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The effect of cross-linking agent amount and type on the sorption properties of starch graft polyacrylamide and poly(acrylic acid) copolymers

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In free radical polymerization initiated by 2,2'-azobis(2-methylpropionamidine) dihydrochloride, grafted starch copolymers with a weight ratio of acrylamide to acrylic acid of 1:2 were obtained. Three acrylic products were used to cross-linking starch copolymers: MBA, PETIA and EBECRYL 40 in amounts of: 0.2, 0.4, 0.6 and 1.0 wt.%. Materials were characterized by Fourier transform infrared spectroscopy, differential scanning calorimetry and reoviscometry. The sorption properties of starch copolymers were confirmed by sorption tests: water absorption, swelling in water and sorption of cations: trivalent iron and divalent copper. The highest water absorption is characteristic of materials cross-linked with MBA (1800%), then PETIA (1400%) and EBECRYL 40 (850%). On the other hand, the best swelling results are in the sequence PETIA > MBA > EBECRYL (1050% > 900% > 570%). The most effective sorbent of cations is the copolymer cross-linked with MBA. Solution purifications of 90% and 45% were obtained for Fe^{+3} and Cu^{+2}, respectively.

Keywords: superabsorbents, starch graft copolymers, potato starcha, cross-linking agent.

INTRODUCTION

Cross-linked polymers are becoming increasingly popular as sorbents in various fields of science and industry. Polymer cross-linking is a result of chemical or physical bonding between polymer chains. Cross-linked polymers are characterized by a three-dimensional network with high mechanical, chemical and thermal stability. In comparison to linear polymers, cross-linked structures are also characterized by better solvent resistance. The degree of cross-linking, i.e. the number of cross-links between polymer chains, has a direct effect on the properties of these materials. A high degree of cross-linking increases resistance to solvents and improves mechanical stability, but may limit their sorption capacity, reducing the availability of free active sites[1]. In turn, a lower degree of cross-linking promotes greater porosity, which allows for more effective absorption of pollutants, but may negatively affect the stability and durability of the material[2–4]. Due to the flexibility of the structural design and the possibility of chemical modification, these materials can be adapted to selectively bind specific substances related to water purification, gas separation, environmental protection, as well as in medicine and pharmacy[5–11].

Cross-linked polymer technologies are also evolving towards sustainable development. Modern polymers are designed with biodegradability or recycling capabilities in mind, which is crucial in the context of contemporary ecological challenges[12, 13]. Starch is a natural polymer which, due to its availability, low price and relatively easy modification[14–20], can be a component of biodegradable or partially biodegradable sorbents[1, 21, 22].

In this article, the results of sorption efficiency for copolymers of potato starch (St) grafted polyacrylamide (PAM) and poly(acrylic acid) (PAA) are presented. Starch copolymers were synthesized in a free radical reaction using twice the amount of PAA compared to PAM (St--AM-2AA), contrary to the literature[23]. The polymerization initiator was 2,2'-azobis(2-methyl propionamidine) dihydrochloride. The starch modified materials were characterized by Fourier transform infrared spectroscopy, differential scanning calorimetry and reoviscometry. The results of volumetric and mass swelling of differently cross-linked sorbents in water are presented. The aim of the work was to determine the effect of three acrylic cross-linking agents and their amounts on the sorption properties of water and Fe^{+3} and Cu^{+2} cations by starch superabsorbents. The presented results for acrylamide starch copolymers complement the knowledge for similar sorbents obtained by reactive extrusion[24, 25] or in a batch reactor[23].

MATERIALS AND METHODS

Materials: Acrylamide (~99%, AM) was purchased from Sigma Aldrich and acrylic acid (~98%, AA) from Fluka Chemica. Potato starch (super standard quality, St) with moisture content of ca. 16.5 wt.% and ca. 30/70 wt.% of amylose/amylopectin from Potato Industrial Enterprise "Nowamyl" S.A., Poland was used for syntheses. 2,2'-azobis(2-methyl propionamidine) dihydrochloride (97%, AAPH, Sigma Aldrich) was used as the free radical polymerization initiator. Crosslinking agents with different functionalities were used to crosslink starch-co-polyacrylamide/poly(acrylic acid) copolymers: two-functional N,N'-methylenebisacrylamide (99%, MBA, Sigma Aldrich), mixture of six-functional penthaerythritol triacrylate and eight-functional pentaerythritol tetraacrylate (99%, PETIA, CYTEC) and four-functional alkoxylated tetraacrylate - EBECRYL 40 (99%, EBEC, CYTEC). Acetone (~99,9%) and iron(III) and copper(II) sulphates (~99,9%,) were purchased from Chempur, Poland.

