

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/281344367>

New routes to prepare superabsorbent polymers free of acrylate cross-linker

Article in *Iranian Polymer Journal* · September 2015

DOI: 10.1007/s13726-015-0373-9

CITATIONS

0

READS

247

7 authors, including:



Othman A Hamed

An-Najah National University

71 PUBLICATIONS 491 CITATIONS

[SEE PROFILE](#)



Feras AbuJaber

University of Castilla-La Mancha

8 PUBLICATIONS 3 CITATIONS

[SEE PROFILE](#)



Kamel M Adwan

An-Najah National University

86 PUBLICATIONS 892 CITATIONS

[SEE PROFILE](#)



Shehdeh Jodeh

An-Najah National University

261 PUBLICATIONS 444 CITATIONS

[SEE PROFILE](#)

Some of the authors of this publication are also working on these related projects:



The waste of saffron crop, a cheap source of bioactive compounds [View project](#)



Theoretical Tools for corrosion inhibition study: DFT, Monte Carlo and Molecular dynamic simulations [View project](#)

New routes to prepare superabsorbent polymers free of acrylate cross-linker

Othman A. Hamed¹ · Firas Jaber¹ · Emad M. Hamed² · Kamel Adwan³ · Shehdeh Jodeh¹ · Rachid Salghi⁴ · Haythem Saadeh⁵

Received: 17 November 2014 / Accepted: 17 August 2015 / Published online: 30 August 2015
© Iran Polymer and Petrochemical Institute 2015

Abstract In this study, new series of superabsorbent polymers, which were free of acrylate cross-linkers, were synthesized and their absorbent properties were evaluated. The new superabsorbent polymers showed high free swell and absorbency under loading. They were synthesized in a single-step process through a solution polymerization of partially neutralized acrylic acid in the presence of cross-linking agents allyl sucrose (AS) and epoxy allyl sucrose (EAS). Allyl sucrose was synthesized by reacting sucrose with allyl chloride in an alkaline medium. Allyl sucrose was then converted into EAS by oxidation with peracetic acid. The synthesis and absorbent properties of superabsorbent polymers (SAPs) cross-linked with commercially available non-sucrose-based epoxy cross-linking agents, e.g., glycerol diglycidyl ethers (GDGE), 1,4-butanediol diglycidyl ether (1,4-BDGE) and 1,4-cyclohexanedimethanol diglycidyl ether (1,4-CHDDMDGE) have been evaluated, as well.

Absorbent properties of the prepared superabsorbent polymers were evaluated in saline solution and results showed high dependency of the absorbent properties on the cross-linking agent polarity and concentration. Superabsorbent polymers cross-linked with EAS and GDGE showed the highest absorbency under loading and indicated that they formed gels with high strength in the aqueous solution. Absorbent properties of the prepared SAPs showed reversible correlation with cross-linking agent concentration. The pH of the reaction mixture was optimized to achieve the highest free swell and absorbency under loading. The biodegradation properties of the superabsorbent polymers cross-linked with sucrose-based cross-linking agents were also evaluated and they showed degradation behavior under the influence of organisms *Pseudomonas aeruginosa* and *Trichophyton rubrum*.

Keywords Superabsorbent polymer · Polyacrylic acid · Allyl sucrose · Epoxy allyl sucrose · Cross-linking agent · Gel

Electronic supplementary material The online version of this article (doi:10.1007/s13726-015-0373-9) contains supplementary material, which is available to authorized users.

✉ Othman A. Hamed
ohamed@najah.edu

- ¹ Department of Chemistry, An-Najah National University, Nablus, West Bank, Palestine
- ² Department of Basic Sciences, College of Science and Health Professions, King Saud Bin Abdul Aziz University for Health Sciences, Jeddah, Saudi Arabia
- ³ Department of Biology, An-Najah National University, Nablus, West Bank, Palestine
- ⁴ Department of Chemistry, University of Jordan, Amman 11942, Jordan
- ⁵ Team of Environmental and Biotechnology, ENSA, University Ibn Zohr, 1136, 80000 Agadir, Morocco

Introduction

Superabsorbent polymers (SAPs) are defined as highly polar hydrogels that can absorb and retain large amounts of water or aqueous solutions [1, 2]. The hydrogels have the ability to absorb deionized water as high as 10–1000 g water/g SAP. The first commercial SAP was developed 40 years ago by alkaline hydrolysis of starch-graft-polyacrylonitrile (SPAN) [3, 4]. Since then, the applications of superabsorbent polymer have grown extensively. They are currently used in a wide array of applications, which include personal disposable hygiene [5, 6], agriculture [7, 8], biomedical applications [9], food [10],

cosmetics [11], surgical pads [12], controlled release [13], spill control [14], packaging materials [15], chemical sensors [16, 17], filtration applications [18, 19], wound dressing [12] and many other applications [20].

Superabsorbent polymers are usually made from natural or synthetic polymers that are hydrophilic and have high affinity for water. When these polymers chemically or physically are cross-linked, they can become water-swella-ble, and not water-soluble.

There are several approaches for synthesis of the superabsorbent polymers. The main approach for making SAP is by solution polymerization of acrylic monomers such as acrylic acid (AA) or its salts in the presence of a cross-linking agent [21, 22]. Other approaches involve the synthesis of superabsorbent polymers by emulsion polymerization [23], inverse suspension polymerization [24, 25] and foaming polymerization [26, 27]. Natural product based superabsorbent polymers are usually prepared by graft copolymerization in an aqueous solution [28, 29] or by a radiation-induced copolymerization [30].

One major disadvantage in the superabsorbent polymers natural based such as cellulose or starch-based SAPs is the formation of tacky materials with poor gel texture and low gel strength during the polymerization [31]. Generally, SAPs are prepared by either simultaneous polymerization and cross-linking with a poly-functional acryl cross-linking agent, or cross-linking of water-soluble prepolymer with poly-functional materials capable of forming covalent bonds with the prepolymer functional groups. The poor absorption against pressure is one major disadvantage of SAPs prepared by either of these two pathways, which makes them unsuitable for certain application such as in baby diapers.

Since semi-swollen gel can cause what is known as gel blocking, particles tend to swell rapidly on the top layer of the gel bed and form an insulating layer, which inhibits the flow of fluid to the lower parts of the gel bed, leading to a less absorbency under loading. The gel-blocking phenomenon was solved by a process known as surface cross-linking [7, 20]. It is normally performed on a dried, milled and sized SAP as the final stage of the process. A cross-linking solution is applied to the particles which then cured through heating at high temperature (150–200 °C) for about 30–60 min. Suitable reagents for surface cross-linking are those able to form multi ester or amide linkages simultaneously with several poly(acrylic acid) chains such as polyhydric alcohols glycerin. Relatively high temperatures and long reaction time are required for the surface cross-linking reactions [20, 22]. Therefore, an important challenge is to prepare a superabsorbent polymer free of these disadvantages in a single step process.

In this study, we report a useful natural product (sugar) based cross-linking agents that allow the preparation of superabsorbent polymers with desired properties such as high swelling capacity, high swelling rate, and superior absorbency under loading in a single step. The biodegradability of the prepared SAPs was also evaluated.

