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Synthesis and characterization of cellulose-based hydrogels

PhD Theses

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1. Introduction and literature

Hydrogels are systems consisting of a three-dimensional polymer network filled with water. Superabsorbents are hydrogels which can absorb water tens or even hundreds of times of their dry weight. While their biomedical application is the most widely studied, there is a growing interest in their use in other fields, as well. The majority of the commercially available superabsorbents are based on synthetic polymers, usually on acrylates.[1] However, the use of various renewable materials is becoming increasingly important as they not only provide an environmentally friendly alternative for the synthetic polymer-based systems, but they also have numerous advantageous properties.

Cellulose is the most abundant renewable material. Due to its low cost and favorable properties it is widely used in the industry and its significance is still growing, While several studies investigated its application for hydrogel preparation, its insolubility in water is a major drawback as special solvents are required for the process. Thus, the interest shifted mainly to its derivatives as water solubility is easily and cheaply achieved by chemical modification of the cellulose.

Cellulose derivative based systems can form both physical and chemical gels.[2] Chemical crosslinking is achieved either by crosslinking agents – compounds containing two or more reactive groups – or by free-radical crosslinking. For the initiation of the free radical formation, chemical initiators such as persulfates and high-energy irradiation (most notably electron beam or gamma irradiation) are both commonly used. Radiation-initiated crosslinking is becoming more dominant as the chemical gelation can be achieved without the use of additives. As the gels are synthesized from aqueous solutions of the derivatives, the reactive intermediates formed during the radiolysis of water also play a major role besides the direct macroradical formation in the process. The macroradicals participate in further reactions, which can result both crosslink formation (due to the recombination of the radicals) and chain degradation. The gelation of cellulose derivative solutions by radiation-initiated crosslinking was discovered only recently as the gel formation occurs only at high polymer concentrations.[3] There is a major focus on the gelation of carboxymethylcellulose systems, but other major derivatives such as the alkyl, hydroxyalkyl and alkylhydroxyalkyl celluloses were also investigated. However, studies comparing the gelling behavior of different derivatives are not available. The free-radical crosslinking of pure cellulose derivative

[1] Ahmed, E. M., *J. Adv. Res.* 6:105-121 (2015)
[2] Chang, C., Zhang, L., *Carbohyd. Polym.* 84:40-53 (2011)
[3] Fei, B., Wach, R. A., Mitomo, H., Yoshii, F., Kume, T., *J. Appl. Polym. Sci.* 78:278-283 (2000)

systems in the presence of ***crosslinking agents*** was not investigated, either, despite its importance in synthetic polymer-based systems.

Beside pure cellulose derivative gels, there is a large interest in its ***copolymers and composites***, as well. In such systems the incorporation of other components allows the modification of the gel properties depending on the application requirements. This can be achieved either by the addition of inorganic components (composites) or by blending/copolymerization with other polymers. In the latter case, the copolymerization of cellulose derivatives with synthetic polymers was most in-depth studied. ***Acrylates*** are the most important group in this field. As their polymerization and crosslinking occur through free-radical reactions, the use of the high energy radiation for cellulose derivative/acrylate systems is very advantageous. While such systems were already investigated, studies involved gels containing relatively low amounts (<20%) of polysaccharide, thus the properties were mainly determined by the acrylate component.[4] Cellulose derivative/acrylic acid systems containing low concentrations of acrylic acid were not investigated, despite the latter component possibly significantly improving the gelation behavior, while the advantageous properties of the cellulose component are still dominant.

The modification of cellulose derivative systems with other renewable polymers, most notably ***polysaccharides*** such as alginate and chitosan, also holds a major interest. In such systems the copolymerization is easily achieved due to the similar chemical structure. While ***starch*** is, similarly to the cellulose, one of the most abundant, low cost polysaccharide, for the hydrogel preparation mostly its copolymers with synthetic polymers were investigated. Studies regarding cellulose derivative/starch blends are limited to the preparation of films and membranes; for copolymer gel synthesis only the carboxymethyl derivative of starch was used. The preparation of blends with other polysaccharides offers a convenient route for the modification of the gel properties without the introduction of synthetic polymer components. This is especially important in applications where properties like good biodegradability are crucial.