Synthesis of cross-linked starch copolymers: The procedure for obtaining of cross-linked starch-g-polyacrylamide/poly(acrylic acid) (St-AM-AA) has been thoroughly presented in the literature[23]. In free radical polymerization, polyacrylamide (PAM) and poly(acrylic acid) were grafted onto starch and then the copolymer was cross-linked using various cross-linking agents in 0.2, 0.4, 0.6 and 1.0 wt.%. AAPH was used based on the weight

of acrylic monomers (1.0 wt.%). Gelatinized starch (30 min at 82°C) was used regarding acrylic monomers in a ratio of 1:0.3. Acrylic monomers (AM and AA) were used in a fixed weight ratio of 1:2, respectively.

Polymerization was carried out at a nitrogen atmosphere. Polymerization and cross-linking of the starch copolymer were carried out at 42°C±2°C for 3.5 h. The cross-linked acrylamide starch graft copolymers were precipitated in excess acetone, filtered under reduced pressure, dried and ground in a knife mill. The starch sorbent was used in the form of powder with a grain diameter below 0.3 mm (fraction obtained from vibrating sieves).

Methods

Fourier transform infrared (FTIR) spectroscopy. FTIR spectra of dried samples were obtained in the range of 500–4000 cm^{-1} using a Nexus FTIR spectrometer (Thermo Nicolet Corp., USA) with a Golden Gate (ATR) attachment. The spectra were processed with the OMNIC computer program.

Differential Scanning Calorimetry (DSC). DSC of the materials was performed using Q100 DSC (TA Instruments Inc., USA) with a heating rate of 10 °C/min, from –10 °C to 250 °C in a nitrogen atmosphere. The average sample weight was ~ 5–6 mg. Hermetically sealed aluminum pans were used.

Viscosities of post-reaction mixtures. Viscosity values for post-reaction mixtures were measured using a Brookfield rheometer, model DV III Rheometer V2.0 HB PC-Steverung, using the plate-cone method (CP-42 cone with a measuring range of 20.48 to 512 000 mPa·s, measurement was performed for two shear rates of 10 and 20 rpm).

Sorption tests: The sorption properties of starch and acrylamide copolymers were checked on samples weighing 0.50 g ± 0.02 g. The moisture content of the materials was determined using a RadWag moisture analyzer and the results were included in the water sorption calculations.

Water absorption and swelling tests were performed on 3 samples of the same material and the results are averaged.

Water absorption. The water absorption of starch copolymers was determined by placing the weighed amounts of the material in 50 cm^3 of distilled water at room temperature for 30 minutes. After the designated time, the entire material was filtered and weighed. The mass swelling (W) was calculated using formula (1):

$$W = [(W_{30} - D) \cdot 100\%] / D [\%] \quad (1)$$

where:

D – the dry sorbent mass [g],

W_{30} – the mass of swollen sample after time 30 min [g].

Water swelling. The swelling was assessed in measuring cylinders by measuring the volume of material exposed to water after 30 minutes. The volumetric swelling (V) was calculated using formula (2):

$$V = [(V_{30} - V_D) \cdot 100\%] / V_D [\%] \quad (2)$$

where:

V_D – the dry sorbent volume [cm^3],

V_{30} – the volume of swollen sample after time 30 min [cm^3].

Sorption of Fe(III) and Cu(II) cations. Sorption tests of Fe^{+3} and Cu^{+2} cations from the aqueous solution by starch grafted copolymers were carried out according to the literature[23]. The sorbent weights were 0.4 g and the initial concentrations of Fe^{+3} and Cu^{+2} cations solutions were 50 mg/L for Fe^{+3} and 100 mg/L for Cu^{+2} ions, respectively. The sorption material was magnetically stirred in 100 cm^3 of the tested cation solution, during which samples were taken for analysis every 10 minutes. The measurements of absorbance changes of Fe^{+3} and Cu^{+2} ions were performed spectrophotometrically (UV-9000 device from BioSens) using the following wavelengths: 480 nm for solutions containing Fe^{+3} ions and 608 nm for Cu^{+2} ions. The removal of the cation from the solution was determined based on the calibration curves of cations concentrations in aqueous solutions.

