Thermal degradation of biopolymer binders: the example of starch-poly(acrylic acid)

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Summary

To characterise a polymer, it is of fundamental importance to determine its parameters, like the temperatures of destruction, vitrification, melting point, specific mass losses or polymorphic transformations, which frequently determine the quality of the product and its applications. Thermal analyses were conducted of samples of a biopolymer binder: a starch-poly(acrylic acid) composition and a moulding sand with a biopolymer binder previously hardened with microwaves. In order to determine the thermal stability of the examined samples by determining the destruction temperature and the thermal effects of transformations taking place during heating, FTIR spectroscopy and thermal analysis (DSC, DTG, TG) methods were used. In addition, volatile products of degradation were analysed using the thermogravimetry (TG) method coupled online with mass spectrometry (MS). These examinations were also aimed at identifying the changes that can take place in the moulding sand when it comes into contact with liquid metal.

Key words: biopolymer binders, thermal degradation, destruction, moulding sand

1. Introduction

During use, polymers are exposed to the effects of many physical factors, including physical stress, temperature, UV radiation, ultrasounds, electrical discharges and ionising radiation [1-4]. As a result of the action of these factors, the chemical and physical structure of polymers is destructively changed, which includes degradation. During degradation, the molar mass is reduced as a result of breaking polymer chains and forming new molecules with shorter chains. Polymer degradation usually occurs as a result of physical and biological factors (Fig. 1).

The general mechanism of polymer degradation is radical in its course and the initiation which causes the degradation process may be due to heat, electromagnetic radiation, ionising radiation or mechanical stress (Fig. 2).

Macro-radicals formed in the above fashion may undergo many reactions, including the depolymerisation process (the release of a monomer brought about by high temperature), the transfer of a free radical both in intra- and extra-molecular reactions, the dismutation reaction during which a new macroradical and a macromolecule with a double bond are formed, and also mutual recombination, forming branched or cross-linked structures.

Individual bonds within the macromolecule may dissociate into free radicals if energy exceeding the bond energy is supplied to them (the bond dissociation energy) (table 1) [1].

Fig. 1. Diversity of processes causing polymer degradation
When polymers are heated, reversible and irreversible changes take place. Reversible changes occur due to phase transitions, the disaggregation of supramolecular structures and the polymer transiting into the plastic state. Irreversible changes occur above the flow temperature, when polymers are thermally degraded, which is often accompanied by the emission of volatile low-molecular substances. The polymer degradation temperature depends on the chemical structure of the macromolecule, the phase state of the polymer and the admixture content. The majority of polymers are thermally degraded at a temperature greater than their flow temperature (amorphous polymers) or melting point (crystalline polymers). During this process, quite a large quantity of low-molecule products of polymer degradation are emitted. Depending on the structure, carbon oxide (IV), carbon oxides (II), water, methane, ethane, propylene, acetylene and benzene may be produced. The final product is usually a carbonised polymer sample [1, 4-6].

2. Research methods

Materials
The following materials were used in the research conducted:

- binder: a biopolymer composition (KOMP. A) made up of a synthetic polymer: poly(acrylic acid) produced by BASF (Fig. 3a) and a natural polymer: starch by Xenon, in the 1:1 weight ratio (Fig. 3b and 3c);
- matrix: standard quartz sand from the Jaworzna-Szczakowa sand mine.

Preparing samples for examinations
- samples of moulding sand with a biopolymer binder, 1:1 weight ratio [8, 9];
- cross-linking and hardening samples with microwaves: RM 2001 Pc microwave reactor by Plazmatronika (800 W, 90s) [8, 9].

Infrared spectroscopic examinations, FT-IR
Infrared spectroscopic examinations were carried out using a Digilab Excalibur FTS 3000 Mx spectrometer with a DTGS detector, electrically cooled. The spectrometer is equipped with two attachments: ATR with a ZnSe crystal for multiple reflections and a transmission attachment.

Thermal analysis examinations
The NETZSCH model STA 449 F3 Jupiter® simultaneous thermal analyzer can be used to measure the mass change and transformation energetics of a wide range of materials. The top-loading STA can be equipped with various easy exchangeable TG, TG-DTA or true TG-DSC sensors and with different furnaces to accommodate different application areas. The system employed for this work was equipped with a steel furnace capable of operation from -150 to 1,000°C. For control of the measurements as well as for data acquisition, modern digital electronics and the well established NETZSCH PROTEUS® 32-bit Software are employed. Several Advanced Software packages like c-DTA® (calculated DTA-signal), Super-Res® (rate-controlled mass change) or Thermokinetics® are available. Furthermore, combining both thermogravimetric and spectroscopic methods such as MS enables identification of the evolved gases.

