



Hybrid hydrogel based on pre-gelatinized starch modified with glycidyl-crosslinked microgel

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Abstract

Hybrid hydrogels based on pre-gelatinized starch were synthesized by inverse emulsion polymerization through modifying the starch with a glycidyl-crosslinked microgel. Glycidyl-crosslinked microgel is a special latex with high ability to impart hydrophilic characteristics to various substrates. Glycidyl-crosslinked microgel latexes with various structures were synthesized, and the effect of latex type on swelling capacity of the hybrid hydrogels based on pre-gelatinized starch was investigated. The highest swelling capacity was achieved for a pre-gelatinized starch modified with a glycidyl-crosslinked microgel latex based on poly(acrylic acid, sodium acrylate, acrylamide, 2-acrylamide-2 methyl propane sulfonic acid) (AA–SA–AM–AMPS). The swelling values of this hybrid hydrogel in distilled water and saline solution were 52.4 and 28.8 g/g, respectively. A key advantage of these hybrid hydrogels is that starch constitutes 64% of their structure. Given the fact that such hybrid hydrogels display low absorbency under load (AUL), they were surface crosslinked using microwave heating instead of conventional heating. Ethylene glycol diglycidyl ether was used as surface crosslinker. The AUL of the surface crosslinked hybrid hydrogels was increased by 85%. The hydrogels were characterized using FTIR, thermogravimetric analysis, scanning electron microscopy, and rheological measurements.

Keywords Hydrogel · Inverse emulsion polymerization · Pre-gelatinized starch · Surface modification · Surface crosslinking

Introduction

Starch is the second most readily available natural polymer [1]. As a polysaccharide, it consists of repeating D-glucopyranose units, linked together with α -1,4 and α -1,6 glycosidic bonds [2]. Pre-gelatinized starch is a modified starch that, in addition to its solubility in cold water, it possesses a high water holding capacity. It is a preferred starch, which is used in industry to avoid highly viscous gels [3]. The potential advantages of using starch in its gelatinized state have been extensively reviewed [4].

Superabsorbent hydrogels are hydrophilic polymer networks that can absorb and retain large amount of water and aqueous solutions [5, 6], and have been used in both

hygienic and non-hygienic applications extensively [7]. Superabsorbent hydrogel structures can be synthetic, natural, or synthetic-natural hybrid [5]. Hybrid hydrogels are mostly prepared through graft polymerization of acrylic monomers such as acrylic acid and acrylamide, 2-acrylamido-2-methyl propane sulphonic acid (AMPS) onto natural polymers [5, 6]. Although hybrid hydrogels can be prepared based on proteins or polysaccharides, those based on polysaccharides are being extensively used due to their variety and accessibility, low price, and remarkable rheological properties in aqueous media [8–10].

Preparation of hybrid hydrogels through graft polymerization has several shortages such as low grafting efficiency, homopolymerization of acrylic monomers, low content of natural component, and low absorbency under load (AUL). A lot of work has been done on hybrid hydrogels containing natural polymers such as collagen [11], starch [12], carrageenan [13], agarose [14], and chitosan [15].

Glycidyl-crosslinked microgels have been recently prepared using inverse emulsion polymerization of acrylic monomers and diglycidyl chemicals as crosslinker. These

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glycidyl-crosslinked microgels possess considerably higher thickening properties than microgels crosslinked with the conventional multifunctional acrylic crosslinkers such as methylene bisacrylamide or poly(ethylene glycol) diacrylate [16]. Moreover, glycidyl-crosslinked microgel latex has the ability to induce absorbency to different substrates. The promotion of high water absorbency to polyester fiber was reported using glycidyl-crosslinked microgel, where swelling capacity of the polyester fiber was increased to 75 g/g [17].

Due to their low AUL, the conventional hybrid hydrogels based on starch cannot be used in hygiene or agricultural applications. Therefore, as a common practice to increase AUL of synthetic superabsorbent materials, such hydrogels need to be crosslinked at their surface to achieve desirable mechanical and swelling properties [18]. The AUL enhancement after surface modification depends on several parameters including surface crosslinker type, surface crosslinker concentration, surface treatment temperature, and surface treatment time. Surface crosslinking reaction is carried out between acrylic acid of SAP and surface crosslinking agents, i.e., ethylene glycol diglycidyl ether, polyethylene glycol diglycidyl ether, and epoxy silanes for AUL enhancement in full acrylic superabsorbents [18–20].