RESULTS AND DISCUSSION

Figure 1 shows the FTIR spectra of potato starch (St), starch-co-polyacrylamide/ poly(acrylic acid) with AM to AA ration 1:2 (St-AM-2AA) and cross-linked St-AM-2AA by 0.2 wt.% cross-linking agent for PETIA (St-co-PETIA02), MBA (St-co-MBA02) and ECRCRYL 40 (St-co-EBEC02) – Figure 1A and Figure 1B for starch copolymer with different amount of PETIA: 0.2 wt.% (St--co-PETIA02), 0.4 wt.% (St-co-PETIA04) and 1.0 wt.% (St-co-PETIA1). FTIR studies confirm the chemical modification of starch with acrylamide and acrylic acid and the cross-linking of the material. FTIR for St has a broad band in the wavelength range of 3650–3000 cm^{-1}, which indicates the presence of OH groups and at 2900 cm^{-1} corresponding to the vibrations of the C-H and CH_2 groups. In addition, a characteristic combination of three peaks from C-O-C at 1160, 1080 and 1015 cm^{-1} can be seen[26]. The spectra of the non-crosslinked copolymer skr-2AAm1AA, in addition to the characteristic bands of starch, have characteristic bands of AM at 3400, 1650 and 1600 cm^{-1} originating from the vibrations of N-H, C=O and N-H[27] and from AA, the sharp peak at about 1640 cm-1 originates from the vibrations of the COO- group of acrylic acid[28]. However, cross-linked copolymers with the lowest cross-linking agent content of 0.2 wt.% have more diffuse peaks and lower intensity, e.g. bands at wavelengths of 3650–3000 cm^{-1} and 2900 cm^{-1}.

On the other hand (Fig. 1B), increasing the amount of acrylic cross-linker causes sharpening of peaks and increase of their intensity for bands corresponding to OH, CH and CH_2 groups. At the same time, a broad band of 1500–1700 cm^{-1} is formed where signals from characteristic groups (C=O, N-H and COO^-) of used acrylates overlap.

The DSC test results were presented graphically (Figure 2) and tabularly (Table 1) with maximum peak temperatures from DSC studies. Figure 2 displayed the DSC curves of St-AM-2AA with different amount of cross-linking agent 0.2, 0.4 and 1.0 wt.% and pure cross-linking agent; Figure 2A for MBA, Figure 2B for PETIA and Figure 2C for EBECRLY 40. The DSC of each crosslinker is characterized by two or three characteristic transition temperatures in the tested range. Regardless of the type of crosslinking agent, increasing its amount in the material results in a temperature shift for the characteristic phase transition towards higher temperatures. This is due to the stiffening of the poly-

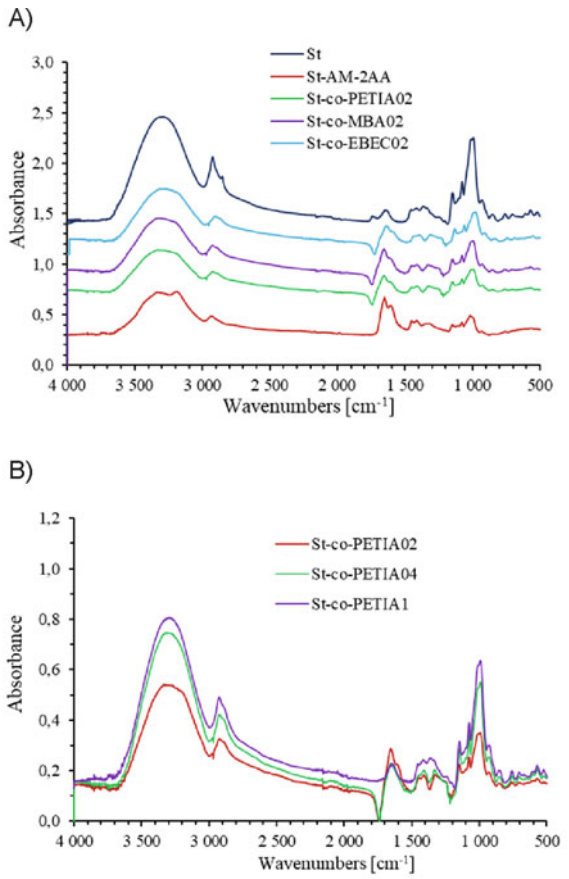

Figure 1. Fourier-transform infrared spectra of A) starch (St), starch-co-polyacrylamide/poly(acrylic acid) with AM to AA ration 1:2 (St-AM-2AA) and cross-linked St-AM-2AA by 0.2 wt.% cross-linking agent for PETIA (St-co-PETIA02), MBA (St-co-MBA02) and ECRCRYL 40 (St-co-EBEC02); B) for starch co-polymer with different amount of PETIA: 0.2 wt.% (St-co-PETIA02), 0.4 wt.% (St-co-PETIA04) and 1.0 wt.% (St-co-PETIA1)

