

**Beata Grabowska, Karolina Kaczmarska**

## FT-IR studies of the polymeric binder BioCo1 with modified biopolymer – part I

### Badania FT-IR polimerowego spoiwa BioCo1 z udziałem skrobi modyfikowanej – część I

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#### Abstract

This paper presents structural studies of polymeric water soluble compositions consisting of acrylic derivatives/modified biopolymer. The research FT-IR was focused on novel polymer composition poly(acrylic acid)/modified starch (PAA/CMS) designed for application in the foundry industry – a novel group of polymeric BioCo binders. It was found, that the structure changes occur within groups: carboxyl present in poly(acrylic acid) and carboxyl and hydroxyl groups contained in carboxymethyl starch (vibrations:  $\nu_3$ -C=O,  $\nu_3$ -COO<sup>-</sup> and  $\delta$ -C-O-H).

**Keywords:** polymeric composition, polymeric binder, moulding sands, FT-IR

#### Streszczenie

Przedstawiono analizę strukturalną wodnej kompozycji polimerowej składającej się z syntetycznych pochodnych akrylowych i modyfikowanych polimerów naturalnych. Badania FT-IR skoncentrowano na wodorozcieńczalnej kompozycji poli(kwas akrylowy)/modyfikowana skrobia (PAA/CMS) przeznaczonej do zastosowania w przemyśle odlewniczym – nowa grupa spoiw BioCo. Stwierdzono, że podczas mieszania składników kompozycji zmiany strukturalne zachodzą w obrębie grup: karboksylowych obecnych w poli(kwasie akrylowym) oraz karboksylanowych i hydroksylowych, obecnych w karboksymetyloskrobi (drgania:  $\nu_3$ -C=O,  $\nu_3$ -COO<sup>-</sup> oraz  $\delta$ -C-O-H).

**Słowa kluczowe:** kompozycja polimerowa, spoiwo, masa formierska, FT-IR

## 1. Investigations

The polymer composition poly(acrylic acid)/modified starch (PAA/CMS), due to its physical and chemical properties found its application as a new binding agent of moulding

sands (binder BioCo1) [1]. The main loose component of a moulding sand is sand grains of the determined mineralogical, chemical and granular composition (the most often high-silica sand). A component providing a determined mechanical strength and able to bind sand grains is the binding agent (binder). The selection of the proper binder cross-linking moulding sands components, to obtain the binding power sufficient to retain the mould shape – during pouring it with liquid metal – is essential in the foundry technology [2]. Thus, a binder is crucial in the foundry process since it has to bring about obtaining of dimensional castings. In addition, the proper selection of the cross-linking factor has a significant influence on a binder bounding power in moulding sands. Therefore, when designing new polymer binders or modifying already known ones, one should penetrate into its structure and recognize its binding mechanism [3–5]. The results concerning the structure analysis (FT-IR) of the designed binder BioCo1 (polymeric composition PAA/CMS) are presented in the paper.

Structural investigations on the determination of the moulding sand hardening process, *i.e.* binding agent cross-linking process in the system: binding agent-mineral matrix in relation to its technological properties, will constitute the second part of the publication.

### **1.1. Materials**

The following samples BioCo1 were used as a new polymer binding agent in the form of a two-component polymer composition formed by mixing in water a synthetic polymer (poly(acrylic acid), PAA, BASF) and a modified biopolymer (modified starch: carboxymethyl starch, CMS, Xenon, DS 0.2) in the weight ratio 1:1 was used in the performed investigations. After mixing components the mixture in the form of the water homogeneous polymer composition of pH = 2.5, viscosity 850 mPa·s and 78% of water content, was obtained.

### **1.2. Structural investigations**

Spectroscopic FT-IR tests were carried out by means of the spectrometer Digilab Excalibur FTS 3000 Mx with detector DTGS, electrically cooled. This spectrometer is equipped with two attachments: ATR with ZnSe crystal for multiple reflection and the transmission attachment. Transmission spectra of the investigated samples were recorded in a range: 4000–400  $\text{cm}^{-1}$ , at the resolution of 4  $\text{cm}^{-1}$ . Number of scans was selected in dependence on the level of the obtained signal (within 32–64 scans). The correction of the obtained spectra base line was performed by means of the Merlin (FTS 3000) software.

### **1.3. The microscopic studies**

Then the formed samples of aqueous composition polymer of PAA/CMS were dried by vacuum and after converting to microscopic examination were conducted of the solid

form using ultra-high resolution scanning electron microscope NOVA Nano SEM 200 (by FEI EUROPE COMPANY) cooperating with the analyzer EDAX EDS company.

