Study of Thermal Degradation
of Starch-Based Binder by TG-DTG-DSC,
Py-GC/MS and DRIFTS

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Abstract

This paper focuses on the thermal behavior of the starch-based binder (Albertine F/1 by Hüttenes-Albertus) used in foundry technology of molding sand. The analysis of the course of decomposition of the starch material under controlled heating in the temperature range of 25-1100°C was conducted. Thermal analysis methods (TG-DTG-DSC), pyrolysis gas chromatography coupled with mass spectrometry (Py-GC/MS) and diffuse reflectance spectroscopy (DRIFT) were used. The application of various methods of thermal analysis and spectroscopic methods allows to verify the binder decomposition process in relation to conditions in the form in both inert and oxidizing atmosphere. It was confirmed that the binder decomposition is a complex multistage process. The identification of CO_2 formation at set temperature range indicated the progressive process of decomposition. A qualitative evaluation of pyrolysis products was carried out and the course of structural changes occurring in the presence of oxygen was determined based on thermo-analytical investigations the temperature of the beginning of binder degradation in set condition was determined. It was noticed that, significant intensification of Albertine F/1 sample decomposition with formation of more degradation products took place at temperatures above 550°C. Aromatic hydrocarbons were identified at 1100°C.

Keywords: Foundry binders, Starch-based binder, Thermal analysis, Thermal decomposition

1. Introduction

Starch is a natural biopolymer composed of linear polysaccharide amylose with α-1,4-linked glucopyranose units and branched polysaccharide amylopectin with α-1,4-glucopyranose chains having branch-points (1,6)-linkages [1]. Due to its numerous advantages and the possibility to modify its properties, it is widely used in various branches of industry [2]. Starch and its derivatives are also an interesting polymers used in the mold technology [3-6]. Known starch-based binders meet the specific requirements set by the foundry industry while reducing their negative impact on the environment [7-9].

An example of a material intended for application in moulding sand is Albertine F/1 (Hüttenes-Albertus). It is a blend of starch with aluminosilicates and used to modify the wet molding sands most often used for hand-made molds. Starch and starch-based binders have a positive effect in wet molding materials on tendency to dry or scabs, erosive action of metal, the ability to bind water and tensile strength wet of green sands [10]. However, our own research [11, 12] has shown that this material can be an effective main binder in physically (thermally) cured

moulding sands. As a result of heating up to approx. 100°C in the binder-quartz matrix system, the binder can become cross-linked.

In order to verify the phenomena occurring in the mold during pouring it with liquid alloy, it is essential to carry out thermal investigation. In the test cycle it is important to determine the thermostability of the binder, but also to assess the quality of its degradation products and determine the influence of high temperature on its structure [13]. The thermal degradation of the binder in the mold takes place with the limited participation of oxygen (oxygen-free conditions corresponding to the process of pouring the liquid metal/alloy into a mold). During casting the mold, due to strong stresses at the liquid metal/mold interface phases and the spreading heat, it can be also expect oxidative degradation. In addition, cured mold with organic binder is a heterogeneous system, which can include air in space between sand grains, by which the oxygen presence may cause thermal decomposition according to oxidative degradation [13].

In this paper, the aim of the study was to give more information about the course of thermal decomposition of organic-inorganic binder Albertine F/1. Analysis of the thermal decomposition under controlled heating in an inert and oxidizing atmosphere in temperature range 25-1100°C was based on the results of thermal analysis methods (TG-DTG-DSC) in combination with the results of pyrolysis gas chromatography mass spectrometry (Py-GC/MS) and spectroscopic technique DRIFT in "on-line" system.

Cycle of studies on Albertine F/1: the course of curing [12], selected properties of the mold [11], and thermo-analytical studies will prove helpful to verify physical and chemical properties of binder in order to create a database of materials used in foundry technology. Moreover, based on obtained results, it is possible to assess the quality of binder degradation products in contact with liquid alloy, which is important in the context of environmental protection.

2. Experimental

2.1. Materials

The Albertine F/1 binder (Hüttenes-Albertus) is a mixture of products with different swelling capacity in cold water with aluminosilicates. The composition of the commercial binder is described in the Table 1.

