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Hydrogels of starch-g-(*tert*-butylacrylate) and starch-g-(*n*-butylacrylate) copolymers

Synthesis and formation

**Mohammad M. Fares · Adeeb S. El-faqeeh ·
Hasan Ghanem · Mohammad E. Osman ·
Elfatih A. Hassan**

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Abstract The synthesis, characterization, and hydrogel properties of starch-g-(*tert*-butylacrylate) and starch-g-(*n*-butylacrylate) copolymers were studied. The optimum conditions for the grafting process of *tert*-butylacrylate into 1.0 g of starch were as follows: [*tert*-butylacrylate] = 0.04 mol/L, [CAN] = 9.0×10^{-4} mol/L, temperature = 20 °C in 100 mL solution, whereas the results using *n*-butylacrylate monomer were as follows: [*n*-butylacrylate] = 0.04 mol/L, [CAN] = 4.0×10^{-3} mol/L, temperature = 30 °C in 100 mL solution. The grafting evidences of monomers into starch were done through TG and its derivative DTG for thermal changes and mass losses, scanning electron microscope (SEM) for morphological changes, powder X-ray for crystallinity measurements and FTIR for functional group changes. Acid hydrolysis method was used efficiently to allow the calculations of the viscosity average molecular weight (M_v) of the grafted chains on starch and consequently the real percent of grafting efficiency (i.e. %GY). The capability of starch-g-(*n*-BAC) hydrogel to absorb water were found 10 times more than starch-g-(*tert*-BAC) hydrogel, which were clarified through the X-ray and SEM results.

Keywords Hydrogels · Starch-g-(*tert*-BAC) · Starch-g-(*n*-BAC) · Viscosity average molecular weight (M_v)

Introduction

The hydrogels of modified natural polymers is finding an increasingly interest due to its noticeable applications such as thermoresponsive polymers [1, 2]. Furthermore, its applicability is finding wide interest in drug delivery studies [3–5]. The modification of natural polymers such as chitosan [6, 7], starch [8], and pectin [9] through grafting with synthetic polymers were made to meet certain applications especially in drugs sustained release studies. The applicability of such copolymers to make thermoresponsive [10], and pH-sensitive materials [11] was finding a growing interest in uprising industries. Recently, starch/ethylmethacrylate were synthesized and used as excipients for matrix tablets [12], starch/acrylic acid as super-absorbents [13] and starch/*N*-isopropylacrylamide as smart core–shell polymer in supercritical carbon dioxide [14].

The grafting process have been widely accepted using different initiators such as AIBN [15], $K_2S_2O_8$ [16], Fe^{+2}–H_2O_2 [17], $KMnO_4$ [15], KVO_4 [18], and ceric ammonium nitrate (CAN) [19], where CAN was distinguished due to simple mechanism electron transfer, low activation energy and formation of free radicals on starch [20]. In our laboratory, the syntheses of different grafted copolymers were performed such as chitosan-g-ethylmethacrylate [6], starch-g-(*N*-*tert*-butylacrylamide) [21, 22]. The goal of this study focus the attention on the synthesis, optimization conditions and hydrogel properties of starch grafted with two different monomers one at a time namely *tert*-butylacrylate (*tert*-BAC) and *n*-butylacrylate (*n*-BAC) on maize starch.

M. M. Fares (✉) · A. S. El-faqeeh
Department of Applied Chemistry, Jordan University of Science & Technology, P.O. Box 3030, 22110 Irbid, Jordan
e-mail: fares@just.edu.jo

H. Ghanem
Department of Applied Physics, Jordan University of Science & Technology, P.O. Box 3030, 22110 Irbid, Jordan

M. E. Osman · E. A. Hassan
Department of Chemistry, Sudan University of Science & Technology, P.O. Box 857, Khartoum, Sudan

Experimental

Materials

tert-Butylacrylate (*tert*-BAC) (99%, Fluka) and *n*-butylacrylate (*n*-BAC) (99%, Acros Organics) were stored in refrigerator and were brought to desired temperature before use. Maize starch (food grade) supplied by Riedel-Dehaen (Germany) was first dried at 110 °C, and then stored over anhydrous $CaCl_2$. Ceric ammonium nitrate (CAN) was dried at 100 °C, kept in a desiccator over $CaCl_2$, and was used as 0.1 M in molar HNO_3 solution.