Experimental

Materials

All chemicals were purchased from Aldrich (USA) and used without any further purification unless otherwise stated. All new compounds were purified by flash chromatography on silica gel (100–200) mesh.

Characterization

Characterization was performed using ^1H NMR, ^{13}C NMR, and FTIR spectroscopy methods. Nuclear magnetic resonance spectra were recorded on Varian Gemini 200, 300 MHz instrument (Palo Alto, California). All ^1H NMR experiments are reported in δ units, (ppm) downfield from tetramethylsilane (TMS). All ^{13}C NMR spectra are reported in ppm relative to the signal of the deuteriochloroform (77.0 ppm). The FTIR instrument was a Nicolet 6200 spectrometer from Thermal Scientific (WI, Madison) equipped with a Split Pea ATR accessory which was used as the sample interface. The scanning electron microscope (SEM) Hitachi S-3400N (Japan) was used to obtain greater details of the sample morphology. The absorbent properties and various physical characteristics of the prepared superabsorbent polymers were examined by the following test methods.

Absorbency under load

This test method was used to determine the ability of superabsorbent polymer to absorb and retain fluid under load [4]. The absorbency test was carried out in a plastic cylinder “cell” with one inch inside diameter having a 100-mesh metal screen adhering to the cylinder bottom, containing a plastic spacer disk having 0.995 in. diameter and a weight of about 4.4 g. In this test, the weight of the cell containing the spacer disk was determined to the nearest 0.0001 g, and then the spacer was removed from the cylinder and about 0.1 g (dry weight basis) of superabsorbent polymer was placed in the cylinder. The spacer disk then was inserted back into the cylinder with the superabsorbent polymer, and the cylinder and contents were weighed to the nearest 0.0001 g. A load of 0.3 psi was then applied to the SAP pad

by placing a 100 g weight on the top of the spacer disk, and the SAP pad was allowed to equilibrate for 60 s, after which the cell and its contents were hanged in a petri dish containing a sufficient amount of saline solution (0.9 % by weight saline) to touch the bottom of the cell. The cell was allowed to stand in the petri dish for 10 min, and then it was removed and hanged in another empty petri dish and allowed to drip for 30 s. The 100 g weight was then removed and the weight of the cell and contents was determined. The weight of the saline solution absorbed per gram superabsorbent polymer was determined and expressed as absorbency under 0.3 psi load (g/g).

The cell containing the polymer was hanged again under zero loading in the tray containing the saline solution. The cell was left in contact with the saline solution for 10 min, and then it was removed and hanged in another empty petri dish and allowed to drip for 30 s. The weight of the cell and contents was determined. The weight of the saline solution absorbed per gram superabsorbent polymer was then determined and expressed as absorbent capacity (g/g). Cell and contents were then centrifuged for 3 min at 1400 rpm (centrifuge model HN, International Equipment Co., Needham HTS, USA) and weighed. The weight of the saline solution retained was determined and expressed as the centrifuge retention capacity (CRC) (g/g). The absorbency was also determined under loads of 0.6 and 0.9 psi loads in the same manner.

Vortex time

In this test, a 400 mL beaker containing 50.0 mL of saline solution and magnetic stir bar was placed on a magnetic stir plate rotating at 600 revolutions per minute. While the saline solution was being stirred, 2.00 g of the superabsorbent polymer was added quickly to it between the center of the vortex and the side of the beaker. The time required for the vortex to become flat was recorded in seconds and reported as the vortex time. The vortex time represents the free swell absorbing rate of the superabsorbent material. While increasing the absorption rate counterpart, vortex time was reduced.

Preparation of allyl sucrose

Allyl sucrose was prepared by two methods (A and B). In method A, the following procedure was performed. The reaction was carried out in a three-neck round-bottomed flask, fitted with a magnet stir bar, pressure-equalized addition funnel, and a condenser connected to a nitrogen gas line. The flask was dried using a Bunsen burner and cooled down to room temperature under dry N_2 . Sodium hydride was added to the flask (20.0 g, 415.0 mmol, 60 % in oil) and washed with dry hexane (4×15 mL), residual hexane

was removed with a syringe fitted with a Teflon tubing. To the NaH in the flask was added anhydrous DMAc (50 mL). In a separate round bottomed flask (200 mL) a solution of sucrose (10.0 g, 29.0 mmol) in DMAc (100.0 mL) solvent was prepared by stirring a mixture of sucrose in DMAc at about 60 °C under an inert atmosphere of dry N_2 . Then the solution was transferred to a pressure-equalized addition funnel via a cannula. The sucrose solution was added to the suspension of DMAc and sodium hydride over a period of 30 min at 10 °C. The mixture was further stirred for 30 min. To the produced sodium sucrate mixture at 10 °C was then added dropwise allyl chloride (25.0 mL) over a period of 30 min via a pressure-equalized addition funnel. After completing the addition, the temperature equilibrated to about 50 °C, and the content was stirred for about 2 h. Later, the content was cooled to about 10 °C, quenched with 5 % aqueous sodium hydroxide (50 mL), diluted with water (500 mL), and extracted with ethyl acetate (3×100 mL). The organic extracts were combined, washed sequentially with water and brine (3×150 mL each), dried over anhydrous sodium sulfate, filtered and concentrated in vacuum to provide the desired products (18.0 mmol, 11.9 g) in 62 % yields.

The average degree of allyl substitution was calculated from the relative peaks area of the 1H NMR to be 7.2. 1H NMR (Fig. S1) ($CDCl_3$) δ (ppm): 3.26–4.28 sucrose[s] hydrogens; 5.23 (terminal olefin hydrogens, Hb'); 5.24 (terminal olefin hydrogens, Hb); 5.65 Ha of the glucopyranosyl moieties; 5.89 (internal olefin Hd). ^{13}C NMR (Fig. S2) of allyl sucrose ($CDCl_3$) δ (ppm): 68.23–88.70; 104.13–104.44 (C-3 resonances of the fructofuranosyl moieties of allyl sucrose); 118 (CH_2 -1 vinyl), 135.21 (CH_2 -2 vinyl).

In method B sucrose (100 g, 0.29 mol, 2.33 mol hydroxyl groups) and aqueous NaOH (140.2 g in 140 mL water, 3.5 mol, 1.5 eq/hydroxyl group) were placed in a Parr pressure vessel (Buchiglasuste, BMD 300, Switzerland). The vessel was sealed, heated with stirring to about 80 °C over 30 min, and maintained at this temperature for about 1 h to dissolve the reagents. The content was then cooled to about 40 °C, the vessel opened, and charged with cold allyl chloride (300 mL, 3.5 mol, 1.5 eq/hydroxyl group) in one portion. The reactor was then sealed and pressurized with nitrogen gas to about 50 psi. The internal temperature was maintained at about 100 °C over a period of 2 h. Subsequently, the vessel was cooled to the room temperature by placing it in an ice water bath, depressurized, opened, and diluted with cold water (500 mL) to dissolve the salts. The content was transferred to a separatory funnel and the mixture was extracted with ethyl acetate (3×150 mL). The combined organic layers were then washed serially with water (1×200 mL) and brine (1×200 mL), and then dried over sodium sulfate, filtered, and concentrated in vacuo (40–50 °C). Allyl sucrose

$C_{36}H_{54}O_{19}$, 178.7 g, 0.27 mol) was obtained in 80.3 % yield. The average degree of allyl substitution was 6.0 (calculated by 1H NMR).