Table 1.
Characteristic of Albertine F/1 by distributor [10]

Form	Composition		pH
extra fine powder; white and yellow color	water content	10.0-12.0%	4.5
	the content of starch products with different swelling capacity	75.0-79.0%	
	ash content	<1.0%	
	aluminosilicates	<14.0%	

2.2. Methods

Thermal analysis methods

Thermal analysis was performed by using a thermal analyzer TA Instruments DSC SDT Q600 Thermogravimetric Analyzer & Differential Scanning Calorimeter. The system allows simultaneous analysis of TG-DTG (detection of sample mass change and temperature change as a function of a given temperature or time) and TG-DSC from room temperature to 1500°C with a programmable heating rate.

The analyses in open Al_2O_3 crucibles using sample mass ca. 10 mg under an inert atmosphere (argon) and in an oxidizing atmosphere (synthetic air) (flow rate 40 mL·min^{-1}) and at temperatures between 25 and 1100°C have been performed. The rate of heating of the test sample was: 10°C·min^{-1}.

Argon is used in most of TG-DTG-DSC tests in temperature range to 1500°C. The main reason is the lower thermal conductivity as it increases the sensitivity in the low temperature range. Regarding inertness, there might not be a significant difference between argon or helium. In addition, helium as the high thermal conductivity gas generates a good baseline but a low sensitivity of the DSC sensor heads.

Diffuse reflectance infrared Fourier transform spectroscopy

The measurement of the 25-500°C temperature spectra using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was performed on an attachment connected to a temperature control device and water cooling system. Range of measurements temperature (max. 500°C) was limited by instrument. The spectra for the selected sample were recorded in the range of 4000-600 cm^{-1} wavenumbers, assuming a resolution of 8 cm^{-1} and a number of 64 scans. The data were collected in conditions of increasing temperature in oxidizing atmosphere and maintained temperature regime: the spectra were recorded after 1 min after reaching the set temperature. The spectra were normalized by comparing the spectrum obtained with the background spectrum (KBr).

Pyrolysis-gas chromatography-mass spectrometry

Sample (2-4 mg) were thermally degraded in Pyroprobe 5000 pyrolyser (CDS Analytical) in an inert atmosphere (helium). The sample was heated to a set temperature at a rate of 10 000°C/s for a time interval of 3-4 seconds. Then chromatographic separation (Focus GC, Thermo Scientific) was carried out according to the assumed measurement conditions: initial heating at 40°C lasted for 3 min, then the temperature was increased to 100°C (at a rate of 3°C·min^{-1}) and heated for 3 min. Products of pyrolysis were separated on a non-polar TR-SQC tested column (30 m length, 0.25 mm diameter). The next temperature increase to 250°C was carried out at the rate of 20 °C·min^{-1} and the sample was heated for 3 min at the rate of helium flow in the column of 1 ml·min^{-1} and at the division of the sample at the ratio of 1:30. The injector was maintained in the SPLIT mode. The last stage of the study included detection (ISQ, Thermo Scientific) according to the following parameters: ion source temperature 250°C, electron energy 70 eV at full range m/z. The qualitative analysis was performed with the use of Xcalibur 2.2 software based on the

NIST MS Search 2.0 database as well as on mass spectral data and retention time comparisons reported in literature.

3. Results and discussion

Thermal analysis

On the basis of TG-DTG and DSC curves the following parameters characterizing the decomposition process were determined: weight losses (Δm), temperature of the maximum of weight loss rate (T_{peak}), temperature corresponding to 10% (T_{10}) and 50% (T_{50}) weight loss, temperature of exo- or endothermic effects occurring. On the course of thermal curves it is possible to determine the subsequent stages of degradation of the binder. The changes in the material due to the rising temperature for Albertine F/1 binder samples depends on the conditions under which the measurement was carried out (Figs. 1-2).
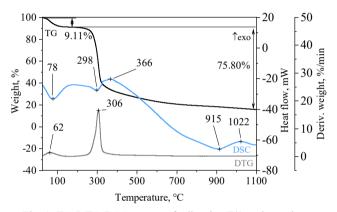

