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The cross-linking influence of electromagnetic radiation on water-soluble polyacrylan compositions with biopolymers

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Abstract

The results of examinations of the cross-linking influence of electromagnetic radiation - in a microwave range – on polyacrylan compositions with biopolymers, are presented in the hereby paper. The cross-linking process of the tested compositions was determined on the basis of the FT-IR spectroscopic methods. It was shown that microwave operations can lead to the formation of new cross-linked structures with strong covalent bonds. The adsorption process and formation of active centres in polymer molecules as well as in high-silica sand were found due to microwave radiations. In this process hydroxyl groups (-OH) - present in a polymer - and silane groups (Si-O-H) - present in a matrix - are mainly taking part. Spectroscopic and strength tests performed for the system: biopolymer binding agent – matrix indicate that the microwave radiation can be applied for hardening moulding sands with biopolymer binders.

Key words: biopolymer binders, cross-linking, microwaves, moulding sands

1. Introduction

One of the main directions of science and technique developments in the world is now-a-days a complex utilising of renewable raw materials – including polymers - in industry. Apart from a significant cognitive meaning this subject area has also a practical aspect, which is shown by numerous references concerning the use of biopolymers in various industrial branches [1-3]. Therefore endeavours were undertaken to utilise natural raw materials for obtaining casting binding materials. Development of binding agents consisting entirely of natural substances of a vegetable origin, easily biodegradable and simultaneously having good technological properties, constitutes an important scientific challenge. Solution of this problem has an essential ecological and economic meaning. Research concerning application of polymers as binding agents and methods of hardening them in moulding sands has been carried on by the Environment Protection Team of the Faculty of Foundry Engineering for several years [4-8]. Investigations on the development of polymer compositions with a participation of biopolymers, on the cross-linking methods and possibilities of their application as binding agents – are presently carried on. A certain part of this research, namely the one related to the cross-linking reactions of biopolymers under the influence of micro wave radiations, as well as the process of bonding the polymer composition by means of micro waves to be used as binders in moulding sands - are presented in the hereby paper.

2. Examination method

2.1 Materials

The following materials were used in the performed tests:

► Binding agent: polymer composition consisting of acrylic polymer (Fig. 1a) and biopolymer of a vegetable origin (Fig. 1b);

a) b)

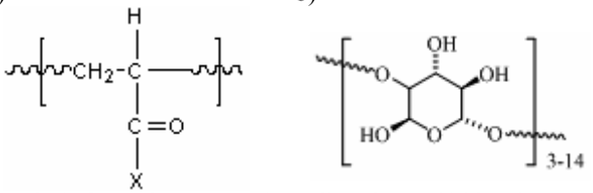


Fig.1. General structure: a) acrylic polymer, b) biopolymer

► Matrix: standard high-silica sand from the sand-pit Jaworzno – Szczakowa (Fig. 2).

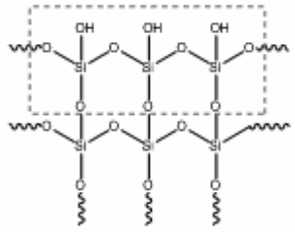


Fig.2. Structure of high-silica sand showing distribution of hydroxyl groups on the sand surface

2.2 Cross-linking of samples

Cross-linking of samples by microwaves was carried on by means of the microwave reactor „RM 2001 Pc" of Plazmatronika Company. The microwave device was equipped with an electronic system of a temperature regulation inside the reactor as well as a regulation of the duration and power of microwaves operations. Samples were subjected to microwaves operations of a power of 800 W for a constant time of 90 s. A temperature inside the device during the radiation was approximately 150°C. After the cross-linking of samples their spectroscopic examinations were performed by the FT-IR method.

The following stages constitute the FT-IR spectra series:

- ►Before a cross-linking – solution of a polymer composition;
- ►After a cross-linking without a matrix – solution of a polymer composition subjected to microwave operations;
- ►Before a cross-linking with a matrix – mixture of a polymer composition solution and a matrix;
- ►After a cross-linking with a matrix – mixture of a polymer composition solution and a matrix subjected to microwave operations.