Preparation of epoxy allyl sucrose

In method A to synthesis of epoxy allyl sucrose (EAS), to a mechanically stirred solution of allyl sucrose (10 g), urea (120 g), sodium bicarbonate (0.6 g), and manganese sulfate (0.02 g) in 20 mL water and 110 mL of dichloromethane at 25 °C was added dropwise over a period of 4 h 20 mL of 30 % of aqueous hydrogen peroxide. After 4 h, the reaction mixture was extracted with (4 × 50 mL) ethyl acetate. The combined organic layer was dried over anhydrous sodium sulfate and evaporated to provide the desired product in 20 % yield.

In method B, the reaction was carried out in a three-neck round bottomed flask, equipped with a stir bar, pressure-equalized addition funnel, and a condenser connected to a nitrogen gas line. The flask was placed in an ice water bath and charged with allyl sucrose 10.0 g (average molecular weight 660.0 g, 15.2 mmol, 93.0 mmol of double bonds), ethyl acetate (50 mL), and sodium acetate (1.0 g, 10 % the number of moles of peracetic acid solution was added later). The content was stirred and cooled to about 5 °C, and over a period of 2 h a solution of peracetic acid (26.3 g, 32 % in acetic acid, 110.0 mmol) was added dropwise to it. The temperature of reaction mixture was then raised to about 10 °C and stirred for 2 h. Subsequently, the mixture was diluted with ethyl acetate (200 mL), transferred to a separatory funnel, and washed serially with cold water (2 × 50 mL), cold aqueous saturated sodium carbonate (1 × 50 mL), and brine (2 × 50 mL). The organic layer was then separated, dried over anhydrous sodium sulfate, filtered, and concentrated in vacuo (at 50 °C) to yield EAS as a clear light yellow in 93 % yield (9.24 g, 11.7 mmol.).

A sample of the product was purified by flash chromatography (hexane:ethyl acetate, 60:40). The 1HNMR (Fig. S3) of epoxy allyl sucrose (EAS) ($CDCl_3$) δ (ppm): 2.67 (H-c, epoxy group) 3.0–4.3 (sucrose protons and methylenes), 4.82–4.98 (residual terminal olefin hydrogens), 5.55 (H-1 signal of the glucopyranosyl moieties of the epoxy methallyl sucrose isomers). $^{13}CNMR$ (Fig. S4) of epoxy allyl sucrose ($CDCl_3$) δ (ppm): 19.24 (residual allylic CH_3 -d), 51.5 (terminal epoxy allyl carbon CH_2 -c'), 56.1 (internal epoxy allyl carbon C-b'), 66–86 (sucroses carbons and methylenes CH_2), 89.6 (C-1 resonances of the glucopyranosyl moieties of the epoxy allyl sucrose), 104.2 (C-2' resonances of the fructofuranosyl moieties of epoxy allyl sucrose isomers) and 105 (C-2' residual resonances of the fructofuranosyl moieties of unepoxidized allyl sucrose isomers), 111.7 (residual CH_2 -c), 141.3 (residual tetra substituted olefin carbons C-b).

Preparation of superabsorbent polymer

The reaction was carried out in a Pyrex reaction kettle (1.0 L). The reaction kettle was equipped with a thermocouple inserted through a rubber septum, a Teflon bladed agitator on a glass shaft attached to a mechanical mixer, gas inlet polyethylene tubing inserted through an adapter fitted with a rubber septum, and a gas outlet adapter connected to a gas trap partially filled with oil. Acrylic acid (300.0 g, neutralized to pH 6.0 with 615 g of 25 % aqueous NaOH) and desired amount of cross-linking agent, followed with 0.6 g of surfactant Triton X-100 were added into the reaction kettle. The mixture was agitated and purged with nitrogen gas for at least 30 min to remove oxygen. Then potassium persulfate (0.5 g in 50 mL distilled water) was added via a syringe followed by sodium thiosulfate solution (0.15 g in 5.0 mL water). Gelation accompanied with an exothermic reaction was started after about 15.0 min from the addition of the initiator. After the exothermic reaction had subsided (50 min), the reaction mixture was heated to 70 °C and maintained at that temperature for about 2 h. The produced solid mass was dried for 24 h at about 80 °C. The dried solid was then ground in a Wiley mill to pass through a 20-mesh screen and retained on a 40-mesh screen.

Biodegradability

Test microorganisms

The microorganisms used in the degradation experiments were *Pseudomonas aeruginosa* and *Trichophyton rubrum*. Isolated *P. aeruginosa* was maintained on Nutrient Agar (NA) (Oxoid) plates and incubated for 48 h at 37 °C prior to use. *Trichophyton rubrum* was isolated from the superficial skin of a human dermatomycosis patient. The isolated fungal was maintained on Sabouraud Dextrose Agar (SDA).

Biodegradation testing method

Biodegradation experiment was performed using the plate assay, which detects polymer-degrading activity based on either the formation of a clear zone surrounding the fungal colonies or the growth of bacterial isolates as clear colonies on media with the polymer as a sole carbon source [26].

The assay medium used in the study was mineral salt media (MSM). The MSM per 1000 mL distilled water was prepared as follows: K_2HPO_4 1.0 g; KH_2PO_4 0.2 g; NaCl 1.0 g; $CaCl_2 \cdot 2H_2O$ 0.002 g; boric acid 0.005 g; $(NH_4)_2SO_4$ 1.0 g; $MgSO_4 \cdot 7H_2O$ 0.5 g; $CuSO_4 \cdot 5H_2O$ 0.001 g; $ZnSO_4 \cdot 7H_2O$ 0.001 g; $MnSO_4 \cdot H_2O$ 0.001 g and $FeSO_4 \cdot 7H_2O$ 0.01 g.

Fungal biodegradation experiment was screened using MSM containing 0.5 % (w/v) of the polymer either allyl

sucrose or epoxy sucrose as a sole carbon source, which was solidified with 1.0 % agar at pH 6.0.

For bacterial biodegradation, the MSM containing about 0.5 % (w/v) of dry polymer (either allyl sucrose or epoxy sucrose) as a sole carbon source and solidified with 2 % agar at pH 7.0 was used. After autoclaving, the media were poured into plates and the agar was allowed to set, a loopful of the bacterium or fungal strain were then inoculated on the agar and the inoculated plates were sealed with parafilm. The plates inoculated with bacteria were incubated at 37 °C for 7 days under aerobic conditions, while plates inoculated with fungi were incubated at room temperature for 1–3 weeks [32].

