

# Analysis of the Stability Selected Properties of Polymeric Binder on the Example of an Aqueous Solution of the Modified Starches

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## Abstract

The aim of this study was to determine the stability of the physicochemical properties of foundry binders based on modified starch. On the basis analysis of structural changes (FT-IR), thermal characteristics (TG / DSC), were conducted an initial assessment of the stability of the binder during the 3-month duration of the measurement cycle. Additionally, there were studied the strength of moulding sand bonded by starch binder prepared at the beginning of the test cycle and starch binder after 3-month storage period.

**Keywords:** Innovative foundry materials, Polymeric binders, Starch derivatives, Stability

## 1. Introduction

Starch as a natural and inexpensive material is used on a wide scale [1], and in over the last few years there has been an increased interest in this polymer and its derivatives in a various industries, including as a binder material for moulding. According to the data suggest that the native starch is rarely used as the main or only one binder in the moulding sand [2], which is related to the physicochemical properties of the native form. Additional starch are used as auxiliary substances improving the hardness and strength of, e.g. moulding sands with bentonite [2-9]. A side effect of the presence of starch in the composition of moulding was molding flowability and resistance to erosion and penetration of metal into the mould [2]. Moreover, its disadvantage is the

insolubility in cold water - only at temperatures around 70 °C begins to partially dissolve and swell [10]. The method of introducing the component to the moulding sand can be awkward, because in the native form shows no adhesiveness, does not bind the sand grains, and therefore it is necessary to prepare the starch paste in hot water (a colloidal solution of starch in water) [1].

Improvement of properties, including soluble in cold water, can be prepared by modification of starch where one or more of its initial physical or chemical characteristics are changed [11,12].

From the group of modified starch with altered properties, such as molecular weight, gelation temperature, solubility, viscosity, water-binding capacity, and resistance to acids and enzymes, its widest application in the casting formulations are prepared by chemical modification [13 -21].

In this work the study of assessing the stability of selected physicochemical properties of a new binder based on water soluble etherified starch were conducted. The aim of the study was to determine the impact of storage time on selected properties of the binder and the ability to store a binder in specified conditions during the three months (similar to those in the foundry). The analysis of changes in the physicochemical properties of starch binders were carried out on the basis of spectroscopic studies in the infrared, the pH changes, the viscosity, and thermal analysis. In addition, studies were conducted bending strength of samples moulding sands bonded by freshly drawn up and stored binder.

## 2. Methodology of research

### 2.1. Materials

The research was carried on the solid powder of modified starch as a non-cross-linked Polvitex Z (by Xenon) with degree of substitution (DS) about 0.2. This material was used to prepare a new starch binder as an aqueous 5-% solution (starch pasta). Brookfield viscosity of the solution is about 18 000 mPa·s, a pH is equal to 11.52.

Samples of binder were stored in sealed vessels for a period of three months in a thermostatic cold storage at 10 °C.

### 2.2. The samples cross-linking

Cross-linking of the modified starch solution was carried out by physical means (evaporation of solvent water) in a microwave radiation with a microwave power of 800 W. The crosslinking process was carried out in a microwave INOTEC MD 10940 with adjustable the power and the irradiation duration. Irradiation time of binder samples was 60 seconds and temperature in the microwave apparatus was about 100 °C.

### 2.3. pH measurement

The pH measurement was carried out cyclically by using a pH-meter CP-105

### 2.4. Viscosity measurement

The measurement was performed on a rotational viscometer Rotowisko ® Haake RV30 with M5 drive system and measuring system type coaxial cylinders NV with a double slit, DIN 54453. Apparatus was controlled by a computer program RheoWin Pro Job Manager Haake.

The measurement was conducted after introduced into the cylinder 9 cm<sup>3</sup> of sample. After that the set of rollers was accelerated for 120 seconds to 100 rotations per second, then maintained for 60 seconds at a constant speed of 100 rotations per

second, and finally was stopped for 120 seconds to 0 rotations per second. The results were interpreted using RheoWin Pro Data Manager Haakeanager Haake

## 2.5. Infrared spectroscopy

Structural studies were carried out using Thermo Scientific spectrometer Nicolet™ 6700 FT-IR. The resolving power was  $\pm 4$  cm<sup>-1</sup>.

## 2.6. Thermal analysis

Thermal analysis was performed using a thermal analyser NETZSCH STA 449 F3 Jupiter®, which allow the simultaneous execution of TG and DSC measurements. The measurement was performed in an oxygen atmosphere within a temperature range of 22 - 500 °C at a gas flow rate of 40 l/min and the sample heating rate of 10 °C/min.