Graft copolymerization

The grafting process as been previously reported [21] illustrated as follows. A 1.0 g of dried and 75 mL distilled water was stirred magnetically under N_2 atmosphere, and then was treated with CAN for 15 min. Then this treatment was followed with dropwise addition of monomer and completed to a total volume of 100 mL by distilled water, and then polymerization proceeded at 30 °C for 300 min unless mentioned elsewhere. After polymerization was over, the solution was allowed to cool and 50 mL of distilled water was added and stirred for 10 min to extract homopolymer. Furthermore, washing was continued until no precipitation of homopolymer in the filtrate was observed. The precipitation was done using non-solvent methanol. Eventually the precipitate was collected by suction filtration and dried to constant weight. The percentage of grafting was evaluated using grafting efficiency (%GE) [23], which could be calculated from the relation

$$\%\mathrm{GE} = \frac{W_2 - W_1}{W_3} \times 100 \qquad (1)$$

where W_1, W_2 and W_3 are weights of starch, starch-g-(*tert*-BAC) or (*n*-BAC) copolymers and the monomer, respectively.

Characterization of grafted starch

Different techniques used to characterize the target hydrogels such as thermogravimetric analysis (TG), FTIR, X-ray diffraction (XRD) and scanning electron microscope (SEM) techniques as follows:

Thermogravimetric analysis (TG)

Shimadzu TGA-50 (Japan).All samples were carried out under N_2 atmosphere at a heating rate of 10 °C/min.

FTIR

Spectra were recorded via Thermo Nicolet (avator-360, USA) FTIR spectrophotometer in the range of 4000–400 cm^{-1} using KBr pellets.

X-ray diffraction (XRD)

Philips-Holland diffractometer (model PW 1729) was used for the X-ray diffraction studies with copper as target material in an X-ray tube under the operational conditions of 30 KV, 40 mA and wavelength between 1.54060 and 1.54438 Å. The samples were scanned between 3° and 100°.

Scanning electron microscopy (SEM)

DSM 950 (ZEISS) model (USA) was used to study the morphology of the surface of all samples. The SEM was of Polaroid films. The samples in the form of films were mounted on the specimen stabs and coated with gold ion by sputtering method with Polaron (E6100) model. The micrographs were taken at a magnification of 500 and 2500.

Properties of grafted starch

Optimization of reaction conditions

The reaction conditions such as monomer concentration, initiator concentration, temperature, time, and volume of solution were checked each one at a time and were monitored throughout the percent of grafting efficiency (%GE).

Acid hydrolysis and MW measurements

0.2 g of starch-g-(*tert*-BAC) or starch-g-(*n*-BAC) were acid hydrolyzed using 100 mL, 0.5 M HCl reflux for 2 h, where all starch chains were converted into glucose units. The solution after cooling is poured in a large amount of methanol, and the precipitate collected by filtration is expected to be chains of poly(*tert*-BAC) or poly(*n*-BAC) bounded to starch, which was checked by FTIR spectra. The viscosity average molecular weight (M_v) of these branches of poly(*tert*-BAC) or poly(*n*-BAC) were determined from the relation [24]: $[\eta] = 2.56 \times 10^{-4} M_v^{0.74}$, using 0.03 g/mL in THF solvent at 30 °C. The real amount of starch involved in each copolymer could be determined by acid hydrolysis as previously mentioned by subtracting weight of grafted chains of poly(*tert*-BAC) or poly(*n*-BAC) deduced from acid hydrolysis from total weight of starch-g-(*tert*-BAC) or (*n*-BAC) samples and consequently %Grafting Yield (%GY) [21] could be determined by the formula:

$$\%\mathrm{GY} = \frac{W_2 - W_4}{W_3} \times 100 \qquad (2)$$

where W_2, W_3 and W_4 are the weights of starch-g-(*tert*-BAC) or (*n*-BAC) copolymer, monomer and real amount of starch involved in grafting. respectively. Thus, %GY formula can simultaneously present the best mathematical formula for the grafting process under the condition that the synthetic grafted polymer onto starch must resist acid hydrolysis.