In this research, glycidyl-crosslinked microgel latex was used to induce absorbency to pre-gelatinized starch in preparation of starch-based hybrid hydrogels. We first prepared glycidyl-crosslinked microgels by inverse emulsion polymerization of 1,4-butanediol diglycidyl ether or poly(ethylene glycol) diglycidyl ether, and then modified the pre-gelatinized starch with the prepared glycidyl-crosslinked microgel to induce absorbency to its hybrid hydrogel. Finally, the surface of the hydrogel was crosslinked to enhance its AUL. Surface crosslinking of superabsorbent hydrogels is carried out mostly through the conventional heating at high temperature for long period of time [18]. In this research, the surface crosslinking was achieved using a more efficient microwave process.

Experimental

Materials

Acrylic acid (AA, Merck), acrylamide (AM, Merck), and 2-acrylamide-2-methyl propane sulfonic acid (AMPS, Fluka) as monomers, and 2,2'-azobis-isobutyronitrile (AIBN, Fluka, recrystallized in ethanol) as initiator were used. Pre-gelatinized starch from Glucozan Co., Iran, was used. Poly(ethylene glycol) diglycidyl ether (PEGDGE), 1,4-butanediol-diglycidyl-ether (1,4-BDDGE), and ethylene glycol diglycidyl ether (EGDGE) (Sigma-Aldrich) as crosslinker were used as received. Sorbitan monooleate (Span 80, HLB 4.3) and poly(ethylene glycol) sorbitan monooleate (Tween 80, HLB 15) were purchased from Merck and used as emulsifier. Liquid paraffin ($\rho = 0.85 \text{ g/cm}^3$) from Farshid Shahrza Co., (LP140) was used as continuous phase in inverse emulsion polymerization.

Synthesis

Synthesis of glycidyl-crosslinked microgel through inverse emulsion polymerization

Synthesis of microgel latex was performed in a 250 mL four-neck glass reactor equipped with an agitator, a condenser, a nitrogen inlet gas, and an injection inlet pump. The continuous phase was composed of paraffin, Span 80, and Tween 80 was stirred for 15 min using a magnetic stirrer, and then transferred into the reactor. The aqueous phase including monomers, crosslinker, and water were mixed and added dropwise to the continuous phase for 30 min. The mixture under nitrogen blanket was kept under mixing at 350 rpm for 30 min. The slurry was then heated to 70 °C, kept at this temperature, the initiator was added into, and the reaction was continued for 4 h. The formulation for the synthesized latexes is shown in Table 1.

Table 1 Materials and their amounts used in synthesis of microgel latexes

Microgel structure	Monomers mol (%)	Crosslinker type	Weight of crosslinker (g)	Span 80 (g)	Tween 80 (g)	Paraffin (g)	Reaction time (h)
Poly(AA–SA)	90–10	1,4-BDDGE	0.4	3.44	1.16	64.12	4
Poly(AA–SA)	90–10	1,4-BDDGE	0.2	3.44	1.16	64.12	4
Poly(AA–SA–AM–AMPS)	54–6–32–8	PEGDGE	0.2	5.316	1.793	64.749	1.5
Poly(AA–SA–AM–AMPS)	54–6–32–8	PEGDGE	0.1	5.316	1.793	64.749	1.5
Poly(AA–SA–AM)	72–8–20	1,4-BDDGE	0.2	3.44	1.16	64.12	4

Degree of neutralization: 90%, temperature: 70 °C, HLB: 7, amount of initiator: 0.2 g

Preparation of the hybrid hydrogel

A certain amount of the glycidyl-crosslinked microgel was added to a certain amount of pre-gelatinized starch to carry out a chemical reaction on starch surface for achieving superabsorbency. After mixing, the mixture was placed in an oven at 70 °C for 2 h, and then washed several times with acetone to remove paraffin, impurities and unreacted polymer latex. Finally, the product was dried out in an oven at 50 °C for 3 h.

Surface crosslinking of pre-gelatinized starch hybrid hydrogel

EGDGE was used as a crosslinker in surface modification of the hybrid hydrogel. Given amounts of water and acetone (10:90) and crosslinker were added to 1.5 g of hybrid hydrogel prepared in the previous step. Surface treatment was carried out using both conventional heating and microwaving for a given time and temperature. Figure 1 shows a general outline of the steps involved in the reaction.

Characterization

Viscosity measurements

The apparent viscosity of the synthesized latex powder in distilled water (1 g sample in 100 mL solvent) was measured at room temperature with a digital rotational viscometer (model Brookfield, Selecta, Spain).

FTIR spectroscopy

A model EQUINOX55 spectrophotometer (Germany) was used to obtain FTIR spectrum of the plates containing the sample with KBr matrix.

Microstructural and elemental analysis

A scanning electron microscope (model S360, Cambridge Company) equipped with an energy-dispersive X-ray spectrometer (EDX, INCA model, Ofordinst) was used to perform a microstructural study on the samples. A thin layer of palladium–gold alloy was used to coat the samples.

