Chemical Engineering Journal 145 (2008) 154–159

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Radiation-induced kappa carrageenan/acrylic acid graft-copolymers and their application as catalytic reagent for sucrose hydrolysis

H.L. Abd El-Mohdy*, H.A. Abd El-Rehim

National Center for Radiation Research and Technology, P.O. Box No. 29 Nasr City, Cairo, Egypt

ARTICLE INFO

Article history:
Received 20 May 2008
Received in revised form 26 August 2008
Accepted 29 August 2008

Keywords:
Hydrolysis
Sucrose
Kappa carrageenan
Acrylic acid
Radiation
Grafting
Hydrogels
Kinetics

ABSTRACT

Kappa carrageenan/acrylic acid graft-copolymers (kC-g-AAc) were prepared by using γ-radiation. The prepared graft-copolymer was acidified to convert the sulfate group ($-OSO_3^-$) in kappa carrageenan into sulfuric group ($-OSO_3H$) to be used as catalytic reagent for sucrose hydrolysis. The hydrolysis of sucrose to glucose and fructose by kC-g-AAc copolymers was investigated. The kinetics of the reaction was determined for various kC/AAc compositions and the reaction rate constants were obtained in a temperature range of 40–70 °C. The catalytic activity of the copolymers was found to be dependent on the reaction temperature and kC/AAc compositions, it increased with high reaction temperature and enhanced kC content (high $-OSO_3H$ groups) in the feed solution. The obtained results suggest that the prepared kC-g-AAc copolymers considered as catalytic reagent for sugar hydrolysis.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Sucrose continues to constitute a significant part of the human diet and therefore, it is widely used in the food industry as such and as a precursor of invert sugar through its partial or total hydrolysis [1]. Other uses in the non-food industry, such as the use of sucrose as a starting material for the formation of high added value furanic derivatives (5-hydroxymethylfurfural) are also appealing [2,3]. Sucrose is a dimer composed of two sugar monomers, β-D-fructose and a-D-glucose, and is non-reducing. In commercial processes, sucrose is hydrolyzed to invert, glucose and fructose monomers using acids, enzymes, or cation resins. Under strong acidic conditions, sucrose glycosidic bonds hydrolyze rapidly at temperatures greater than 160 °C [4–6], but typical commercial acid invert processes operate below 120 °C to minimize fructose and glucose degradation. So fructose and glucose are known to degrade at temperature (>106 °C) and pH (<2.0) conditions encountered in dilute acid pretreatment of lignocellulosic biomass. The primary degradation pathway is a dehydration of the sugar to 5-hydroxymethylfurfural (5-HMF), which hydrolyzes and further degrades to levulinic and formic acid [7–11]. Enzymes are the most used catalysts to hydrolyze sucrose and transform it into inverted sucrose on the industrial scale [12], invertase enzymes are the most catalysts that often use on the industrial scale to transform sucrose into invert sugar. 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 [13]. To overcome this problem strongly acidic ion exchange resins containing sulfonic acid groups are used and allowed a complete conversion of sucrose in the temperature range compatible with their stability, but with a relatively high level of impurities [14,15]. Acid ion exchange resins are also used and allow a complete conversion of sucrose in the temperature range compatible with their stability, but some of them invert sugar with a relatively high level of impurities [14]. Ion exchange resins composing of divinylbenzene crosslinked polystyrene (PS–DVB) network structure containing sulfonic acid groups, inhibit the access of reactants with sizes larger than the interstices of the polymer chains [16]. Unlikely, polystyrene–polypropylene fibrous ion exchange catalysts showed more effective catalytic activity toward sucrose hydrolysis due to the increase in their surface area together with the increase in the reactant molecular size accessibility [17].

Radiation-induced grafting using high energy radiation has been found to be powerful method to produce graft-copolymers capable of hosting sulfonic groups and having more effective catalytic activity toward sucrose hydrolysis, Aiba et al.

---

* Corresponding author at: National Center for Radiation Research and Technology, Polymer Chemistry Department, P.O. Box No. 29 Nasr City, Cairo, Egypt. Tel.: +002 0102538878.

E-mail address: hatem_lotfy@yahoo.com (H.L.A. El-Mohdy).

