ARCHIVES OF METALLURGY AND MATERIALS
Volume 54 2009 Issue 2

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STRUCTURAL EXAMINATION OF THE CROSS-LINKING REACTION MECHANISM OF POLYACRYLATE BINDING AGENTS

BADANIA STRUKTURALNE NAD MECHANIZMEM REAKCJI SIECIOWANIA SPOIW POLIAKRYLANOWYCH

The results of structural investigations (FTIR, Raman, NMR) performed in order to determine mechanisms of cross-linking reactions of samples of polyacrylic binding agents: sodium polyacrylate. Chemical methods ($Ca(OH)_2 + CO_2$) as well as physical ones (microwave and UV radiations) were applied as cross-linking factors.

During the chemical cross-linking reaction of sodium polyacrylate by means of $Ca(OH)_2$ and CO_2 divalent Ca^{2+} cations are built-in into a polymer chain in place of monovalent Na^+ cations. The reaction is ionic and no changes in the position of absorption bands - before and after cross-linking – are seen on the obtained spectra.

The cross-linking reaction of sodium polyackrylate by electromagnetic radiation (microwaves and UV) occurs with a formation of new chemical bonds with a participation of carbonyl groups (ester, anhydride, aldehyde or ketone). Position changes of absorption bands before and after the cross-linking reaction are observed on the obtained spectra.

In cross-linking done by microwaves the active centres on polymer particles are formed. Atomic excitations and the polymer reactivity increase occurs simultaneously and as the result the cross-linking reaction between polymer chains takes place (with a participation of carboxyl or carboxylate groups).

The cross-linking reaction by the UV radiation occurs with the formation of active radicals in polymer particles. Those radicals can further react with each other an in consequence the cross-linked product of a complicated structure is formed.

The performed structural examinations have proved that the kind of the applied cross-linking factor is essential for the reaction mechanism as well as for the final physical and chemical properties of the hardened moulding sands.

Keywords: polyacrylates, cross-linking, microwaves, UV radiation, foundry engineering

W prezentowanym artykule przedstawiono wyniki badań strukturalnych (FTIR, Raman, NMR) wykonanych w celu opracowania mechanizmu reakcji sieciowania próbek spoiwa poliakrylanowego: poli(akrylan sodu) Sokalan CP10, BASF. Jako czynniki sieciujące zastosowano metody chemiczne ($Ca(OH)_2 + CO_2$) oraz fizyczne (promieniowanie mikrofalowe, promieniowanie UV).

W procesie sieciowania chemicznego poli(akrylanu sodu) za pomocą $Ca(OH)_2 + CO_2$ następuje wbudowywanie się w łańcuch polimerowy dwudodatnich kationów Ca^{2+} w miejsce jednododatnich kationów Na^+. Reakcja ma przebieg jonowy i nie obserwuje się zmian w położeniu pasm absorpcyjnych przed i po sieciowaniu na otrzymanych widmach.

Reakcja sieciowania poli(akrylanu sodu) promieniowaniem elektromagnetycznym (mikrofalowym i UV) zachodzi przy utworzeniu nowych wiązań chemicznych z udziałem grupy karbonylowej (grupy estrowe, bezwodnikowe, aldehydowe, ketonowe). Na otrzymanych widmach obserwuje się zmiany w położeniu pasm absorpcyjnych przed i po sieciowaniu związane z przebiegiem reakcji sieciowania.

W procesie sieciowania mikrofalami poli(akrylanu sodu) powstają centra aktywne w cząsteczkach polimeru. Zachodzi jednoczesne wzbudzenie atomów oraz wzrost reaktywności polimeru, a w następstwie reakcja sieciowania między łańcuchami polimerowymi z udziałem grup karboksylowych lub karboksylanowych.

Reakcja sieciowania poli(akrylanu sodu) promieniami UV przebiega z utworzeniem w cząsteczkach polimeru aktywnych rodników, które dalej mogą ze sobą reagować, co w konsekwencji prowadzi do powstania usieciowanego produktu o skomplikowanej strukturze.

Przeprowadzone badania strukturalne dowiodły, że rodzaj zastosowanego czynnika sieciującego ma istotny wpływ na mechanizm reakcji sieciowania polimeru, jak również na późniejsze właściwości fizykochemiczne utwardzonej masy odlewniczej.

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1. Introduction

Reference data [1, 2, 3] indicate that cross-linking of polymer plastics can be done by various ways: in chemical reaction (poly-condensation, copolymerisation), under a temperature or electromagnetic radiation influence. Strong covalent bonds formed in cross-linking reactions have a substantial influence on the final mechanical properties, especially strength, of the polymer. Weaker ionic bonds, especially hydrogen bonds form reversible lattices, which at higher temperatures are melting without decomposition and return into the lattice state after cooling. During cross-linking of macromolecules also weaker secondary chemical bonds such as hydrogen bonds, van der Waals intermolecular forces, or lateral covalent bonds (Fig.1) are formed. Products formed in actual cross-linking processes contain various structures different than the ideal lattice.