TGA thermogram

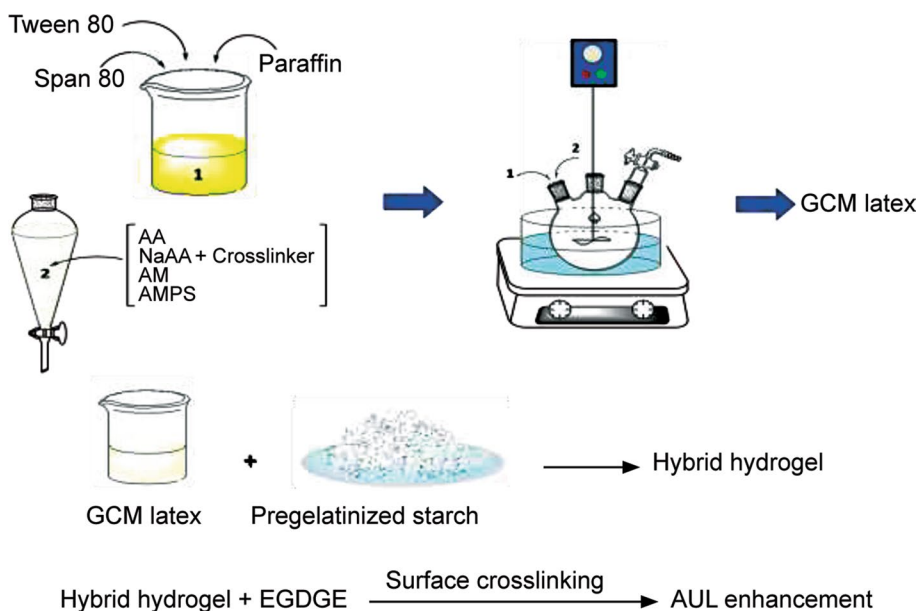
Thermogravimetric analysis (TGA) was performed on powder samples using a TGA-PL (PL1500, England) under nitrogen at a heating rate of 10 °C/min. Samples used in FTIR, TGA, and SEM–EDX tests were immersed in distilled water to remove their sol content before analysis.

Swelling measurements

A tea bag method [21] was used to measure the swelling capacity of the hydrogel samples. Thus, 0.2 g of the hydrogel was added into 100 mL distilled water and allowed to fully swell at room temperature. The swelling capacity was calculated using the following equation:

$$\text{Swelling} = \frac{w_s - w_d}{w_d}, \quad (1)$$

Fig. 1 Schematic for different steps of surface crosslinked hybrid hydrogel preparation



where w_s and w_d are the weights of the swollen and dried gels, respectively.

Absorbency under load (AUL) measurements

A weighed dried SAP sample (0.5 g) was uniformly dispersed on the surface of polyester gauze, which had been located on a macro-porous sintered glass filter plate placed in a Petri dish. A cylindrical solid load (Teflon, $d = 60$ mm) was put on the dry SAP particles, while it could be freely slipped in a glass cylinder. The desired load of 0.3 psi was applied on each sample. Then, a 0.9% saline solution was placed in a Petri dish. After 30 min, the maximally swollen particles were removed and re-weighed [20]. AUL value was calculated by Eq. (1).

Rheology

The rheological measurement was performed on the swollen samples with the concentration of 10% (1 g sample in 10 g distilled water). A para-physical vibrational device (model MCR 300 with parallel pages at 25 °C) was used where the page diameter and distance were 25 and 3 mm, respectively [22].

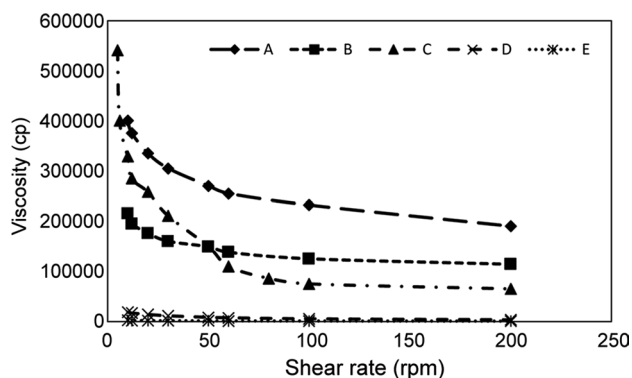


Fig. 2 Viscosity-shear rate curves of: **a** poly(AA–SA–AM–AMPS) with 0.2 g PEGDGE, **b** poly(AA–SA–AM–AMPS) with 0.1 g PEGDGE, **c** poly(AA–SA) with 0.4 g 1,4-BDDGE, and **d** poly(AA–SA–AM) with 0.2 g 1,4-BDDGE; **e** poly(AA–SA) with 0.2 g 1,4-BDDGE

