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Thermal decomposition of binder based on etherified starch to use in foundry industry

TG–DTG–DSC and DRIFT investigations

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Abstract In this work, the main purpose was the determination of the thermal stability of the modified starch: sodium carboxymethyl starch (CMS-Na) used in foundry technology as organic binder for molding sand. The analysis of the course of decomposition of the starch material under controlled heating in the range of 20–500 °C was based on the results of thermal analysis methods (TG, DTG, DSC) in combination with the results of spectroscopic technology (DRIFT). The use of various methods of thermal analysis and spectroscopic methods was possible to determine more entirely the mechanism of the binder decomposition process comprising reactions at the molecular level with regard to the conditions prevailing in the mold. The onset temperature of degradation of the binder and at the same time the temperature at which it begins to lose binding properties were determined. It was found that the mechanism of the binder is multistage process. The decomposition of the starch binder CMS-Na involves the gradual evaporation of the water bound at a temperature of 20–120 °C and water constitutional starch in the range of 120–200 °C, degradation of the binder in the temperature range 200–342 °C by breaking the glycosidic bonds in the polymer chains with the formation of volatile compounds and finally detaching the side groups and partial combustion of the starch material within a temperature range 342–500 °C.

Keywords Foundry polymer binders · Modified starch · Thermal analysis · TG–DTG–DSC · Thermal decomposition

Introduction

The binders in sand molds are a key component of determining the properties of the mold and castings produced by the binding strength of the matrix grains of sand. Although the binders currently used in foundries provide a production of durable molds and casting without defects, mostly they pose a serious threat to the environment. Thus, in the era of searching ecological solutions for foundry, there are observed strong interests in receiving new materials based on natural raw materials [1].

A potential replacement for toxic ingredients in sand molds is starch and its derivatives, which are tested for application not only as a binder but also an auxiliary material in the molding and core sands. The legitimacy of starch application in the technology of molding sand is dependent on the properties of the formulation starch (the conditioned by the biological origin), such as the ability to form viscous solutions, wetting ability and binding of the matrix grains of sand, susceptibility to cross-linking agents. Most frequently in technologies of molding sand, the potato and corn starches are used, but due to the fact that the prevalence of this biopolymer is almost limitless around the world, and the research on the possibility of use in the casting of starch derived from other plant species is conducted too. The starch as the polymer is not uniform in structure, and it is composed of two fractions: branched chains of amylopectin and linear chains of amylose [2].

However, the results of studies of the properties of molding sand bonded by starchy binders show that

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adhesives based on native starch are not a fully effective alternative to the currently used commercial products, and only its derivatives can guarantee obtaining molding sands with the relevant binding strength and functional parameters [3–6]. The example of modified starch with suitable properties for the foundry industry is carboxymethyl starch as a sodium salt (CMS-Na) produced by etherification of native starch in monochloroacetic acid (or its sodium salt) in the presence of sodium hydroxide [7, 8]. During the etherification, the polymer chains in place of the hydroxyl groups are substituted by hydrophilic groups (Fig. 1). The amount of hydrophilic groups in the polymer chains can be controlled quantitatively, and the structural effect of the modification process is characterized by a degree of substitution (DS). The presence of the hydrophilic group causes that the CMS-Na effectively swells up in cold water and affects the clarity of films and pastes. The etherification process also results in the stabilization of aqueous solutions of starch and reduces its tendency to retrogradation—thus all of the phenomena occurring during storage of the starch colloids, based on the creation of bonds between the starchy polymer chains starch and lead to an increase in its crystallinity at a low temperature [8].

The conducted own research related to application of CMS-Na in molding sands technology proved the legitimacy of using this modified starch as a binding material in the molds cured by chemical or physical agent (through conventional heating and exposure to electromagnetic radiation) [5, 6, 9]. However, from the point of view of pouring a liquid alloy into cured sand mold is to evaluate the thermal stability of a starch binder. Namely, too rapid thermal degradation of the organic binder in molding sand can result in the formation of significant casting defects (shape deformation, cracks, surface defects) [10, 11]. On the other hand, the high thermal resistance may limit knockout properties or adversely affect the efficiency of thermal reclamation methods of used molding sands [12–14]. Thus, in this paper, the aim of the study was to characterize the mechanism of thermal decomposition of alternative organic binder on the example of CMS-Na with low degree of substitution.

