomposition, however on the 28th day the required degree was obtained, which means that the investigated polymer composition can be considered as fully biodegradable.

An attempt to perform the biodecomposition process of polyacrylic acid (PA) was undertaken, but in accordance with expectations, this substance caused an inhibition of microorganisms metabolism which significantly increased the sample turbidity and its COD (more than 12 times) during three days.

The reference GE sample biodegrades practically in 100% on the 26th day of the test.

4. Biodegradation in a soil

The sample of the cross-linked by microwaves biopolymer composition PA/S placed in half in a garden soil was removed after 6 months to determine its visual changes occurring during the biodecomposition (Fig. 4).

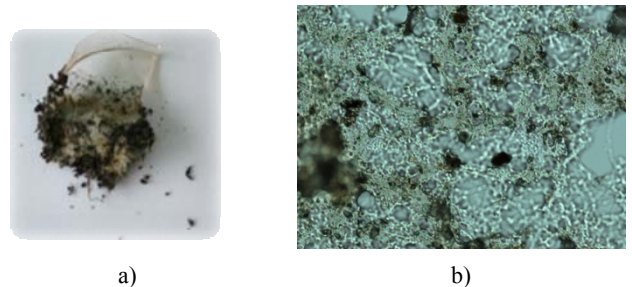


Fig.4. PA/S sample: a) Placed in half in a garden soil for 6-month, after its removal; b) Microscopic picture after 6 months of being in a soil

Morphological changes are visible only on this part of the surface which was in s soil (tarnish), while the part which did not contact with a soil remained without changes. Thus, it seems that the sample placed in a soil undergoes gradual biodegradation. The passage of time caused tarnish formation on PA/S sample. Therefore microscopic and structural examinations were additionally performed.

The surface roughness change of the PA/S sample cross-linked by microwaves visible in AFM pictures (Fig. 5) before and after the 6 months biodecomposition indicates that the biodegradation was due to microorganisms activities. The surface roughness of the initial not degraded PA/S sample expressed by the RMS indicator is smaller ($RMS = 1 \text{ nm}$) than of the sample which underwent the partial biodecomposition ($RMS = 26 \text{ nm}$).

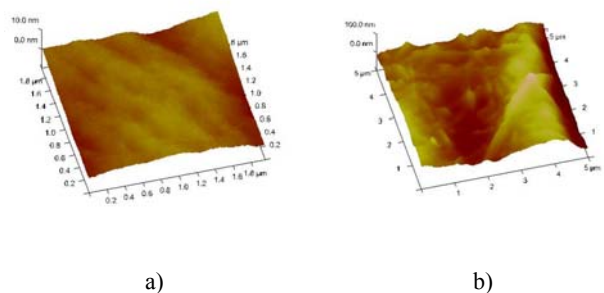
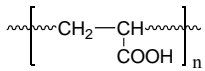


Fig.5. AFM pictures of PA/S samples: a) Before degradation b) After 6 months of biodecomposition

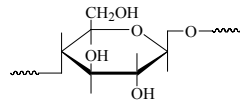
Structure investigations were performed by means of the Raman spectroscopy for the initial (not degraded) sample and for the sample after the 6-months biodecomposition (Fig. 6).

The polymer composition containing polyacrylic acid and starch exhibits characteristic bands for both components (Fig. 6, spectrum a). The Raman spectrum analysis confirmed the presence of groups characteristic for carboxylic acids (from

polyacrylic acid, formula I) in a range 1719 cm^{-1} corresponding to stretching vibrations of carbonyl group -C=O , while in a lower range bands of 1257 cm^{-1} and 1637 cm^{-1} occur – corresponding to stretching vibrations of C-O and to deformation vibrations of group C-O-H (from starch, formula II).



formula I



formula II

As a result of biodegradation within the wave numbers $3700\text{--}2900\text{ cm}^{-1}$ an intensification of the absorption band, corresponding to stretching vibrations of -OH groups, can be observed (Fig. 6, spectrum b). This fact is related to hydrophilicity of the sample being degraded, which can absorb water facilitating the hydrolysis process, which favours biodegradation.