3. FT-IR examinations and their analysis

In order to explain processes taking place in the analysed biopolymer composition as a result of its heating, spectroscopic (FT-IR) examinations were conducted. Temperature spectra were recorded for a sample of the biopolymer composition at 25°C-180°C (the operating range of the temperature attachment of the IR spectroscope). Heating progressed continuously with the spectrum being recorded at the set temperature.

Within the 25°C-180°C temperature range, the spectra discussed (Fig. 4) show a wide band in the 3,700-3,000 cm⁻¹ wave number region which corresponds to the tensile vibrations of the hydroxyl group (the band of the free OH group from water and O-H - O=C hydrogen bonds). At the temperature of 120°C, a number of changes in spectrum shapes can be observed. The reduced intensity of the absorption band corresponding to the tensile vibration of -OH groups is mainly connected with water evaporating due to the temperature impact. At 120°C, two bands disappear in the 1,800-1,500 cm⁻¹ area (vibrations of COO⁻ and C-OH), and a new band appears: 1,700 cm⁻¹ (C=O vibrations). These changes are connected with degradation processes.
occurring due to the impact of the temperature: polymer chain fragment, and a result of this some bonds disappear and new ones are formed, which is obvious in the shape of the spectra.

Fig. 4. FT-IR temperature spectra for the biopolymer composition

Figure 5 shows the FT-IR temperature spectra at the 300°C-500°C range for a moulding sand composed of a biopolymer binder on a quartz matrix within the 4,000-800 cm⁻¹ range.

Fig. 5. FT-IR temperature spectra for the moulding sand with a biopolymer binder hardened with microwaves

Between the 3,700 cm⁻¹ and 2900 cm⁻¹ wave numbers, the absorption corresponding to tensile vibrations of hydroxyl groups within hydrogen bonds gradual can be seen to gradually fade. Conversely, the band in the 2900 cm⁻¹ region, connected with C-H symmetrical and asymmetric tensile vibrations, changes its shape and becomes more intensive. This may be due to the progressive fragmentation of the polymer chain and the formation of new, shorter hydrocarbon chains in various structural configurations. In addition, the band in the 2300 cm⁻¹ region, associated with the formation of CO₂, can be seen to grow in intensity.

4. Thermal analysis examinations

Figure 6 depicts the TG-DSC results for the sample KOMP.A. At sub-ambient temperatures, no effects were observed. Three mass loss steps of 8.1%, 25.5% and 41.7% occurred which were accompanied by endothermic effects visible in the DSC signal. Maxima in the rate of mass change occurred at 133°C, 276°C and 422°C.

At the -100°C-0°C temperature range no polymorphic transformations were detected. The shape of thermal curves is complex because the degradation process progresses in stages, which is due to the structure and the physical chemistry properties of the two-component biopolymer composition in question. Shapes of thermal curves support the claim that the degradation process starts at the temperature of 132°C.

To analyse the volatile products of decomposition, the thermogravimetry (TG) method coupled online with mass spectrometry (MS) was used in this research. Within the 140°C-400°C temperature range, signals of low molecular weights were detected, proving the occurrence of processes of degradation, polymer chain fragmentation and the formation of low molecular compounds (molar masses: 15, 18, 22, 37, 38, 39, 41, 43, 44, 45, 46, 51 and 55 g/mol), during which mainly the following low molecular compounds are formed: H₂O, CO₂ and alkyl radicals among others CH₃; (Fig. 7) [10].

A microscopic photograph taken of a moulding sand sample with a biopolymer binder baked at the temperature of 500°C shows carbonisations of the binder resulting from the action of high temperature, which means that the polymer has suffered partial destruction (Fig. 8).
5. Summary

Infrared (IR) spectroscopic examinations at higher temperatures have confirmed the results of the thermal analysis (DSC) aimed at determining the thermal stability of the polymer. Based on the research conducted, it can be said that, starting at the temperature of 130°C, a gradual process of degradation occurs, associated with the progressive fragmentation of polymer chains and the formation of new, shorter hydrocarbon chains in various structural configurations. It can also be said that during baking, low molecule organic compounds (alkyl radicles) and inorganic ones (mainly CO₂ and H₂O) are formed. Microscopic examinations have confirmed that at 500°C, the polymer under consideration suffered partial destruction.

Bibliography


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