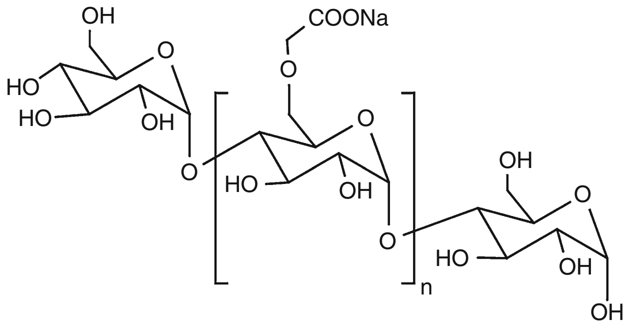

Fig. 1 Amylose fragment with the substitution of the hydrophilic group –CH_2–COONa in positions 6

Analysis of the thermal decomposition under controlled heating in the aerobic atmosphere in the temperature range of 20–500 °C was based on the results of thermal analysis methods (TG, DTG, DSC) in combination with the results of spectroscopic (technique DRIFT) in *online* system.

Experimental

Material

In the study, an etherified starch was used in the form of the sodium salt of carboxymethyl starch (CMS-Na; Polvitex® Z by Xenon) with a degree of substitution DS 0.2 prepared on the basis of native potato starch Superior Standard (80–82%) comprising: monochloroacetic acid (6–8%), sodium hydroxide (3–5%), sodium carbonate (3–5%) and diethylene glycol (3–5%). Moisture content of the starting product was 6.7%.

Methodology

Methods of thermal analysis (TG–DTG–DSC)

Thermal analysis was performed by using a thermal analyzer NETZSCH STA 449 F3 Jupiter® design to simultaneous measurements TG–DTG–DSC, which ensure to obtain independent signals recorded under the same measurement conditions: heating rate, atmosphere and pressure. This method of analysis provided a higher efficiency and allowed obtaining a comprehensive information on the thermal characteristics of the samples of starch products. The measurement was taken under aerobic atmosphere in a temperature range of 20–500 °C at a gas flow rate of 40 mL min^{-1}. The rate of heating of the test sample was 10 °C min^{-1}.

DRIFT spectroscopy

The diffuse reflectance infrared Fourier transform spectroscopy (DRIFTs) is an infrared spectroscopy technique; it can provide both chemical information and structural information for all types of solid surfaces. The DRIFT measurements were taken on the IR spectrometer type FTS 3000 Digilab Excalibur Mx with detector DTGS Bio-Rad, combined with a device for controlling the temperature and cooling system. Spectra were recorded *online* in the wavenumber range 4000–600 cm^{-1} assuming a resolution of 8 cm^{-1}, and the number of scans 64. Interferograms of 64 scans were automatically averaged to a single spectrum.

To measure the diffuse reflectance spectrum of CMS-Na sample, firstly, powdered potassium bromide (KBr) (grain

