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Radiation-induced eco-compatible sulfonated starch/acrylic acid graft copolymers for sucrose hydrolysis

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ABSTRACT

Radiation-induced graft-copolymers capable of hosting sulfonic groups and having more effective catalytic activity towards sucrose hydrolysis were prepared. Acrylic acid monomer (AA) was copolymerized with sulfonated starch (SS) at different compositions using ionizing radiation. Swelling behavior of the prepared copolymers at different environmental conditions was studied as well as thermal stability. The hydrolysis of sucrose to glucose and fructose by sulfonated starch/acrylic acid (SS/AA) graft copolymers was investigated. The kinetics of the reaction was determined for various (SS/AA) graft copolymers compositions and at a temperature range of 40–60 °C. The catalytic activity of the copolymers was found to be dependent on the reaction temperature and (SS/AA) graft copolymers compositions, it increases as the reaction temperature and sulfonated starch content (in the feed solution) increases. The obtained results suggest that the prepared SS/AA copolymers could be considered as catalytic reagent for sucrose hydrolysis.

1. Introduction

The inverted sugar produced has been used as fructose-rich syrups, principally for beverage industries. The application of enzymes has long been used as the most used catalysts to hydrolyze sucrose and transform it into inverted sucrose on the industrial scale [Bussière, Nowak, & Cotillo, 1990]. However, their use is restricted to the food industry with a conversion of sucrose below 95% because the formed glucose and fructose tend to inhibit the hydrolysis reaction through the blocking of the receptor sites on the enzyme in addition to the production of waste, low thermal stability, and problems with separation and recovery of the enzyme from the product. To overcome these problems strongly acidic ion-exchange resins containing sulfonic acid groups were introduced and allowed a complete conversion of sucrose in the temperature range compatible with their stability, but with a relatively high level of impurities Yoshioka and Shimamura (1984). In addition to inhibiting the access of reactants with sizes larger than the interstices of the polymer chains [Mizota, Tsuneda, Saito, & Sugo, 1994]. The acid catalyzed hydrolysis of sucrose was perhaps the earliest catalytic reaction observed and nowadays belongs to the best investigated reactions at all. The reaction is generally considered to follow a first order reaction mechanism in which a fast pre-equilibrium protonation is followed by a unimolecular, rate-determining heterolysis of the fructosyl oxygen bond [Mega, Nishikawa, & Ikenaka, 1983; Younes, Pauli, Korb, & Siegers, 1985].

Sucrose hydrolysis was carried out over different solid catalysts (as zeolites [Moreau et al., 2000], silica with sulfonic acid groups [Heyraud & Rinaudo, 1982], poly(vinyl alcohol) with sulfonic acids [Pito, Fonseca, Ramos, Vital, & Castanheiro, 2009], heteropolyacids on silica [Dhepe, Ohashi, Inagaki, Ichikawa, & Fukuoka, 2005]).

In the respect of the increasing sensitiveness to environmental protection and of the increasing demand of eco-compatible products, to reduce the environmental impact; a global interest in polymers of renewable resources has evolved. The development of new products and materials, especially those which are non-petrochemicals and based on natural sources, are of increasing interest nowadays and deserves the attention of both academic and industrial research.

Among polymers of renewable resources; starch and its derivatives such as carboxymethyl starch (CMS) and sulfonic starch [Fa & Gui, 2006; Vieira, Klemm, Einfeldt, & Albrecht, 2005; Zhang, Ju, Zhang, & Yang, 2008] are currently enjoying increased attention owing to its biodegradability, availability and economic feasibility. Chemically modified starches with improved properties are becoming of more importance in industrial applications, not only because they are low in cost but mainly because the polysaccharide portion of the product is biodegradable.

The objective of this study is the incorporation of sulfonated groups onto starch backbone followed by radiation-grafting with

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acrylic acid to obtain non-soluble starch/acrylic acid graft copolymer. The reaction kinetics of the hydrolysis of sucrose using newly prepared hydrogel from chemically modified starch is investigated.

2. Experimental

2.1. Materials

A commercially corn starch of 8.2×10^5 MWt, Acrylic Acid (AA) was obtained from ACROS organics, USA. All other chemical, such as solvents, inorganic salts organic compounds, and other reagents were reagent grade, supplied by AlGomhorya Company, Cairo, Egypt and used without further purification.

2.2. Apparatus and methods

2.2.1. Gamma radiation source

The samples were irradiated with the ^{60}Co Indian irradiated facility gamma rays at a dose rate (3.5) kGy/h. The irradiation facility was constructed by the National Center for Radiation Research and Technology (NCRRT), Egyptian Atomic Energy Authority (EAEA).

2.2.2. pH measurements

The pH solutions were prepared using (citric acid/trisodium citrate) and (sodium dihydrogen phosphate/disodium hydrogen phosphate) and measured using Jenway 3310 pH Meter.

2.2.3. FTIR spectroscopy

The FTIR spectra were obtained from KBr pellets of native and modified starch samples using FTIR spectrophotometer (JASCO FT/IR-6300, Japan) in the range of 400–4000 cm^{-1}.

2.2.4. Thermal gravimetric analysis (TGA)

The thermo-grams of sulfonated starch, acrylic acid & sulfonated starch-g-acrylic acid (SS/AA) samples were recorded using Perkin Elmer (Pyris6 TGA, USA). Temperature is ranged from 35 °C to 600 °C at flow rate 10 °C/min. and under inert atmosphere of N_2 (at a flow rate of 20 mL/min.).