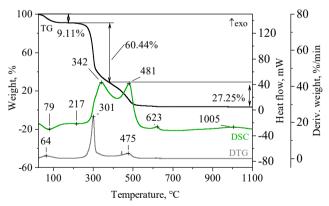Fig. 1. TG-DTG-DSC curves of Albertine F/1 under an inert atmosphere

Fig. 2. TG-DTG-DSC curves of Albertine F/1 under an oxidizing atmosphere

In an inert atmosphere the binder is decomposed with two-stage weight loss. The first weight loss within the temperature range 25-189°C is 9.11% with maximum rate of change in temperature 62°C. In this temperature range one endothermic

effect was recorded at 78°C. The second loss of 75.80% was attributed to irreversible degradation of the binder. In the range of temperature 189-1100°C were observed: two endothermic effects at 298°C and 915°C, and two exothermic effects at 366°C and 1022°C. Sample of binder in an inert atmosphere was not completely decomposed and its residual mass determined at 1100°C was 15.09%. Next changes of mass are assigned to an irreversible process of polymer chains fragmentation (breakage of glycosidic bonds), glucopyranose ring opening and formation of volatile products progressively (CO, CO_2 and H_2O). Peak at approx. 300°C (DTG) is characteristic for the group of natural and modified polysaccharides - it indicates on formation the volatile products during thermal degradation [14, 15]. At 1100º, the residual mass of sample probably contained carbonized carbon and aluminosilicates.

Under the presence of the oxygen (synthetic air atmosphere), the decomposition of the binder takes place with a three-stage weight loss: 9.11% in the range 25-169°C (T_{peak} = 64°C), 60.44% in the range 169-368°C (T_{peak} = 301°C) and 27.25% in the range 368-1100°C (T_{peak} = 475°C). At 1100°C the sample is not completely degraded and the sample residue was 3.20%. The residual mass of the sample is probably formed by small amount aluminosilicates which have been glassed at the bottom of the crucible.

It was found that the same value of the first loss of weight of Albertine F/1 in both atmospheres was caused by evaporation of water absorbed on the starch/aluminosilicate product and dehydration of the material. To evaluate and compare the thermal behavior of binder in different heating condition, the parameters T_{10} and T_{50} were considered (Tab. 2). Analyzing these characteristic temperature of weight losses by thermal decomposition, it can be affirmed that the binder presents similar thermal stability in both types of atmosphere to the ~310°C.

Table 2.
Thermal data selected from the TG-DTG-DSC analysis for Albertine F/1 sample

Atm.	Stage	Temp. range., °C	Δm, %	T_{peak}, °C	Temp. of thermal effect peak, °C	T_{10}, °C	T_{50}, °C
inert	I	25-189	9.11	62	78/endo	225	311
	II	189-1100	75.80	306	298/endo 366/exo 915/endo 1022/exo		
	Residual mass: 15.09% (at 1100ºC)						
oxidizing	I	25-169	9.11	64	79/endo	227	305
	II	169-368	60.44	301	217/endo 342/exo		
	III	368-1100	27.25	475	481/exo 623/exo 1005/exo		
	Residual mass: 3.20% (at 1100ºC)						

Pyrolysis product

Based on data obtained from TG-DTG-DSC tests, qualitative analysis of decomposition products released at a selected temperature was performed for Albertine F/1 samples using the method of pyrolytic gas chromatography coupled with mass spectroscopy (Py-GC/MS). Measurements were conducted at 350°C (around temperature of strongest exothermic effect in inert atmosphere on DSC curve), 550°C (temperature at which aromatic compounds may be released from native starch [16]) and 1100°C (end of stage II). Figure 3 shows the results of analysis of recorded pyrolysis products of the Albertine F/1.
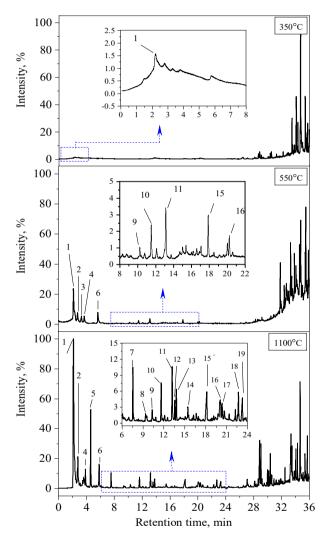
decomposition and H_2O is formed by inter- and intramolecular condensation of hydroxyl groups in starch chains. So, taking into account the results of thermal analysis indicating a significant weight loss in the second stage of decomposition (Fig. 1), with T_{peak} at 306°C, it was found that pyrolysis in 350°C could occur with the release of H_2O. However, the column type used in measurements does not allow to detect signals from the polar components of the sample decomposition.