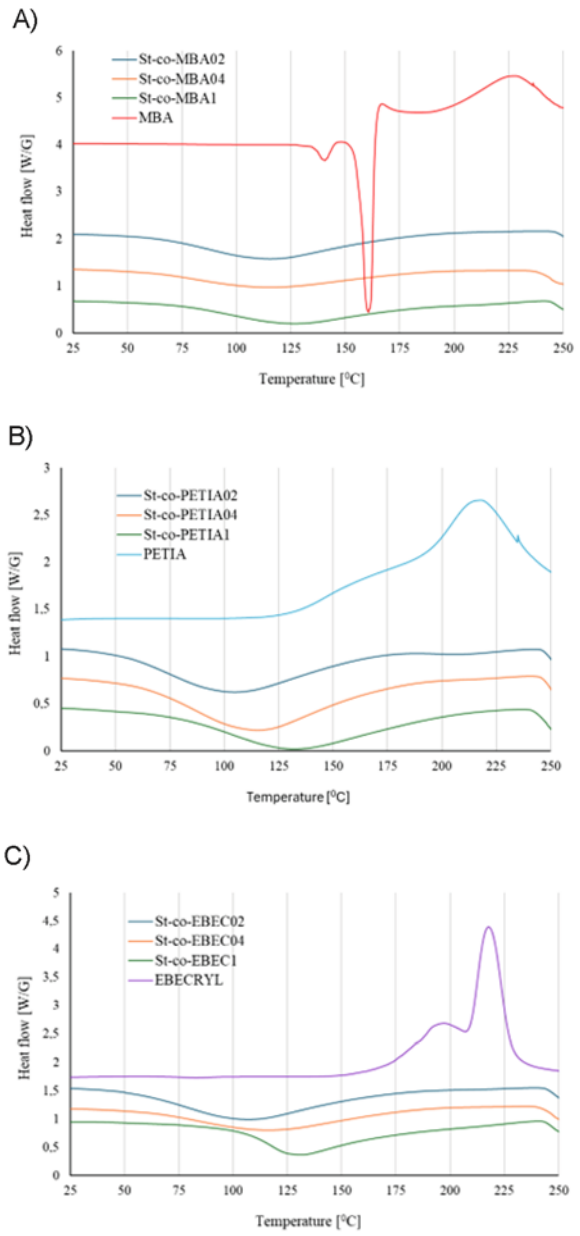

Figure 2. Differential scanning calorimetry of St-AM-2AA with different amount of cross-linking agent 0.2, 0.4 and 1.0 wt.% and pure cross-linking agent A) MBA, B) PETIA, C) EBECRLY 40

mer chains. T_{max} mainly depends on the amount and not the type of crosslinker. The temperatures for the max peaks on the DSC curves are practically similar for the three crosslinkers for the same amounts used. The only difference is observed for MBA, where at 0.2 and 0.4 wt.% T_{max} is similar and equal to 114–115 °C.

The influence of changes in the viscosity values of post-reaction mixtures depending on the type of cross--linking agent and its amount in the system for two spindle rotational speeds (10 and 20 rpm) is shown in Figure 3. Starch materials exhibit typical properties of non-Newtonian, pseudoplastic fluids, since increasing the shear rate causes a decrease in the viscosity of the post-reaction mixtures[29]. The viscosity values for the MBA cross-linked materials increased significantly from 1500 mPa·s for 0.2 wt.% to 3200 mPa·s for 0.4 wt.% of MBA and are still maintained despite the increase in the amount of MBA in the system (Fig. 3A). The viscosity of PETIA cross-linked materials increases proportionally with the increase in the amount of PETIA in the system up to 0.6 wt.% (3200 mPa·s), while at 1.0 wt.% it decreases to 2900 mPa·s (Fig. 3B). However, for EBECRA 40 the highest viscosity value is 0.4 wt.% and then systematically decreases with the increase of crosslinker amount in the system (Fig. 3C). It is likely that with increasing concentration of crosslinker in the system, the cross-linking density increases and the material loses its swelling ability[10].