Results and discussion

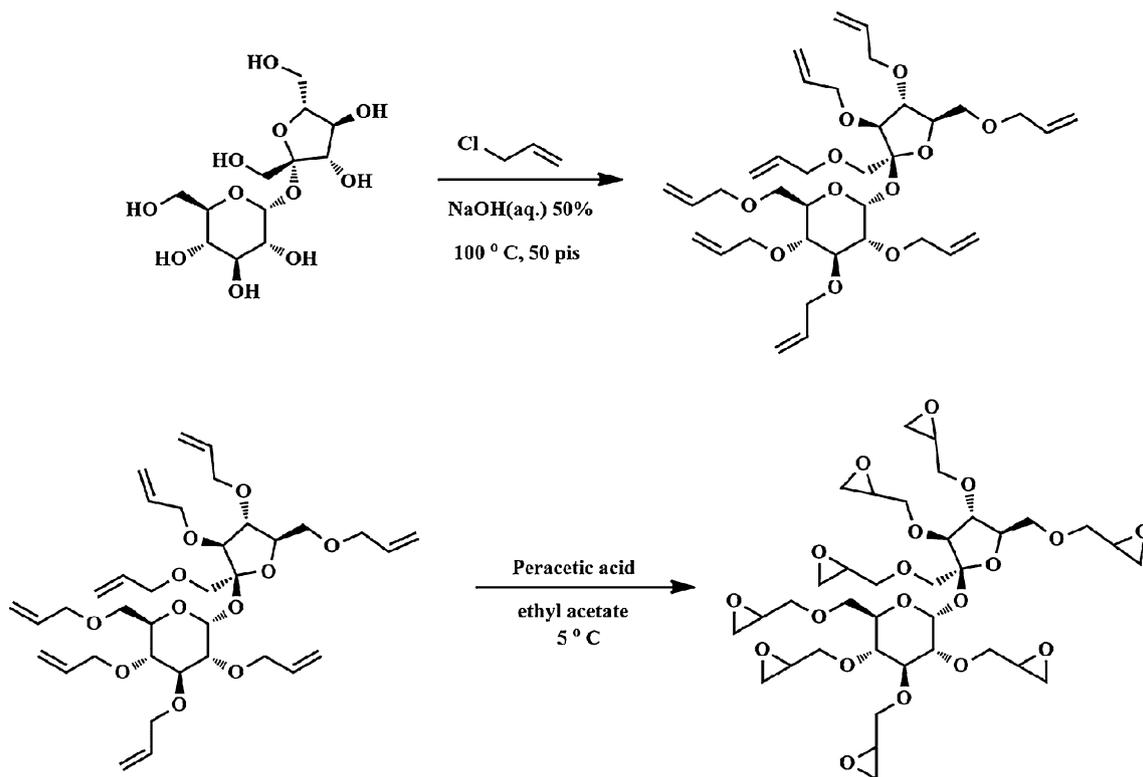
Monomers synthesis

Allyl sucrose (AS) and epoxy allyl sucrose (EAS) based monomers were chosen for this study. Sucrose is a particularly appropriate material for use in the formation of specialty monomers since it is naturally occurring (biodegradable), relatively inexpensive, poly-functional, and non-reducing sugar, thus does not have the potential for

the wide variety of side-reactions that reducing sugars have.

Both monomers AS and EAS were prepared according to the procedures published in the literature [33, 34]. As shown in Scheme 1, allyl sucrose was first prepared from the allylation of sodium sucrate with allyl chloride, which is then converted into EAS via epoxidation using two different methods as shown in the experimental section. In the first method epoxidation was carried out in an aqueous solution of hydrogen peroxide and catalytic amount of magnesium sulfate. By this method a yield of 20.0 % was obtained, the low yield could be due to the reaction of epoxy groups as they form with water that is part of the reaction mixture, which form water soluble glycols. However, the second method which was carried out in ethyl acetate using the epoxidation reagent peracetic acid produced EAS in high yield.

In addition to these two monomers, SAPs were also prepared using other commercially available epoxy monomers such as glycerol diglycidyl ether (GDGE), 1,4-butanediol diglycidyl ether (1,4-BDGE), and 1,4-cyclohexanedimethanol diglycidyl ether (1,4-CHDGE). Commercial SAP collected from Pampers® Cruisers Diapers size 3, (Procter & Gamble Co., Cincinnati, OH, USA) and SAP cross-linked with ethylene glycol diacrylate (EGDA) were also used in the study for a comparison purposes.



Scheme 1 Synthetic routes of allyl sucrose and epoxy allyl sucrose

Polymer preparation

Polymerization was performed in a partially neutralized aqueous mixture of acrylic acid (30 %) and cross-linking agents initiated with sodium persulfate. The reaction was ended in about 30 min. To ensure the reaction was complete it was continued for about 2 h. Cross-linking agents were used at various concentrations to determine optimum amount of cross-linking agent. Prepared superabsorbent polymers were ground to a conventional particle size using Wiley mill by passing it through a 20-mesh screen and retaining on a 40-mesh screen before testing. In the polymerization reaction of AS and sodium acrylate a radical was developed on both AS and sodium acrylate which causes a chain growth polymerization and a cross-linking reactions to occur simultaneously. As a result of that a cross-linked polymer with high M_w was formed, the possible structure of the resulted polymer is shown in Scheme 2.

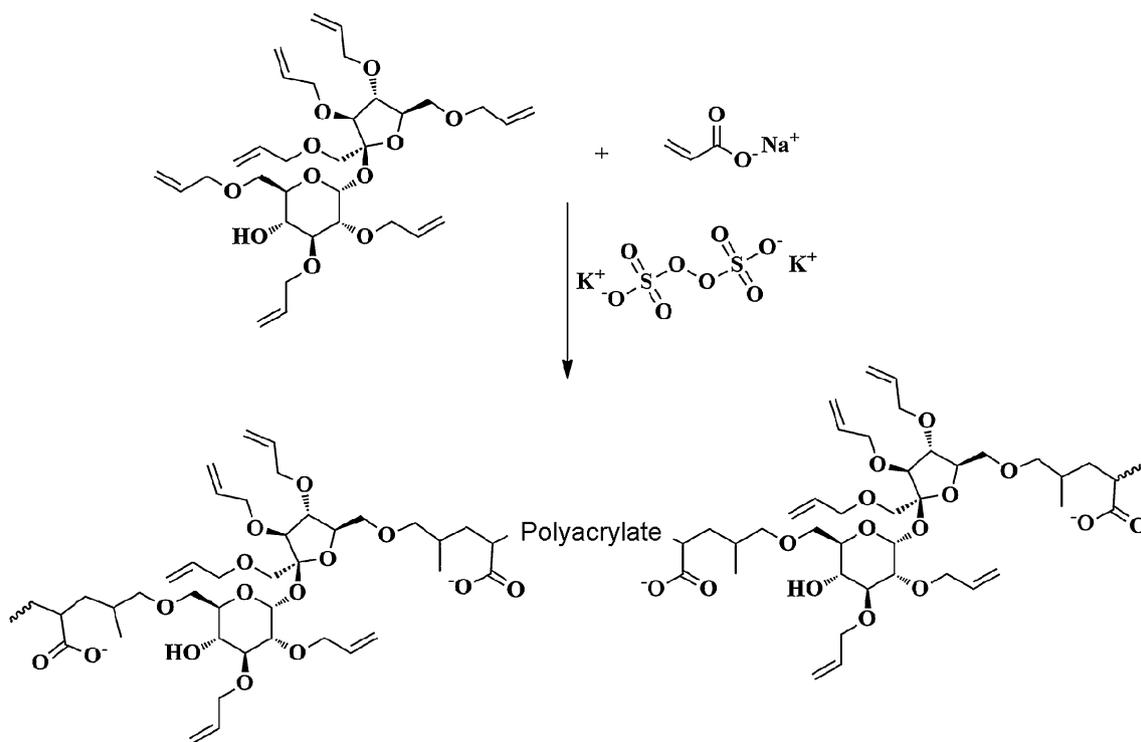
However, in the case of EAS, radical was developed on sodium acrylate only which caused it to undergo exothermic chain growth polymerization. The heat evolved from the free radical polymerization reaction initiates the S_N2 reaction between carboxylate anion and epoxy group which results on cross-linked polymer via an ester linkage (Scheme 3) [35]. Once the S_N2 reaction begins it liberate heat to the reaction mixture. Other side products were also formed during the course of the reaction; they were