2.2.5. Scanning electron microscope (SEM)

SS/AA gel was soaked in water, quickly frozen in liquid nitrogen and freeze-dried under vacuum for 15 h with Freeze Dry system until all water was sublimed. The freeze-dried samples were fractured carefully and mounted onto brass stubs and coated with thin layer of gold under reduced pressure for 3 min. The surface topology of the lypholized dried gel was examined using JOEL JSM-5400 scanning electron microscope.

2.2.6. Gel permeation chromatography (GPC)

Molecular weight determination was carried out using Gel Permeation Chromatography Agilent 1100 instrument using deionized water as the mobile phase with flow rate of 1 mL/min, maximum pressure 150 bar, minimum pressure 5 bar, injection volume 20 μL and column temperature thermostat of 25 °C. The eluent was monitored by refractive index detector of optical unit temperature of 25 °C and peak width of 0.1 min. Polymer concentration was 0.1 (wt%). The Mwt was determined from a calibration curve using polyethylene oxide standard.

2.2.7. Starch sulfonation

According to the method of Khan, Mariotti, Navarini, Gilli, and Roberto, 1997; 50 g of starch were suspended in dichloroethane. 10 mL chlorosulphonic acid were added drop-wise under stirring for 15 min. in ice-bath till starch is turned brown this is followed by filtration of the solution and air drying.

The degree of substitution was determined by acid/base volumetric titration method of sulfonated starch (SS).

For sulfur content estimation, a known weight of SS is dissolved in 100 mL distilled water and then 10 mL was titrated against 0.06 N NaOH using phenolphthalein as an indicator. The final point of the valuation is when the color is changed into Mexican pink (dark pink). Duplicated samples were treated the same way.

Sulfur content was determined according to the following equation:

$$S\% = \left(\frac{0.06 \times V \times 32 \times (100/10)}{W} \right) \times 100$$

where V is the volume of 0.06 N NaOH used to titrate the sample. W is the weight of the sample used in mg; 32 is the molecular weight of sulfur.

Sulfur% is used to calculate the degree of substitution according to the following equation [Chiovitti et al., 1998; Liao et al., 1996]:

$$DS = \frac{162 \times S\%}{3200 - 102[S\%]}$$

2.2.8. Preparation of the SS/AA copolymer gels

A known concentration of the prepared sulfonated starch (SS) is mixed with different concentrations of acrylic acid (AA) in the presence of distilled water where (SS/AA):H_2O is 1:1 (w/w). The samples were then irradiated at different irradiation doses using gamma irradiation. The formed gel is then neutralized using 10% sodium carbonate. Followed by; immersion in distilled water for 6 h this is repeated for several times. The prepared gel was then air dried and grinded in powder form.

2.2.9. Gel content measurements

In order to determine the insoluble parts of the gel, the prepared samples were extracted with water for 24 h at 60 °C. The gelled part, was taken out and washed with water to remove the soluble fraction, then dried and weighed.

The gel (%) in the prepared hydrogel was determined from the following equation:

$$\text{Gel} \quad (\%) = \left(\frac{W_E}{W_g} \right) \times 100$$

where W_E and W_g; represent the weights of the dry gel after and before extraction, respectively.

2.2.10. Swelling measurements

The dry sample was weighed (0.2 g) and immersed in water for 24 h to reach equilibrium at 25 °C. The fully swollen gel was then weighed and the relative water absorbency was calculated as follows:

$$\text{Swelling} \quad (\%) = \left[\frac{W_g - W_o}{W_o} \right] \times 100$$

wherein W_o and W_g are weights of dry sample and of fully swollen gel, respectively.

2.2.11. Catalytic activity of the SS/AA copolymer gels

The catalytic activity of the SS/AA hydrogel containing sulfonic acid groups was tested for sucrose hydrolysis. The gel of known degree of swelling was cut into small pieces (of definite size), soaked in 40 mL of sucrose solution having a concentration of 0.58 $\text{mol}\,\text{l}^{-1}$ hosted in a small glass reactor placed in thermostat controlled oil bath and equipped with condenser and a round-shaped Teflon blade stirrer. At prescribed time, samples (size 0.6 mL) were extracted and analyzed for concentration of glucose.

Analyses were performed by using Jasco V-550 UV–vis spectrometer at wavelength 500 nm using a calibration curve.

The kinetic analysis was made based on the variation in the reaction temperature from 25 to 60 °C and SS/AA composition.

3. Results and discussion

3.1. Preparation conditions

Among the sulfating reagents mentioned in the literature, there is concentrated sulfuric acid [Yalpani, 1999] or its mixture with organic solvents [Malm, Rowley, & Hiatt, 1961], SO_3 complexes with pyridine, DMF [Daicel, 1983], liquid SO_2, trialkylamine [Kruger & Wurzburg, 1968], DMSO [Whistler, Unrau, & Ruffini, 1968] and also chlorosulfonic acid in formamide [Koerdel & Schierbaum, 1975] or pyridine [Gilbert, 1965]. In this work starch sulfonation was prepared according to the method of Khan et al. (1997). Utilization of these sulfating agents could result in extreme hydrolysis or degradation of starch chains during reaction. To reduce the hydrolytic or degradative effect, ethylene dichloride has been used as reaction medium [Beck, Fitton, & Kricheldorf, 1992; Schweiger, 1968].