Hydrogels have a wide array of potential application in several fields. For cellulose derivative-based systems, similarly to the synthetic polymer-based gels, medical applications have the largest share, especially as controlled drug release systems, wound dressings and matrixes for tissue engineering; such products are already commercially available. However, nowadays their potential application in wastewater treatment and ***agriculture*** is also

[4] Said, H. M., Abd Alla, S. G., El-Naggar, A. W. M., *React. Funct. Polym.* 61:397-404 (2004)

becoming more apparent. In the latter field they show a big potential as ***soil conditioners***. Water retention of the soil is one of the most important factors in agriculture as the plants need adequate humidity for growth. The addition of superabsorbents leads to improved water retention, thus even sandy soils with low water holding capacity may be suitable for cultivation. Their use as ***controlled release systems for fertilization and pest control*** is another potential application. The incorporation of bioactive molecules in the gel matrix allows exhibiting their beneficial effect over a longer period of time. While studies indicate that such application is very advantageous, most of them focused on acrylate based superabsorbents.[5] However, their poor biodegradability – which may take decades – hinders their practical use.[6] Therefore, recently the demand towards biodegradable soil conditioners based on renewable materials increased.[7]

The goal of my work was the preparation of such cellulose derivative-based superabsorbents with radiation-initiated crosslinking which may be an alternative for the currently commercially available synthetic polymer-based products. First, the gelling behavior of the most common cellulose derivatives was compared and the effect of various synthesis parameters was studied. Besides the determination of the optimal synthesis parameters, the further improvement of the properties with crosslinkers or copolymerization with other components was also investigated. In this case the main goal was the achievement of the best gel properties while the concentration of the non-cellulose derivative component was kept as low as possible. Their potential application in various fields was also investigated: the properties were compared with various commercially available products and their suitability for agricultural use was in-depth studied.

2. Experimental

Superabsorbent gels were prepared from aqueous solutions of carboxymethyl, hydroxyethyl, hydroxypropyl and methyl derivatives of cellulose via radiation-initiated free-radical crosslinking (Co^{60} source, 9 kGy/h dose rate). The effect of the molar properties of the cellulose derivatives and the synthesis parameters (absorbed dose, solute concentration, pH, salt concentration) on the gel properties was investigated and the optimal synthesis conditions were determined for each system. Besides pure cellulose derivative solutions, the

[5] Zohuriaan-Mehr, M. J., Omidian, H., Doroudiani, S., Kabiri, K., *J. Mater. Sci.* 45:5711-5735 (2010)
[6] Wilske, B., Bai, M., Lindenstruth, B., Bach, M., Rezaie, Z., Frede, H. G., Breuer, L., *Environ. Sci. Pollut. R.* 21:9453-2014 (2014)
[7] Guilherme, M. R., Aouada, F. A., Fajardo, A. R., Martins, A. F., Paulino, A. T., Davi, M. F. T., Rubira, A. F., Muniz, E. C., *Eur. Polym. J.* 72:365-385 (2015)

modification of the properties by introducing *N,N'*-methylenebisacrylamide crosslinking agent or the partial replacement of the cellulose derivative component with acrylic acid or potato starch was also studied.

The gel fraction and the degree of swelling were determined for the characterization of the prepared hydrogels. Scanning electron microscope (SEM) was used to study the morphology of the gels, while their chemical composition was determined by FTIR-ATR. The swelling properties of the superabsorbents were in-depth studied. Besides the swelling kinetics, the sensitivity of the swelling to the solvent properties was determined. Various test solutions were used for simulating environmental conditions during application. Commercially available acrylate-based superabsorbents were also characterized and compared to the prepared samples. The potential application of the superabsorbents as agricultural soil conditioners was also investigated. Four soil samples with significantly different properties were used for the experiments. The superabsorbent was mixed in different concentrations with the soil samples and its effect on various soil properties such as the water capacity and the water infiltration rate was studied and the optimal gel concentration was determined.