beyond the scope of this study and did not affect polymer absorbency.

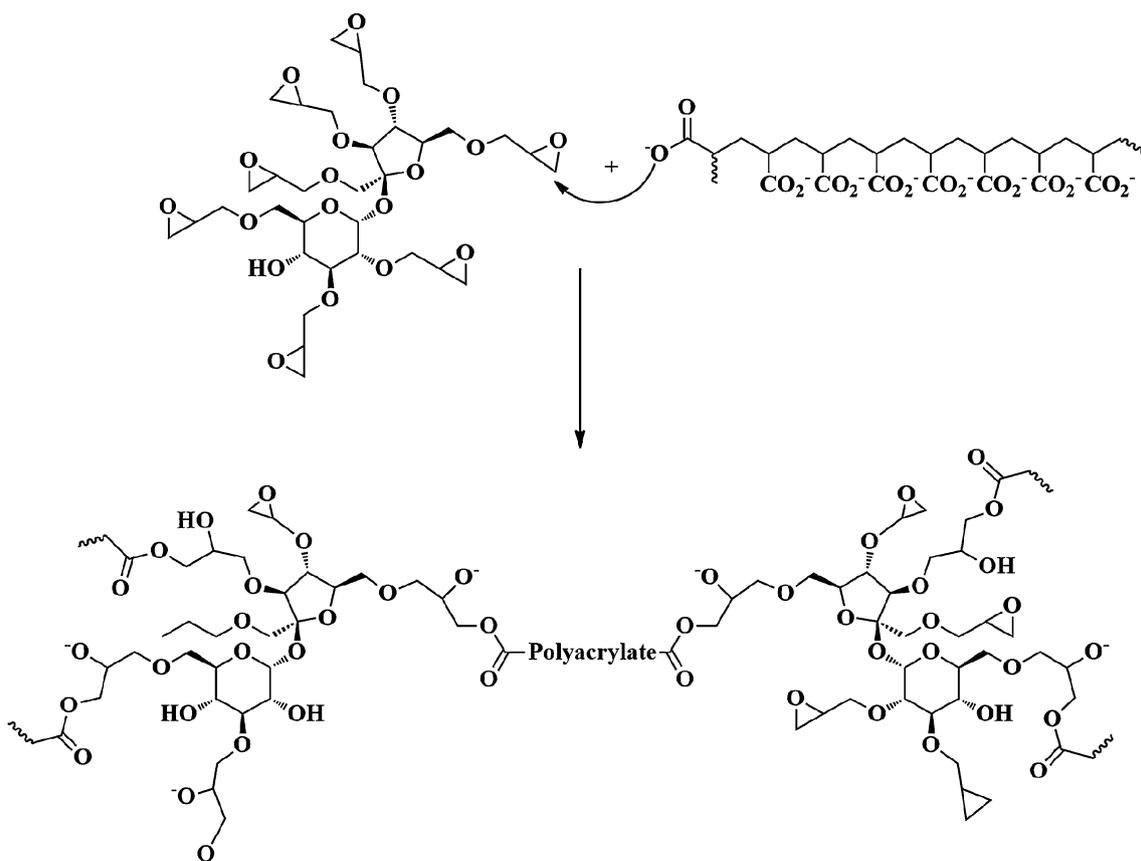
FTIR of prepared SAP polymers cross-linked with AS and EAS

An overlaid FTIR spectra of SAPs cross-linked with EGDA and EAS are shown in Fig. 1. Figure 1a represents the FTIR spectrum of SAP cross-linked with EAS and Fig. 1b is for SAP cross-linked with EGDA. The main characteristic peaks in both spectra are similar. The FTIR does not reveal the differences between the two networks polymers, since the only difference between the two polymer networks are the cross-linking agents that were used at low concentrations.

Both spectra show a broad peak that extends from 3600 to 2700 cm^{-1} corresponding to O–H stretching vibration of carboxylic groups and moisture, aliphatic C–H stretching vibration appears at 2950–2990 cm^{-1} , several small stretching vibration peaks of C=O of ester links appear between 1710 and 1650 cm^{-1} , this is because the epoxy groups of the sucrose moiety are not equivalent, therefore produce no equivalent ester links. A strong peak at 1530 cm^{-1} corresponding to asymmetric stretching vibration and at 1380 cm^{-1} corresponding to symmetric stretching vibration peak of COO carboxylate groups. A small peak appears as a shoulder at about 1280 cm^{-1} could be related to C–O–C (ether) stretching of sucrose.



Scheme 2 Possible structures of superabsorbent polymers made from sodium acrylate AS



Scheme 3 Possible structures of superabsorbent polymers made from sodium acrylate and EAS

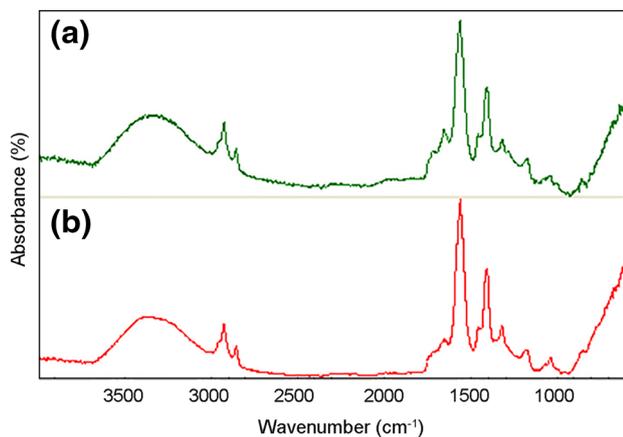


Fig. 1 FTIR spectra of SAP (neat) cross-linked with sugar-based monomers of **a** EAS and **b** EGDA

Morphological analysis

SEM micrographs of SAP cross-linked with EGDA and EAS are shown in Fig. 2. The differences between the polymers surfaces are noticeable. Conventional superabsorbent

polymer made from acrylic acid and 1.5 % EGDA cross-linking agent (Fig. 2a) has a solid smooth surface. While superabsorbent polymers cross-linked with EAS (Fig. 2b1) shows surface covered with the large number of bumps which could be attributed to porous polymeric network [36], the porosity can be seen clearly in the cross-sectional micrograph (Fig. 2b2). The porosity in SAP cross-linked with EAS could be attributed to the sucrose structure and the multi cross-linking sites it provides (Scheme 1).