Table 2 Effect of latex type on swelling capacity of hybrid hydrogel in water, saline solution, and AUL

Microgel structure	Crosslinker type	Weight of crosslinker (g)	Absorption in water (g/g)	Absorption in saline solution (g/g)	AUL (g/g)
Poly(AA–SA)	1,4-BDDGE	0.4	39.4	18.1	6.6
Poly(AA–SA)	1,4-BDDGE	0.2	12.4	7.5	5.2
Poly(AA–SA–AM–AMPS)	PEGDGE	0.2	52.3	28.8	7
Poly(AA–SA–AM–AMPS)	PEGDGE	0.1	18	8.2	4.4
Poly(AA–SA–AM)	1,4-BDDGE	0.2	18.1	12.4	4.5

Results and discussion

Glycidyl-crosslinked microgel synthesis

Glycidyl-crosslinked microgel latexes with different structures were synthesized. The products displayed high thickening properties which made them suitable for imparting hydrophilic properties to substrate.

Figure 2 shows the apparent viscosity of synthesized latexes versus shear rate. According to this figure, viscosity decreases with increasing shear rate. This behavior can be seen in all the microgels swollen in water. Such observation refers to the pseudoplastic behavior of the synthesized microgels [23, 24]. At low shear rates, the relaxation time was long, while at high shear rates, the microgels were deformed easily and apparent viscosity was reduced. Poly(acrylic acid, sodium acrylate, acrylamide, 2-acrylamide-2-methyl propane sulfonic acid) (AA–SA–AM–AMPS) having 0.2 g of PEGDGE crosslinker shows the highest apparent viscosity.

Effect of latex type on swelling capacity of the modified pre-gelatinized starch

Table 2 shows the swelling capacity of the modified pre-gelatinized starch with different latexes. The swelling capacities of pure sample in distilled water and saline solution (NaCl 0.9% solution) are 9.2 and 6.1 g/g, respectively. Swelling of modified pre-gelatinized starch was considerably increased after treatment with the acrylic latex. For the pre-gelatinized starch modified by poly(AA–SA–AM–AMPS) latex, the highest swelling capacities in distilled water and saline solution are 52.3 and 28.8 g/g, respectively.

The higher absorbency of poly (AA–SA–AM–AMPS)-based hydrogel in saline solution can be attributed to the ionizing part of polymer latex. The increased ionic contribution in a hydrogel increased ionic mobility inside the gel phase, which led to swelling enhancement. Furthermore, the presence of AMPS in hydrogel structure generally causes increased salt absorbency [25].

Modification of the pre-gelatinized starch by poly(AA–SA–AM–AMPS) and addition of 0.2 g of

crosslinker was carried out more efficiently than other latexes, and enhanced the swelling capacity. Therefore, the hybrid hydrogel prepared using the above latex was chosen for further study, including other analyses and surface crosslinking.

FTIR analysis

Figure 3 shows the FTIR spectrum of the unmodified pre-gelatinized starch, poly(AA–SA–AM–AMPS) and the pre-gelatinized starch modified by poly(AA–SA–AM–AMPS) latexes.

In poly(AA–SA–AM–AMPS) FTIR spectrum, the peak at 1569.8 cm^{-1} corresponds to the asymmetrical tension of CO group of carboxylate ions. In addition, the medium intensity peak at 1455.6 cm^{-1} is due to the symmetrical tension of CO group of carboxylate ions. The absorption peaks at

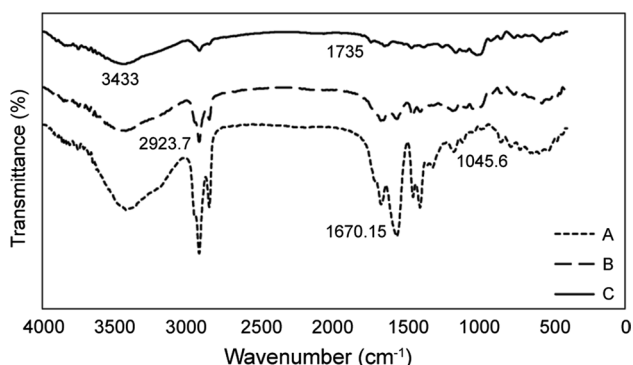


Fig. 3 FTIR spectra of: **a** poly(AA–SA–AM–AMPS), **b** pre-gelatinized starch modified by poly(AA–SA–AM–AMPS) latexes, and **c** unmodified pre-gelatinized starch

1045.6 cm^{-1} which were observed for AMPS revealed the existence of SO group [26–28].