Table 1. Maximum peak temperatures from DSC studies for cross-linking starch-co-polyacrylamide/poly(acrylic acid) with AM to AA ration 1:2 with different amount of cross-linking agent 0.2, 0.4 and 1.0 wt.% and pure cross-linking agent

Sample name	T [°C]	Sample name	T [°C]	Sample name	T [°C]
PETIA	217	ERECRYL 40	196 218	MBA	140 160 229
St-co-PETIA02	105	St-co-EBEC02	105	St-co-MBA2	114
St-co-PETIA04	114	St-co-EBEC04	116	St-co-MBA04	115
St-co-PETIA1	135	St-co-EBEC1	132	St-co-MBA1	129

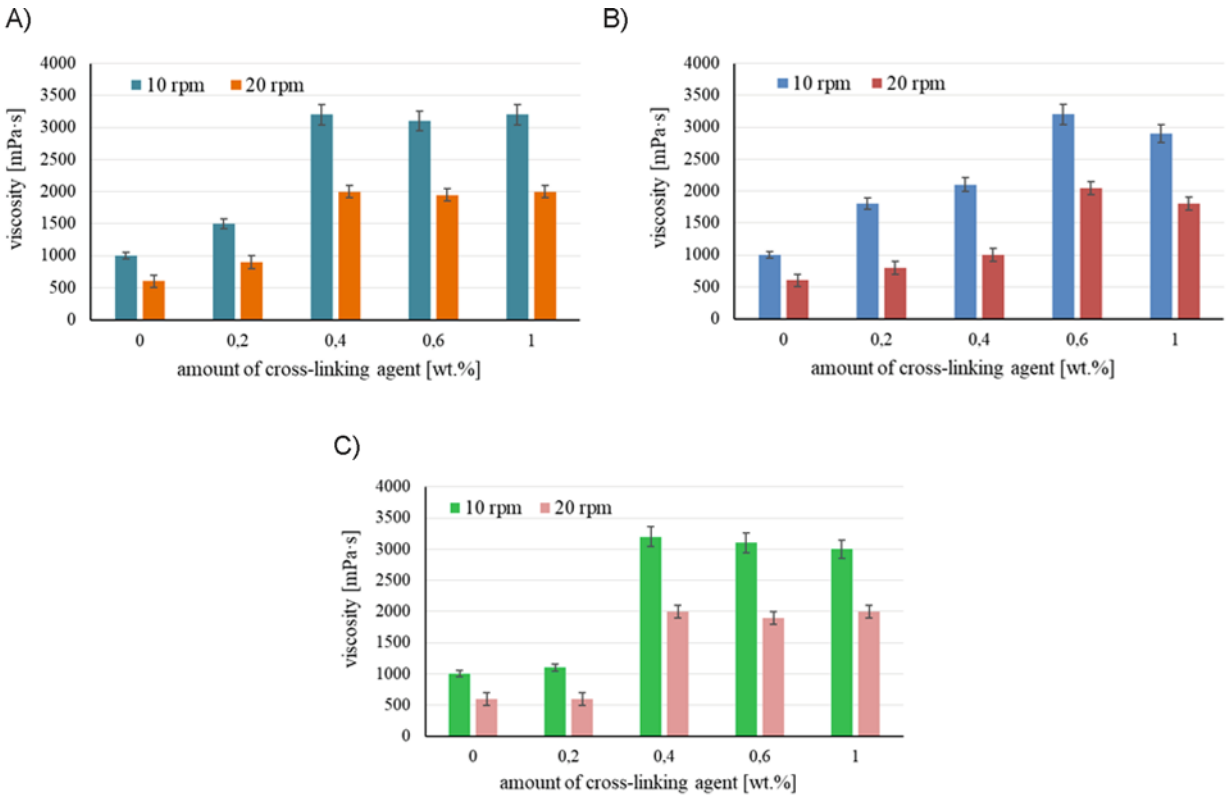

Figure 3. Viscosity values for post-reaction mixtures of non-cross-linking St-AM-2AA and St-AM-2AA with different amount of cross-linking agent 0.2, 0.4, 0.6 and 1.0 wt.% A) MBA, B) PETIA, C) EBECRLY 40