Effect of type of cross-linking agent on hydrogels absorbency

Desired features of superabsorbent polymers are high swelling capacity, high swelling rate and high gel strength. These properties make SAPs ideal for use in the fluid absorbing applications such as disposable diapers, feminine napkins, and agriculture, cosmetic and absorbent pads. The swelling properties of the prepared SAPs in saline were measured using the absorbency underload method, and the results are summarized in Tables 1, 2, 3 and 4.

Table 1 shows the effect of type of cross-linking agent on absorbent properties of the prepared SAPs. Variation of

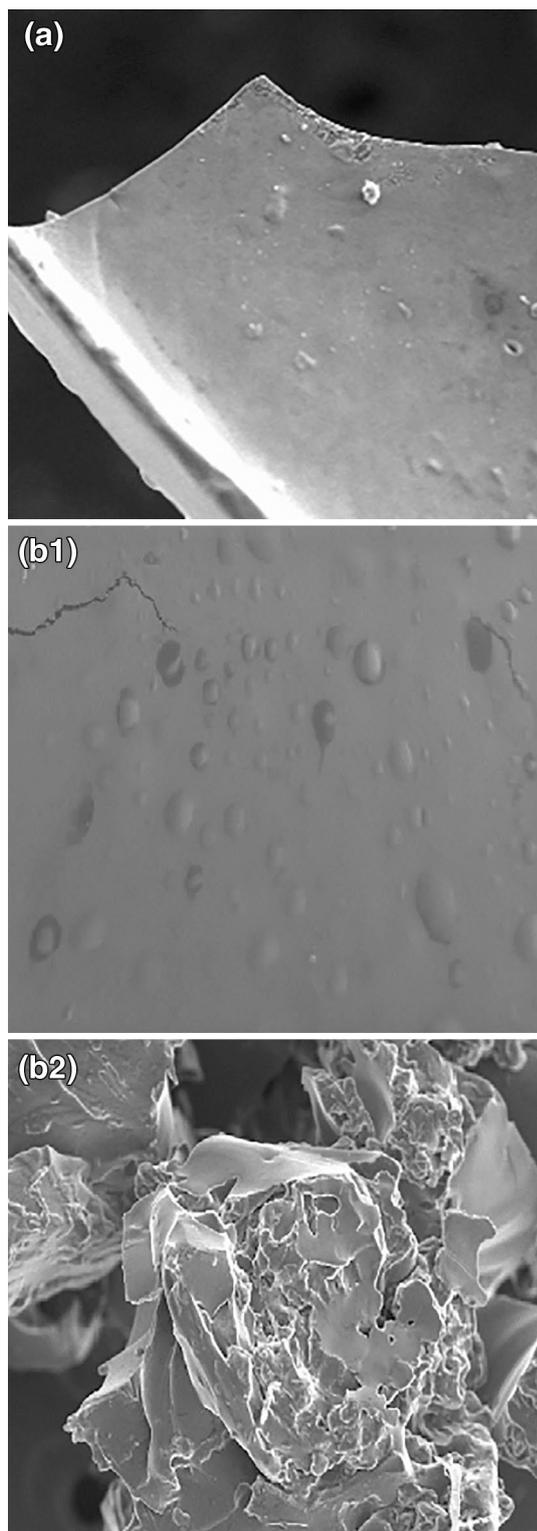


Fig. 2 SEM micrographs of prepared SAPs **a** micrograph of superabsorbent polymer cross-linked with 1.5 % EGDA at magnification $\times 1000$; **b1** micrograph of superabsorbent polymer cross-linked with 1.5 % EAS at magnification $\times 1000$; **b2** a cross-sectional micrograph of superabsorbent polymer cross-linked with 1.5 % EAS at magnification $\times 500$

Table 1 Effect of type of cross-linking agent on absorbency under load (in all runs 1.0 wt% cross-linking agents was used) (pH 6.2)

Cross-linking agent	Absorbency under load (g saline/g SAP)				
	0.01 (psi)	0.3 (psi)	0.6 (psi)	0.9 (psi)	CRC
AS	30.7	17.6	11.4	10.2	11.3
EAS	35.2	29.2	23.3	19.4	18.2
GDGE	35.6	31.2	24.1	20.2	19.2
1,4-BDGE	27.5	20.2	15.2	13.4	17.6
1,4-CHDGE	34.9	19.6	12.9	11.9	25.9
EGDA	39.0	10.5	10.5	10.5	33.5
Commercial SAP ^a	36.4	18.1	11.8	11.0	21.3

^a Collected from Pampers® Cruisers Diapers size 3, Procter & Gamble Co., Cincinnati, Ohio, USA

Table 2 Vortex time of prepared superabsorbent polymers

Cross-linking agent	Vortex time (s)			
	Run 1	Run 2	Run 3	Average
AS	76	75	75	75.0
EAS	53	54	51	52.6
GDGE	57	56	56	56.0
1,4-BDGE	65	67	63	65.0
1,4-CHDGE	73	70	70	71.0
EGDA	108	114	111	111.0
Commercial SAP	105	103	105	104.0

the cross-linking agent type caused considerable difference in the absorbent properties and swelling rate. As can be seen from the results in Tables 1 and 2, polar cross-linkers GDGE and EAS show the highest absorbency under load and the highest rate of swelling (the lowest vortex time). Cross-linkers GDGE and EAS produced polymers with relatively higher hydrophilicity than other cross-linking agents, thus more functional groups are getting hydrated.

Commercial SAP made using cross-linking agent such as EGDA showed the highest swelling capacity under low pressure (0.01 psi). However, its absorbency under load was the lowest. For this reason commercial SAP requires surface cross-linking. Its absorbency under load was higher than that for SAP cross-linked with EGDA but still lower than those prepared in a one step process using epoxide cross-linking agents.

Superabsorbent polymers cross-linked with various cross-linking agents were also evaluated by vortex time method. Vortex time is related to the rate of swelling, the lower the vortex time, the higher the swelling rate. In this method, the time in seconds required for 2 g of a superabsorbent polymer to close a vortex (becomes flat) created by stirring 50 mL of saline solution at 600 revolutions per minute was measured. As can be seen from the results summarized in Table 2,

Table 3 Effect of amount of cross-linking agent (GDGE) on absorbency of SAPs in saline under load (pH 6.2)

Sample no	Cross-linking agent (%)	Absorbency under load (g saline/g SAP)				
		0.01 (psi)	0.3 (psi)	0.6 (psi)	0.9 (psi)	CRC
1	0.5	31.6	23.5	20.7	15.7	21.1
2	0.75	34.3	26.9	23.0	16.7	20.8
3	1.0	35.6	31.2	24.1	20.2	19.2
4	1.5	26.5	20.4	22.2	19.0	16.1
5	2.0	25.0	18.5	19.6	16.1	15.1
Commercial SAP		36.4	18.1	11.8	11.0	21.3

GDGE and EAS as the polar cross-linking agents produced SAP with higher rate of absorbency (low vortex time).