3. Results

The ***derivative type*** had a major impact on the gelling behavior, thus the optimal dose and solute concentration was different for the derivatives. While gels with excellent water uptake were synthesized from carboxymethylcellulose due to the charged groups on the polymer chain, the electrostatic repulsion also hindered the crosslinking process, leading to lower gel fraction. The other three derivatives required milder synthesis conditions as ionic interactions did not hinder the crosslink formation due to their non-ionic character. The ***molecular mass*** also proved to be a major factor: the gelation improved significantly with the increasing molecular mass. The gelation of the solutions was observed only over a critical dose and solute concentration (**Figure 1.**). Increasing the dose initially led to higher gelation, but at high doses the degradation processes dominated. An optimal polymer concentration range was observed: the gelation was hindered in both dilute solutions (high chain distance) and high polymer concentrations (low chain mobility). For carboxymethylcellulose systems the pH and the ionic strength of the solution also affected the gelation. As higher gel fraction could be achieved usually at the expense of lower water uptake, choosing synthesis conditions where both properties are simultaneously acceptable was crucial.

Carboxymethylcellulose systems (15-20 w/w%, 20 kGy) showed the highest water uptake (200-250 g_{water}/g_{gel}), but relatively low gel fraction (35%) was achieved at the same time. Gels based on the other two derivatives had inferior swelling properties; however, the gelation was significantly higher. While the water uptake of hydroxypropylcellulose and methylcellulose gels was relatively low (20-25 g_{water}/g_{gel}), for hydroxyethylcellulose based systems good swelling (100 g_{water}/g_{gel}) and high gel fraction (50-70%) could be achieved. Therefore, carboxymethylcellulose and hydroxyethylcellulose proved to be the most suitable for superabsorbent preparation.

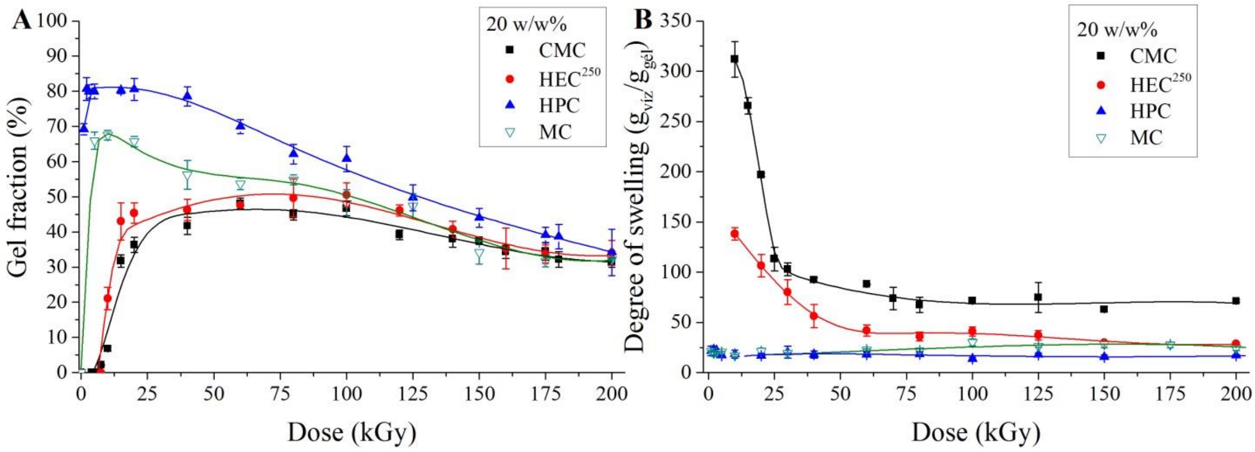

Figure 1. The effect of the dose on the gel fraction (A) and the degree of swelling (B) for different cellulose derivative systems

The gelation improved significantly in the presence of additives such as ***N,N'-methylenebisacrylamide***, thus very mild synthesis conditions (low dose and solute concentration) were sufficient for the gel formation. The gelation improved with the crosslinker concentration, but even 1 $w/w_{polymer}$% MBA proved to be very efficient. Compared to the pure cellulose derivative systems, the simultaneous decrease of the dose and the solute concentration led to the best gel properties. Gels prepared from carboxymethylcellulose solutions containing 1 $w/w_{polymer}$% MBA in sufficiently mild synthesis conditions (7,5-10 w/w%, 5-10 kGy) showed both superior gelation (35-45%) and water uptake (250-350 g_{water}/g_{gel}) compared to crosslinker-free systems.