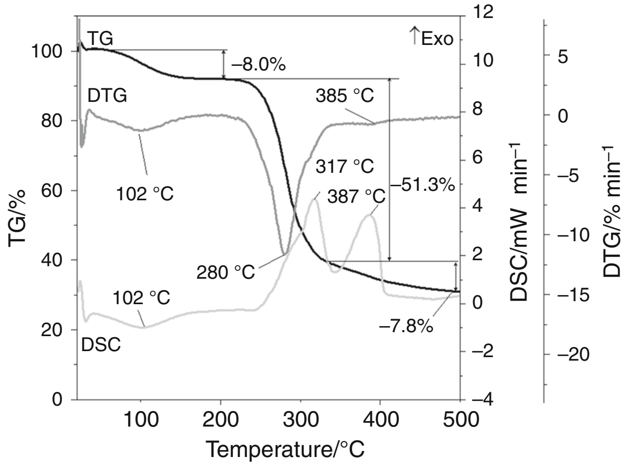

Fig. 2 TG–DTG–DSC curves obtained in an aerobic atmosphere for sample of CMS-Na

size ≤2 μm), acting as control, was placed in the diffuse reflectance cup and mounted on the DRIFT attachment to prepare the background measurement. In the next step, the initial sample of CMS-Na (Polvitex® Z) was prepared for DRIFT measurements by mechanically grinding to a fine powder with KBr (CMS-Na/KBr 1:5 ratio) and mounted in DRIFT attachment in the similar manner as described above. Dilution of sample CMS-Na in KBr was necessary to reduction the intensity of the bands and distortions in the course of DRIFT spectra. Prepared sample was gradually heated in aerobic atmosphere (air) in the range of 20–500 °C. The first DRIFT spectrum of initial sample was recorded at 20 °C; the next DRIFT spectra of heated sample were recorded after 1 min from reaching the next desired temperature values during heating of sample to 500 °C (at 50, 100, 120, 150, 180, 200, 220, 250, 280, 300, 320, 350, 380, 400, 420, 450, 480 and 500 °C). The heating rate of the test sample was 10 °C min^{-1}.

Results and discussion

TG–DTG–DSC thermal analysis

The course of TG curve proves that the decomposition of CMS-Na takes place with a three-step mass loss: −8.0, −53.1, −7.8% in an aerobic atmosphere at speeds of maximum mass changes at temperature 102, 280, 387 °C, respectively (Fig. 2).

The first mass loss of the sample CMS-Na within a temperature range of 20–120 °C is interpreted as the evaporation of the water molecules adsorbed on the starch granules and in the range 120–188 °C assigned to gradual dehydration of the material [15, 16]. On DSC curve, a weak endothermic effect, related to the removal of moisture from initial sample CMS-Na, is detected around 102 °C.

The degradation process of the sodium salt of carboxymethyl starch begins at temperature above 188 °C. It is evidenced by the highest mass loss in the temperature range of 188–342 °C. This change of mass is assigned an irreversible process of polymer chains fragmentation (breakage of glycosidic bonds), glucopyranose ring opening and formation of volatile products progressively, mainly CO, CO_2 and H_2O [17]. In the defined temperature range in 280 °C, there was noticed a maximum rate of mass change on DTG curve and the strong exothermic effect on a DSC curves at a temperature of 317 °C. Thermal effects at approx. 300 °C are typical for the group of natural and modified polysaccharides, and it is associated with receiving the volatile products during thermal degradation [18]. Boki et al. [19] conducted similar research related to thermal decomposition of CMS-Na with DS ≤ 0.3 in the temperature range of 200–350 °C. Based on above-mentioned paper and our results, it can be noted that the course of mass changes on TG curves and onset temperature of decomposition of CMS-Na (Polvitex® Z) approx. 260 °C are comparable. The most visible difference is the presence of the two strong exothermic effects at 260 and 295 °C on DCS curves detected by Boki et al. [19] in the defined temperature range.

In the temperature range of 342–500 °C, the mass loss is associated with much less efficient course of material degradation and detachment of the side groups –COONa. At the temperature of 387 °C, a strong exothermic peak is detected, which may be associated with a combustion of carboxymethyl starch sodium in an aerobic atmosphere.

In the analyzed temperature range of 20–500 °C, the sample is not completely decomposed and at a temperature of 500 °C the residual mass of sample is 30.9%.

Table 1 Analysis of TG–DTG–DSC curves in the range of 20–500 °C obtained for sample of CMS-Na

Stage	Mass loss Δ*m*/%	Range of temperature/°C	Temperature of maximum rate of mass loss/°C	DSC effect temperature/°C
I	−8.0	20–188	102	Endo-102
II	−53.3	188–342	280	Exo-317
III	−7.8	342–500	385	Exo-387
Residual mass: 30.9% (500 °C)				

Incomplete decomposition of CMS-Na is probably related to the presence of sodium atoms in the sample. Sodium plays a key role in thermal decomposition of modified starch by influence on the efficiency of the dehydration, decarboxylation, carbonizing the material and the volatile substances of higher molecular mass and carbon oxides formation [15, 20]. Table 1 summarizes the characteristic thermal data selected from the TG–DTG–DSC curves for a sample of CMS-Na (Polvitex® Z).