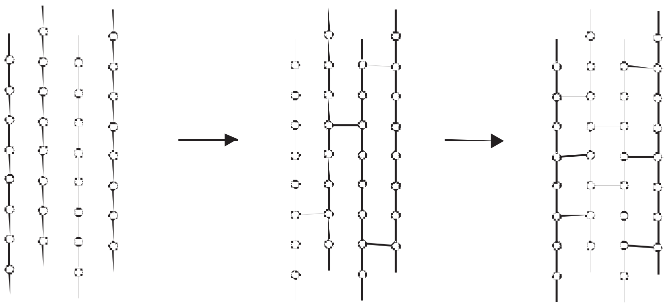

Fig. 1. Cross-linking of long-chain molecules [1]

Acrylic polymers obtained from acrylic acid and its derivatives such as esters, amides or chlorides are characterized by the mer structure presented in Fig. 2 (acrylic series), where X can be: -OH, -OMe, -OR, -NH_2 or -Cl [1].

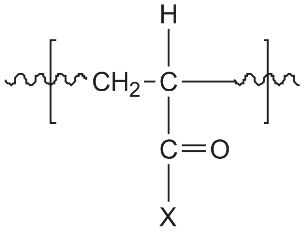

Fig. 2. General formula of an acrylic polymer

Acrylic acid polymers, due to their physical and chemical properties, have found application in several industry branches [5, 6, 7, 8]. Foundry engineering is one of the fields where trials of the technological utilisation of acrylic polymers were undertaken. Those polymers are applied as binding agents in castings (moulding and core sands) [7, 9, 10, 11].

Investigations on applying various cross-linking methods of binding agents from the group of acrylic polymers and attempts of the explanation of their cross-linking mechanisms were undertaken in the paper.

2. Investigation methodology

Materials

The following samples were used in tests:

1. Binding agent: sodium polyacrylate, Sokalan CP10, molar mass 4 000 g/mol, concentration 45 %, pH 8.5, viscosity 500 mPa.s, produced by BASF Company;
2. $Ca(OH)_2$ (analytically pure), Polish Chemical Reagents S.A. Gliwice;
3. CO_2 gas.

Cross-linking of samples

The list of the applied cross-linking methods together with the equipment used and cross-linking conditions is given in Table 1. Structural tests were performed after the cross-linking procedure.

TABLE 1

List of the applied cross-linking methods

Hardening factor	Equipment	Conditions of hardening
CO_2	Run-purging device supplying CO_2	CO_2 run-purging time 60 s
Microwaves	Microwave device RM 2001 Pc of Plazmatronica Company	Microwave power 800 W Time of operation 150 s
UV radiation	Photochemical reactor RAYONET	Wave length 300 nm Time of operation 1h

3. Structural investigations

Spectroscopic tests in **infrared FT-IR** were carried on 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.

Raman spectroscopic measurements were performed by the trinetlike spectrometer of the Yobin Yvon Company, model T64000 and the Fourier spectrometer of the Bio-Rad Company.

13C NMR spectra of the tested polymers were obtained by the Bruker AMX spectrometer 500 MHz. Polymer samples were dissolved in D_2O. All measurements were done at the room temperature.

4. Structure analysis of samples chemically cross-linked – with the participation of calcium cations

FT-IR spectra of sodium polyacrylate before and after cross-linking performed by means of calcium hydroxide and CO_2 in the range of 4000-400 cm^{-1} are presented in Figure 3. A wide band corresponding to stretching vibrations of the hydroxyl group (band of a free OH group [from water] and hydrogen bonds) occurs in the range of wave number 3700-3000 cm^{-1}. Negligible differences in the shape of this band – before and after the cross-linking – are the result of -OH groups participation in hydrogen bonds. Characteristic absorption bands at the wave number 1651 cm^{-1} corresponding to deformation vibrations C-OH and two bands at 1559 cm^{-1} and 1324 cm^{-1} typical for salts of carboxylic acids (symmetrical stretching vibrations of carboxyl anions $-COO^{-}$) occur on the obtained FT-IR spectra. Small changes in the shape of those bands indicate structural and conformation changes occurring during material hardening and are solely related to building-in of Ca^{2+} cations in place of Na^{+} cations in a polymer chain. The band corresponding to stretching vibrations of C-O bond and deformation vibrations of C-O-H group occurs at the wave number 1246 cm^{-1}. An exchange of ions is accompanied by conformation changes in the polymer structure, what exhibits itself in a general shape of spectra. However, there are no changes in absorption band positions before and after cross-linking.