3.2. Determination of Mwt change and degree of substitution of starch

The reaction with chlorosulfonic may affect the MWt of starch. Thus Mwt of starch was determined before and after reaction. The MWt of starch was reduced from 8.2×10^5 to 5.6×10^5. It is clear that the treatment of starch with chlorosulfonic in the presence of dichloethane has a slightly effect on starch Mwt degradation. The degree of substitution (DS) is the number of substituted hydroxyl groups per anhydroglucose unit (AGU) in the starch polymer by SO_3H. The degree of substitution was determined by acid/base volumetric titration method of the sulfonated starch. S% and the DS was determined to be 16.8, and DS = 1.5, respectively.

3.3. SS/AA copolymerization

Trails were made to crosslink past-like structure sulfonated starch (SS) by using ionizing radiation. Ionizing radiation has a great effect on SS. It degrades the SS into low fragment. Thus, the prepared sulfonated starch (SS) was copolymerized with different amount of acrylic acid (AA) using gamma irradiation at various irradiation doses and the obtained hydorgel was then neutralized using Na_2CO_3 (5%) as shown in Scheme 1.

3.3.1. Structure analysis of the SS/AA

3.3.1.1. *FTIR.* FTIR was performed to confirm the starch modification by chlorosulfonic acid and elucidate the structure of SS.

As shown in Fig. 1, IR spectrum of SS had two new characteristic absorption peaks at 1515 cm^{-1} and 1239 cm^{-1} for asymmetric and symmetric stretching vibration of $–SO_2–$, respectively, which indicated that sulfonic acid groups were introduced into the corn starch molecule [Xing, Zhang, Ju, & Yang, 2006]. The FTIR spectra of sulfonated starch also showed, characteristic band at 829 cm^{-1} with a shoulder at 940 cm^{-1} for a symmetrical C–O–S vibration assigned to a $C–O–SO_3$ group. The band at 829 cm^{-1} suggested that equatorial 6-sulfonated groups on the galactosyl units had been formed [Yang, Du, Huang, Wan, & Li, 2002]. The shoulder peak at 940 cm^{-1} indicated the presence of axial sulfate ester at O-4 of some β-D-glucose residues [Chiovitti et al., 1998; Liao et al., 1996]. The data obtained suggested that equatorial primary hydroxyl group at O-6 and axial secondary hydroxyl group at O-4 of glucose residues are substituted easily.