## 2.7. The preparation and curing of moulding sands

Preparation of moulding sands was carried out in ribbon mixer (LM-R1). Into sand grains (quartz sand, Szczakowa SA., 0,2/0,16/0,32) were introduced a binder starch in an amount of 3 pbw per 100 pbw of sand.

Sand and the binder was stirred for 3 minutes. The conditions for the moulding sands preparing - humidity in laboratory: 35%, and ambient temperature: 23 °C.

Curing was carried out by microwave irradiation in the microwave INOTEC MD 10940 (800 W microwave power, for 120 s at 100 °C).

The bending strength tests ( $R_g^b$ ) was performed according to the standard as a binding material using freshly prepared starch solution and a solution stored for 3 months [22].

## 3. Results and discussion

### 3.1. FT-IR studies

The high water content in the sample (95%) causes that the bands derived from modified starch, are overshadowed by the bands derived from the solvent, i.e. broad band extending  $\nu$ -OH vibration with a peak at 3336 cm<sup>-1</sup> and H<sub>2</sub>O deforming oscillation wave number region with a peak at 1636 cm<sup>-1</sup> (fig. 1). On the basis of spectra no significant changes during storage binder. The bands are shifted only within the limits of sensitivity of the method ( $\pm 4$  cm<sup>-1</sup>).

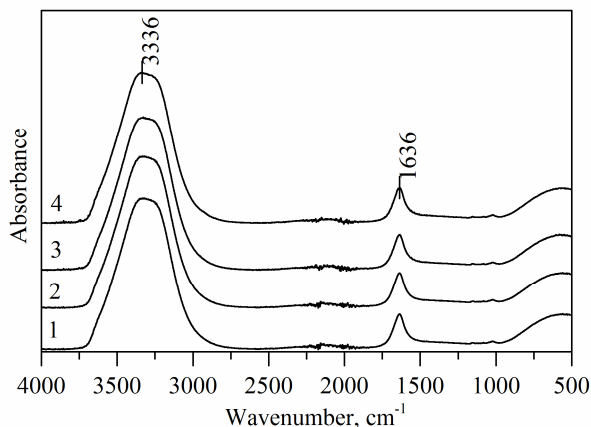


Fig. 1. IR spectra for the non-cross-linked binders: 1 - the first week, 2 - after 1 month, 3 - after 2 months, 4 - after 3 months

To evaporate the water from the binder samples were subjected to exposure to microwave irradiation for 60 s. Then structural studies FT-IR were carried out on these physically cross-linked samples (fig. 2).

The bands with a maximum occurring at 929  $\text{cm}^{-1}$  confirm the present in binder a  $\alpha$  configuration of the glycosidic bond, typical for native starch [19]. In all the IR spectra of the samples tested was observed the presence of the bands surrounding peaks at a wavenumber 995  $\text{cm}^{-1}$ , 1078  $\text{cm}^{-1}$  and 1153  $\text{cm}^{-1}$  on the vibration characteristic of the groups of native starch (C-O stretching, C-H bending, stretching C-O and C-C). Maxima of the bands observed at 1415  $\text{cm}^{-1}$  and 1595  $\text{cm}^{-1}$  are associated with the presence of carboxyl groups in the considered modification of the starch.

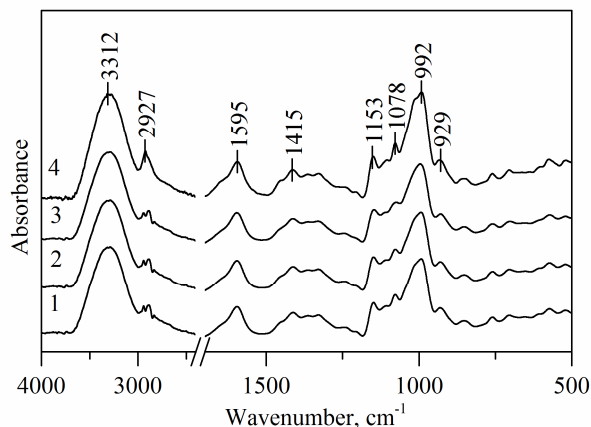


Fig. 2. IR spectra for the cross-linked starch binders: 1 - the first week, 2 - after 1 month, 3 - after 2 months, 4 - after 3 months

In the IR spectra of modified starch in the range of wave number 2800-3000  $\text{cm}^{-1}$  bands were observed originating from  $\text{CH}_2$  stretching vibrations. The intensity of the vibrations in this area may be related to the amount of amylose and amylopectin. The IR spectrum wave numbers in the area 3000 - 3600  $\text{cm}^{-1}$  revealed the presence of characteristic OH stretching vibration.