Spectroscopic analysis

The analysis of the impact of increasing temperature on the structure of the investigated material was carried out with regard to the disappearance or the formation of bands on the spectra. The DRIFT spectra recorded within the temperature range of 20–500 °C for sample of low-substituted CMS-Na are presented in Fig. 3.

Initially, within the temperature range of 20–200 °C there are observed changes in the area assigned to inter- and intramolecular O–H groups [21]. These changes are associated with the elimination of water from the polymer chain (bound water and constitutional water). As a result of temperature rising, in the range of the wavenumber 3900–2900 cm^{-1}, there is observed change of the position of the two maxima of the bands assigned to hydroxyl groups. At 20 °C in the range of wavenumber 3000–2900 cm^{-1}, there is one band with a maximum at 3586 cm^{-1} and a second band with a peak at around 3199 cm^{-1}. At rising temperature, maxima of this bands are shifted to the 3545, and 3291 cm^{-1}, respectively. This shows the intensive evaporation of water and the partially disappearance of existing hydrogen bonding between polymer chains of CMS-Na. However, the intensity of the bands assigned to OH group in the DRIFT spectra is not completely reduced in the temperature range of 20–200 °C, so there also may indicate to cross-linking of the polymer chains by hydrogen bonds [5].

Furthermore, the process of eliminating water adsorbed on the starch macromolecules from the sample CMS-Na is confirmed by the change of intensity of band near the wavenumber 1643 cm^{-1}, which disappears completely above 120 °C [21, 22].

On the DRIFT spectra recorded at above 120 °C, a new band in the range of wavenumber 1670–1820 cm^{-1} (maximum of peak at 1664 cm^{-1}) 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 [17, 21, 23]. In the subsequent heating steps above 300 °C,