The release of acyclic and cyclic hydrocarbons (e.g. 2-hydroxycyclopent-2-en-1-one, furan-2-carbaldehyde and 5-methylfuran-2-carbaldehyde) was observed on chromatograms of binder sample pyrolyzed at 550°C. Peaks from aromatic compounds were not registered at this temperature.

Significant intensification of Albertine F/1 sample decomposition with formation of more degradation products took place at temperatures above 550ºC. The identification of CO_2 (high peak) at 1100ºC indicated the progressive process of decomposition. Aromatic hydrocarbons were formed by decomposition of the binder at 1100ºC in the form of benzene and its derivatives (Tab. 3).

Fig. 3. Py-GC/MS chromatograms of Albertine F/1 under the different pyrolysis temperature

From the Fig. 2-3 it was found that found that at 350ºC the decomposition of Albertine F/1 sample took place with the formation of a CO_2 registered with the chosen measurement method (Tab. 3), but the course of the chromatogram indicates that the share of CO_2 in degradation products is unnoticeable. In this temperature water could be the main product of

Table 3.
Results of Py-GC/MS measurements for CMS-Na samples in different pyrolysis temperature

No.	IUPAC Name	No. CAS	M_w	R_T
1	carbon dioxide	124-38-9	44	2.22[a] 2.16[b] 2.17[c]
2	2-oxopropanal	78-98-8	72	2.75[b] 2.79[c]
3	acetic acid	64-19-7	60	3.33[b]
4	2-hydroxyacetaldehyde	141-46-8	60	3.70[b] 3.88[c]
5	benzene	71-43-2	78	4.63[c]
6	1-hydroxypropan-2-one	116-09-6	74	5.66[b] 5.85[c]
7	toluene	108-88-3	92	7.57[c]
8	1-hydroxybutan-2-one	5077-67-8	88	9.39[c]
9	2-hydroxyethyl acetate	542-59-6	104	10.22[b] 10.34[c]
10	methyl 2-oxopropanoate	600-22-6	102	11.51[b] 11.63[c]
11	furan-2-carbaldehyde	98-01-1	96	13.12[b] 13.22[c]
12	ethynylbenzene	536-74-3	102	13.58[c]
13	styrene	100-42-5	104	13.81[c]
14	2-oxopropyl acetate	592-20-1	116	15.47[c]
15	2-hydroxycyclopent-2-en-1-one	10493-98-8	98	17.87[b] 18.19[c]
16	5-methylfuran-2-carbaldehyde	620-02-0	110	20.22[b] 20.11[c]
17	2~{H}-furan-5-one	497-23-4	84	20.27[c]
18	1-ethynyl-3-methylbenzene	766-82-5	116	22.73[c]
19	2-hydroxy-3-methylcyclopent-2-en-1-one	80-71-7	112	23.30[c]

M_w- mass weight, u; R_T- retention time, min
[a] compound detected in 350°C
[b] compound detected in 550°C
[c] compound detected in 1100°C

Structural changes in an oxidizing atmosphere

Due to the large number of recorded spectra, the changes occurring in the individual DRIFT spectra were not discussed. The analysis was carried out taking into account the disappearance or formation of bands, at the same time separating on the list of spectra the areas of temperature occurrence of the interpreted changes. The DRIFT temperature spectra recorded for the Albertine F/1 sample are shown in Figure 4.
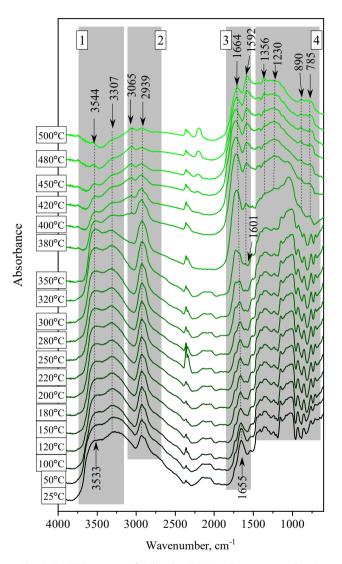