1385-8947/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2008.08.034

[18] prepared polystyrene sulfonic acid grafted poly (tetrafluoroethylene) (PTFE) membranes by radiation-induced grafting of styrene onto PTFE films with γ-rays followed by sulfonation and tested their catalytic activity for hydrolysis of dextrin. Nasef et al. [19] prepared poly(tetrafluoroethylene-co-perfluorovinyl ether)-graft-polystyrene sulfonic acid (PFA-g-PSSA) membranes by simultaneous radiation-induced grafting of styrene onto poly(tetrafluoroethylene-co-perfluorovinyl ether) films using γ-radiation followed by sulfonation with chlorosulfonic mixture.

The objective of this study is report on the probability of using the radiation grafted kappa carrageenan/acrylic acid copolymers as catalytic reagents for sugar hydrolysis.

2. Experimental

Kappa carrageenan was purchased from Condinson Co., Denmark. Acrylic acid (Merck, Darmstadt, Germany) was used as received. Glucose kit was purchased from Biolabo Reagents, France. Sucrose was supplied by El-Nasr Pharmaceutical Chemicals Co. (Egypt).

3. Methods

3.1. Preparation of the kC/PAAc graft-copolymers

Kappa carrageenan was dissolved in distilled water at 80 °C for 2 h. The hot kC solution was mixed with AAc, and then poured into a glass tube of diameter 15 mm. The final concentrations in the mixture of kC and AAc were 20%. The samples were cooled and then irradiated at room temperature by a ^{60}Co-γ source. The prepared graft-copolymer was acidified with HCl to convert the $-OSO_3^-$ group in kappa carrageenan into $-OSO_3$ H group.

3.2. Gel fraction

To extract the insoluble parts of the hydrogels (i.e., the gelled part), the prepared hydrogels were soaked in water for 48 h at 100 °C. Then, they were taken out and washed with hot water to remove the soluble part, dried, and weighed. The gel percent in the hydrogel was determined from the following equation:

$$\text{gel}\,(\%) = \frac{W_e}{W_g} \times 100 \tag{1}$$

where W_e and W_g are the dry hydrogel weights after and before extraction, respectively.

3.3. Swelling measurement

The dried hydrogels of known weights were immersed in distilled water or saline solution at 25 °C until the swelling equilibrium was reached (almost 24 h). The gel was removed, blotted quickly with absorbent paper, and then weighed. For accuracy, the experiment was repeated twice for each sample. The following equation was used to determine water uptake:

$$\text{swelling} = \frac{W_s - W_g}{W_g} \tag{2}$$

where W_s and W_g are the weights of wet and dry gel, respectively.

3.4. Measurement of sulfate and sulfuric groups in graft-copolymers

In some extent, R-OSO_3Na is a weak alkali, $-OSO_3$Na group amount in the hydrogel can be measured by titrating with stronger acid HCl. A hydrogel samples varied with kC/AAc compositions (0.5 g) were weighed, then drips HCl standard solution into the sample solution slowly, and the titration end point was judged by potentiometer. The molar percentage of $-OSO_3$Na in the sample was calculated by following equation:

$$-OSO_3Na\,(\text{mol\%}) = C_{HCl} V_{HCl} \frac{71}{W_{\text{sample}}} \times 100 \tag{3}$$

The $-OSO_3$H group in the acidified copolymers can be neutralized by NaOH and its amount can be measured by electrochemistry method. A sample (0.5 g) was immersed in overweight NaOH solution for 24 h to allow $-OSO_3$H group transfer to $-OSO_3$Na group completely. The residual NaOH was titrated by using HCl standard solution and the end point of the neutralization reaction was judged by potentiometer. The molar percentage of $-OSO_3$H in the sample was calculated according to the following equation:

$$-OSO_3H\,(\text{mol\%}) = C_{NaOH} V_{NaOH} - C_{HCl} V_{HCl} \frac{71}{W_{\text{sample}}} \times 100\% \tag{4}$$

3.5. Hydrolysis of sucrose

The catalytic activity of the kC-g-AAc copolymer containing $-OSO_3$H groups was tested for sucrose hydrolysis. The copolymer of known composition was cut into small pieces (5 mm × 5 mm), soaked in 100 mL of sucrose solution having a concentration of 7 mol L^{-1}. At prescribed time, samples were extracted and analyses were detected by colorimetry using UNICAM UV/Vis Spectrometer (1000 Model spectrophotometer) for measuring the glucose concentration using a calibration curve, absorbance was detected at wavelength 500 nm. Residual or non-hydrolyzed sucrose concentration was calculated by subtract the measured glucose concentration from initial sucrose concentration (7 mol L^{-1}). The kinetic analysis was made based on the variation in the reaction temperature from 40 to 70 °C and kC/AAc copolymer compositions.