Considering the spectrum obtained for pre-gelatinized starch, the peak at 3433 cm^{-1} could be related to OH group. The band at 2922.6 cm^{-1} was attributed to the C–H tension vibration and the band at 1054.2 cm^{-1} was due to the tension of $\text{CH}_2\text{--O--CH}_2$ [21, 29]. Considering the spectrum of the unmodified and modified pre-gelatinized starch, the high intensive peak at 1735 cm^{-1} disappeared after the modification of pre-gelatinized starch by poly(AA–SA–AM–AMPS), confirming that a chemical reaction was carried out between the acrylic latex and pre-gelatinized starch.

The peak related to carboxamide which appeared in poly(AA–SA–AM–AMPS) spectral absorption at 1670.1 cm^{-1} disappeared after the modification reaction with pre-gelatinized starch, indicating that a reaction occurred between the carboxamide and functional groups on the pre-gelatinized starch.

Morphology

The images from scanning electron microscopy (SEM) taken for pre-gelatinized starch, pre-gelatinized starch modified by poly(AA–SA–AM–AMPS), and surface crosslinked hydrogel are demonstrated in Fig. 4. The pre-gelatinized starch particles have smooth surface with no porosity. A new morphology was observed for the samples modified by glycidyl-crosslinked microgel latex. The latex has uniformly covered the starch surface. After the modification reaction, the surface area between the pre-gelatinized starch and poly(AA–SA–AM–AMPS) was increased.

Figure 5 demonstrates the elemental map of the elements including Na, S, and N (Na map, S map, and N map) obtained from the surface of the

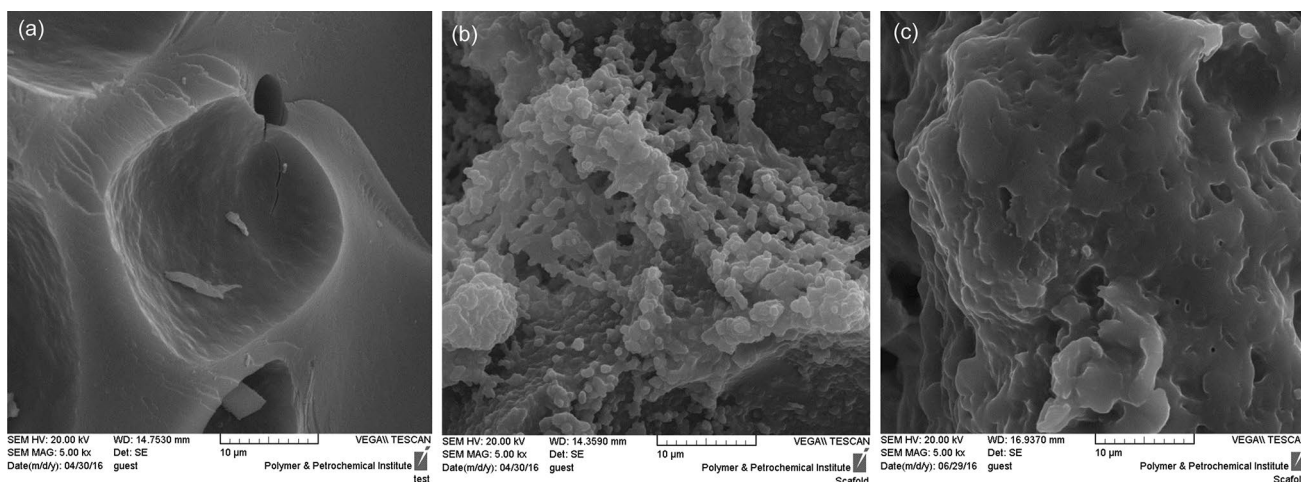


Fig. 4 SEM image of: **a** unmodified pre-gelatinized starch, **b** pre-gelatinized starch modified by poly(AA–SA–AM–AMPS), and **c** surface crosslinked hydrogel