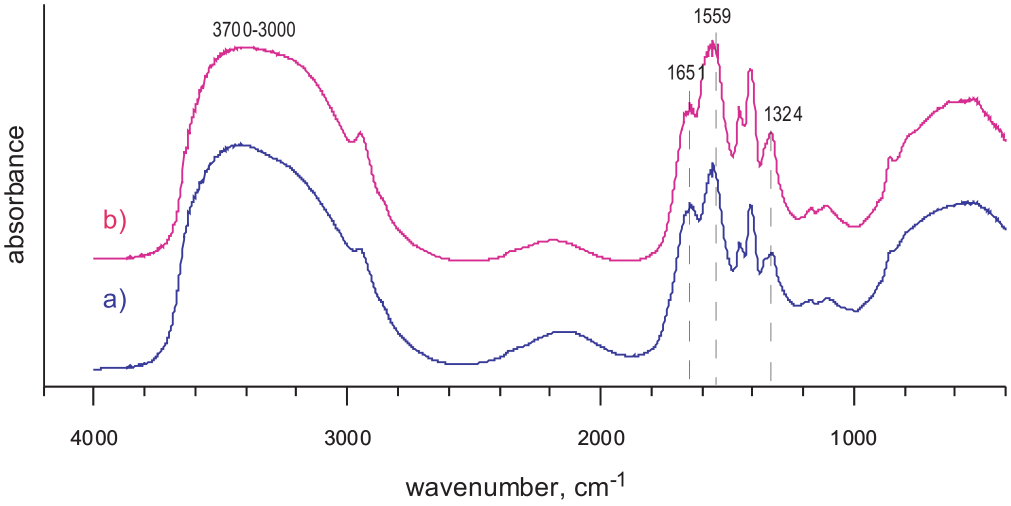

Fig. 3. FT-IR spectra: a) sodium polyacrylate solution, b) sodium polyacrylate solution $+Ca(OH)_2+CO_2$

Polyacrylate structure before and after cross-linking was confirmed on the basis of ^{13}C NMR spectrum. Signals at 184.8 ppm and 183.4 ppm originated from carbon atoms of carbonyl group in carboxylic acids are seen in NMR spectrum presented in Figure 4.

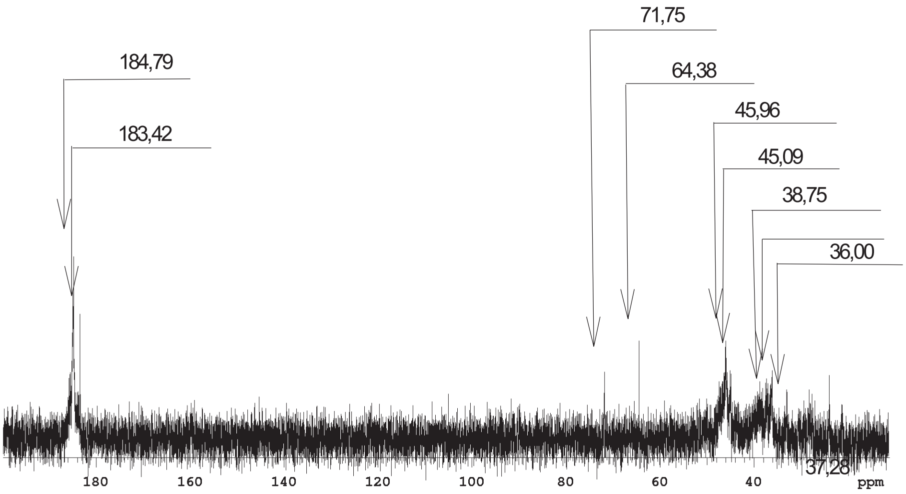

Fig. 4. ^{13}C NMR spectrum of sodium polyacrylate solution in D_2O

Three signals 64.38 ppm, 45.9 ppm and 45.1 ppm can be assigned to C_α carbon atoms while signals 38.7 ppm, 37.3 ppm, 36 ppm belong to C_β carbon atoms (Fig. 5).

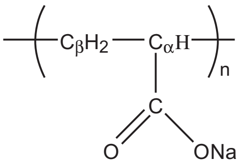

Fig. 5. Sodium polyacrylate structure

After polyacrylate cross-linking by means of $Ca(OH)_2$ with the participation of CO_2 – on the NMR spectrum presented in Figure 6 – a decrease of the signal intensity from -C=O group ($\delta^{1)}$=184.9 ppm, δ=183.4 ppm) can be noticed. Additionally the weak signal appears at 183.9 ppm. This new signal occurring in the NMR spectrum – after hardening – is probably related to calcium atoms building-in into a polymer chain. A weak signal at 45.6 ppm originates from C_α carbon atoms and a signal at 36 ppm from C_β carbon atoms (Fig. 6). A decrease of number and intensity of signals in this spectrum can be explained by more difficult (after hardening) solubility of calcium polyacrylate sample in D_2O.

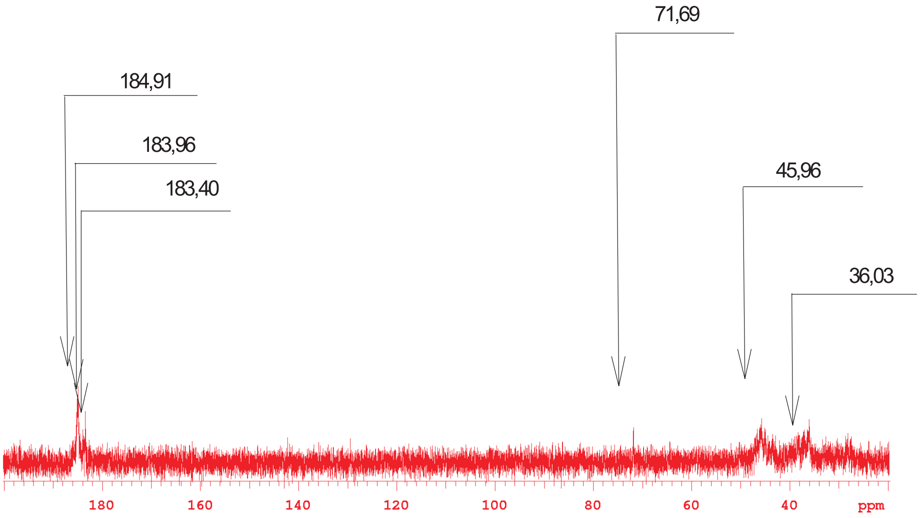

Fig. 6. ^{13}C NMR spectrum of sodium polyacrylate + $Ca(OH)_2$+CO_2 solution in D_2O

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1) δ – chemical shift – determines the difference in constant screening of the nucleus in a standard and in a sample. δ value is an abstract number of the order 10^{-6}, thus, pseudo-unit "part per million" [ppm].