3.6. Scanning electron microscopy (SEM)

The lyophilized dried hydrogels were examined with JEOL JSM-5400 scanning electron microscopy. The surfaces of the polymers were sputter-coated with gold for 3 min.

4. Results and discussion

4.1. Gel content

Gel content and crosslinking network density of prepared polymer have a great influence on its swelling character. There are many factors affecting the polymer gel content among them, polymer compositions and irradiation doses. The gel content of kC/AAc of different compositions prepared at various irradiation doses was investigated and shown in Fig. 1. It is clear that the gel content of kC-g-AAc hydrogel increases with increasing the AAc content in the copolymer feed solutions as well as irradiation dose. The maximum gel content obtained for pure PAAc gels at compared with other kC/AAc compositions as well as irradiation dose. PAAc is well known as a crosslinked polymer by radiation. Consequently, as the polyacrylic acid increases in the graft-copolymer, the gel content increases.

4.2. Sucrose hydrolysis

The rate of acid-catalyzed sucrose hydrolysis has been extensively studied due to its importance to both the commercial sugar industry and as a means to study thermal degradation in the food processing industry [5]. As the rate of degradation of fructose

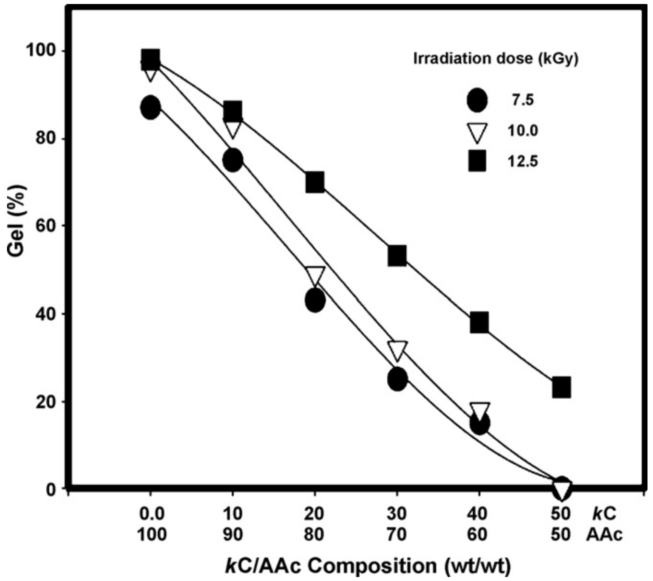

Fig. 1. Effect of kC/AAc composition on the gel content of kC-g-AAc copolymers at different irradiation doses.

was high, the residual concentration in solution was often very low. Thus, calculating the fructose degradation kinetic parameters required numerical integration of the reaction rate based on the temperature profile. Since the rate of degradation of glucose was much slower, glucose was always detected after hydrolysis and then sucrose concentration can be calculated. The reaction of the hydrolysis of sucrose to glucose and fructose using $-OSO_3H$ group bearing kC-g-AAc copolymers which prepared by radiation-induced graft-copolymerization of kC and AAc, proceeds according to the following equation:

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6} \qquad (3')$$

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

$$\frac{dC}{dt} = -kC \qquad (4')$$

where k is the reaction rate constant.

4.2.1. *Kinetics of the sucrose hydrolysis*

To begin investigating the kinetics of the hydrolysis of sucrose, a kC-g-AAc copolymer was used as a catalyst and the reaction was conducted with various hydrolysis temperatures and kC/AAc compositions at various time intervals.

4.2.1.1. Hydrolysis temperature. The intention of the author to monitor the sucrose conversion into glucose and fructose in terms of variation of sucrose concentration at certain time (C) with respect to initial concentration (C_0). The time courses for the hydrolysis of sucrose into glucose and fructose by kC-g-AAc copolymer with kC/AAc composition (40/60, w/w) at temperatures ranging from 30 to 80 °C is shown in Fig. 2. The ratio C/C_0 was plotted against time to provide kinetic data that can best explain the effect of reaction variables on the overall conversion. At all temperatures, the C/C_0 ratio decreases 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 decreases until it reach almost zero at 80 °C and 70 °C after 50 and 70 min, respectively, 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.