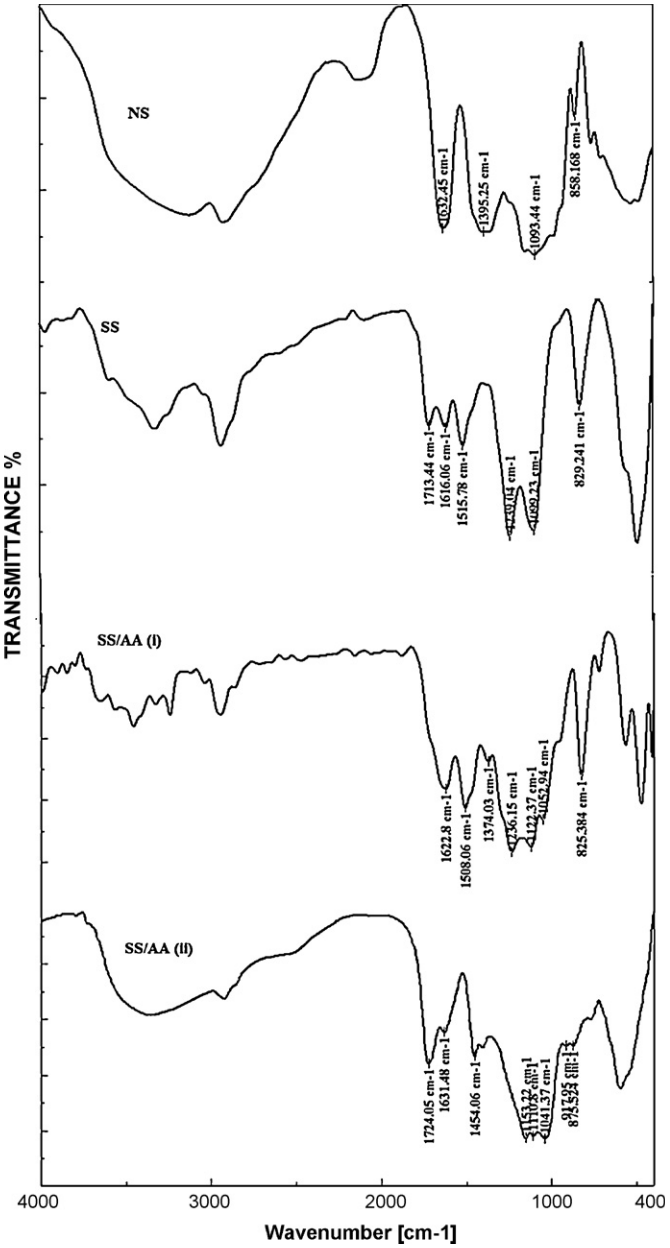
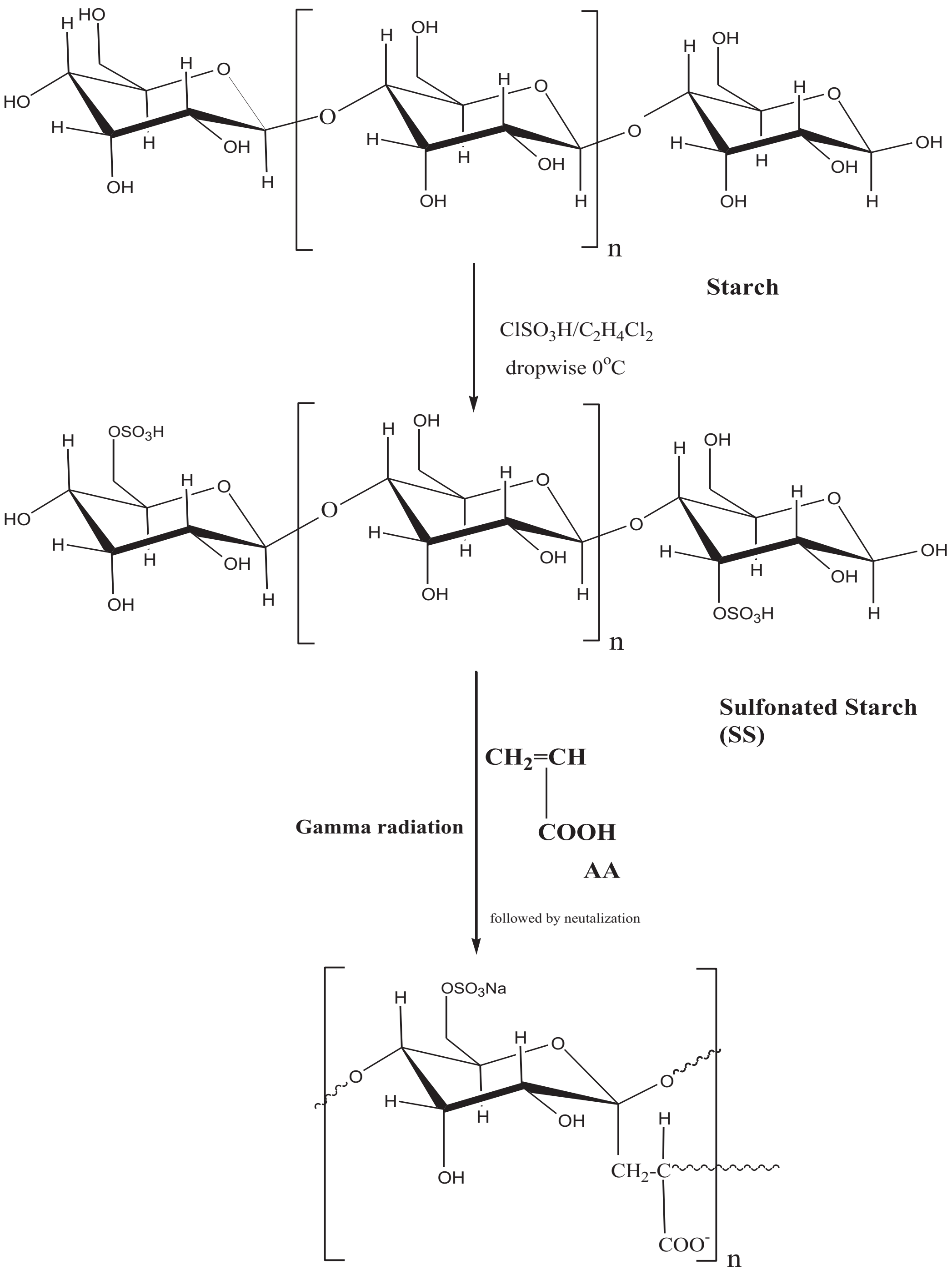


Fig. 1. FTIR of native starch (NS), sulfonated starch (SS) and SS/AA copolymer (i) before, (ii) after catalytic reaction at 60 °C.

Since SO_3 has strong properties of dehydration, it can be assumed that the anhydroglucose residues were formed during the process of the sulfonation and this can be detected from the band appearing at 1099 cm^{-1} that associated with the presence of C3–O–C6 bridge of the anhydro glucose residue [Pereira, Amado, Critchley, van de Velde, & Ribeiro-claro, 2009]. Interestingly, a new band appeared at 1713 cm^{-1}, and this band could be related to the unsaturated band formed in sulfonation, or the deformation vibration of H_2O as suggested by Yang, Du, Huang, Wan, and Wen (2005). The appearance of vibrational band at 1622 cm^{-1} in SS/AA (i) related to the formation of H-bonding between C=O of acrylic and H-of glucopyrnose ring.

3.4. Gel content measurements

There are many factors affecting the polymer gel content among them, the applied irradiation doses and the polymer composition.



Scheme 1. Representation of sulfonation reaction followed by grafting with AA.

In general, crosslinking and chain scission normally proceed simultaneously but the most prevalent process determines the outcome of irradiation treatment [Peppas & Mikos, 1986].

Gel content of SS/AA copolymers prepared at different compositions and irradiated with various doses was determined. As it can be seen from Fig. 2-I the increase in the applied irradiation dose, up to 25 kGy, leads to a significant increase in the gel content for the same copolymer composition. This can be attributed to the formation of intermolecular crosslinks and three-dimensional network structure. After that, any further increase in the absorbed dose (30 kGy) leads to a non-significant increase in the gel content and in all cases; gel percent reaches a plateau at a value lower than 100%. This is may be due to chain scission becoming more important than crosslinking during the final stage of the reaction and the ratio between the yields of scission and crosslinking will probably equals to one and this explains the plateau values.