Changes in the range of $1600\text{--}1500\text{ cm}^{-1}$ can be also seen.

The absorption band corresponding to vibrations of C=O (characteristic for carboxylic acids, 1719 cm^{-1}) fades out, while new bands are formed: 1715 , 1163 , 1239 and 1024 cm^{-1} corresponding to deforming vibrations of C-O-H and C-O and asymmetric deforming vibrations COO^- , respectively. These changes can be the result of superimposing vibrations related to the decomposition of certain groups, within the functional group, and to formation new bonds during the biodecomposition.

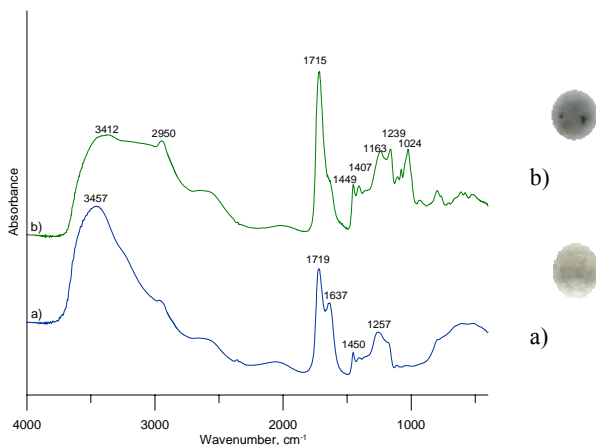


Fig.6. Raman spectra of: a) Polymer composition PA/S before the biodegradation, b) Polymer composition PA/S after 6 months of biodecomposition

Thermal analysis was performed for the initial PA/S cross-linked polymer composition sample (not degraded biologically) and for the PA/S cross-linked polymer composition partially degraded sample (after 6 months of being in a soil). It was found that staying in the soil influences the sample thermal stability. Mass changes presented in the TG curves for the biodegraded sample and for the initial one reveal several stages of thermal decomposition (Fig. 7).

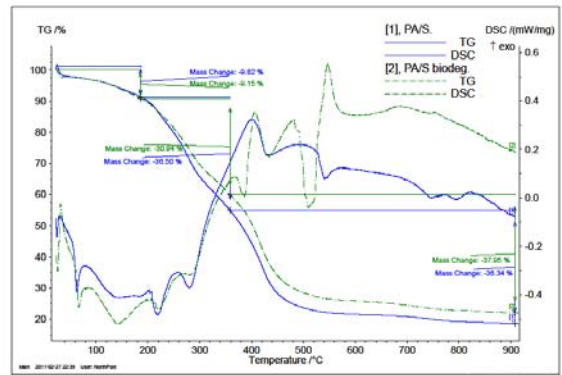


Fig. 7. TG/DSC curves

Changes in the TG curves for both samples are very similar. Within low temperatures, to 200°C , a small (of some %) mass loss is observed, which can be caused by dehydration. Above this temperature a further significant mass loss occurs corresponding to endothermic maximum at temperatures of 220 and 280°C recorded in the DSC curves. Above 360°C the last stage of the thermal decomposition begins, in which exothermic effects occur exhibiting differences between the degraded and not degraded sample. The DSC signal for the sample after the biodegradation contains in this range several sharp exothermic peaks occurring one after another. Such effects were not observed for samples, which were not undergoing the biodegradation. The analysis of the results indicate a similar pathway of the thermal decomposition (similar mass losses in the same temperature ranges) of the initial sample and after a partial biodegradation, however different energy values of these changes and the maximum location in the DSC curves at the last decomposition stage, confirms structure differences between the analysed samples.