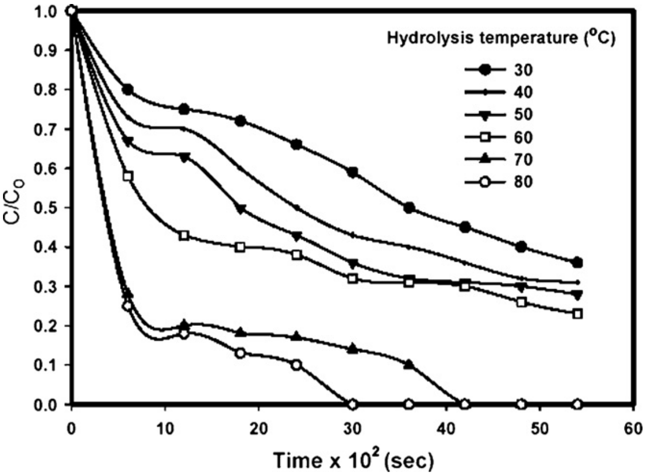

Fig. 2. Time courses for the hydrolysis of sucrose into glucose and fructose at various temperatures. kC/AAc composition: 40/60 (w/w); irradiation dose: 12.5 kGy.

Hence, hydrolysis of sucrose with kC-g-AAc copolymer is favored at high temperature. The reaction rate constant (k) for the hydrolysis of sucrose at various temperatures was obtained from Eq. (4′) using a standard integral method and can be expressed by:

$$kt = -\ln\frac{C}{C_0} \qquad (5)$$

To obtain k graphically, $\ln(C/C_0)$ was plotted against the reaction time at temperatures ranging from 30 to 80 °C as shown in Fig. 3. All reactions showed linear relationships and the rate constants obtained from the slopes are shown in Table 1. This kinetic data confirms that the reaction is first order.

4.2.1.2. kC/AAc compositions. A kC-g-AAc copolymer of various compositions was used as a catalyst and the reaction was conducted at specified temperature and various time intervals. The time courses for the hydrolysis of sucrose into glucose and fructose at 50 °C are shown in Fig. 4. As can be seen, the sucrose concentration decreases gradually with the increase in the reaction time and kC content in the kC/AAc feed mixture, due to carrageenan rich with $-OSO_3H$ groups which accelerate the sucrose hydrolysis, this is cleared in Table 2, it shows that the content of $-OSO_3H$

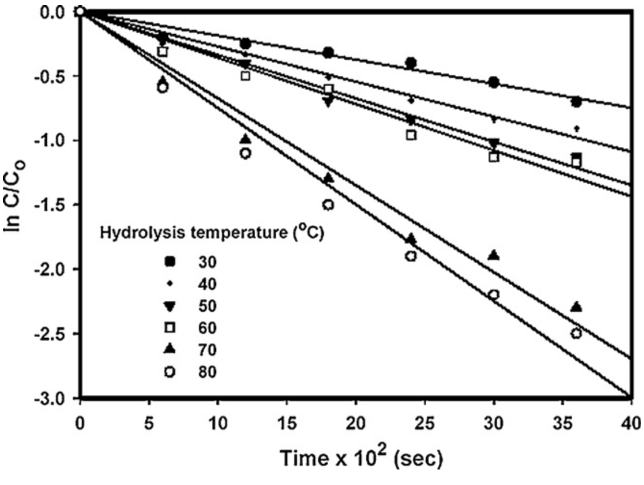

Fig. 3. Kinetics of hydrolysis of sucrose into glucose and fructose using kC-g-AAc copolymers at various temperatures.

Table 1
Reaction rate constants for hydrolysis of sucrose by kC-g-AAc copolymer at various temperatures

Temperature (°C)	k obtained from the slopes in Fig. 3 ($\times 10^{-4}\,\text{s}^{-1}$)
30	1.9
40	2.6
50	3.1
60	6.0
70	7.7
80	8.3

kC/AAc composition, 40/60 (w/w).