2.3 Spectroscopic examinations in infrared FT-IR

Spectroscopic examinations in infrared were performed by means of the spectrometer Digilab Excalibur FTS 3000 Mx type with the DTGS detector, electrically cooled. This spectrometer is equipped with the ATR attachment with ZnSe crystal for multiple reflections and with the transmission attachment.

3. FT-IR results and their analysis

Microwave radiation causes significant changes in the structure of the prepared biopolymer composition, which manifests in changes of intensity and distribution of the characteristic bands (Fig. 3). Absorption bands at 1715 cm^{-1} and 1634 cm^{-1} corresponding to vibrations of C=O and C-O-H decay and form a new band at 1723 cm^{-1}. Those changes can be the result of overlapping vibrations related to new bonds (with the participation of carbonyl group C=O of ester or anhydride type) being formed during a cross-linking process. In addition, a band shifting from 1254 cm^{-1} (spectrum 3) in the direction of lower wave numbers 1241 cm^{-1} (spectrum 4) is observed. Decay of bands at 1715 cm^{-1} and 1634 cm^{-1} as well as the creation of a new band as a result of microwave operations indicate that hydroxyl and carbonyl groups take part in the cross-linking reaction.

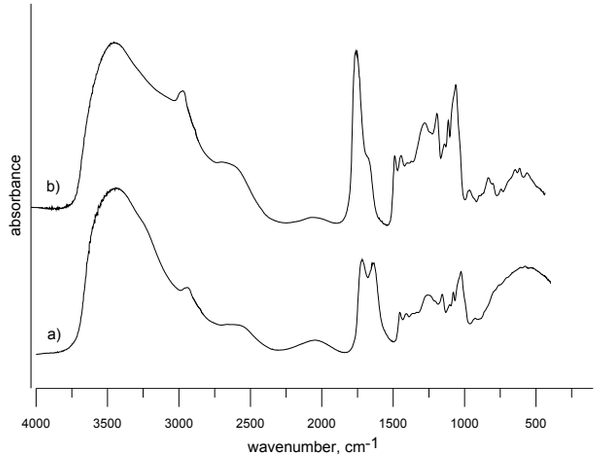


Fig. 3. FT-IR spectra of the polymer composition with the participation of acrylic polymer and biopolymer: a – solution of a polymer composition, b – solution of a polymer composition after microwave operations

FT-IR spectra for the examined system in the range of 4000-400 cm^{-1} are presented in Figure 4 – with taking into account the following stages:

- ►Before a cross-linking – solution of a biopolymer composition;
- ►Before a cross-linking with a matrix participation – mixture of a biopolymer composition solution and a matrix;
- ►After a cross-linking with a matrix participation – mixture of a biopolymer composition solution and a matrix after microwave operations.

Within the wave number range 3700-2900 cm^{-1} a decrease of the absorption band corresponding to stretching vibrations of –OH group can be seen. This happens due to water evaporation during microwave operations. However, even after microwave operations this band is still visible, because hydrogen bonds of the Si-O-H···O-H, or Si-O-H···O=C type are formed. Those bonds are formed in between Si-O-H silane group and COOH carboxyl (on account of the possibility of partial hydrolysis of sodium polyacrylate the presence of COOH groups is probable) or COO^- carboxylane group.