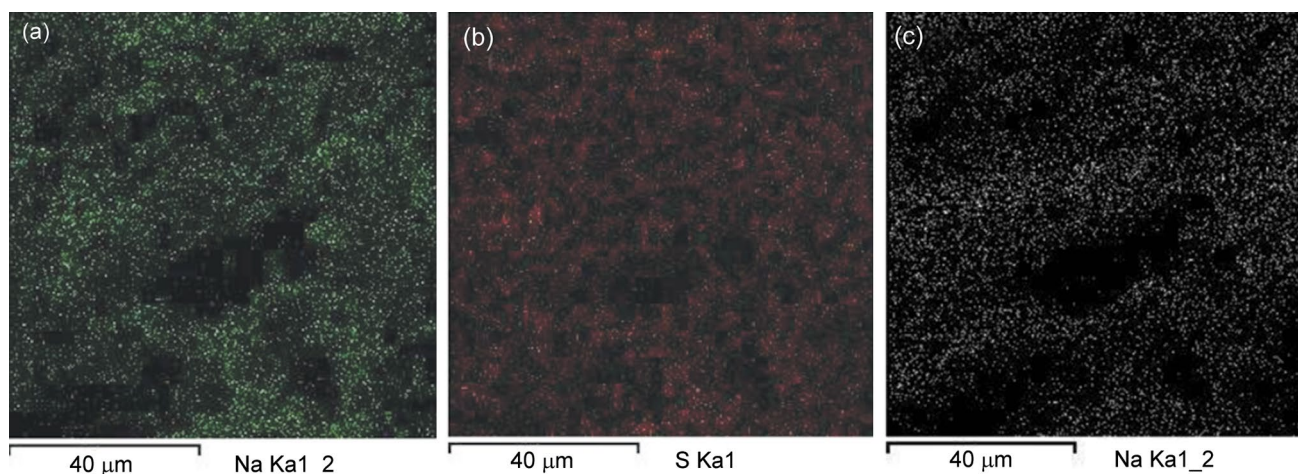


Fig. 5 Elemental maps of: **a** Na, **b** S, and **c** N atoms of the surface of hybrid hydrogel

Table 3 Scattering percentage of different atoms for (A) poly(AA–SA–AM–AMPS) and (B) hybrid hydrogel

Elements	A	B
C	39.67	40.52
N	28.99	22.09
O	27.72	36.06
Na	3.06	1.16
S	0.57	0.16

hydrogel synthesized from pre-gelatinized starch modified by poly(AA–SA–AM–AMPS) polymer latexes. This figure confirms the presence of sulfur and sodium elements in the sample modified by glycidyl-crosslinked microgel latex. Since these elements are not present in the pre-gelatinized starch, they certainly originated from poly(AA–SA–AM–AMPS). In addition, the image revealed a uniform dispersion of these elements on the surface of the pre-gelatinized starch, which could be attributed to the uniform reaction between the starch and glycidyl-crosslinked microgel latex.

Contribution of different atoms in the structure of two samples of poly(AA–SA–AM–AMPS) and pre-gelatinized starch modified by poly(AA–SA–AM–AMPS), shown in Table 3, was obtained by SEM–EDX. By the substitution of the data in Table 3 into Eq. (2), the percentages of natural and synthetic components present in the basic hydrogels of pre-gelatinized starch were calculated as follows:

$$\text{Weight percent of synthetic component (} w\% \text{)} = \frac{w_2}{w_1} \times 100. \quad (2)$$

In this equation, w_2 is the atomic percentage of the elements Na, S, or N in the synthesized hydrogel and w_1 is the atomic percentage of the above-mentioned elements in poly(AA–SA–AM–AMPS). After performing the above

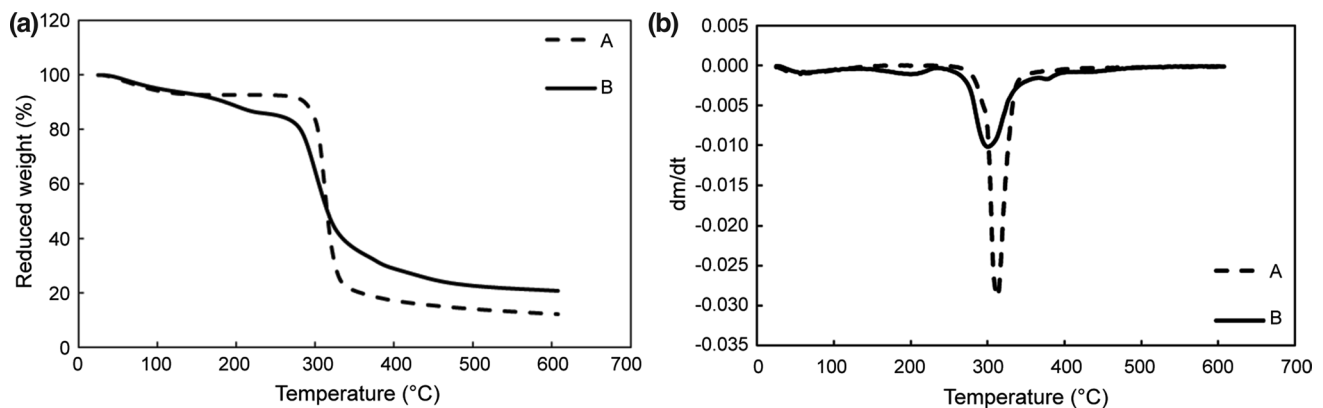
calculations, the percentage of natural component in the hydrogel synthesized from the pre-gelatinized starch was found to be almost 64% and the percentage of synthetic component in these products was about 36. This result shows that the contribution of natural part in the hybrid hydrogel is significantly high, and it is much higher than that in those prepared by grafting method. Table 4 shows the natural part contribution in hybrid hydrogels reported in the literature previously. Natural parts of the hybrid hydrogels based on starch [30], tara gum [31], chitosan [32], and sodium alginate [33] have been already reported (15, 2, 1, and 6), respectively. The results for other natural-based hybrid hydrogels are also seen in this table [34–36]. The results indicate that this new method has great potential in the economic production of environmentally friendly hybrid hydrogels based on glycidyl-crosslinked microgel latex due to high contribution of natural part in the structure of these hydrogels.