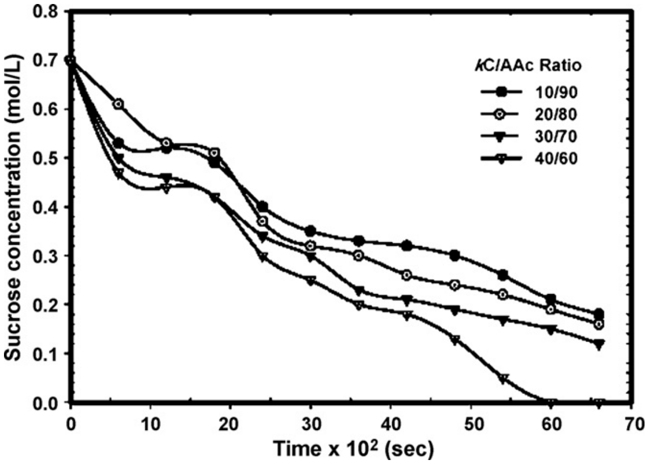

Fig. 4. Effect of kC/AAc composition in kC-g-PAAm copolymer on the rate of sucrose hydrolysis at 50 °C. Irradiation dose, 12.5 kGy.

groups increased with enhanced carrageenan content in acidified kC-g-AAc copolymers.

The effect of various kC/AAc compositions in the grafted copolymers on kinetics of the sucrose hydrolysis was studied and the data obtained at a temperature of 70 °C is shown in Fig. 5. The ratio C/C_0 was plotted against time to provide kinetic data that can best explain the effect of reaction variables on the overall conversion. At all kC/AAc compositions, the C/C_0 ratio decreases steeply with the increase in time intervals until it reaches minimum values, which varies depending on the kC content in the kC-g-AAc copolymer. For instance, the C/C_0 ratio decreases until it reach almost zero for kC/AAc copolymer composition; 40/60 (w/w), after 100 min, whereas the time is getting longer at other copolymers have lower kC content. This clearly shows that raising the kC content in the kC-g-AAc copolymer causes a remarkable increase in the rate of the reaction coupled with lower diffusion resistance that helps achieving complete conversion rapidly. The rate constant of the reaction calculated from the slopes was found to rise with the increase in the kC content in the kC/AAc ratio from $2.8 \times 10^{-4}\,\text{s}^{-1}$ at 10/90 to $7.2 \times 10^{-4}\,\text{s}^{-1}$ at 40/60 (w/w) (Table 3). This behavior can be explained based on the fact that, the increase in the kC content leads to an increase in the number of $-\text{OSO}_3\text{H}$ groups found on the chain of kC-g-AAc copolymer. Consequently, the number of fixed $-\text{OSO}_3\text{H}$ groups increases in the micropores providing more accessible sites to the chemical reaction i.e., the catalytic activity of the copolymers increases with the increase in the kC content in the kC/AAc feed mixture. This is enhanced by improving the hydrophilicity of the copolymers and increasing polymer chains mobility leading to a reduction in the diffusional resistance to sucrose molecules and allowing more accessibility to the ionic sites.

Table 2
Variation of the amount of sulfate and sulfuric groups in kC-g-AAc copolymers with different kC/AAc compositions

kC/AAc composition (w/w)	Group amount (%)		
	$-\text{OSO}_3\text{Na}$[a]	$-\text{OSO}_3\text{Na}$[b]	$-\text{OSO}_3\text{H}$[c]
10/90	23	5	17
20/80	37	9	28
30/70	52	11	40
40/60	64	13	51

Irradiation dose, 12.5 kGy.

[a] The original $-\text{OSO}_3\text{Na}$ content in copolymer.

[b] The $-\text{OSO}_3\text{Na}$ content in acidified copolymer.

[c] The $-\text{OSO}_3\text{H}$ content in acidified copolymer.

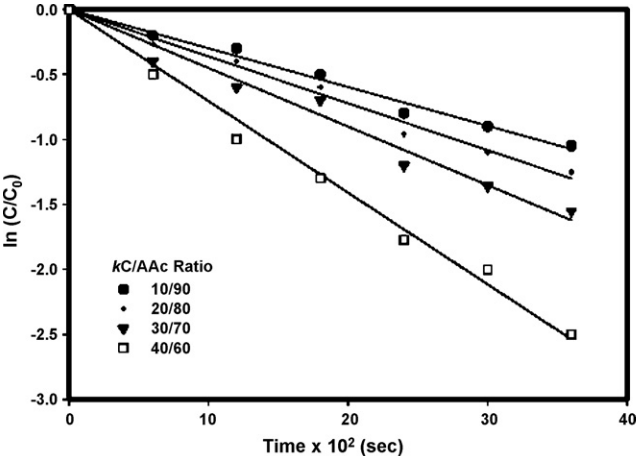

Fig. 5. The relationship between C/C_0 ratio and the reaction time for kC-g-AAc copolymers having various kC/AAc compositions.