In general by the increase in the applied dose, there is an increase in the radical concentration in the reaction media and consequently, the grafting sites on the starch backbone [Huglin & Zakria, 1986; Rosiak & Ulanski, 1999], these alkoxy macroradicals, initiate the AA copolymerization with starch sulfate.

At the same time, there is a relationship between the AA composition in the feed solution and the gel content value, where the

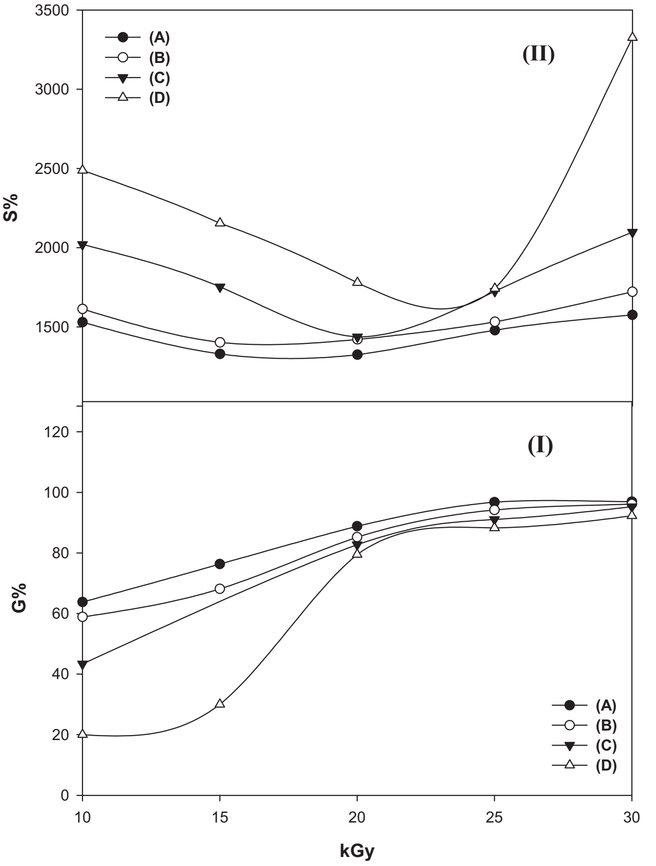


Fig. 2. Effect of different irradiation doses on the gel content% at different compositions (I) and swelling% of copolymer at different compositions of (SS/AA), A = (1:1), B = (1:0.75), C = (1:0.5), D = (1:0.25) (II).

increase in the AA composition is accompanied by an increase in the gel content value. Where low gel content at lower AA composition is due to the lower polymerization rate of AA due to its low concentration which leads to lower conversion of PAA chains and thus lower gel content. Thus the presence of the synthetic polymer, represented in AA, improves the crosslinking of the SS natural polymer.

3.5. Swelling measurements

3.5.1. Effect of irradiation dose and copolymer composition

Several factors affect the swelling capacity of the gel; the nature of the polymer, the temperature, ionic strength and pH of the swelling medium and the degree of crosslinking.

It can be observed from Fig. 2-II that the swelling% measured at room temperature and the same polymer composition is reduced by increasing the applied irradiation doses up to 25 kGy. Meanwhile, at higher doses (25–30 kGy), the increase in the doses is accompanied by an increase in the swelling% which correlates with the gel content results. At low doses (10–15 kGy) the swelling% is low due to low density network structure in agreement to the gel content measurements; at high doses (25–30 kGy) the swelling is again high indicating again a low density network. At high doses the density of the network decreases because of the scission reactions, which break connecting chains. However the broken chains are still connected to the crosslinking points, which make the gel content to stay high.

On the other hand, at the same irradiation dose (30 kGy) but at different copolymer composition, the increase of the AA concentration in the feed mixture is accompanied by a reduction in the swelling%. Since gels with higher crosslinking degree has tighter structure and less swelling compared to the gels with lower crosslinking degree. The grafted starch backbone containing –COO$^-$, groups are quite polar and bounded with water, resulting in enhancing the copolymer swelling. The extent of swelling is directly dependent on both irradiation dose and AA concentration. Also, the gel content or crosslinking ability of the copolymer has an influence on the hydrogel swelling property. The higher the gel content the lower the water absorbency.

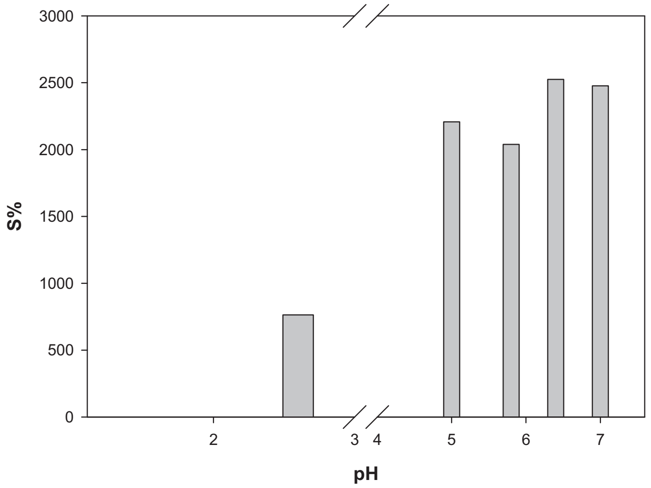


Fig. 3. Effect of pH on the swelling% of (SS/AA) composition (1:0.5) prepared at 30 kGy.

