



Crosslink the Novel Group of Polymeric Binders BioCo by the UV-radiation

B. Grabowska*, K. Kaczmarek, A. Bobrowski, Ż. Kurleto-Koziol, Ł. Szymański
AGH University of Science and Technology, Department of Casting Process Engineering,
Faculty of Foundry Engineering, Reymonta 23 St, 30-059 Krakow, Poland
*Corresponding author: E-mail address: beata.grabowska@agh.edu.pl

Received 08.04.2016; accepted in revised form 10.05.2016

Abstract

The spectroscopic FT-IR and FT-Raman methods allowed to identify the cross-linking process of the aqueous composition of poly(acrylic acid)/sodium salt of carboxymethyl starch (PAA/CMS-Na) applied as a binder for moulding sands (as a novel group binders BioCo). The cross-linking was performed by physical agent, applying the UV-radiation. The results of structural studies (IR, Raman) confirm the overlapping of the process of cross-linking polymer composition PAA/CMS-Na in UV radiation. Taking into account the ingredients and structure of the polymeric composition can also refer to a curing process in a binder - mineral matrix mixture. In the system of binder-mineral matrix under the influence of ultraviolet radiation is also observed effect of binding. However, the bonding process does not occur in the entire volume of the investigated system, but only on the surface, which gives some possibilities for application in the use of UV curing surface of cores, and also to cure sand moulds in 3D printing technology.

Keywords: Cross-linking, UV radiation, Spectroscopy, Polymeric binder BioCo, Moulding sands

1. Introduction

The excited state of an electron is related to the transition of an electron with lower energy state to higher energy state. In this case, selection rules are in force, defining the probability of an electronic transition. Electron excitation occurs under the influence of electromagnetic radiation in the ultraviolet (UV) light. Ultraviolet radiation breaks the chemical bond in a selective manner. Energy of ultraviolet light with a wavelength of 254 nm is already sufficient to break the covalent bonds C-C as well as the C-H bond in organic compounds, but not enough to ionize molecules, so photochemical reaction is a radical reaction. Rupture of covalent bonds in the field of UV radiation occurs easily within the tertiary carbon atoms. Molecule that includes a group capable of absorbing ultraviolet radiation within its structure undergoes so many reactions as the mechanism of the

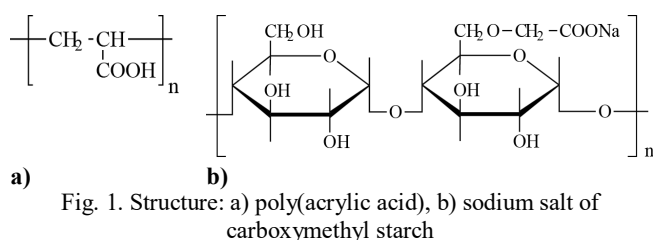
free radical reaction. Most often the three step reaction takes place. The first step consists of photoinitiation, further propagation, and termination [1-3]. To ensure an efficient course of the photochemical reaction of the UV-treated system, photoinitiators are often added to absorb radiation readily and dissociate themselves, which is then the beginning of further steps of the photoreaction, leading to the cross-linking system. For more complex structures of polymers in presence of mobile hydrogen atoms in the construction, a tertiary carbon atom may be involved in the photocrosslinking [2, 3]. In this paper, in the part of research on identifying possibilities for crosslinking by physical and chemical agents, a new group of polymeric binders BioCo was presented [4, 5]. Studies of the course of the process of crosslinking by UV radiation were described. In the electromagnetic field in the ultraviolet range, binder BioCo1 was exposed as an aqueous polymer composition involving poly (acrylic acid) and a modified biopolymer. In order to explain the

photocrosslinking process, FTIR spectroscopy and Raman spectroscopy were used. The results of research and analysis became the starting point in planning the implementation of further work on defining the possibility of selection and use of certain crosslinking agents aimed at curing molding sands bonded by binder BioCo [6, 7].