4.2.1.3. The activation energy of sucrose hydrolysis. The activation energy (E) of the reaction was obtained using Arrhenius equation given below:

$$\ln k = \ln k_0 - \frac{E}{RT} \tag{6}$$

where k_0 is the Arrhenius constant. Fig. 6 shows Arrhenius plot for hydrolysis of sucrose into glucose and fructose using kC-g-AAc copolymer with kC/AAc composition, 40/60 (w/w) at temperatures ranging from 30 to 80 °C. The activation energy calculated from the slope is found to be 36.4 kJ mol^{-1}. The lower activation energy is due to mass transfer limitation to the observed reaction rate. This agrees with the explanation of other authors and with the intermediated value compared to other results [15,16,20]. The membranes studied may have an intermediated level of effect of mass transfer. In their study, Mizota et al. [16] 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. However, the value of activation energy in this work is less than that for the hydrolysis of sucrose conducted by free acid (HCl) in a homogenous system [20]

Table 3
Reaction rate constants for hydrolysis of sucrose by kC-g-AAc copolymer at various kC/AAc compositions

kC/AAc ratio	k obtained from the slopes in Fig. 5 ($\times 10^{-4}\,\text{s}^{-1}$)
10/90	2.8
20/80	3.3
30/70	4.6
40/60	7.5

Reaction temperature, 70 °C.

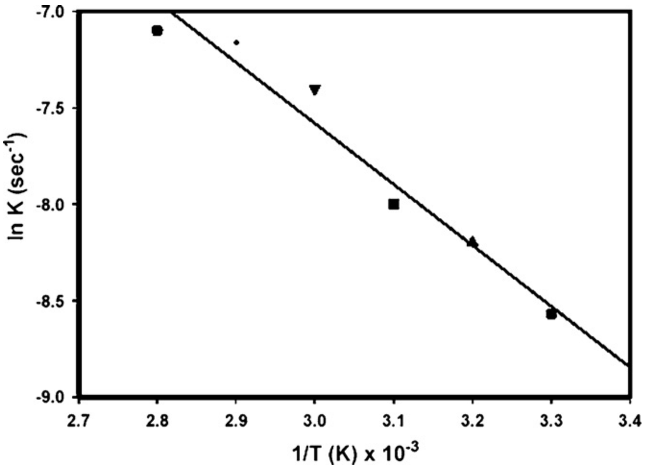

Fig. 6. Arrhinus plot for hydrolysis of sucrose into glucose and fructose using kC-g-AAc copolymer.

and also by sulfonic acid containing porous hollow fiber membrane prepared by radiation-induced grafting of styrene sodium sulfonate followed by conversion of Na-form to H-form [15], both of which equal 95 kJ mol^{-1}. This may be attributed to the used acidified kC-g-AAc copolymers which contains weak and low sulfonic groups and not all sulfonate groups converted into sulfonic groups on acidification according to Table 2. Also, this is due to the reduction in water flux or copolymer swelling caused by the small average pore diameter of the copolymer prepared in this study, which gives rise to the diffusional resistance and reduce the accessibility to the ionic sites.

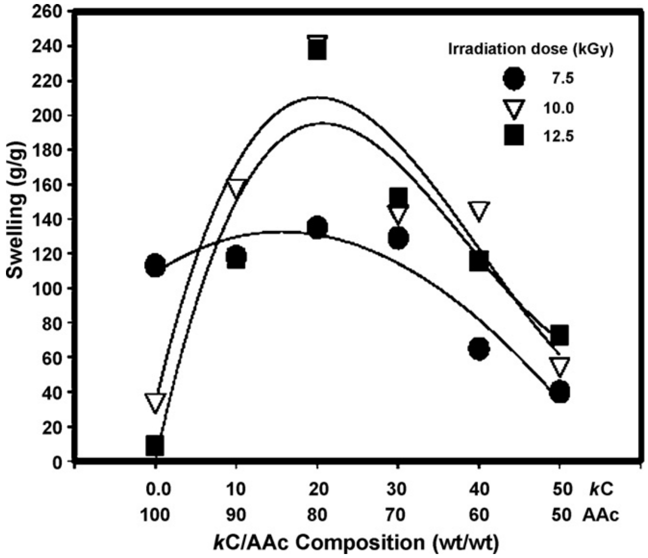

Fig. 7. Effect of kC/AAc composition on the swelling of kC-g-AAc copolymers at different irradiation doses.