5. Structure analysis of samples cross-linked by the microwave radiation

Figure 7 presents FT-IR spectra of sodium polyacrylate sample cross-linked by means of microwaves in the range of 4000-400 cm^{-1}. A decrease of the absorption band corresponding to stretching vibrations of -OH groups, caused by water evaporation due to microwaves action, can be seen in the range of wave numbers 3700-2900 cm^{-1}. The absorption band of sodium polyacrylate solution at 1557 cm^{-1} (spectrum a) corresponding to asymmetric vibrations of COO^{-} during cross-linking by microwaves shifts in the direction of a higher wave number 1567 cm^{-1} (spectrum b), while the band at 1651 cm^{-1} (deformation vibrations of C-OH) smears and shifts with an additional appearance of a broad band at 1750 cm^{-1} (spectrum b). The formed smeared band has no distinct maximum. Those changes can be the result of overlapping of vibrations related to the formation of new bonds with the participation of carbonyl group (of ester or anhydride type).

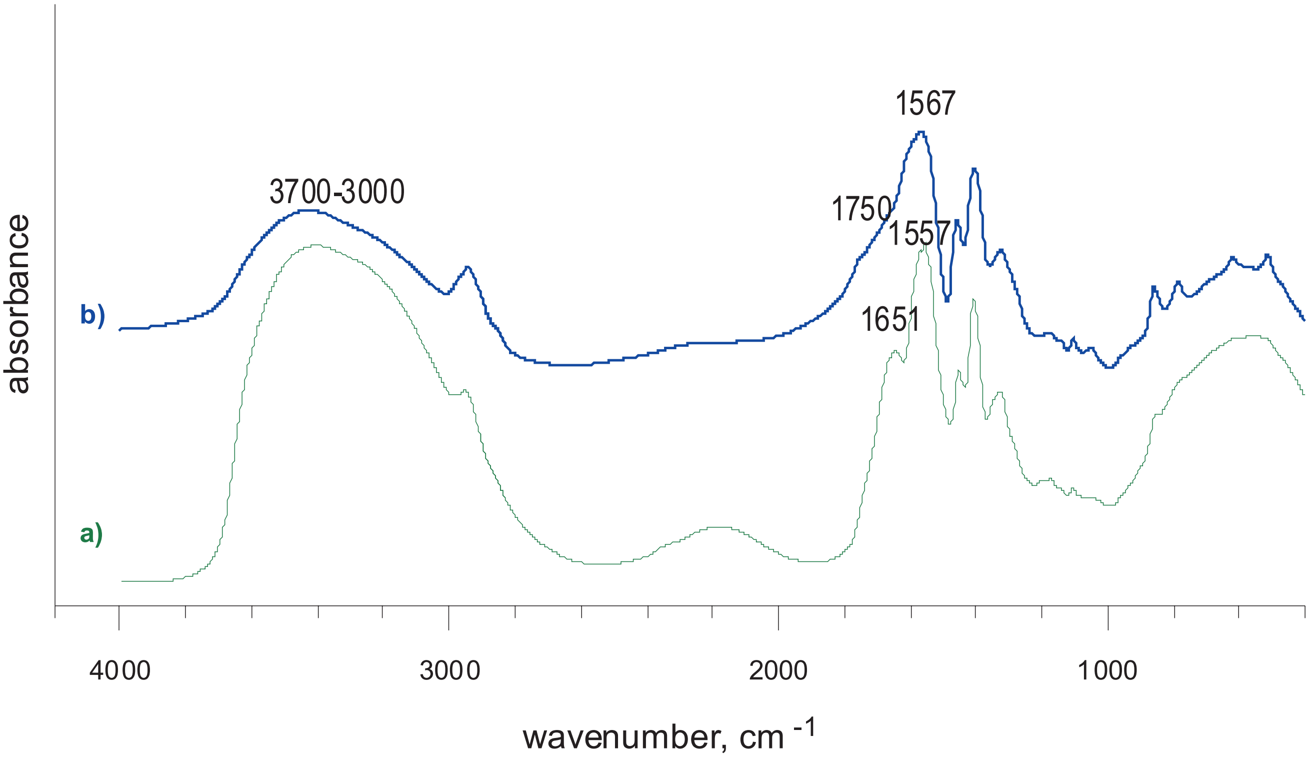


Fig. 7. FT-IR spectra: a) sodium polyacrylate solution), b) sodium polyacrylate solution + microwaves

On the Raman spectra (Fig. 8) within wave numbers 3700-2900 cm^{-1} a decay of an absorption band corresponding to stretching vibrations of -OH groups (3420 cm^{-1}) – in the case of cross-linking done by microwaves – can be seen (spectrum b). The absorption band at 1583 cm^{-1} shifts in the direction of higher wave numbers (spectrum b: 1613 cm$^{-1)}$, while the band within wave numbers 1358-1320 cm^{-1} (spectrum a) is shifted towards lower wave numbers (spectrum b: 1337 cm$^{-1)}$. It can be assumed that band shifts are the result of overlapping of vibrations related to the new ester bonds formation during the cross-linking reaction (spectrum b).