The partial replacement of the cellulose derivative with ***acrylic acid*** also improved the gelation (**Figure 2.**). While higher monomer concentrations were required compared to the systems containing crosslinker, the solutions gelled easily and even better gel properties were achievable. For carboxymethylcellulose/acrylic acid systems 10% acrylic acid content was optimal: while 7,5 w/w% solute concentration and 5 kGy dose led to similar gel fraction (40%) as the MBA-crosslinked systems, the water uptake of the former was significantly higher (700 g_{water}/g_{gel}). In case of hydroxyethylcellulose systems, the addition of acrylic acid was most efficient up to 5%. For HEC/AAc systems containing high molecular mass (1 300 000 Da) derivative, 60-80% gel fraction and 150-300 g_{water}/g_{gel} water uptake were achieved at 2-2,5 w/w% solute concentration and 5 kGy dose. The swelling further improved after the neutralization of the acrylic acid component with short (15-30 s) NaOH treatment at room temperature. Even gels containing only 5% acrylic showed 2,5-3 times higher water uptake than before the treatment. Therefore, the neutralization proved to be an efficient method to improve the swelling properties even for systems containing low concentrations of acrylic acid.

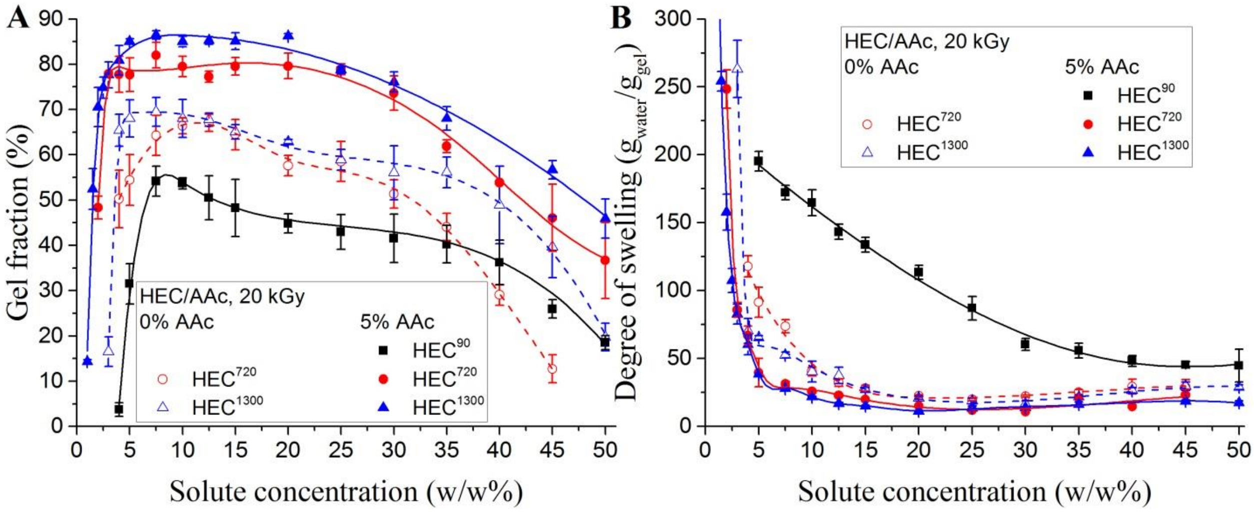

Figure 2. The effect of the solute concentration on the gel fraction (A) and the degree of swelling (B) for hydroxyethylcellulose/acrylic acid gels

The partial replacement of the cellulose derivative with ***starch*** in carboxymethylcellulose systems also had a positive impact on the gel properties. Not only the gel fraction increased significantly with the starch content, but even the water uptake showed a small increase. The properties improved up to 30% starch content, over which the addition of more starch led to poorer properties. The optimal synthesis conditions, unlike systems containing crosslinker or acrylic acid, were similar to those of pure CMC solutions. A major advantage of the CMC/starch systems is the improvement of the gel properties without toxic additives, thus offering an environmentally friendly and low-cost alternative.

The ***swelling kinetics*** proved to be similar for all gels. The swelling process followed second-order kinetics in all cases, while the diffusion mechanism of the water molecules into the gel structure was anomalous based on the Fickian diffusion model. The swelling of carboxymethylcellulose gels was very sensitive to the ***properties of the solvent such as ionic strength, salt type and pH***. On the other hand, the water uptake of the other three derivatives was unaffected by the solvent properties. For copolymer gels, the responsive behavior also changed with the chemical composition. For hydroxyethylcellulose systems, even adding as low as 5% acrylic acid led to a significant sensitivity to the changes of the ionic strength, while for carboxymethylcellulose gels the introduction of starch led to weaker responsivity. This allows the modification of the swelling properties based on the application requirements.