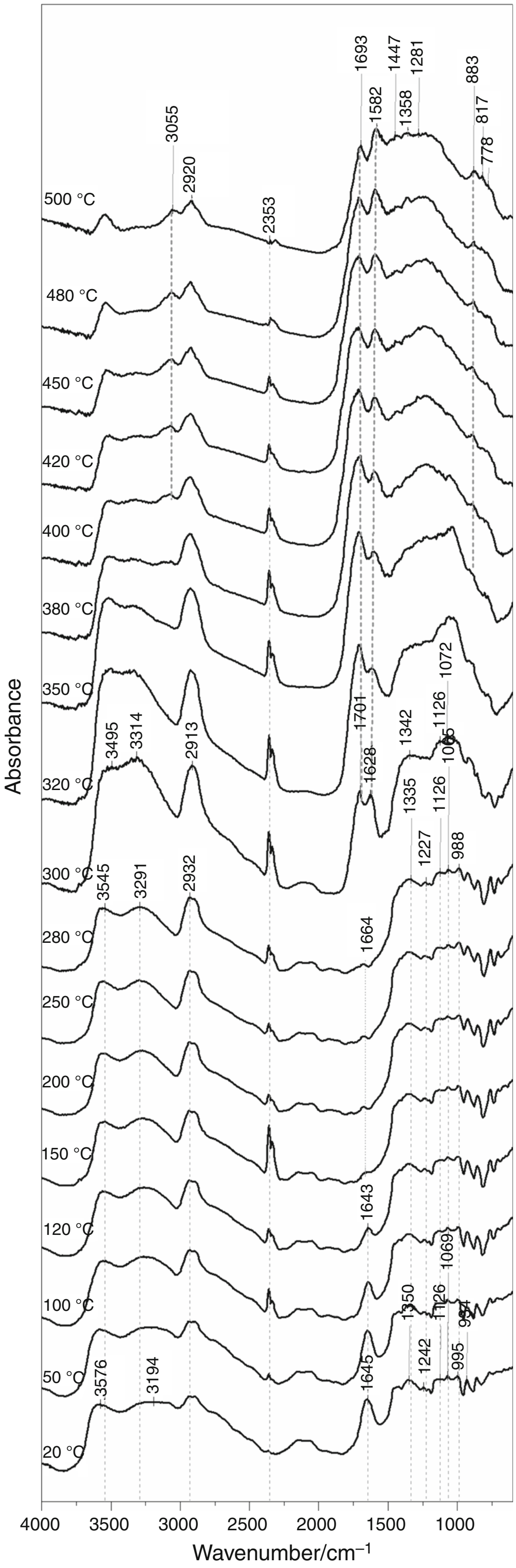

Fig. 3 DRIFT spectra recorded in the range of 20–500 °C for samples of CMS-Na

two bands are separated from this band, and maximum of band corresponding to the C=O group is shifted to higher wavenumbers. Boki et al. [19] in their research also carried out research on structural changes between initial and decomposed sample of CMS-Na with DS $\leq$ 0.3. Based on IR spectra obtained by transmittance spectroscopy, Boki et al. noticed that main result of thermal decomposition of CMS-Na in temperature range 200–350 °C was change of the intensity band with maximum at 1600 cm^{-1} assigned to vibration of carbonyl (C=O) and carboxylate (–COO^{-}) groups. This effect was probably caused by partial decomposition of carboxymethyl group in low-substituted CMS-Na [19]. That effect is not clearly observed on DRIFT spectra obtained for initial and thermally decomposed sample of CMS-Na (Polvitex® Z) analyzed in this paper. But optical phenomena that generate DRIFT signals are different from those involved in transmittance spectroscopy; therefore, the spectra obtained by these methods cannot be considered equivalent.

The irreversible structural changes in the sample indicating degradation of the material are recorded in the temperature range of above 300 °C. The new bands appear in area of the wavenumber 3000–3100 cm^{-1} (peak at 3055 cm^{-1}), 1700–1500 cm^{-1} (maximum ~1574 cm^{-1}) and 900–650 cm^{-1} (three peaks at 876, 814, 777 cm^{-1}). They are identified as: stretching vibration of the C–H vibrations of the C=C stretching of the ring, and a few bands in the fingerprint range (800–1500 cm^{-1}) relating to aromatic C–H out-of-plane bending vibrations. The presence of these bands and increase in their intensity can indicate the progressive process formation of aromatic compounds [21]. In the lower wavenumber above 300 °C, it is also observed the disappearance of the band corresponding to the bonding characteristic C–O–C in modified starch and shifting its maximum from 930 cm^{-1} to the lower wavenumbers. The changes in the wavenumber range are associated with irreversible cracking of many glycosidic linkages between glucopyranose ring of amylose and amylopectin chains in CMS-Na [24].

Conclusions

The results of thermal stability studies obtained by methods of thermal analysis TG–DTG–DSC and spectroscopic method by DRIFT technique allowed to determine a complex course of the next stages of thermal decomposition of the binder under the aerobic atmosphere measurement conditions. Thermal decomposition mechanism of the binder in the form of CMS-Na is a multistage process, and based on the curve TG–DTG–DSC and DRIFT spectra course, it can be concluded that:

- evaporation of adsorbed water molecule sodium carboxymethyl starch occurs at the temperature of 20–120 °C;
- dehydration and formation of the network of hydrogen bonds are observed in the range of 120–200 °C;
- breakage of glycosidic bonds in the polymer chains intense the fragmentation chain, the formation of carbonyl groups (it indicates the presence of aldehydes, ketones or esters as a decomposition product) and the formation of volatile compounds are recorded in the range of ~200–342 °C;
- above the temperature of 188 °C, the process of degradation of the binder begins, but the most intense structural changes are recorded over 280 °C. In this temperature range, the thermal decomposition reactions were observed associated with the formation of bonds characteristic for aromatic moieties.

Sample of CMS-Na is not completely decomposed in the temperature range of 20–500 °C, leaving a residual mass of 30.9% at 500 °C.

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