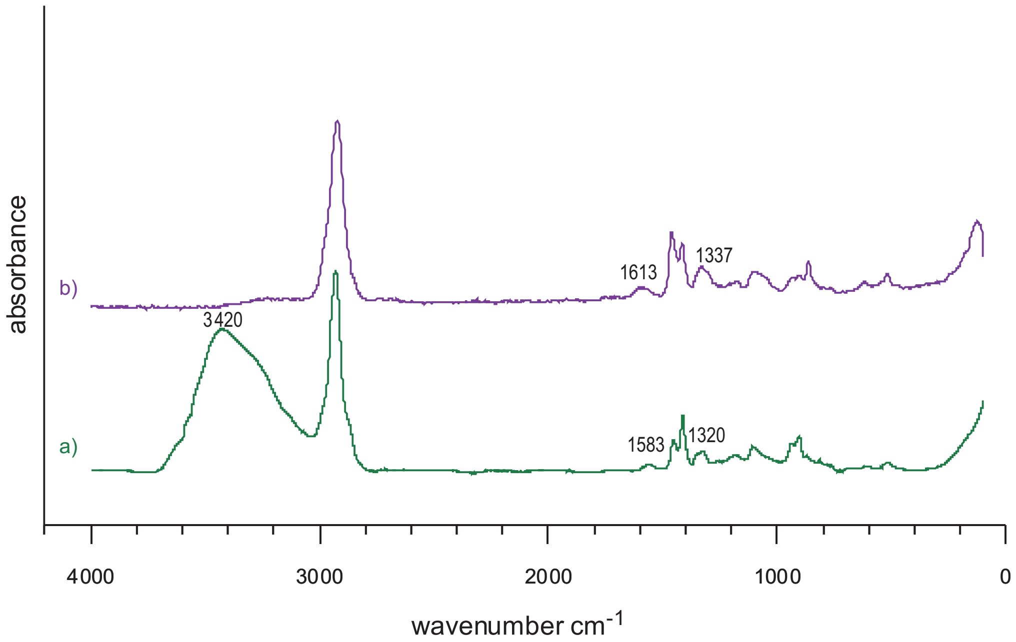


Fig. 8. Changes in the Raman spectra: a) sodium polyacrylate solution, b) sodium polyacrylate solution + microwaves

NMR spectrum presented in Figure 9 exhibits a new signal at 220.92 ppm, after cross-linking done by microwaves. It can be assigned to carbon atoms appearing in ester or anhydride group. A decay of the signal originated from carbonyl group -C=O (δ=183,4) can be also observed, which indicates that this part of carbon atoms might be participating in the formation of new bonds. Signals at 45.96 ppm and 45.09 ppm belong to carbon atom C_α, while signals at 38.75 ppm, 37.28 ppm and 36 ppm to carbon atom C_β.

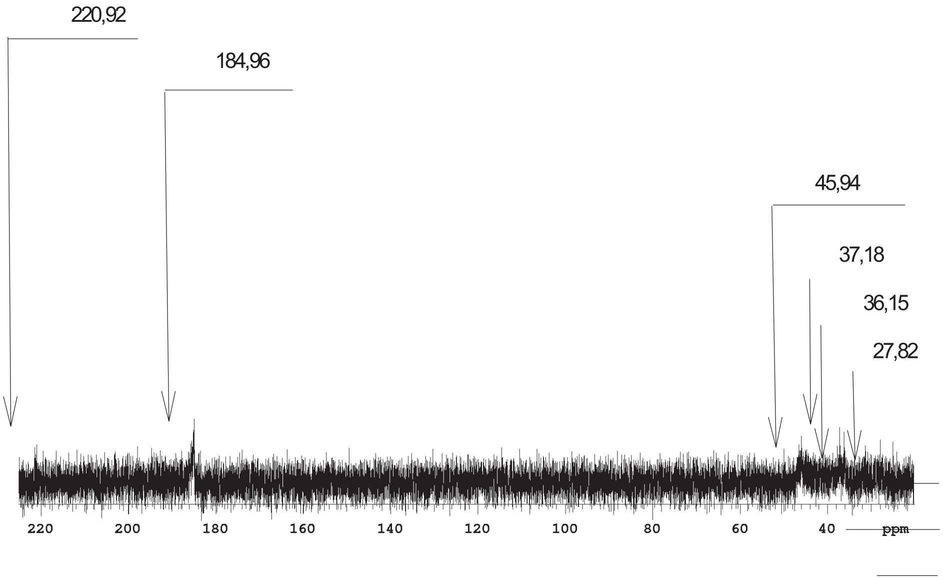


Fig. 9. ^{13}C NMR spectrum of sodium polyacrylate solution in D_2O + microwaves

6. Structure analysis of samples cross-linked photochemically by the UV radiation

Investigations of structure analysis concerning a time-history of the cross-linking reaction of sodium polyacrylate under the influence of the UV radiation were carried on. FT-IR spectra of sodium polyacrylate within the range of 4000-400 cm^{-1} are presented in Figure 10. In the range of wave numbers 3700-2900 cm^{-1} a certain decrease of the absorption band corresponding to stretching vibrations of -OH groups can be observed. It is caused by water evaporation. However, after the cross-linking procedure this band becomes also visible due to the presence of hydrogen bonds.