Its importance is also apparent from the comparison of the gels with ***commercial superabsorbent products*** (**Figure 3.**). Pure CMC gels showed excellent swelling properties like the acrylate-based superabsorbents in distilled water, but in the presence of salt (e.g. in Ringer's solution) their water uptake also decreased significantly. Out of the non-ionic cellulose derivatives, hydroxyethylcellulose gels had the most advantageous properties. HEC systems showed superior swelling in an environment of high electrolyte concentration as they were not sensitive to the ionic strength. Cellulose derivative/acrylic acid copolymer gels proved to be even better than pure cellulose derivative based systems. While the addition of acrylic acid to HEC led to salt sensitivity, due to their excellent water uptake such systems showed the best swelling properties even in the test solutions. This is especially advantageous as the acrylic acid content of such systems is still relatively low (5-10%).

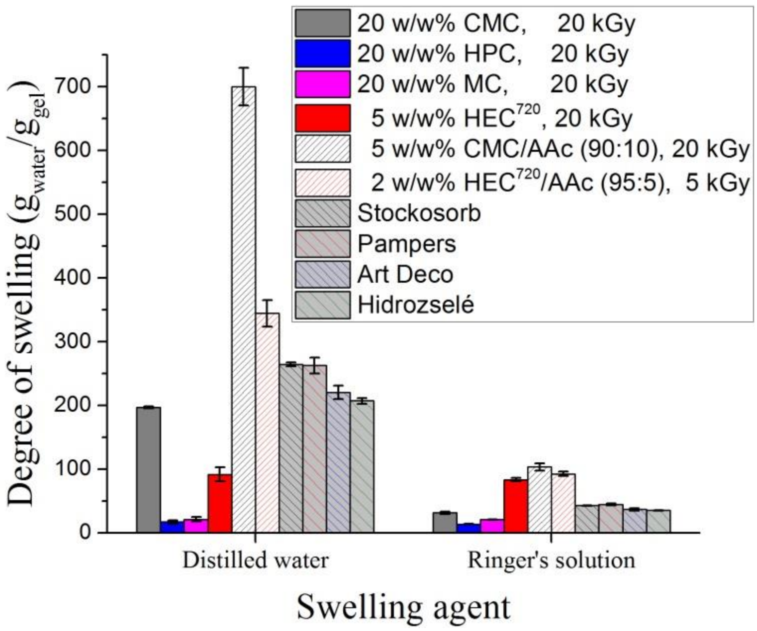

Figure 3. Comparison of swelling properties of cellulose derivative-based and various commercially available acrylate-based superabsorbents in distilled water and Ringer's solution

The water capacity of the various soil samples improved significantly even when only a few permille superabsorbent was added (**Figure 4.**). While the water uptake of the superabsorbent decreased due to the salt present in the soil and the irrigation water, they still showed excellent swelling. The water absorbed in the gel was bound relatively strongly, thus it was not affected by the gravitational drainage and improved the water retention of the upper soil layer. Moreover, the water bound in the soil pores and the gel decreased simultaneously and only minimal water was present in the gel matrix at the permanent wilting point. Therefore, the superabsorbent does not only increase the humidity of the soil, but the absorbed water is also nearly fully available for the plants. The addition of the gel also led to slower water drainage, thus longer period was available for the swelling of the gel particles. The superabsorbent proved to be an excellent soil conditioner especially for sandy soils with poor water holding capacity.