Effect of cross-linking agent concentration on hydrogels absorbency

The effect of the amount of GDGE cross-linking agent on the absorbent properties was also evaluated. Results summarized in Table 3 show that, there is a noticeable effect of cross-linking agent concentration on absorbency underload and swelling capacity, both increase by increasing concentration of cross-linking up to 1 % over that the absorbency declined. Higher cross-link density may cause weaker thermodynamic force that leads to slower diffusion of water.

As a result, a denser network with lower spaces between the polymer chains was formed in a higher concentration of cross-linker. Consequently, the resulted highly cross-linked rigid structure expanded less and did not able to hold a large quantity of water [1, 37]. According to the results summarized in Table 3, maximum swelling (35.6 g saline/g) was obtained with 1.0 % of GDGE, lower or higher than 1.0 % showed lower swelling capacity.

Effect of pH on hydrogels absorbency

The relationship between the pH of SAP and water absorbency values was also studied by varying the initial pH of acrylic acid solution. Several studies have been shown that superabsorbent polymers exhibit swelling dependency on pH values [38]. Therefore, in this series of experiments, a set of superabsorbent polymers with pH ranged from 5.3 to 8.3 have been synthesized from acrylic acid that was neutralized to the desired pH prior the polymerization stage. The absorbency underload and swelling capacity of the prepared SAPs were then evaluated. Results are summarized in Tables 4 and 5. Cross-linking agents used were GDGE and EAS which are the most polar compounds among the evaluated agents.

As shown in Tables 4 and 5, maximum swelling capacity of “anionic” hydrogels (35.6 g saline/g) was obtained at pH 6.2. Under slightly acidic (pH <6.2) conditions, most of the carboxylate anions were protonated, and consequently

Table 4 Effect of pH of acrylic acid solution on absorbency under load (in all runs 1.0 wt% of GDGE was used)

pH	Absorbency under load (g saline/g SAP)				
	0.01 (psi)	0.3 (psi)	0.6 (psi)	0.9 (psi)	CRC
5.3	29.6	22.4	20.6	17.9	17.9
6.2	35.6	32.4	25.3	21.7	20.5
7.2	30.1	19.2	18.0	17.0	17.0
8.3	28.2	18.7	16.3	14.1	18.5

Table 5 Effect of pH of acrylic acid solution on absorbency under load (in all runs 1.0 wt% of EAS was used)

pH	Absorbency under load (g saline/g SAP)				
	0.01 (psi)	0.3 (psi)	0.6 (psi)	0.9 (psi)	CRC
5.3	32.6	30.4	23.6	19.9	18.9
6.2	35.2	31.2	24.1	20.2	19.2
7.2	33.0	27.8	23.4	18.9	17.7
8.3	31.8	25.6	21.4	16.6	16.2

swelling values decreased. At higher values of pH some of carboxylic acid groups were ionized and the electrostatic repulsion between carboxylate anionic groups caused an enhancement of the swelling capacity. Then, at higher pH 6.2, a charge screening effect of the counter ions (cations) reduced the swelling.

Biodegradability

The biodegradability test results showed the formation of *P. aeruginosa* colonies and the presence of clear zones around *T. rubrum* colonies. The results were an indication that the cross-links between the polymer chains that were made up of sugar monomers were degrading and the polymer chains were breaking apart (Fig. 3). Therefore, superabsorbent polymer cross-linked with sugar monomers can be classified as biodegradable materials.

More works need to be carried out to confirm the biodegradability which is beyond the scope of this study.

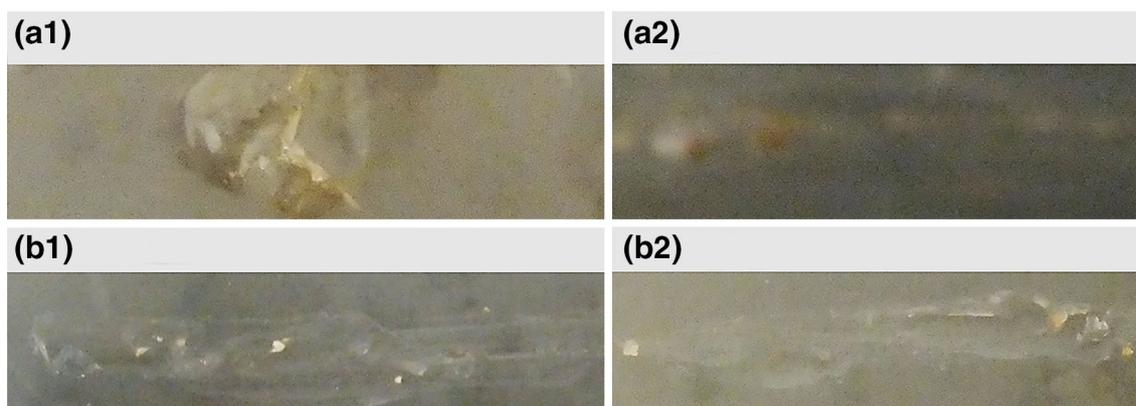


Fig. 3 Plate assay to visualize biodegradation by *P. aeruginosa* **a1** allyl sucrose, **a2** epoxy allyl sucrose and by *T. rubrum* **b1** allyl sucrose, **b2** epoxy allyl sucrose

Conclusion

In the present study, new series of cross-linking agents were used for making superabsorbent polymers with enhanced absorbent properties and free of acrylate cross-linkers. Among the cross-linking agents, sucrose-based allyl and epoxy agents were used. Superabsorbent polymers were prepared in a one-step process via free radical polymerization, using a persulfate initiator. Certain variables (i.e., type of cross-linker and its concentration and pH of the monomers) for the preparation of SAP were systematically optimized to achieve a hydrogel with maximum AUL. The optimum reaction conditions to obtain maximum absorbent capacity of saline (35.6 g/g) were found to be with GDGE at 1.0 % and a pH 6.2. Under these conditions the highest AUL and liquid uptake were also obtained. Morphological examination of the prepared SAP by SEM indicated the porosity nature of the SAP cross-linked with epoxy allyl sucrose. Superabsorbent polymers cross-linked with sucrose-based cross-linking agents were subjected to biodegradability test using the organisms *P. aeruginosa* and *T. rubrum*. Results showed that these polymers can be classified as biodegradable materials.

Acknowledgments The authors would like to extend their sincere gratitude to An-Najah National University and the Palestinian Ministry of High Education for the financial support received for this study.