3.5.2. Effect of swelling medium pH

Fig. 3 shows the effect of different pH on the swelling behavior of the prepared gel. The increase in the solution pH led to an increase in the gel swelling%. This can be explained on the basis of copolymer nature, the presence of acrylic acid is highly affected by the swelling medium pH. At high pH values the negative charges present on the polymer backbone, represented by both the COO$^-$ groups of acrylate and the $SO_3{}^-$ groups of starch backbone, aid on enhancement the swelling% of the gel due to the created repulsive forces between the network structures. In addition to the increase of the osmotic pressure as a result of the concentration of ions bounded to the network increases which will lead to an increase in the swelling%.

On the other hand, at low pH, these groups are protonated leading to a reduction in the swelling%.

3.6. Thermogravimetric analysis

The thermal stability of (SS/AA) was studied as a function of applied irradiation dose used for preparation. Fig. 4 shows the effect of the applied irradiation dose on the thermal stability of (SS/AA) gel at the same composition. At low applied irradiation dose (10 kGy) only two weight change stages are observed in the thermogram. One weight loss values 20% observed at 220 °C, followed by another weight loss value 40% at 250 °C. At higher doses the gel showed three weight change stages which are 16%, 30% and 40% around 230 °C, 320 °C and 450 °C, respectively. This clearly indicates that the increase in the applied dose led to the enhancement in the thermal properties of the prepared hydrogel. This could be attributed to the formation of crosslinked network as a result of grafting of AA monomers on to SS.

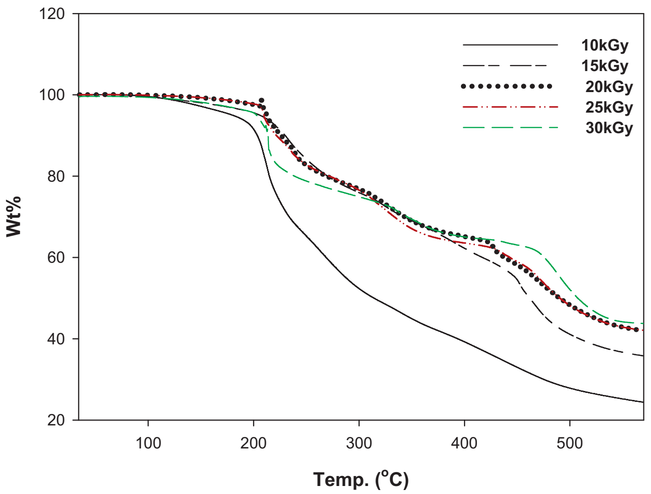


Fig. 4. TGA thermogram curves for (SS/AA); (1/0.25) at different irradiation doses.

4. Application of SS/AA copolymer (in its acid-form) as catalytic reagent for sucrose hydrolysis

A SS/AA gel of degree of gelation (80%) was used as a catalyst and the reaction was conducted at specified temperature (25 °C) and various time intervals. A sample of small volume is extracted from the reaction vessel and analyzed by UV for glucose using glucose kit.

The reaction of the hydrolysis of sucrose to glucose and fructose using sulfonic acid bearing cation exchange hydrogel proceeds according to Eq. (1)

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H+} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6} \qquad (1)$$

The reaction is irreversible and first order with respect to the concentration of sucrose (C) at time t and SO_3H concentration.

$$\frac{dC}{dt} = -kC_o \qquad (2)$$

where k is the reaction rate constant.

The time courses for the hydrolysis of sucrose into glucose and fructose at 25 °C is shown in Fig. 5. As it can be seen, the sucrose concentration decreases gradually with the increase in the reaction time. Inversely, the concentration of both glucose or fructose increases with the increase in the reaction time and the increase in glucose and fructose concentration is equivalent to the decrease in the sucrose concentration. This is going along with the mass balance consideration. Therefore, it is the intention of the author to monitor the sucrose conversion into glucose in terms of variation of sucrose concentration at certain time (C) with respect to initial concentration (C_0).

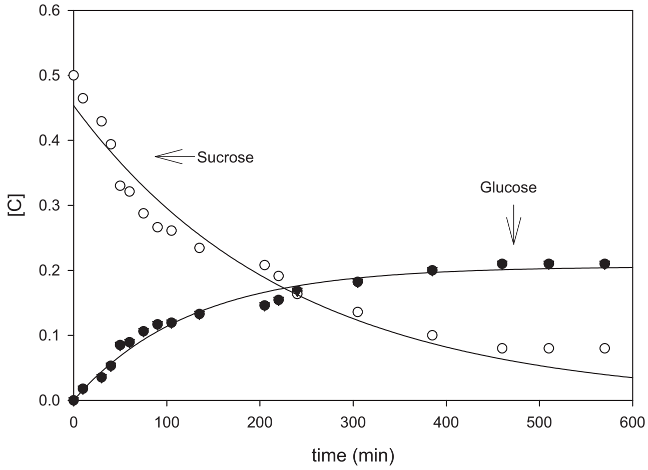


Fig. 5. Time courses for concentrations of: (○) sucrose and (▼) glucose at 25 °C; SS:AA (1:0.25).