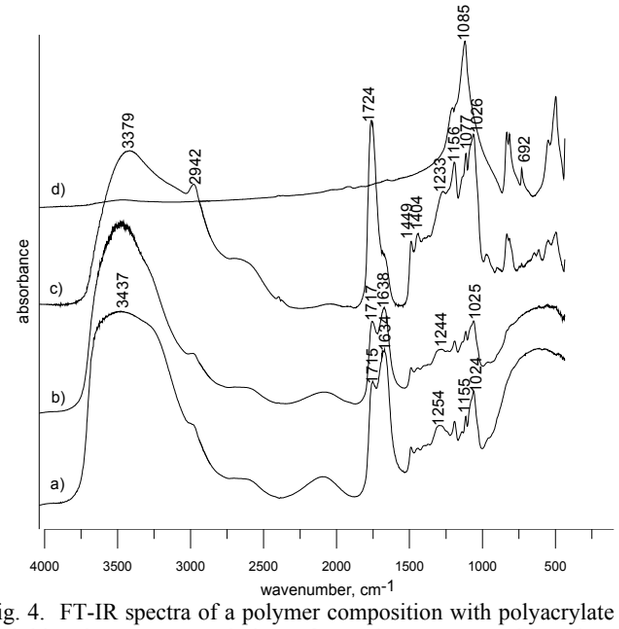
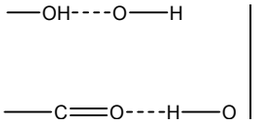


Fig. 4. FT-IR spectra of a polymer composition with polyacrylate and biopolymer: a – solution of a polymer composition, b – solution of a polymer composition + high-silica sand, c – solution of a polymer composition + high-silica sand after microwave operations, d – high-silica sand

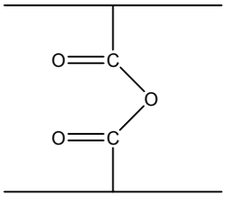
Analysis of the FT-IR spectra (Fig. 4) allowed to observe changes after a cross-linking done by a microwave radiation corresponding to the presence of:

►Hydrogen bonds:



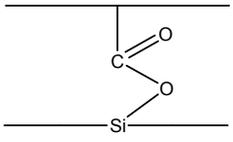
►Band in the range 3700-3000 cm^{-1} (FT-IR spectra a, b, c,) changes of the shape and of the band maximum.

►Anhydride bonds formed due to a dehydration reaction under an influence of a temperature:



►Decay of bands at 1715 cm^{-1} and 1634 cm^{-1} (FT-IR spectra a, c)
►Formation of a new band at 1724 cm^{-1} (FT-IR spectrum c)

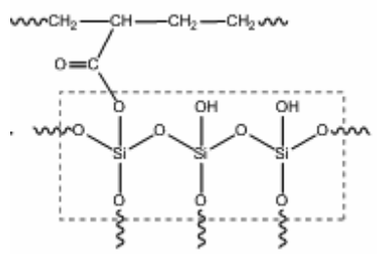
►Bonds with silane groups:



►Band at 1750 cm^{-1} (FT-IR spectrum c)
►Band shifting from 1254 cm^{-1} (FT-IR spectrum a) to → 1233 cm^{-1} (FT-IR spectrum c)
►Band shifting from 1085 cm^{-1} (FT-IR spectrum d) to → 1077 cm^{-1} (FT-IR spectrum c)

4. Polymer adsorption on a matrix surface during microwave operations

Interfacial reaction in the system: binding agent – matrix in the first contact of both phases (polymer and high-silica sand) occurs by physical adsorption related to attraction forces: dispersial, electrostatic or van der Waals. However, significant increase of a temperature created by microwave radiations weakens this type of interfacial binding and therefore a physical adsorption process is here meaningless. A significant role plays a chemical adsorption due to which stable chemical bonds between a polymer and matrix are formed:



The chemical adsorption is a process thermally activated and can occur in the determined temperature range. In the case of the system under testing: binding agent – matrix, this temperature range is within 100-200°C. Below 100°C a reaction rate is too low while above 200°C the state of equilibrium is shifted towards desorption, for thermodynamic reasons. Above a temperature of 300°C a polymer destruction takes place [9-12].

Thus, microwave radiations by activating polymer molecules as well as surfaces of high-silica matrix (silane groups) caused - in consequence – a chemical adsorption and highly cross-linked structures with strong covalent bonds of C-O-Si type (FT-IR spectra, Fig. 4).