TGA analysis

Figure 6 shows the thermogravimetric curves of the unmodified and poly(AA–SA–AM–AMPS)-modified pre-gelatinized starch. There are two degradation stages for unmodified sample. The first stage between 25 and 100 °C is related to water removal. The second stage which can be observed between 280 and 400 °C is related to the degradation of the main chains of polysaccharides where the largest amount of sample is destroyed. The degradation pattern of the modified pre-gelatinized starch is completely different from that of unmodified sample. The thermal degradation process of the modified pre-gelatinized starch has three stages. The first stage is related to the water discharge from the sample. The second stage is for destruction of microgel part (mostly AMPS) and the third stage belongs to the degradation of natural part. In contrast, in an unmodified sample, the TGA

Table 4 Percentage of natural component of hybrid hydrogels reported in the literature

Designate	Natural polymer	Structure	Natural polymer in hybrid hydrogel (%)	References
1	Starch	Polyacrylic acid	15	[30]
2	Tara gum	Acrylic acid	2	[31]
3	Chitosan	Polyvinyl alcohol	1	[32]
4	Sodium alginate	Polyacrylamide	6	[33]
5	Chitosan	Sodium acrylate- <i>co</i> -hydroxyethyl methacrylate	3–12	[34]
6	Durian seed starch	Polyvinyl alcohol	3	[35]
7	Cassava starch	Polyacrylic acid	7.5	[36]
8	Pre-gelatinized starch	Poly(acrylic acid-sodium acrylate-acrylamide-2-acrylamido-2-methylpropane sulfonic acid)	64	Present work

**Fig. 6** **a** TGA and **b** DTG of: **a** unmodified pre-gelatinized starch and **b** pre-gelatinized starch modified by poly(AA–SA–AM–AMPS) latexes

thermogram of the modified pre-gelatinized starch has no sharp transition. The TGA test results showed that pre-gelatinized starch is successfully modified and its thermal degradation behavior is certainly changed.

The initial decomposition temperature (IDT) was reduced from about 280 °C in the unmodified sample to 180 °C in the hydrogel of the modified sample. This reduction was due to the instability of sulfonic acid groups in the polymers containing AMPS and desulfonation reaction. The AMPS-containing hydrogel is very sensitive to heat, and it has a low thermal stability. Due to the presence of less stable sulfonic groups in the structure of pre-gelatinized starch modified by poly(AA–SA–AM–AMPS), it is susceptible to degradation and thus the modified sample shows lower IDT than unmodified one [37].

The char yields of unmodified pre-gelatinized starch and pre-gelatinized starch modified by poly(AA–SA–AM–AMPS) were 12.15 and 20.02%, respectively. The lower char yield of unmodified sample compared with that of the modified sample can be attributed to the lower thermal stability of polysaccharides than acrylic polymers. The hydrogel prepared from modified pre-gelatinized

starch with 36% acrylic part accounts for its higher char yield compared with pure pre-gelatinized starch [26, 38].

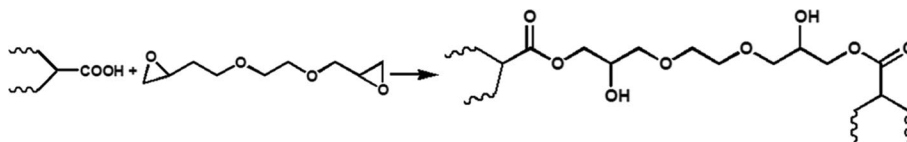
Swelling capacity of hybrid hydrogel after surface crosslinking

Table 5 shows the swelling capacity of surface crosslinked samples of hybrid hydrogel in distilled water and saline solution heated in a conventional oven for 2 h at 120 °C and heated in a microwave for 3, 5, and 7 min. Hybrid hydrogels mostly have low gel strength. To increase their mechanical strength, the hydrogels were subjected to surface crosslinking. After surface crosslinking, the swelling capacity in water and saline solution was decreased due to increasing crosslinking density in the surface of samples, but the AUL was increased.

The absorbency under load (AUL) for surface crosslinked hybrid hydrogels is shown in Table 5. Surface treatment using microwave resulted in achieving hybrid hydrogel with higher AUL. The AUL of surface-treated modified pre-gelatinized starch was increased up to 13 g/g.