The results of the water absorption (mass swelling) (Fig. 4.A) and water swelling (volume swelling) tests for the obtained materials are presented in Figures 4 and 5, respectively. These results complementarily show the application properties of the obtained polymers. Water sorption properties of synthesized materials strongly depend on the type and amount of cross-linking agent used. The highest water retention capacity is shown by the materials cross-linked with MBA (1800%), then PETIA (1400%) and the weakest with EBECRYL 40 (850%) – Figure 4. On the other hand, for swelling in water, the best results were obtained in the sequence PETIA > MBA > EBECRYL (1050% > 900% > 570%) – Figure 5. However, for the amount of cross-linking agent 0.4 wt.% (the smallest amount of additive with excellent sorption), the sequence of results changes to a more favorable one for MBA: MBA > PETIA > EBECRYL 40. All the results obtained for the copolymer with a double amount of AA in the composition (St-AM-2AA) confirm their better sorption properties compared to materials containing a double amount of AM[23].

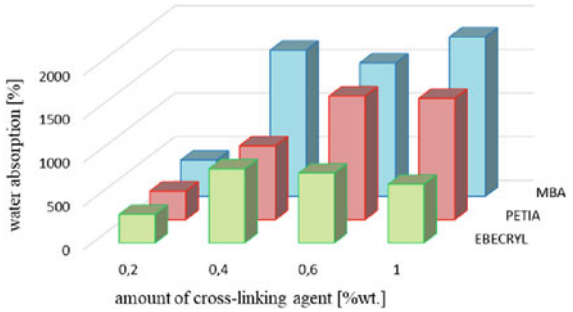

Figure 4. Mass swelling of cross-linking St-AM-2AA by MBA, PETIA and EBECRLY 40 with different amount of crosslinker 0.2, 0.4. 0.6 and 1.0 wt.%

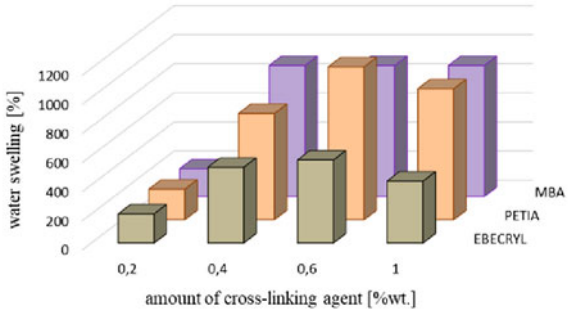

Figure 5. Volumetric swelling of cross-linking St-AM-2AA by MBA, PETIA and EBECRLY 40 with different amount of crosslinker 0.2, 0.4, 0.6 and 1.0 wt.%

Based on the water sorption results, systems containing 0.4 wt.% of a cross-linking agent in the system were selected for cation sorption tests. Figures 6 and 7 show the results of Fe^{+3} and Cu^{+2} sorption tests obtained by starch sorbents, respectively. Each of the figures shows how the absorbance of solutions changed during the sorbent's action (Fig. 6 and 7 A) and the % removal of the cation from the solution (Fig. 6 and 7 B). In both cases the best results were obtained for the MBA cross-linked copolymer with 90% purification for the Fe^{+3} solution and approx. 45% for Cu^{+2}. However, the results for PETIA and EBECRYL 40 can be considered comparable, with slightly better results approx. 30% for Fe^{+3} and 15% for Cu^{+2} were obtained using EBECRYL 40.

The use of a double amount of AA in the starch cross-linked copolymer improves the sorption capacity of the materials compared to materials with a smaller amount of COO- in the structure[23]. This is due to the repulsion of side chains between carboxylate groups[30]. This in turn causes easier penetration of solutions into the interior of the sorbents. Sorption properties are also improved