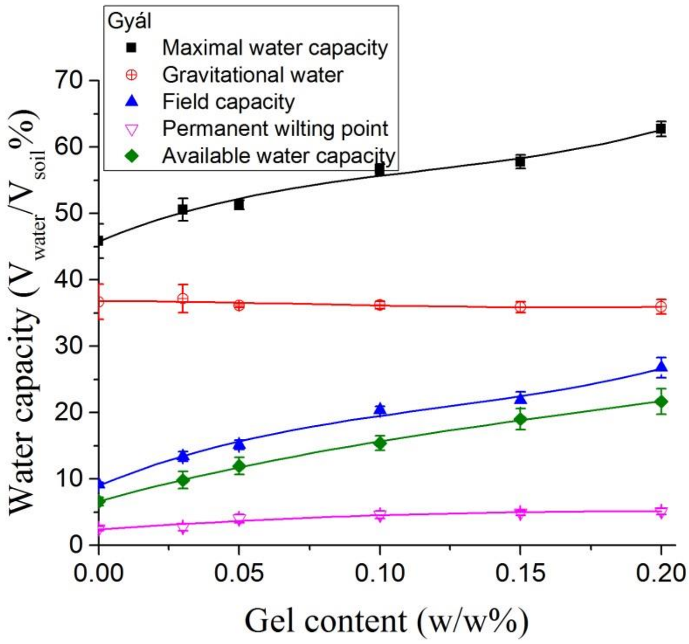

Figure 4. The effect of the gel content on the water capacity of sandy soil (Gyál)

4. Theses

1. In order to prepare biodegradable superabsorbents based on renewable materials I compared the gelling behavior of various cellulose derivative solutions initiated by gamma irradiation. Carboxymethylcellulose (excellent water uptake) and hydroxyethylcellulose (good gel fraction and swelling) proved to be the most suitable for such application. The dose and solute concentration required for good gel properties depended on the derivative type and its molecular weight. The pH and the ionic strength also affected the gelation of carboxymethylcellulose systems. (I, IV)

2. I proved that cellulose derivative systems require significantly milder synthesis conditions for gel formation in the presence of 1 $w/w_{polymer}$% *N,N'*-methylenebisacrylamide crosslinker. The simultaneous improvement of the gel fraction and the water uptake compared to the pure cellulose derivative gels was possible at well-chosen synthesis conditions.

3. I showed that very low dose and solute concentration was required for the gelation after the replacement of the 2-10% of the cellulose derivative with acrylic acid. This also allowed the synthesis of hydrogels from polymers with low molecular mass otherwise showing poor gelling behavior. This method proved to be especially advantageous for non-ionic cellulose derivatives as swelling properties similar to carboxymethylcellulose superabsorbents could be achieved at low solute concentrations. (III, IV)

4. I showed that in carboxymethylcellulose systems the replacement of the cellulose derivative with starch up to 30% significantly increases the gel fraction along with a small increase in the water uptake. The addition of starch had no significant effect on the optimal synthesis conditions. The use of such blends allows the reduction of the synthesis costs. (V)

5. I observed that the swelling properties of the prepared various cellulose derivative-based gels showed different sensitivity to the environmental parameters. As various systems showed excellent swelling properties at different environmental conditions, the sensitivity can easily be modified depending on the application requirements by the derivative type or the introduction of low amounts of acrylic acid or starch. (I, IV, V)

5. Application

The synthesized cellulose based superabsorbents offer a good alternative to the currently commercially available, mainly acrylate-based systems. Due to the lack of non-renewable components or in case of copolymers their very low concentration, they show a large potential in agricultural application. Based on the results, the water retention of the soil increases significantly even in the presence of very low amounts of superabsorbents, thus they are suitable both for the improvement of sandy soils with poor water retention or for the reduction of the irrigation required for soil more suitable for cultivation. Moreover, there is a large potential in their use for the controlled release of fertilizers or bioactive molecules for pest control, as in this field the application of the poorly biodegradable acrylates is restricted.

6. Publications

Publications related to the dissertation

Publications in English:

I. Fekete, T., Borsa, J., Takács, E., Wojnárovits, L., Synthesis of cellulose derivative based superabsorbent hydrogels by radiation induced crosslinking. *Cellulose* 21:4157-5165 (2014) (IF: 3,573, independent citations: 7)

II. Fekete, T., Borsa, J., Takács, E., Wojnárovits, L., Synthesis of cellulose-based superabsorbent hydrogels by high-energy irradiation in the presence of crosslinking agent. *Radiat Phys Chem* 118:114-119 (2016) (IF: 1,315, independent citations: 3)

III. Fekete, T., Borsa, J., Takács, E., Wojnárovits, L., Synthesis of carboxymethylcellulose/acrylic acid hydrogels with superabsorbent properties by radiation-induced crosslinking. *Radiat Phys Chem* 124:135-139 (2016) (IF: 1,315, independent citations: 1)