Table 5 Swelling capacity of surface crosslinked hybrid hydrogels in distilled water and saline solution, and AUL

Sample	Surface treatment condition	Swelling in water (g/g)	Swelling in saline solution (g/g)	AUL (g/g)
Non-treated sample	–	52.3	28.8	7
1	2 h, 120 °C (oven)	28.105	17.24	9.43
2	3 min- MW	32.95	20.55	10.59
3	5 min- MW	35.51	21.23	11.69
4	7 min- MW	38.53	23.61	13.16

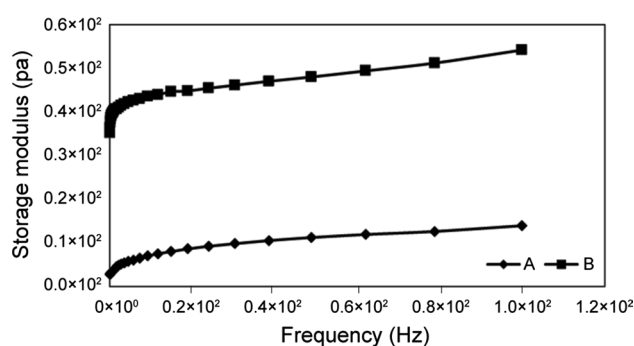
Fig. 7 Surface crosslinking reaction

During surface crosslinking process, as shown in Fig. 7, the carboxylic acid groups of hybrid hydrogels reacted with epoxy groups, leading to creating new crosslinks on the surface of hybrid hydrogels. The AUL has a direct relationship with crosslink density. Therefore, the increase of crosslink density during surface treatment would lead to AUL enhancement.

The surface crosslinking is a necessary step to have a hybrid hydrogel to increase its potential for industrial applications. Before surface crosslinking, the AUL of a hybrid hydrogel is low, but it can be promoted during surface treatment process. During surface treatment, a chemical reaction is carried out mostly between the carboxylic acid of superabsorbent hydrogel with epoxy groups of surface crosslinking agent. The usual method for surface crosslinking is by the conventional heating which requires high temperature and long time. Microwave-assisted surface crosslinking which has been introduced in this paper for crosslinking of hybrid hydrogels significantly reduces the crosslinking time from hours to less than 10 min.

Rheological measurements

The storage modulus versus angular frequency curves for the pre-gelatinized starch hydrogel modified by poly(AA–SA–AM–AMPS) latex and surface crosslinked hybrid hydrogel are shown in Fig. 8. As shown in both cases, with increasing frequency, the storage modulus of both hydrogels is increased. Surface crosslinking reaction of hybrid hydrogel leads to greater crosslink density which has a direct relationship with storage modulus. Modulus increases with increasing frequency due to the relaxation phenomenon in the polymer chains as a result of the applied tensions. At low frequencies, the polymer chains have enough time to relax and they are deformed in response to imposed shear stress. At high frequencies, the polymer

**Fig. 8** Storage modulus-angular frequency curves of: **a** hydrogel of pre-gelatinized starch modified by poly(AA–SA–AM–AMPS) latex and **b** surface crosslinked hybrid hydrogel

chains do not have sufficient time to relax, so their flexibility decreases and the storage modulus increases [16, 39].

Conclusion

In this study, hybrid hydrogels based on pre-gelatinized starch containing 64% natural component and 36% synthetic component were prepared. Hybrid hydrogels were prepared through a new two-step method. First, glycidyl-crosslinked microgel latex was prepared through inverse emulsion polymerization, and the modification of pre-gelatinized starch with glycidyl-crosslinked microgel was performed to impart water absorbency of the starch. After modification of hybrid hydrogel, the maximum swelling values of 52.4 and 28.8 g/g were obtained, respectively, in distilled water and saline solution. In the preparation of hybrid hydrogels, this new method does not have the limitations of grafting procedure such as homopolymerization, low grafting efficiency, and low contribution of natural component in hybrid hydrogel structure.

Surface crosslinking of the hybrid hydrogel was carried out to overcome low gel strength of the hybrid hydrogels. Hybrid hydrogels were surface crosslinked with EGDGE using two methods including, conventional heating and microwave (MW) heating. The AUL of hybrid hydrogel significantly increased (85%) after surface modification. Surface crosslinking was used as a key process to overcome low AUL of hybrid hydrogels. Microwave heating, as a very efficient technology, was employed for surface crosslinking of hybrid hydrogels to enhance AUL and lower the reaction time. High structural contribution of natural component (64%), low cost of pre-gelatinized starch, and reasonable and acceptable value of AUL make these hybrid hydrogels good candidates for industrial applications.

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