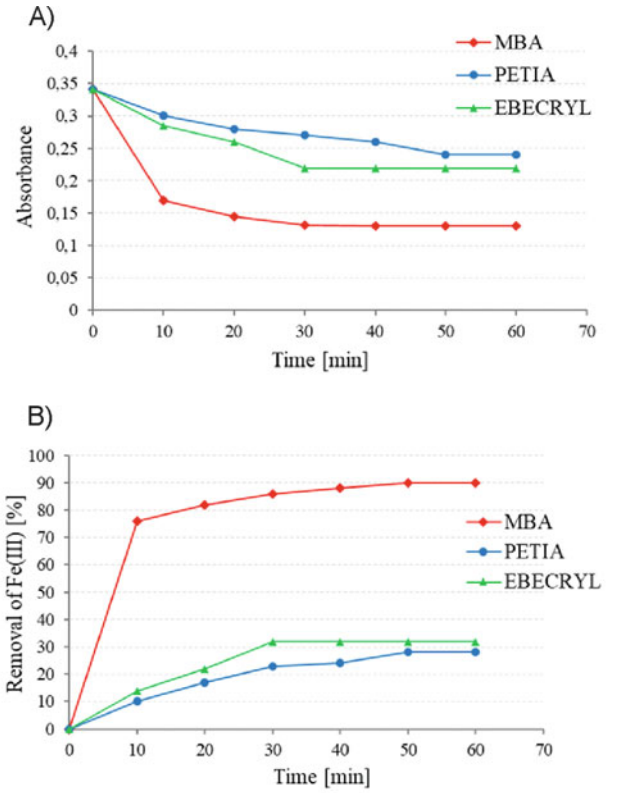

Figure 6. Sorption of Fe(III) cations from aqueous solution for St-AM-2AA copolymer with different cross-linking agents in the amount of 0.4 wt.% A) changes in absorbance of iron solution over time, B) removal of Fe(III) ions

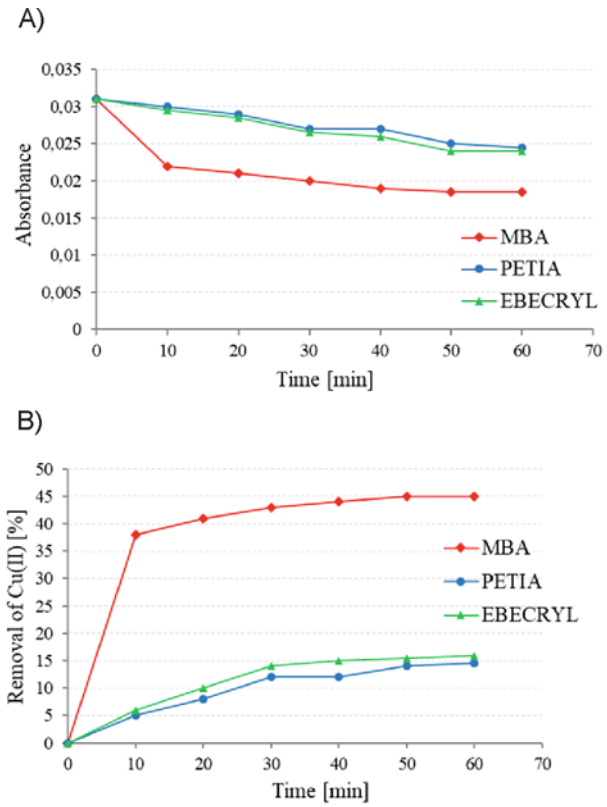

Figure 7. Sorption of Cu(II) cations from aqueous solution for St-AM-2AA copolymer with different cross-linking agents in the amount of 0.4 wt.% A) changes in absorbance of cooper solution over time, B) removal of Fe(III) ions

due to the interaction of negative groups (-COO-) and cations attractive for attachment.

CONCLUSIONS

In a free radical reaction initiated by 2,2'-azobis(2-methyl propionamidine) dihydrochloride, acrylamide graft copolymers of starch with twice the amount of acrylic acidin in relation to acrylamide were obtained. Three acrylic products were used to cross-link starch copolymers: MBA, PETIA and EBECRYL 40. The studies confirmed the synthesis of copolymers, cross-linking, and material diversity. The materials were characterized using FTIR, DSC and viscosimetric studies. The sorption properties of starch copolymers, depending on the type and amount of the cross-linking agent used, were confirmed by sorption tests: water absorption, swelling in water and sorption of cations: trivalent iron and divalent copper.

The highest water absorbance is shown by the materials cross-linked with MBA (1800%), then PETIA (1400%) and EBECRYL 40 (850%). However, the best results for swelling in water were obtained in the sequence PETIA > MBA > EBECRYL (1050% > 900% > 570%). For tests of cation removal from aqueous environments, systems containing 0.4 wt.% of cross-linking agent were selected. The most effective sorbent of metal cations is the St-AM-2AA copolymer cross-linked with MBA. The solution purification was achieved at a very satisfactory level of 90% and 45% for Fe^{+3} and Cu^{+2}, respectively.

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