## 2. The obtained results

Thermodynamic solubility of polymers is their ability to formation of stable, homogenous polymer solutions in the whole range of the components quantitative fraction. The chemical affinity of a solvent to a substance being dissolved and their similar polarity constitutes the condition for solving. The solvent role consists in overcoming the van der Waals forces occurring in between individual macroparticles [6].

Mixtures of two or more polymers by their solving in the same solvent can form complex systems of a single phase or of multiphases (the so-called multi-component polymer compositions) in dependence on the structure and properties of polymers and solvents, their concentrations and mixing temperature.

Taking into consideration the general theory of mixing polymers, the verification of the polymer composition was performed taking into account physical and chemical properties of polymer components (molecular mass, polarity, viscosity, pH, concentration) and their chemical affinity to the solvent (water) [7].

As the first component of the composition the synthetic homopolymer from the group of acrylic polymers: poly(acrylic acid) (Fig. 1) was selected.

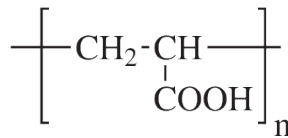


Fig. 1. Structure of poly(acrylic acid)

The second component of the composition was the natural polymer: starch. In order to improve the starch miscibility and solubility in water its chemical modification was performed. The obtained modified carboxymethyl starch (Fig. 2) exhibits better polarity, which means better solubility in water and better miscibility with hydrophilic polymers [8].

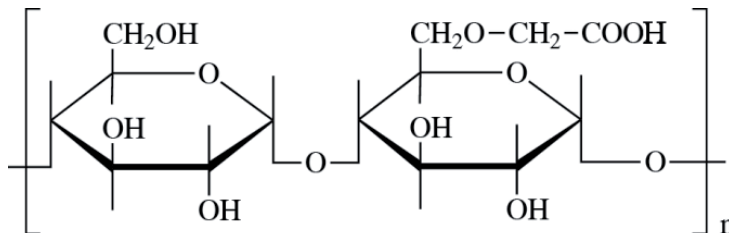


Fig. 2. General formula of carboxymethyl starch

Spectroscopic FT-IR investigations for the initial components (polymers) and after their mixing was performed, which enabled to determine structure changes occurring during the polymer composition formation (Fig. 3).

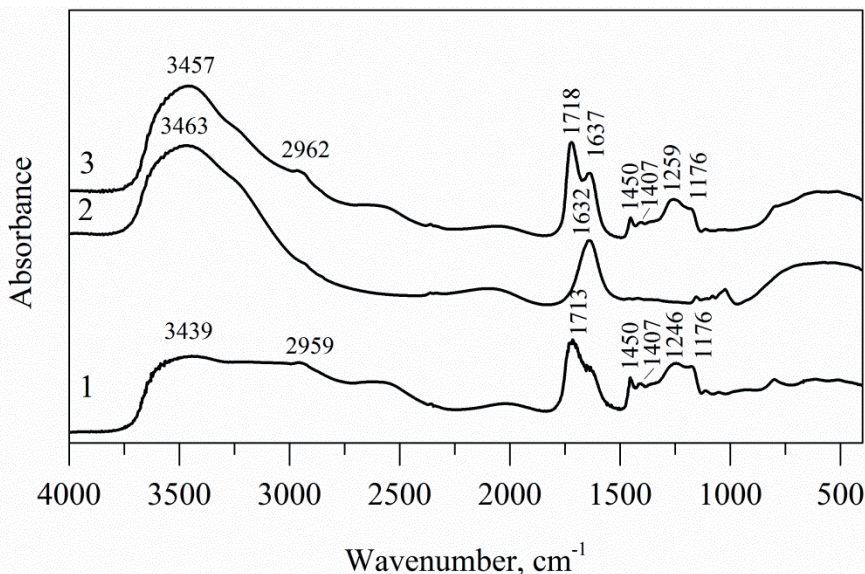


Fig. 3. IR spectra of the PAA/CMS composition: 1 – poly(acrylic acid) solution, 2 – carboxymethyl starch solution, 3 – PAA/CMS solution

Three IR spectra were recorded and the occurrence of a broad band – in the wave number range 3700–3000  $\text{cm}^{-1}$  – corresponding to stretching vibrations of the hydroxyl group (band of free –OH group [water] and hydrogen bond).