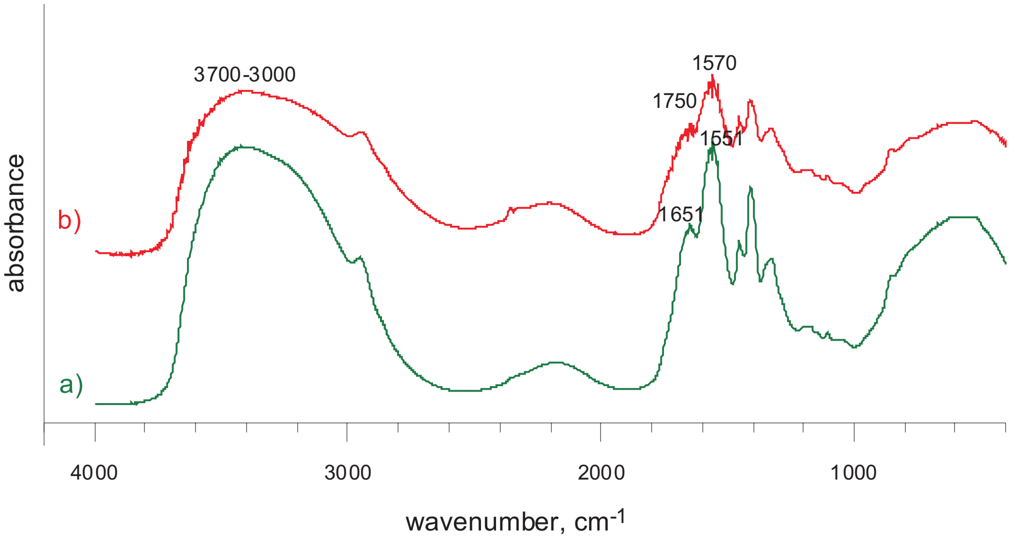


Fig. 10. FT-IR spectra: a) sodium polyacrylate solution, b) sodium polyacrylate solution + UV

The absorption band of sodium polyacrylate solution at 1551 cm^{-1}, corresponding to deformation vibrations of -C-O-H, shifts – during cross-linking caused by the UV radiation – towards higher wave numbers, namely 1570 cm^{-1}, while the band at 1651 cm^{-1} becomes smeared and shifted with an additional appearance of a wide smeared band near 1750 cm^{-1}. This band does not have any distinct maximum. Those changes can be a result of overlapping of vibrations of new carbonyl bonds of aldehyde or ketone type related to a fragmentation of polymer chains during photo-cross-linking as well as to the presence of anhydride groups.

The Raman spectra performed for sodium polyacrylate before and after cross-linking by the UV radiation in the range of 4000 100 cm^{-1} are presented in Figure 11.

Changes related to shifting the absorption band from 3420 cm^{-1} to 3275 cm^{-1} can be seen on the Raman spectra. Intensities and position changes of the band, after hardening, can be attributed to water evaporation and to vibrations of hydrogen bonds of O-H...O=C type, appearing during cross-linking reactions.

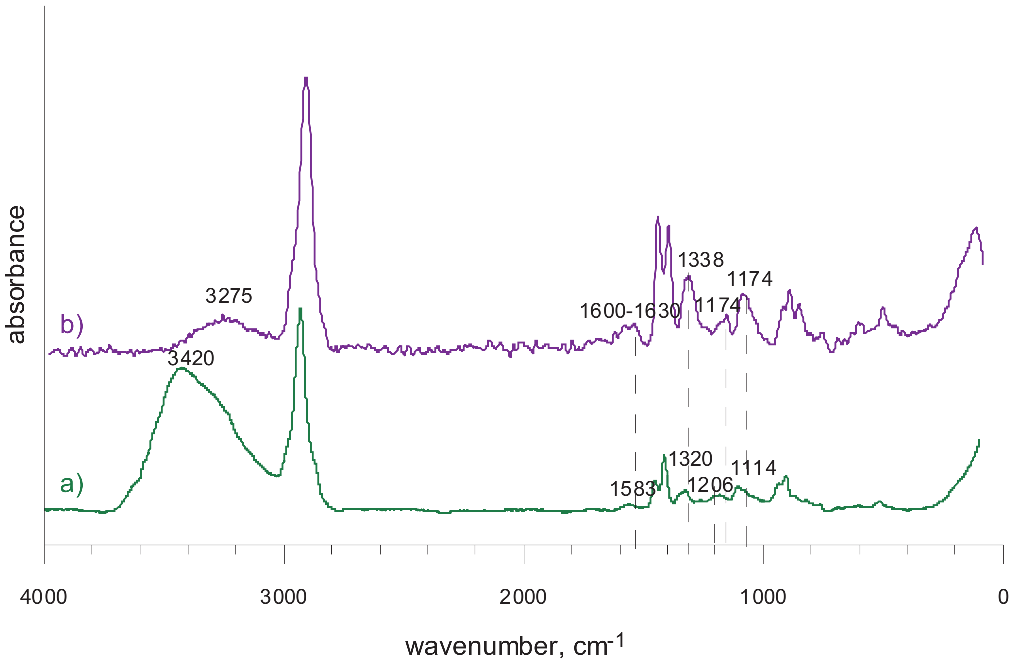


Fig. 11. Raman spectra: a) sodium polyacrylate solution, b) sodium polyacrylate solution + initiator + UV