The bands at wavenumbers 929 and 995  $\text{cm}^{-1}$  are probably related to the occurrence of  $\alpha$ -1,4-glycosidic bonds in the binder.

In the wave number range 3000 - 3600  $\text{cm}^{-1}$ , broad band corresponding to the vibration of the free OH group ( $\text{H}_2\text{O}$ ) and hydrogen bonding does not disappear after crosslinking (after solvent evaporation), but visible is reduction in its intensity as compared to the binder in the form of a solution. Probably the presence of this band is due to the presence of hydrogen bonds in the cross-linked binder and a bound water [2, 3].

There were no significant shifts bands, and any differences are small and within the limits of measurement error (spectrometer resolution:  $\pm 4 \text{ cm}^{-1}$ ). Three-month storage binder does not result in the appearance of new bands or loss of bands characteristic can therefore be concluded that the structure of modified starch is stable.

### 3.2. pH results

Table 1 shows the summarized results of measurements of the pH of the fresh samples and samples after 1, 2 and 3 months of storage. Differences between successive measurements are negligible, so it is considered that the pH of the starch binder is stable in predetermined period the research.

Table 1. Results of pH measurement

Parameter	Binder storage time			
	initial	1-month	2-month	3-month
pH	11,52	11,52	11,50	11,46

### 3.3. Rheological measurements

The flow curves and viscosity curves were plotted for the test binder using a computer program. Obtained curves were fitted to Bingham rheological model. In both cases, the rheological measurements showed that the colloidal solutions exhibit the characteristics of non-Newtonian liquid with flow limit.

Table 2. The viscosity comparison

Parameter	Binder storage time	
	initial	3-month
$\eta_0$ [Pa*s]	2,259	1,643
$\tau_0$ [Pa]	113,4	84,67

The results of the rheological measurements have shown that in keeping the colloidal solution of starch in cold storage caused the plastic viscosity ( $\eta_0$ ) decrease from of 2,259 Pa\*s to a value of 1,643 Pa\*s, and the flow limit offset values ( $\tau_0$ ) of 113,4 Pa to 84,67 Pa.

### 3.4. Thermal analysis TG-DSC

Figure 3 shows TG-DSC curves for the starch binder in the form of the initial 5-% aqueous solution and this solution after 3 months of the test cycle.

Analysing the TG-DSC curve obtained for a sample of the binder in the first week of test (starting measurement) can be stated that in the temperature range 22 - 141 °C was observed a rapid evaporation of water from the binder (first weight loss of 80,94 %, fig. 3a). Presumably, in this temperature range in the binder occurs the crosslinking by dehydration [21, 27].

Under the conditions of atmospheric oxygen above 141 °C is observed onset of degradation (second weight loss - 4,17 %, fig. 3a). The loss of mass above the temperature of the degradation beginning may be due to breakage of glycosidic bonds in starch modifier [27, 28].

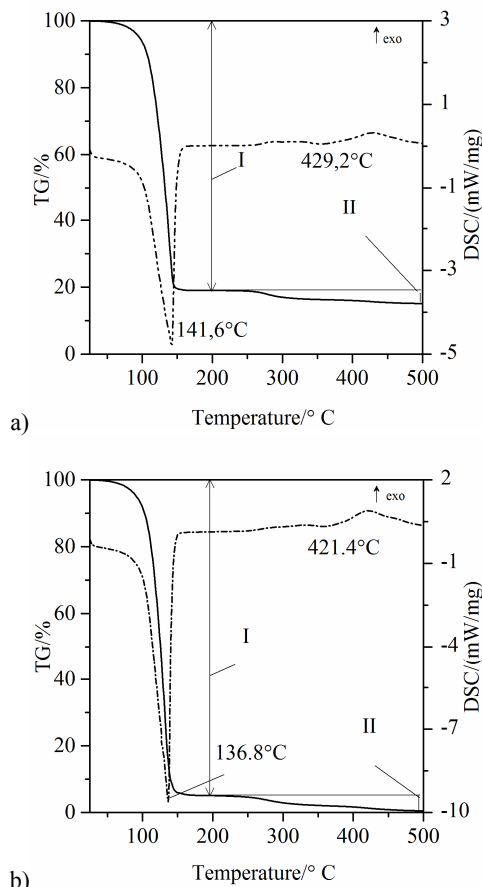


Fig. 3 TG-DSC curves of starch binder: a) after first week b) after 3 months.