IV. Fekete, T., Borsa, J., Takács, E., Wojnárovits, L., Synthesis and characterization of superabsorbent hydrogels based on hydroxyethylcellulose and acrylic acid. *Carbohyd Polym* 166:300-308 (2017) (IF: 4,811 (2016), independent citations: 1)

V. Fekete, T., Borsa, J., Takács, E., Wojnárovits, L., Synthesis of carboxymethylcellulose/starch superabsorbent hydrogels by gamma-irradiation. *Chem Cent J* 11:46 (2017) (IF: 2,442 (2016), independent citations: 0)

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1. Fekete, T., Borsa, J., Chapter 5: Polysaccharide-based hydrogels. In: Thakur, V. K., Thakur, M. J., Polymer Gels: Science and Fundamentals. Springer Singapore. ISBN:978-981-10-6085-4, *In Press*

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1. Fekete, T., Takács, E., Borsa, J., Cellulóz alapú hidrogélek előállítása nagyenergiájú sugárzással. *Magyar Textiltechnika* LXVI. évf./3. szám, 110-114 (2013)
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2. Fekete, T., Takács, E., Wojnárovits, L., Borsa, J., Cellulóz alapú szuperabszorbens gélek előállítása nagyenergiájú sugárzással monomer jelenlétében. Őszi Radiokémiai Napok, 2014. október 13-15., Balatonszárszó. Pp. 58-61. MKE, Budapest (ISBN:9789639970502) (2014)

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1. Fekete, T., Borsa, J., Takács, E., Wojnárovits, L., Synthesis of carboxymethylcellulose/acrylic acid hydrogels with superabsorbent properties by radiation-initiated crosslinking. *13th Tihany Symposium on Radiation Chemistry*, Balatonalmádi, Hungary, August 29-September 3, 2015

2. Fekete, T., Borsa, J., Takács, E., Wojnárovits, L., Synthesis of cellulose derivative/acrylic acid superabsorbent hydrogels crosslinked by gamma-irradiation. *1st International Conference on Radioanalytical and Nuclear Chemistry,* Budapest, Hungary, April 10-15, 2016

3. Fekete, T., Borsa, J., Takács, E., Wojnárovits, L., Synthesis of cellulose derivative/acrylic acid hydrogels by radiation-initiated cross-linking. *The 12th Meeting of the Ionizing Radiation and Polymers Symposium (IRaP 2016),* Peninsula of Giens, France, September 25-30, 2016

Oral presentations in Hungarian:

1. Fekete, T., Takács, E., Borsa, J., Cellulóz alapú hidrogélek előállítása és jellemzése. *MTA Természetes Polimerek Munkabizottságának és MTA Műanyagok Munkabizottságának konferenciája*, 2012. december 12., Budapest

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5. Fekete, T., Borsa, J., Takács, E., Wojnárovits, L., Cellulóz alapú hidrogélek előállítása és jellemzése. *Oláh György Iskola XII. Konferenciája*, 2015. február 5., Budapest

6. Fekete, T., Borsa, J., Takács, E., Wojnárovits, L., Karboximetil-cellulóz/akrilsav alapú szuperabszorbens gélek előállítása nagyenergiájú sugárzással. *Őszi Radiokémiai Napok*, 2015. október 19-21., Balatonszárszó

7. Fekete, T., Borsa, J., Takács, E., Wojnárovits, L., Karboximetil-cellulóz/akrilsav szuperabszorbens gélek előállítása gamma-sugárzással iniciált térhálósítással. *Fiatal Diplomások Fóruma*, 2015. november 24., Budapest

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1. Fekete, T., Takács, E., Wojnárovits, L., Borsa, J., Synthesis of cellulose-based superabsorbent hydrogels crosslinked by gamma irradiation. *International Conference on Bio-Friendly Polymers and Polymer Additives – From Scientific Aspects to Processing and Applications*, Budapest, Hungary, May 19-21, 2014

2. Takács, E., Fekete, T., Borsa, J., Wojnárovits, L., Synthesis of cellulose derivative based superabsorbent hydrogels. *The 12th Meeting of the Ionizing Radiation and Polymers Symposium (IRaP 2016)*, Peninsula of Giens, France, September 25-30, 2016

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