The absorption band at 1583 cm^{-1} undergoes – during cross-linking by UV – splitting into bands at 1600 cm^{-1} and 1566 cm^{-1}. Additionally a new band at 1630 cm^{-1} is formed. It can be assumed that those shifts are related to overlapping vibrations of new bonds formed during the cross-linking reaction with the participation of carbonyl groups (of aldehyde, ketone or anhydride type). Bands shifting and wave number changes: 1320 $cm^{-1} \rightarrow 1338\ cm^{-1}$, 1206 $cm^{-1} \rightarrow 1174\ cm^{-1}$ can also indicate that COO^- group participates in the formation of new groups.

7. Mechanisms of the cross-linking reaction of sodium polyacrylate

During the cross-linking reaction by means of $Ca(OH)_2$ and CO_2 divalent Ca^{2+} cations are building-in into a polymer chain in place of monovalent Na^+ cations (Fig. 12), which means it is done by bridging. Ions replacements are accompanied by conformation changes in the polymer structure, which has been confirmed by the spectroscopic examinations. Thus, the cross-linked component is formed as the result of the reaction of carboxyl and carboxylate polymer group with metal cations in a water medium [7, 12, 13]. This is an ionic reaction.

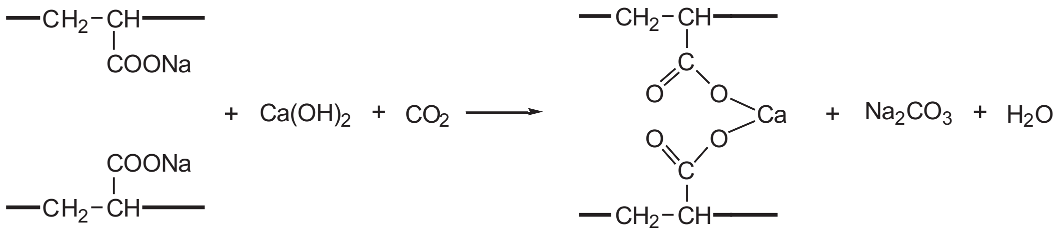


Fig. 12. Reaction of chemical cross-linking between polymer chains

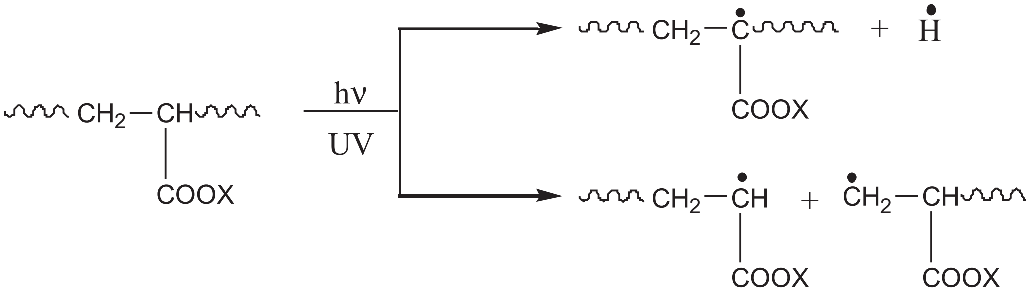
During microwaves action an alternating electric field of a high frequency is interchanging into heat emitting into the examined material. Contrary to other kinds of electromagnetic waves, the microwave radiation causes only molecule rotations in an alternating electric field without disturbing the stability of chemical bonding since the energy transferred by this type of radiation is much lower than the chemical bond dissociation energy. Interactions of the microwave radiation with the matter are done mainly by the reorientation of charged particles or being polar systems in a high frequency electromagnetic field. Active centres are created in polymer particles due to microwave actions, where an increase of reactivity followed by cross-linking reactions in between polymer chains with the participation of carboxyl and carboxylate groups - seems very important [7, 12, 13].

Microwave actions lead to a formation of new intermolecular hydrogen bonds both between polymer chains themselves and between polymer chains and water (O-H···O-H and O-H···O=C).

Additionally microwaves generate an increase of a sample temperature, causing a dehydration reaction between two carboxyl groups belonging to adjacent chains. Strong covalent bonds are being formed in this reaction.