Course of the curves obtained TG-DSC for the freshly prepared starch binder was compared with the curves achieved for binder after 3 months of the measurement cycle, it was found that is very similar (fig. 3b).

In this interval of temperature 20-500 °C, the degradation of binder takes place the two-step weight loss for both of binders: in the fresh samples and after 3 months of storage.

In the temperature 22-140 °C in the stored binder a solvent water evaporation process was followed also (endothermic effect, the maximum rate of change of weight of 136,8 °C, fig. 3b), but the weight loss of the sample in this area is more intense and reaches 94,87 % (first weight loss, fig. 3b). Above a temperature of about 136,8 °C was observed a slow process of destruction of the binder (second weight loss of 4.88%, fig. 3b).

In the predetermined test temperature range 22-500 °C occurs to complete degradation modified starch after 3 months of storage. Intensive solvent water loss in the range of 20-136,8 °C may be indicative of the ongoing process of retrogradation in the solution. During storage its leads to the release of water from the binder macrostructure (syneresis) and delamination of colloid solution on the modified starch and water. When water is not linked to the structure of the starch grain evaporates more easily [24-26].

### 3.5. The strength of moulding sand

The bending strength after 1 h, 4 h and 24 h of samples storage of both, prepared and cured, moulding sands was achieved on 60 N/m<sup>2</sup> level (fig. 4). The obtained results allowed observe that a viscosity changes have only a little influence on the binding capacity of sand grains by the three-month-stored binder. The differences in the measurements  $R_g^u$  are not large, and the obtained results allow to conclude that after three months of starch binder does not lose the essential properties of binding in moulding sands.

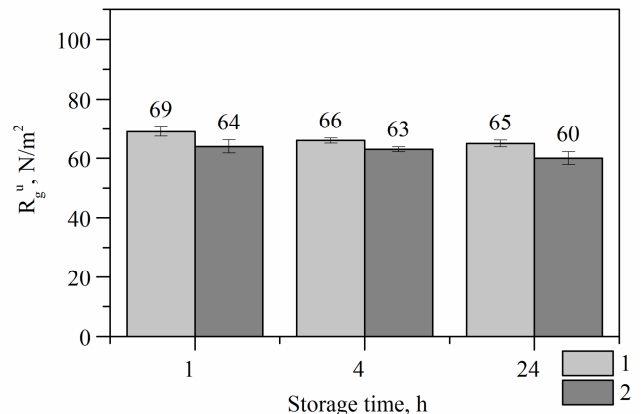


Fig. 4. The bending strength of moulding sand bonded by stored starch binder: 1 – after first week, 2 - after 3 months the measuring cycle

## 4. Summary

Observations of IR spectra of non-cross-linked and cross-linked binder in the microwaves irradiation allow to conclude that the retention time does not affect the structure of the material being tested. During the measurement cycle, there hasn't been observed the appearance of new groups or decay of characteristic bands modified starch, therefore the structure of the tested material is stable over time.

The pH value wasn't change for three months and it was ~11,50.

Plastic viscosity of the binder is significantly lower after 3 months. There is a visible decrease of this parameter from 2,259 Pas to 1,643 Pas, which is probably associated with the occurring starch retrogradation process in the colloidal solution.

Water is pushed out from the inter-gel starch areas and binder is delaminated on unbound solvent and insoluble dendrites of the retrograded starch [24-25].

Thermal analysis of the samples tested showed that the courses of thermal degradation in the temperature range 20-500 °C are similar (two-step weight loss, degradation onset temperature of the binder) are not significantly affected, and the time does not change the thermo stability of the binder. In both cases, the degradation of the binder starts in temperature around 140 °C. Noticeable difference is the intensity of the evaporation of water. After three months of storage of the binder, this process is somewhat more intense, which could result from a possibly ongoing process of elimination water from the solvent solution of the macrostructure (starch paste) by syneresis.

Despite the observed changes of selected physicochemical properties of starch adhesive strength measurements weight bending prove that these changes have not material impact on its binding properties. The moulding sand bonded by fresh and stored for 3 months binder, achieved a similar level of bending strength, about 60 N/m<sup>2</sup>.

## Acknowledgements

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