Strength tests R_c^u performed for the system: biopolymer binding agent – mineral matrix indicated that the microwave radiation can be applied for hardening moulding sands with biopolyacrylic binders. The prepared moulding sand consisted of 100 parts by weight of matrix and 2.9 parts by weight of biopolymer binder. Microwave power was 800 W, and time of operation 90 s. Under these conditions a compressive strength of the prepared samples was equal 2 MPa [13].

In addition, on the basis of testing the strength properties R_c^u of the hardened samples of moulding sands, a slight increase of those properties – as compared to moulding sands with polyacrylate binders [4-7] - was found.

5. Conclusions

The performed analysis of the FT-IR spectra allows to state, that during the microwave radiation the cross-linking processes can occur. New intermolecular hydrogen bonds between polymer chains and surface layers of a matrix are formed. First of all, hydroxyl groups (-OH) - present in a polymer - and silane groups - present in a matrix - are taking part in this process. Moreover, during microwave operations the dehydration reactions occur between two carboxyl groups either from the same polymer chain or from adjacent chains.

As a result of microwave radiations the adsorption processes take place, active centres are formed both in polymer molecules and in high-silica sands. A simultaneous excitation and a reactivity increase of the surface layer of quartz crystals with silane groups followed by their reaction with carboxyl or carboxylate groups – seems to be very important.

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References

[1] Mohanty A. K., Misra M., Drzal L. T.: Natural fibres, biopolymers and biocomposites, Taylor & Francis Group, USA, (2005).
[2] E. Olędzka, M. Sobczak, W.L. Kołodziejski: Polymers in medicine – review of recent studies, Polimery, vol. 52, No 11/12, (2007) p. 795-804.
[3] Zhou X., Yang J., Qu G.: Study on synthesis and properties of modified starch binder for foundry, Journal of Materials Processing Technology, 183, Issues 2-3 (2007) p. 407.
[4] Grabowska B., Holtzer M.: Networking and useing polyacrylate as binders of mould sands Acta Metallurgica Slovaca, No. 3 (2001), (1/2), Year-book 7, p. 56.
[5] Grabowska B., Holtzer M.: Application of a Microwave Radiation as a Cross-linking Factor in the System: Sodium Polyacrylate – Silica Gel, Polimery (2007), 52, No. 11/12, p. 841-847.
[6] Grabowska B.: Biopolimers – structure, properties and applicability in the foundry industry, Archives of Foundry Engineering, (2008) vol. 8 iss. 1 p. 51–54.
[7] Grabowska B., Holtzer M.: Possibilities of using the biopolymers as binders for the moulding and core sands, Przegląd Odlewnictwa, (2008) vol. 58, No. 4, p. 212-215 (in Polish).
[8] Grabowska B., Holtzer M.: Application of Spectroscopic Methods for Investigation of Cross-Linking Process of Sodium Polyacrylate by Various Methods, Polimery, (2008) vol. 53, No. 7/8, p. 531-537.
[9] Sarbak Z.: Adsorption and Adsorbers, (2000) Wydawnictwo Naukowe, Poznań (in Polish).
[10] Jian-Zhong Ma, Jing Hu, Zhi JIe Zhang: Polyacrylate/silica nanocomposite materials prepared by sol-gel process, Europan Polymer Journal 43 (2007) p. 4169-4177.
[11] Vermöhlen K., Lewandowski H.: Adsorption of polyacrylic acid on aluminium oxide: DRIFT specytroscopy and ab initio calculations, Physicochemical and Engineering Aspects, (2000) 170, p. 181.
[12] Spange S., Vilsmeier E.: Colloid Pollym Sci 277 (1999) p. 687-693.
[13] Grabowska: Polimery, Cross-Linking and Application of Polyacrylan Compositions with Biopolymers Used as Moulding Sands Binding Agents Part 1. Polyacrylan Compositions - Containing Dextrin - Cross-Linked by Means of Microwaves (2009) - in print.