2. Experimental

2.1. Polymer binder BioCo

The polymeric binder used to the research was BioCo1 [4], a new polymer binder in the form of a water-based composition of PAA/CMS-Na namely a mixture of a synthetic polymer, poly(acrylic acid) (100 000 g/mol, BASF, Fig.1a) and a modified biopolymer: sodium salt of carboxymethyl starch (modified potato starch, degree of substitution (DS ~0.2), Xenon, Fig. 1b). The polymer composition contained 60% of water. The weight ratio of the PAA:CMS-Na polymers in mixture was 4:1.



2.2. Cross-linking of polymer binder

The cross-linking of the polymer sample (5 g) binder by UV radiation was carried out in a photochemical reactor equipped with RAYONET 16 lamps having a wavelength of 260 nm for 15 minutes. Into the binder mixture was added the photoinitiator Irgacure 500 (Ciba Specialty Chemicals).

2.3. Structural investigations

Spectroscopic FT-IR studies 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 cm^{-1} , at the resolution of 4 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.

Measurements were made by the Fourier Transform Spectroscopy, FTS 6000 of the American Bio-Rad Company with FT – Raman attachment.

Measuring parameters:

- laser power on a sample 120 mW,
- resolution 4 cm^{-1} ,
- measuring range: 4000–80 cm^{-1} .

3. Results and discussion

On the basis of IR and Raman spectra, it was found that under the influence of electromagnetic waves in the ultraviolet range in the structure of the polymer composition PAA/CMS-Na significant changes (Fig. 2) are occurred. In the region of wave number at 3700-3000 cm^{-1} for all spectra before and after curing was observed a broad band corresponding to the stretching vibration of the hydroxyl group (the presence of hydrogen bonds). Visible difference in shape and intensity of the bands are the result of the participation in the -OH groups forming hydrogen bonds. Stretching vibration band symmetric and asymmetric C-H were noticed in the range at 3000-2850 cm^{-1} of wavenumber.

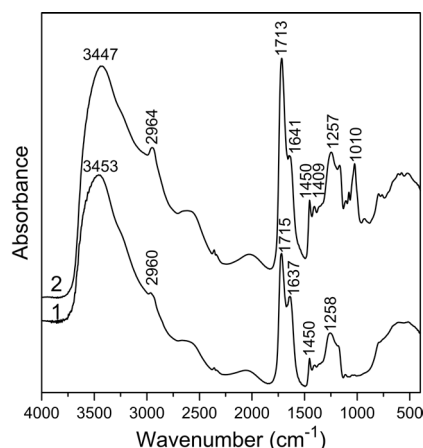


Fig. 2. IR spectra of the polymer composition PAA/CMS-Na: 1 – noncrosslinked form, 2 – UV radiation cross-linked form

Crosslinked polymer composition involving poly(acrylic acid) and sodium carboxymethyl starch was characterized by the presence of characteristic bands for both polymer components of the mixture on the IR spectrum (Fig. 2, spectrum 1: band 1715 cm^{-1} - vibration of C=O, a band of 1637 cm^{-1} - C-O-H vibration and band of 1258 cm^{-1} - vibrations C-O and C-O-H). The cross-linking changed intensity of characteristic bands. Whereas the changing position of the bands was within in the range sensitivity of the method.

On the Raman spectra were observed a distinct change related to the impact of UV radiation on the structure of the polymer composition. Characteristic band in the region of 3000-2900 cm^{-1} was shifted and there was changed its intensity (Fig. 3). This may prove to participate in hydrogen bonding cross-linking process. Furthermore, changes in band position 2940 cm^{-1} may be due to the participation of the C-H photoreaction. A band with peak at 1705 cm^{-1} disappeared and two new - corresponding to the wave numbers of 1690 cm^{-1} and 1645 cm^{-1} (new vibration C-O and C-O-H) - rise of much lower intensity. These changes could be the result of photocrosslinking involving a tertiary carbon atom

(2939 cm^{-1}) and in the carboxyl group (1703 cm^{-1}). Ranges of 1453 cm^{-1} (CH_2 vibration) and 1338 cm^{-1} (C-O-H vibration) were shifted to lower wavenumbers, wherein the intensity was significantly reduced. In addition, after crosslinking, were formed a new bands 1300 cm^{-1} and 1010 cm^{-1} , which probably were associated with vibrations of C-O and C-O-H. In the region of wavenumbers 1340-1100 cm^{-1} was appearing new bands, which can be attributed to stretching vibration of C-C and deformation vibration C-H.