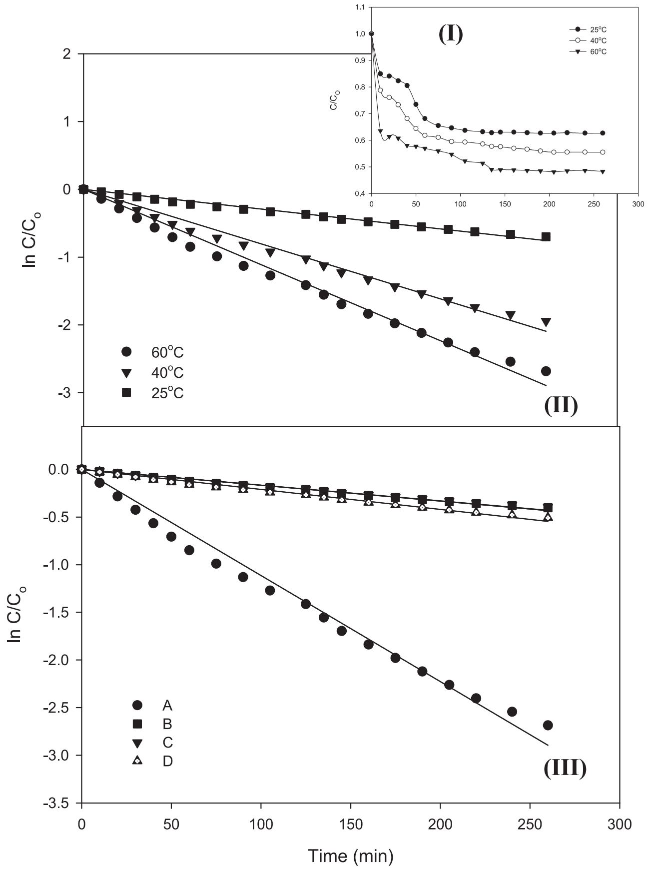


Fig. 6. (I) Time courses for the hydrolysis of sucrose into glucose and fructose at various temperatures; SS/AA (1:0.25). (II) Effect of reaction medium temperature on the kinetics of hydrolysis of sucrose into glucose and fructose using SS/AA (1:0.25). (III) Effect of different SS/AA compositions on the kinetics of hydrolysis of sucrose into glucose and fructose at 60 °C; A = SS/AA(1:0.25), B = (1:0.5), C = (1:0.75), D = (1:1) hydrogel prepared at 25 kGy.

The time courses for the hydrolysis of sucrose into glucose and fructose by SS/AA hydrogel at temperatures ranging from 25 to 60 °C is shown in Fig. 6-I.

The ratio C/C_0 was plotted against time to provide kinetic data that can explain the effect of reaction variables on the overall conversion. At all temperatures, the C/C_0 ratio decrease steeply with the increase in time intervals until it reaches minimum values, which varies depending on the reaction temperature. For instance, the C/C_0 ratio for (SS/AA) (50:50) decreases until it reaches almost zero at 60 °C after 5 h, whereas the time is getting longer at lower temperature. This clearly shows that raising the reaction temperature causes a remarkable increase in the rate of the reaction coupled with lower diffusion resistance that helps achieving complete conversion rapidly. Hence, hydrolysis of sucrose with SS/AA hydrogel is favored at high temperature.

The reaction rate constant (k) for the hydrolysis of sucrose at various temperatures was obtained from Eq. (2) using a standard integral method and can be expressed by:

$$kt = -\ln\left(\frac{C}{C_0}\right) \qquad (3)$$

Table 1
Comparison between the graphically obtained and the calculated reaction rate constants for hydrolysis of sucrose by (SS/AA) (1:0.25) hydrogel at various temperatures.

Temperature (°C)	k obtained from the slops (Fig. 7) $\times 10^{-3}$	k calculated from Eq. (3) $\times 10^{-3}$
25	1.6	1.4
40	1.8	1.6
60	1.98	2.1

To obtain k graphically, $\ln(C/C_0)$ was plot against the reaction time at temperatures ranging from 25 to 60 °C as shown in Fig. 6-II All reactions showed linear relationships and the rate constants obtained from the slops are in a good agreement with their respective values calculated from Eq. (3) as shown in Table 1. This kinetic data confirms that the reaction is first order.

The effect of variation of AA composition in the hydrogel on kinetics of the hydrolysis of sucrose was studied and the data obtained at a temperature of 60 °C is shown in Fig. 6-III. The rate constant of the reaction calculated from the slopes was found to be increased with the decrease in the AA composition; it increased from 1.03×10^{-3} to 1.9×10^{-3}. This is related to the number of fixed sulfonic acid groups that increases with SS contents in copolymer relatively to AA. Similar results were obtained in literatures by different authors [El-Mohdy & El-Rehim, 2008; Nasef, Saidi, & Senna, 2005]. They found that the increase in the catalytic activity is due to the increase in the amount of sulfonic groups in the used catalyst and the rate constant of the reaction was found to rise from 7.5×10^{-3} to 27.5×10^{-3} at 70 °C. Also, the reduction in the gel content with the decrease of AA affects the microspore structure of (SS/AA), improves the hydrophilicity of (SS/AA) copolymer and increasing polymer chains mobility leading to a reduction in the diffusion resistance to sucrose molecules and allowing more accessibility to the ionic sites. These results agree with that obtained in swelling measurements of SS/AA at different compositions, they show that the swelling of SS/AA copolymers decreased with increasing copolymer AA content the results obtained agreed with Mizota et al.; who attributed the lower catalytic activity of the crosslinked ion exchange resin to the decrease in the accessibility of the sulfonic acid groups by sucrose molecules stemmed from the diffusional mass transfer resistance caused by presence of the crosslinked polymer network structure [Zhang et al., 2008].