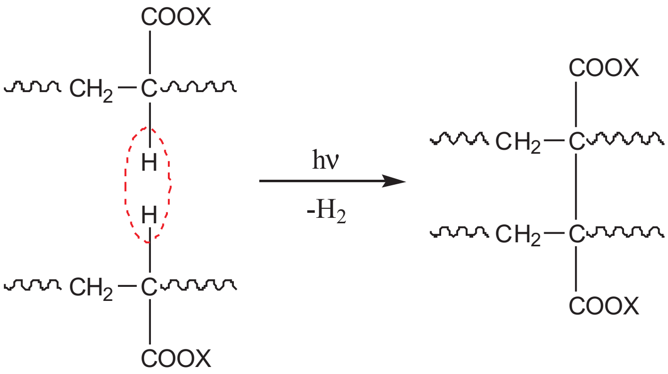
The dehydration reaction is presented below:

The cross-linking reaction of sodium polyacrylate under the influence of the UV radiation occurs with a formation of several intermediate products – active radicals, which can react with each other, what in consequence leads to the cross-linked product of a complicated structure. In addition – under these conditions – polyacrylate undergo a statistic breaking of macromolecule chains in which chain fragments of various length are formed. Energy corresponding to the UV radiation of a wave length 254 nm is satisfactory to chemical bonds C-C or C-H cleavage in examined polymers, but is not sufficient to ionise macromolecules. Therefore a majority of photochemical reactions in polymers is of a radical character. On the basis of the literature data [1, 3, 7, 12, 14] and the performed examinations the following general schemes of mechanisms of polyacrylate cross-linking reactions (with the participation of the UV radiation) – can be proposed (reaction I):

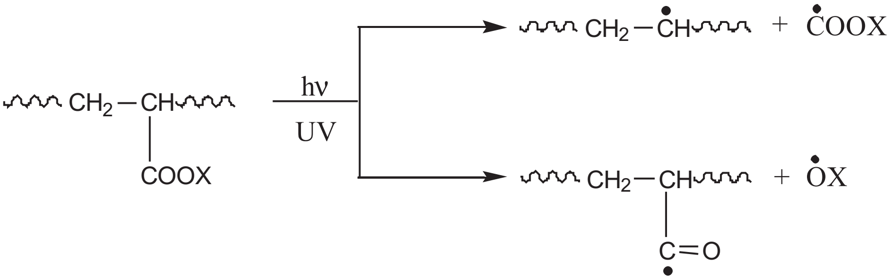


where X means either H or Na atom

Polyacrylates undergo an effective cross-linking also due to the presence of a mobile hydrogen atom at the tertiary carbon atom (reaction II):



Apart the above mentioned processes, reactions of detachment and destruction of side substituents can occur in polyacrylate being radiated (reaction III):



The formed radicals are extremely active and can easily detach hydrogen atoms from adjacent mers as well as can react with atmospheric oxygen. This leads to the formation of new bonds: ketone in the main chain or aldehyde at the macromolecule ends. In addition, the active radicals reacting with each other form branched macromolecules of quite complicated structure. The proposed schemes of the cross-linking reactions under the UV radiation influence are confirmed by the presence of characteristic absorption bands corresponding to hydrogen, anhydride, aldehyde and ketone bonds in FT-IR and the Raman spectra, obtained for the examined sodium polyacrylate. The possible products of the cross-linking reaction done by the UV radiation - with new aldehyde and ketone groups are presented in Figure 13.

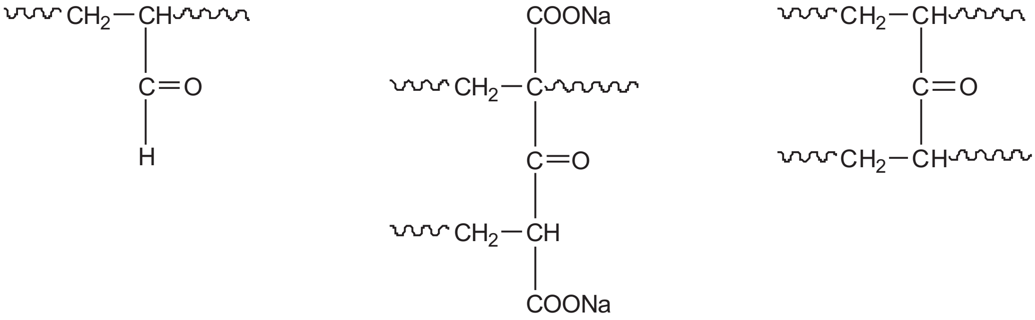


Fig. 13. Products of polyacrylate cross-linking by the UV radiation

8. Conclusions

Phenomena occurring during polyacrylate cross-linking reactions strongly depend on the applied method. Thus, the knowledge of the mechanism of binding agents bonding applied in moulding sands allows for their modification, in a way which will contribute to an improvement of physical, chemical and technological properties and to decrease environment hazards.

It has been shown – on the basis of structure examinations – that the cross-linking reaction of sodium polyacrylate by means of $Ca(OH)_2 + CO_2$ is of a ionic character. On the other hand the cross-linking reaction done by means of the microwave actions is mainly related to dehydration and to formation of inter-chain anhydride covalent bonds. The cross-linking process performed by the UV radiation is done by radicals.

Models of cross-linking mechanisms of the polyacrylic binding agent – proposed in the hereby paper – constitute fully modern approach to the hardening process of moulding sands with organic binding agents. Performing this type of structure examinations at the atomic level, with the application of the most advanced research methods, should allow to design and to manage properly technological processes.

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Preparation of the paper has been supported by scientific project of University of Science and Technology (No 10.10.170.343)

Received: 10 May 2009.