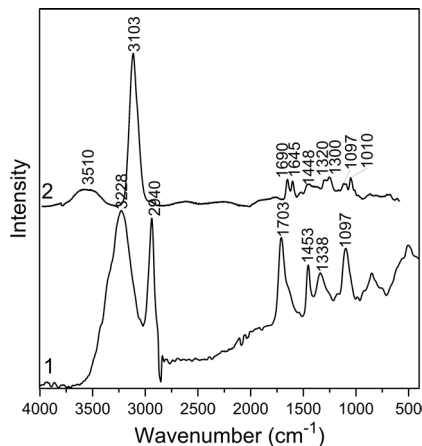


Fig. 3. Raman spectra of the polymer composition PAA/CMS-Na: 1 – noncrosslinked form, 2 – UV radiation cross-linked form

Based on literature data [2, 8-10], and own structural studies it can be concluded that the photocrosslinking the selected polymer composition may occur through excitation in the polymer chain of poly (acrylic acid) a tertiary carbon atom and a carbon atom in the functional group $-\text{COOX}$ (wherein X is H or Na) and the radical reaction course (Fig. 4).

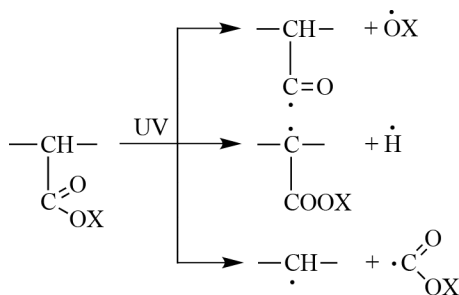


Fig. 4. Diagram of the disintegration process in chain poly(acrylic acid) or its sodium salt

In addition, in the modified polysaccharide under the influence of UV light may occur to breaking the glycosidic bond (photodegradation) to form a cyclic radical [2, 11-13]. Based on structural studies it can be concluded that, in the case of sodium carboxymethyl also occur within the photo-degradation of the glycosidic bond (Fig. 5).

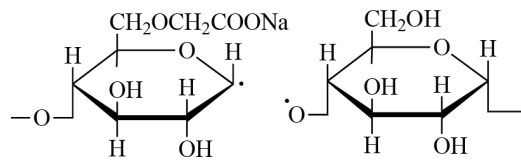


Fig. 5. Scheme of the disintegration process in chain poly(acrylic acid) or its sodium salt

Formed in this way reactive aliphatic or cyclic radicals can undergo further transformations, which in turn leads to permanent cross-linked product of the highly branched structure.

In order to verify the effectiveness of UV radiation in relation to its use in the technology of curing of the polymeric binders from the group BioCo by photocrosslinking, the process was carried out in the binder – mineral matrix system. The test included the preparation of the samples of model binder- mineral matrix mixture, while maintaining the weight ratio of binder to mineral matrix was 10:1.

Proportion of the polymeric binders has been intentionally inflated in relation to the composition used in the moulding sand technology, because of spectroscopic studies planned for the chosen systems. As the matrix was used silica sand from the mine Jaworzno Szczakowa (1K-0.2/0.16/0.32, PN-85/H-11001). The components of each system were stirred for 3 minutes using a mechanical stirrer R-1 (company DANLAB 1000 revolutions/min).

Based on the study, it was found that extending the duration of exposure on UV radiation with a wavelength of 260 nm to 15 minutes does not increase the degree of hydrogenation of the sample of model moulding sand, wherein the samples were still not cured throughout its volume. Exposure samples in UV radiation for one hour resulted in only a surface hardening. This effect may be important in the use of UV curing surface of cores, and also to cure sand moulds in 3D printing technology.