SEM, study was done to investigate the surface structure SS/AA of different compositions. The surface morphology and microspore structure of SS/AA copolymer of composition (1:0.25) seem to be completely different from that of composition (1:0.75) Fig. 7. The copolymer sample of composition (1:0.25) has wide micropore structure that increases the surface area in aqueous medium, causing the fluid to easily diffuse into the hydrogel mass through the gaps and pores leading to substantially increasing of fluid absorption rate. However, the small average pore diameter of composition (1:0.75) causes the reduction in water flux or copolymer swelling, gives rise to the diffusion resistance and reduces the accessibility to the ionic sites.

4.1. Catalyst stability and reusability

In order to study the catalytic stability of SS/AA gel, different batch runs with the same catalyst sample, at same conditions were carried out. The results showed nearly the same rate constant was obtained when the experiment was run up to 5 times as shown in Fig. 8. FTIR was used to follow the structural changes occurred in the SS/AA gel during the sucrose hydrolysis process. After 5 times reusability of SS/AA gel, the intensity of vibrational band at 1622 cm^{-1} related to the formation of H-bonding between the unsaturated groups as C=O of acrylic and H-of glucopyrnose ring in SS/AA is lower than that of Fig. 1 SS/AA (i). Also, free C=O of acrylic appeared at 1724 cm^{-1} Fig. 1 SS/AA (ii). The decrease in this band is due to the raise in the reaction temperature and the reorientation of SS/AA to be fit for sucrose hydrolysis which may result in hydrogen bond broken.

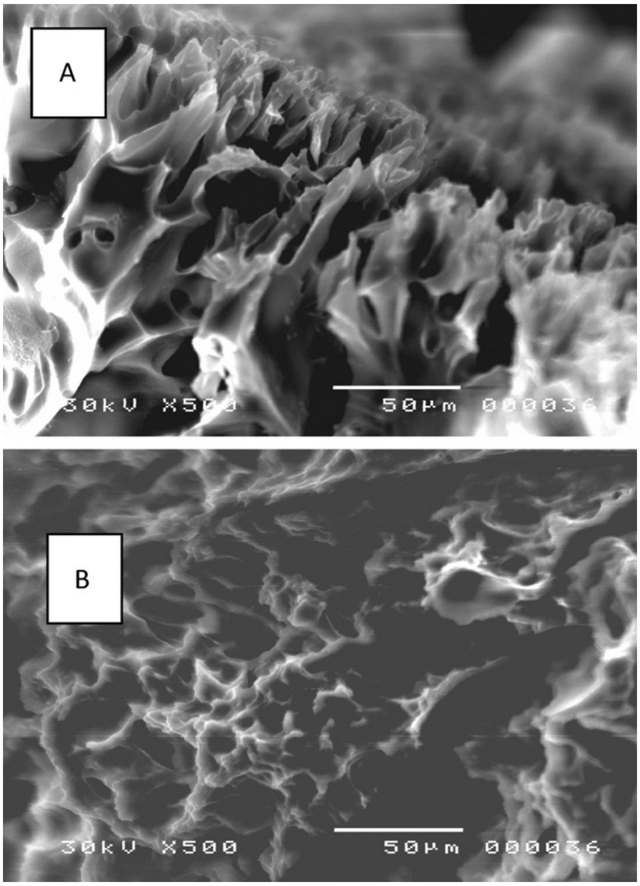


Fig. 7. SEM of SS/AA swelled in sucrose solution (A): SS/AA (1:0.25), B: SS/AA (1:0.75).

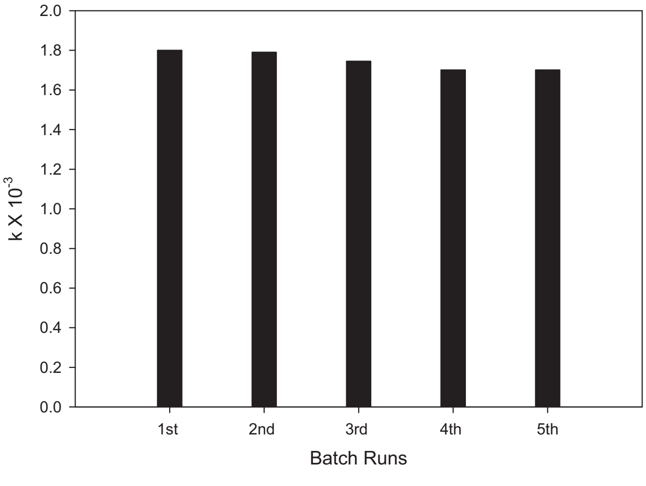


Fig. 8. Reusability of SS/AA (1:0.25) catalyst prepared at 25 kGy in sucrose hydrolysis at 40 °C.

5. Conclusion

Eco-friendly SS-g-AA copolymers were prepared using ionizing radiation for sucrose hydrolysis. Kinetic investigation of the reaction was determined and the reaction rate constants were obtained in a temperature range of 40–60 °C at different copolymer compositions. Hydrolysis of sucrose catalyzed by SS-g-AA copolymers showed that the reaction is favored as the reaction temperature increases because of higher reaction rate constants. The increase in the SS content i.e. concentration of fixed sulfonic groups leads to enhance the catalytic activity of copolymers. The present work demonstrates the potential of radiation-induced grafting method in preparing eco-compatible catalytic copolymers. The results suggest that SS-g-AA copolymers have strong potential to replace liquid sulfuric acid and ion exchange resins using in sugar hydrolysis processes.

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