Fig. 7 can agree with this explanation, it shows that the swelling of kC-g-AAc copolymers decreased at high kC content at kC/AAc composition; 40/60 (w/w) which has low microscale layers that observed in the sample structure (Fig. 8d). These layers cause to increase surface area and in an aqueous medium, the fluid easily diffuses into the hydrogel mass through the gaps of the layers led to substantially increasing of absorption rate, it is shown in Fig. 8 by

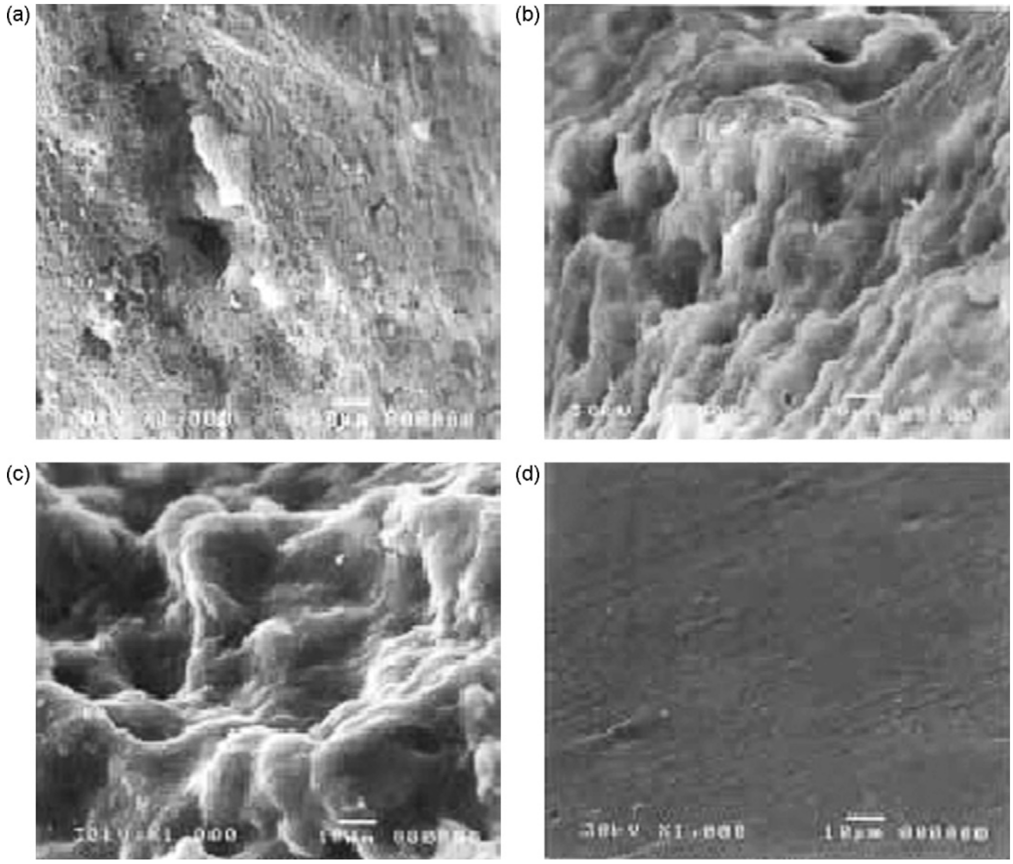

Fig. 8. SEM for various kC/AAc compositions of kC-g-AAc copolymers at irradiation dose, 12.5 kGy. (a) 10/90 (w/w), (b) 20/80 (w/w), (c) 30/70 (w/w) and (d) 40/60 (w/w).

study the surface morphology of kC-g-AAc copolymers with various kC/AAc compositions by using the scanning electron microscopy.

5. Conclusion

Kappa carrageenan/acrylic acid graft-copolymers (kC-g-AAc) were prepared by using γ-radiation. The hydrolysis of sucrose to glucose and fructose by kC-g-AAc copolymers was investigated. The catalytic activity of the copolymers was found to be dependent on the reaction temperature and kC/AAc compositions, it increased with high reaction temperature and enhanced kC content in the feed solution. The obtained results suggested that the prepared kC-g-AAc copolymers considered as catalytic reagent for sugar hydrolysis.

References

[1] C. Moreau, R. Durand, F. Alies, M. Cotillon, T. Frutz, M.-A. Theleyre, Hydrolysis of sucrose in the presence of H-form zeolites, Ind. Crops Prod. 11 (2000) 237.