4. Conclusions

Ultraviolet radiation capable of excitation of atoms on electron level has an impact on radical mechanism of the crosslinking reaction of the polymeric binders BioCo. Studied aqueous polymer compositions contain in their structure a group capable of absorbing ultraviolet radiation. UV exposure results in the formation of active polymer chains and cyclic aliphatic radicals, which then undergo further transformations leads to the formation of a crosslinked product of a highly branched structure. The results of structural studies IR and Raman spectra confirm the overlapping of the cross-linking process of polymer composition PAA/CMS-Na and it can also be applied to the curing process in a binder-mineral matrix mixture. In the system of mineral binder-mineral matrix under the influence of ultraviolet radiation was observed binding effect. However, the bonding process does not occur in the entire volume of the sample, but only on it's the surface, which gives some possibilities for application in the use of UV curing surface of cores, and also to cure sand moulds in 3D printing technology.

Acknowledgements

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

References

- [1] Bielański, A. (2002). *Fundamentals of Inorganic Chemistry*, 1. Warszawa. PWN. (in Polish).
- [2] Pączkowski, J. (2003). *Photochemistry polymers. Theory and Application*. Toruń: WN Uniwersytetu Mikołaja Kopernika. (in Polish).
- [3] Czech, Z., Urbala, M. (2007). UV-crosslinked acrylic pressure-sensitive adhesive systems containing unsaturated ethers. *POLIMERY*. 52(6).
- [4] Grabowska, B. (2013). *New polymer binders in form of aqueous compositions with poly(acrylic acid) or his salts and modified biopolymer for foundry practice applications*. Kraków: WN AKAPIT.
- [5] Grabowska, B., Sitarz, M., Olejnik, E., Kaczmarek, K. (2015). *Spectrochim Acta A*. DOI:10.1016/j.saa.2014.07.031.
- [6] Grabowska, B., Sitarz, M., Olejnik, E., Kaczmarek, K., Tyliczszak, B. (2015) *Spectrochim Acta A*. DOI:10.1016/j.saa.2015.06.084.
- [7] Kaczmarek, K., Grabowska, B., Drożyński, D. & Łątka, P. (2014). Analysis of the stability selected properties of polymeric binder on the example of an aqueous solution of the modified starches. *Archives of Foundry Engineering*. 14(SI3), 25–30.
- [8] Czech, Z. & Butwin, A. (2010). UV-initiated crosslinking of acrylic pressure sensitive adhesives using ultraviolet excimer-laser. *Rev. Adv. Mater. Sci.* 23, 32-36.
- [9] Kaczmarek, H. & Metzler, M. (2014). The Properties of Poly (Acrylic Acid) Modified with NPhenylbenzothioamide as Potential Drug Carriers. *The Open Process Chemistry Journal*. 6, 1-7.
- [10] Czech, Z., Kowalczyk, A., Kabatc, J., Shao, L., Bai, Y. & Świdarska, J. (2013). UV-initiated crosslinking of photoreactive acrylic pressure-sensitive adhesives using excimer-laser, *Polym. Bull.* 70: 479–488. DOI 10.1007/s00289-012-0818-7.
- [11] Nagasawa, N., Yagi, T., Kume, T. & Yoshii, F. (2014). Radiation crosslinking of carboxymethyl starch. *Carbohydrate Polymers*. 58, 109–113.
- [12] Wang, C.C. & Chen, C.C. (2005). Physical properties of the crosslinked cellulose catalysed with nanotitanium dioxide under UV irradiation and electronic field, *Applied Catalysis A: General*. 293, 171-179.
- [13] Sionkowska, A., Kaczmarek, H., Vincini, S., Pedemonte, E. & Wiśniewski, M. (2002). The influence of camphorquinone on the photochemical stability of celoluse. *Polymer Degradation and Stability*. 78, 175-182.