5. Conclusions

Investigations of ecological casting binding agents are presented in the hereby paper for the example of the polymer composition: polyacrylic acid/starch with its biodegradation problem taken into consideration.

On the basis of the performed examinations it was indicated, that the method applied for the biodegradation process analysis (Zahn-Wellens static test) carried out in water environment can be also used in the determination of the biodegradation degree of water soluble foundry binders. The proper preparation of the experimental stand and maintaining appropriate conditions for the biodegradation process (temperature, pH, aeration degree) allows for the biodecomposition process under the microorganisms influence.

On the basis of the obtained results of the chemical oxygen demand (COD) the progress of the biodegradation process of the polymer composition PA/S was observed. The investigated polymer binding material undergoes the gradual biodecomposition. After 28 days of the test the biodegradation

degree (R_t) achieved 74%, which – according to the literature data – indicated its full biodegradability. This fact provides also information that there is a possibility of its biodegradation under storage conditions on wastes dumping grounds, which is important for the environment. This can result from the fact that the investigated polymer material is fully compatible with the environment.

In addition the biodegradation examinations (Raman spectroscopy, microscopic observations and thermal analysis) performed in a soil, indicated that the applied polymer composition undergoes a gradual biodegradation under an influence of moistness and substances contained in the soil. Thus, the following final conclusions can be drawn:

- There is a possibility of utilising the static test as a method for investigating the biodegradability of water soluble foundry binders;
- Since after 28 days of the test duration the biodegradation degree achieved 74%, this polymer composition can be considered as fully biodegradable;
- The investigated polymer composition is compliant to biodecomposition under conditions similar to the ones existing in wastes dumping grounds;
- The indicated biodegradability of the polymer composition: polyacrylic acid/starch locates this material in a group of degradable 'environment friendly' materials.

Acknowledgements

Preparation of the paper has been supported by scientific grant under project No *N N 507 326 836 (2009-2011)*.

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Biodegradacja nowych polimerowych spoiw odlewniczych na przykładzie kompozycji poli(kwas akrylowy)/skrobia

Streszczenie

W pracy przedstawiono badania nad przebiegiem procesu biodegradacji nowych spoiw polimerowych na przykładzie wodorozpuszczalnej kompozycji poli(kwas akrylowy)/ skrobia. Degradację prowadzono w środowisku wodnym i w glebie. Oznaczenie całkowitej tlenowej biodegradacji w środowisku wodnym wykonano w warunkach laboratoryjnych zgodnie ze statycznym wodnym systemem testowym (metoda Zahna Wellensa), w którym poddana biorozkładowi mieszanina zawierała pożywkę nieorganiczną, osad czynny oraz kompozycję polimerową, jako jedyne źródło węgla i energii. Postęp biorozkładu próbki kompozycji polimerowej w środowisku wodnym oceniano na podstawie pomiarów chemicznego zapotrzebowania na tlen (ChZT) i wyznaczenia stopnia biodegradacji R_t w przygotowanych mieszaninach w trakcie trwania testu. Przeprowadzone badania biodegradacji w środowisku wodnym wykazały, że kompozycja poli(kwas akrylowy)/ skrobia jest materiałem w pełni biodegradowalnym w środowisku wodnym. Stopień biodegradacji R_t wyznaczony w ostatnim 28 dniu trwania testu osiągnął poziom 65%, co oznacza iż badaną kompozycję polimerową można uznać za w pełni biodegradowalną. Podczas trwania procesu biodegradacji próbki usieciowanej kompozycji polimerowej w glebie ogrodowej trwającego 6 miesięcy przeprowadzono analizę termiczną (TG-DSC), analizę strukturalną (spektroskopia Ramana) oraz mikroskopową (mikroskopia optyczna, AFM) zmian powierzchniowych i strukturalnych wynikających z rozkładu próbki.

Słowa kluczowe: spoiwa polimerowe, kompozycja polimerowa, masy formierskie, biodegradacja, biorozkład