[2] M. Kunz, Hydroxymethylfurfural, a possible basic chemical for industrial intermediates, in: A. Fuchs (Ed.), Inulin and Inulin-containing Crops, Elsevier, Amsterdam, 1993, p. 149.

[3] C. Moreau, R. Durand, S. Razigade, J. Duhamet, P. Faugeras, P. Rivalier, P. Ros, G. Avignon, Dehydration of fructose to 5-hydroxymethylfurfural over H-mordenites, Appl. Catal. A: Gen. 145 (1996) 211.

[4] K. Vukov, Kinetic aspects of sucrose hydrolysis, Int. Sugar J. 67 (1965) 172.

[5] M.A. Clarke, L.A. Edye, G. Eggleston, Sucrose decomposition in aqueous solution and losses in sugar manufacture and refining, Adv. Carbohyd. Chem. Biochem. 52 (1997) 441.

[6] C. L'Homme, M. Arbelot, A. Puigserver, A. Biagini, Kinetics of hydrolysis of fructooligosaccharides in mineral-buffered aqueous solutions: influence of pH and temperature, J. Agric. Food. Chem. 51 (2003) 224.

[7] F.M. Kuster, H.M.G. Temmink, The influence of pH and weak acid anions on the dehydration of D-fructose, Carbohyd. Res. 54 (1977) 185.

[8] N.S. Mosier, C.M. Ladisch, M.R. Ladisch, Characterization of acid catalytic domains for cellulose hydrolysis and glucose degradation, Biotechnol. Bioeng. 79 (2002) 610.

[9] X. Qian, M.R. Nimlos, D.K. Johnson, M.E. Himmel, Acidic sugar degradation pathways, Appl. Biochem. Biotechnol. 121 (2005) 989.

[10] X. Qian, M.R. Nimlos, M. Davis, D.K. Johnson, M.E. Himmel, Initio molecular dynamics simulations of b-D-glucose and b-dxylose degradation mechanisms in acidic aqueous solution, Carbohyd. Res. 340 (2005) 2319.

[11] Q. Xiang, Y.Y. Lee, R.W. Torget, Kinetics of glucose decomposition during dilute-acid hydrolysis of lignocellulosic biomass, Appl. Biochem. Biotechnol. 113 (2004) 1127.

[12] G. Bussiere, P. Nowak, M. Cotillo, Les sucres invertis, IAA (1990) 645.

[13] B. Hahn-Hagerdal, K. Skoog, B. Mattiasson, The utilization of solid superacids for hydrolysis of glycosidic bonds in di- and polysaccharides: a model study on cellobiose, sucrose, and starch, Eur. J. Microbiol. Biotechnol. 17 (1983) 344.

[14] B. Satyanarayana, Y.B.G. Varma, Heterogeneous catalysis of inversion of sucrose, Indian J. Technol. 8 (1970) 58.

[15] A. Masroua, A. Revillon, J.C. Martin, A. Guyot, G. Descotes, Hydrolyse d'oligo et polysaccharides en prĭesence de rĭesines ĭechangeuses d'ions et de polym‘eres hydrosolubles, Bull. Soc. Chim. Fr. 3 (1988) 561.

[16] T. Mizota, S. Tsuneda, K. Saito, T. Sugo, Hydrolysis of methyl acetate and sucrose in SO_3H-group-containing grafted polymer chains prepared by radiation-induced graft copolymerization, Ind. Eng. Chem. Res. 33 (1994) 2215.

[17] T. Yoshioka, M. Shimamura, Studies of polystyrene-based ion exchanger fiber. II. A novel fiber form catalyst for sucrose inversion and methyl acetate hydrolysis, Bull. Chem. Soc. Jpn. 57 (1984) 334.

[18] S. Aiba, K. Hiratani, T. Nagakawa, Preparation of poly(styrenesulfonic)-grafted microporous polytetrafluoroethylene membranes and their activity as hydrolysis catalysts, Makromol. Chem. Rapid Commun. 7 (1986) 91.

[19] M.M. Nasef, H. Saidi, M.M. Senna, Hydrolysis of sucrose by radiation grafted sulfonic acid membranes, Chem. Eng. J. 108 (2005) 13.

[20] J.V. Rhim, R.V. Nunes, V.A. Jones, K.R. Swartzel, Appearance of kinetic compensation effect in the acid-catalyzed hydrolysis of disaccharides, J. Food Sci. 54 (1989) 222.