References

- Buchholz FL, Graham AT (1998) Modern superabsorbent polymer technology. Wiley, New York. Chap 1–7
- Brannon-Peppas L, Harland RS (1990) Absorbent polymer technology. Elsevier, Amsterdam. Chap 1–4
- Buchholz FL, Peppas NA (1994) Superabsorbent polymers science and technology. ACS symposium series, 573, American Chemical society, Washington, DC. Chap 2, 7, 8, 9
- Zohuriaan-Mehr MJ, Kabiri K (2008) Superabsorbent polymer materials: a review. Iran Polym J 17(6):451–477
- Raju PM, Raju KM (2001) Design and synthesis of superabsorbent polymers. J Appl Polym Sci 80:2635–2639
- Tsubakimoto T, Shimomura T, Irie Y (1987) Absorbent article. U.S. Patent: 4,666,983
- Ben-Hur M, Keren R (1997) Polymer effects on water infiltration and soil aggregation. Soil Sci Soc Am J 61:565–570
- Bakass M, Mokhlisse A, Lallemand M (2002) Absorption and desorption of liquid water by a superabsorbent polymer: effect of polymer in the drying of the soil and the quality of certain plants. J Appl Polym Sci 83:234–243
- Ottenbrite RM, Park K, Okano T (2010) Biomedical applications of hydrogels hand book. Springer, New York
- Weerawarna SA (2009) Method for making biodegradable superabsorbent particles. US Patent 2009/0324731 A1
- Choi SG, Kerr WL (2003) Water mobility and textural properties of native and hydroxypropylated wheat starch gels. Carbohydr Polym 51:1–8
- Kopeček J, Yang J (2007) Review hydrogels as smart biomaterials. Polym Int 56:1078–1098
- More SM, Kulkarni RV, Sa B, Kayane NV (2010) Glutaraldehyde-crosslinked poly (vinyl alcohol) hydrogel discs for the controlled release of antidiabetic drug. J Appl Polym Sci 116:1732–1738
- Colombo P (1993) Swelling-controlled release in hydrogel matrices for oral route. Adv Drug Deliv Rev 11:37–57
- Farris S, Schaich KM, Liu LS, Piergiovanni L, Yam KL (2009) Development of polyion-complex hydrogels as an alternative approach for the production of bio-based polymers for food packaging applications, a review. Trend Food Sci Tec 20:316–332
- Deligkaris K, Shiferaw T, Olthuis W, Berg AVD (2010) Hydrogel-based devices for biomedical applications. Sensor Actuat B Chem 147:765–774
- Shin J, Braun PV, Lee W (2010) Fast response photonic crystal pH sensor based on template photo-polymerized hydrogel inverse opal. Sensor Actuat B Chem 150:183–190
- Zheng Y, Hua S, Wang A (2010) Adsorption behaviour of Cu²⁺ from aqueous solutions onto starch-g-poly (acrylic acid)/sodium humate hydrogels. Desalination 263:170–175
- Carvalho HWP, Batista APL, Hammer P, Luz GHP, Ramalho TC (2010) Removal of metal ions from aqueous solution by chemical polymeric hydrogel. Environ Chem Lett 8:343–348
- Zhang SF, He YF, Wang RM, Wu ZM, Song PF (2013) Preparation of emulsifier-free acrylate cross-linkable copolymer

- emulsion and application in coatings for controlling indoor humidity. *Iran Polym J* 22(6):447–456
21. Zhang W (2013) Synthesis of AA-based SAR interpenetrated with PVA and AM. *Sci Eng Compos Mat* 20(4):379–382
 22. Jiang S, Sun X, Ling L, Wang J (2013) Preparation and properties of anti-salt super absorbent resin. *Adv Mater Res* 807–809:2693–2698
 23. Raihan M, Nadras O, Zulkifli A, Fauzi R (2013) The effects of acrylamide loading on the swelling capacity of superabsorbent polymer in different aqueous medium. *Adv Mater Res* 812:20–29
 24. Bahaj H, Benaddi R, Bakass M, Bayane C (2010) Swelling of superabsorbent polymers in an aqueous medium. *J Appl Polym Sci* 115(4):2479–2484
 25. Wang G, Li M, Chen X (1997) Inverse suspension polymerization of sodium acrylate. *J Appl Polym Sci* 65:789–794
 26. Mohammed AD, Young DA, Vosloo HCM (2014) Synthesis and study of superabsorbent properties of acryloylated starch ester grafted with acrylic acid. *Starch/Staerke* 66(3–4):393–399
 27. Chen Z, Dong F, Liu M, Qi X (2011) Preparation and properties of porous poly(sodium acrylate-co-acrylamide) salt-resistant superabsorbent composite. *Polym Eng Sci* 51(12):2453–2464
 28. Hussain YA, Liu T, Roberts GW (2012) Synthesis of cross-linked, partially neutralized poly(acrylic acid) by suspension polymerization in supercritical carbon dioxide. *Ind Eng Chem Res* 51(35):11401–11408
 29. Shi W, Dumont MJ, Ly EB (2014) Synthesis and properties of canola protein-based superabsorbent hydrogels. *Eur Polym J* 54:172–180
 30. Hemvichian K, Chanthawong A, Suwanmala P (2014) Synthesis and characterization of superabsorbent polymer prepared by radiation-induced graft copolymerization of acrylamide onto carboxymethyl cellulose for controlled release of agrochemicals. *Radiat Phys Chem* 103:167–171
 31. Kalaleh H-A, Tally M, Atassi Y (2013) Preparation of a clay based superabsorbent polymer composite of copolymer poly (acrylate-co-acrylamide) with bentonite via microwave radiation. *Res Rev Polym* 4(4):145–150
 32. Zhang H, Kallimanis A, Koukkou AI, Drinas C (2004) Isolation and characterization of novel bacteria degrading polycyclic aromatic hydrocarbons from polluted Greek soils. *Appl Microbiol Biotechnol* 65:124–131
 33. Sachinvala ND, Winsor DL, Parikh DV, Solhjoo HH, Parks D, Vigo TL, Blanchard EJ, Bertoniere NR (2002) Use of sucrose-based epoxy formulations and cellulosic fibers in the design, preparation, and screening of new composite insulation materials. *Polym Adv Technol* 13(1):66–79
 34. Sachinvala ND, Litt MH (1997) Epoxy monomers from sucrose. US Patent: 5646226
 35. Pham HQ, Marks MJ (2005) Epoxy resins. In: Ullmann's encyclopedia of industrial chemistry. Wiley, Weinheim
 36. Bhattacharya SS, Mazahir F, Banerjee F, Vermaa A, Ghosh A (2013) Preparation and in vitro evaluation of xanthan gum facilitated superabsorbent polymeric microspheres. *Carbohydr Polym* 98:64–72
 37. Jiang JO, Zhao S (2014) Acrylic superabsorbents: a meticulous investigation on copolymer composition and modification. *Iran Polym J* 23(5):405–414
 38. Shah S, Ranjha NM, Javid Z (2013) Development and evaluation of pH-dependent interpenetrating network of acrylic acid/polyvinyl alcohol. *Iran Polym J* 22(11):811–820