Fig. 4. DRIFT spectra of Albertine F/1 (*oxidizing atmosphere*)

As can be seen from DRIFT spectra below 350°C, the structure of the binder does not change. The main changes concern the shift of the bimodal band maxima in the range 3800-3250 cm^{-1} (area 1) and the reduction of the band intensity from the maximum at 1655 cm^{-1} (area 3). The observed changes are the effect of changes in the inter- and intramolecular O-H group network (the fact that the band up to 350°C does not disappear but only changes its shape may indicate that the hydrogen bonds crack, but also that the

components may cross-link) and the evaporation of water bound in the binder. Above 350°C, the band disappears with a maximum at 2939 cm^{-1} (area 2), which is associated with the tensile vibrations of the C-H group.

At 320°C band in the range of wavenumber 1800-1700 cm^{-1} (maximum of peak at 1664 cm^{-1}; area 3) corresponding to the vibration of the carbonyl group forming a C=O is occurred. The recorded vibration of the C=O may be related to both the formation of aldehydes, ketones, esters from the sample [14, 17, 18]. Moreover, above 320°C a new band appeared at 1601 cm^{-1}, the intensity of which increases and the maximum shifts to lower wavenumbers with increasing temperature.

In the wavenumber range 1500-600 cm^{-1}, where the bands are characteristic for starch (*fingerprint region*) [19], no changes in intensity or shifts to 320°C are observed. But the irreversible structural changes in the sample indicating degradation of the material are recorded in the temperature range of above 320-350ºC. Namely, the bands characteristic for vibrations within the glucopyranose ring and the bands attributed to glycosidic bonds disappear, which indicates defragmentation of polymeric chains [1, 19, 20].

In addition, new bands appearing above this temperature are associated with stretching vibration of the C-H vibrations of the C=C stretching of the ring, and a few bands in area of the wavenumber 3100-3000 cm^{-1} (peak at 3065 cm^{-1}; area 2), 1700-1500 cm^{-1} (maximum ~ 1592 cm^{-1}; area 3) and in the fingerprint range (1500-600 cm^{-1}; area 4) relating to aromatic C-H out-of-plane bending vibrations. The presence of these bands and increase of their intensity can indicate the progressive process formation of aromatic compounds [17]. Curves of DRIFT spectrum at 500°C indicates that samples was not complete degraded.

4. Summary

Based on TG-DTG-DSC, Py-GC/MS and DRIFTS investigation of Albertine F/1 it can be concluded that:

- the degradation of the binder regardless of the applied decomposition conditions (both inert and oxidizing atmosphere) is complex and multistage;
- the decomposition of the binder precedes the evaporation of the adsorbed water in the starchy products of the binder at ~169-189°C;
- irreversible changes in structure within the binder have been recorded above ~169-189°C;
- above a temperature of 350°C in presence of oxygen, intensive cracking of the chemical bonds occurs, which results in the breaking of most bond in starch-based binder; at the same time, groups are formed which indicate the formation of aromatic compounds;
- in an inert atmosphere the process formation of volatile decomposition becomes more varied above 550°C, which has an effect of releasing not only volatile low-molecular-weight inorganic (CO_2, H_2O) but also organic compounds (hydrocarbons). Aromatic compounds (benzene and derivatives) were identified at a temperature of 1100°C.

Knowledge about the thermal stability, the quality of degradation products, and the effect of heating on structure of Albertine F/1 obtained from the studies of the TG-DTG-DSC, Py-GC-MS, and DRIFTS methods has allowed to identify the course of binder degradation in the context of its use as a binder and better understanding its thermal behavior in application in molding sand technology.

Acknowledgements

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