The spectrum analysis of the poly(acrylic acid) sample confirmed the presence of groups characteristic for carboxylic acids (1713  $\text{cm}^{-1}$ ) corresponding to the stretching vibrations of carbonyl group: –C=O (Fig. 4, spectrum 1). The band corresponding to stretching vibrations of C–O bond and deforming vibrations of C–O–H was observed in a range of 1246  $\text{cm}^{-1}$ . In the case of the carboxymethyl starch spectrum the band characteristic for the asymmetric vibrations of the carboxylate  $\text{COO}^-$  group and deforming vibrations of C–O–H appears in the wave number range: 1632  $\text{cm}^{-1}$  (Fig. 3, spectrum 2).

During polymer mixing the absorption band of the poly(acrylic acid) from 1713  $\text{cm}^{-1}$  (Fig. 3, spectrum 1) corresponding to asymmetric vibrations of C=O shifts in the direction of higher wave numbers: 1718  $\text{cm}^{-1}$  (Fig. 4, spectrum 3), while bands at 1632  $\text{cm}^{-1}$  and 1246  $\text{cm}^{-1}$  characteristic for vibrations: C–OH and C–O in carboxymethyl starch (Fig. 3, spectrum 2) are also shifted in the direction of higher wave numbers: 1637  $\text{cm}^{-1}$  and 1258  $\text{cm}^{-1}$  (Fig. 3, spectrum 3). These bands can be the result of overlapping vibrations related to the formation – during the composition formation – of new ester type bonds with a participation of carbonyl, carboxyl and hydroxyl groups.

Characteristic absorption bands observed in the IR spectra of the investigated system are given in Table 1.

Table 1. Characteristic bands in the IR spectra of polymers and the polymer composition [9–11]

PAA [cm <sup>-1</sup> ]	CMS [cm <sup>-1</sup> ]	PAA/CMS [cm <sup>-1</sup> ]	Assignment	Remarks
3439	3463	3457	v-OH O-H-O-H O-H-O=C	Band of free OH group (water) Hydrogen bond
2959	–	2962	v-C-H	Bands of stretching vibrations asymmetric and symmetric
1713	–	1718	v <sub>s</sub> -C=O	Stretching vibrations of carbonyl group in carboxylic acids
–	1632	1637	δ-C-O-H v <sub>as</sub> -COO <sup>-</sup>	Deforming vibrations Asymmetric vibration
1450	–	1450	δ (CH <sub>2</sub> ) <sub>n</sub>	Shearing symmetric vibrations
1407	–	–	δ (CH <sub>2</sub> ) <sub>n</sub>	Shearing symmetric vibrations
1246	–	1258	C-O-H C-O	Deforming vibrations Stretching vibrations in a plane
–	1023	–	C-CH <sub>2</sub>	Stretching vibrations

On the grounds of the obtained IR spectra it was found, that there is a possibility of occurrence of the reaction of poly(acrylic acid) and carboxymethyl starch – in the water environment – which reveals itself by changes in a position and intensity of absorption bands in a range of wave numbers: 1700–1600 cm<sup>-1</sup> (Fig. 3). Thus, the structure changes occur within groups: carboxyl (-COOH), present in poly(acrylic acid) and carboxyl and hydroxyl groups (-COO<sup>-</sup> and -OH), contained in carboxymethyl starch.

On the basis of microscopic images, it was found that the composition of PAA/CMS, after drying, are shown separated fractions (starch granules). The obtained results confirm that the polymers PAA and CMS due to the presence of starch grains form a colloidal system (Fig. 4).

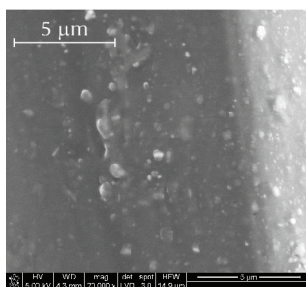


Fig. 4. SEM picture of a polymer composition PAA / CMS.

### 3. Conclusions

On the grounds of the analysis of the IR spectra the structural analysis of the polymer composition PAA/CMS (BioCo1 binder). Spectroscopic investigations for the initial components and after their mixing was performed, which enabled to determine structure changes occurring during the polymer composition formation. On the grounds of the obtained IR spectra it was found, that there is a possibility of occurrence of the reaction in the water environment of poly(acrylic acid) and carboxymethyl starch.

### Acknowledgements

The work was supported by the Project AGH No 11.11.170.318/13

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