Water absorbency

Water uptake

The dry samples were weighed and kept in water for 2 h at 25 °C. The wet weights were determined after sandwiching samples between the filter paper for 10 times. The water uptake of the grafted samples was determined from %water uptake = $100(W_2 - W_1)/W_1$, where W_1 and W_2 are weight of dry and wet values, respectively [25]

Moisture uptake

The weighed dry samples were placed in a desiccator over water (100% humidity) and kept at 25 °C for 24 h, closing the cap of the desiccator. The moisture uptake values of the samples were calculated from their dry and wet weights (i.e. %moisture uptake = $100(W_2 - W_1)/W_1$, where W_1 and W_2 are weight of dry and wet values, respectively) [25].

Results and discussion

Characterization of grafted starch

Gravimetric estimation

The weight difference between grafted starch and pure starch shows an evidence of grafting of *tert*-BAC or *n*-BAC onto starch. This weight difference forms the basis for the determination of grafting efficiency.

Thermogravimetric analysis (TG)

Figure 1 shows the TG curves of (a) pure starch, (b) pure poly(*tert*-BAC), (c) starch-g-(*tert*-BAC) (%GE = 80), (d) pure poly(*n*-BAC) and (e) starch-g-(*n*-BAC) (%GE = 88), It could be clearly seen that from DTG curves that the temperature at which maximum %mass loss takes place ($T_{\max.}$) of the copolymers were as follows. Two important characteristics could be deduced from Fig. 1 and Table 1, the first was that TG curves doubtless prove that grafting process took place where Fig. 1c showed two peaks each one for starch ($T_{\max} = 316$ °C), and the other for poly(*tert*-BAC) ($T_{\max} = 250$ °C). In addition, Fig. 1e showed again the presence of starch ($T_{\max} = 316$ °C), and poly(*n*-BAC) ($T_{\max} = 379$ °C). The other important characteristic was when taking the ratio of the area of DTG curve for poly(*tert*-BAC)/starch and poly(*tert*-BAC)/starch in the copolymer, it showed almost (1:1) ratio, which were very comparative with %GE values (i.e. %GE = 80 for starch-g-(*tert*-BAC) and %GE = 88% for starch-g-(*n*-BAC)), where the molar ratios were (0.8:1) and (0.88:1), respectively. Thus, it could be concluded that TG technique could be strong tool in investigation of grafting process and grafting efficiency values (%GE).

FTIR

Figure 2 shows the FTIR spectra of (a) pure starch (b) pure poly(*tert*-BAC), (c) starch-g-(*tert*-BAC) (%GE = 80), (d) pure poly(*n*-BAC) and (e) starch-g-(*n*-BAC) (%GE = 88).

It could be observed that the intensity of the OH stretching in glucosidic ring of starch that have a broad band at 3450 cm^{-1}, were reduced due to grafting of poly(*tert*-BAC) and poly(*n*-BAC), Furthermore the carbonyl stretching of the ester group located at around 1735 cm^{-1} have clearly appeared in both starch-g-(*tert*-BAC) and starch-g-(*n*-BAC) along with its presence in pure poly(*tert*-BAC) and pure poly(*n*-BAC) and its absence in pure starch, which confirmed the grafting process.

X-ray diffraction (XRD)

Figure 3 shows the diffraction patterns of pure starch, starch-g-(*n*-BAC) and starch-g-(*tert*-BAC) copolymers.

Starch was known as semi crystalline material, which was attributed to the presence amylopectin fraction into it. The grafting process leads to the decrease in %crystallinity due to capability of grafted chains (i.e. poly(*n*-BAC) or poly(*tert*-BAC) to bind the crystalline chains and consequently loosen and open up the crystalline region. This could be noticed from relatively large decline of number of accounts from 1000 to 400 or 200 accounts, respectively, which suggests that the crystalline region largely contributes in the grafting process. By referring to the TG results, in spite of some similarities that seem to be in *n*-BAC and *tert*-BAC structures, the $T_{\max.}$ for poly(*n*-BAC) equals

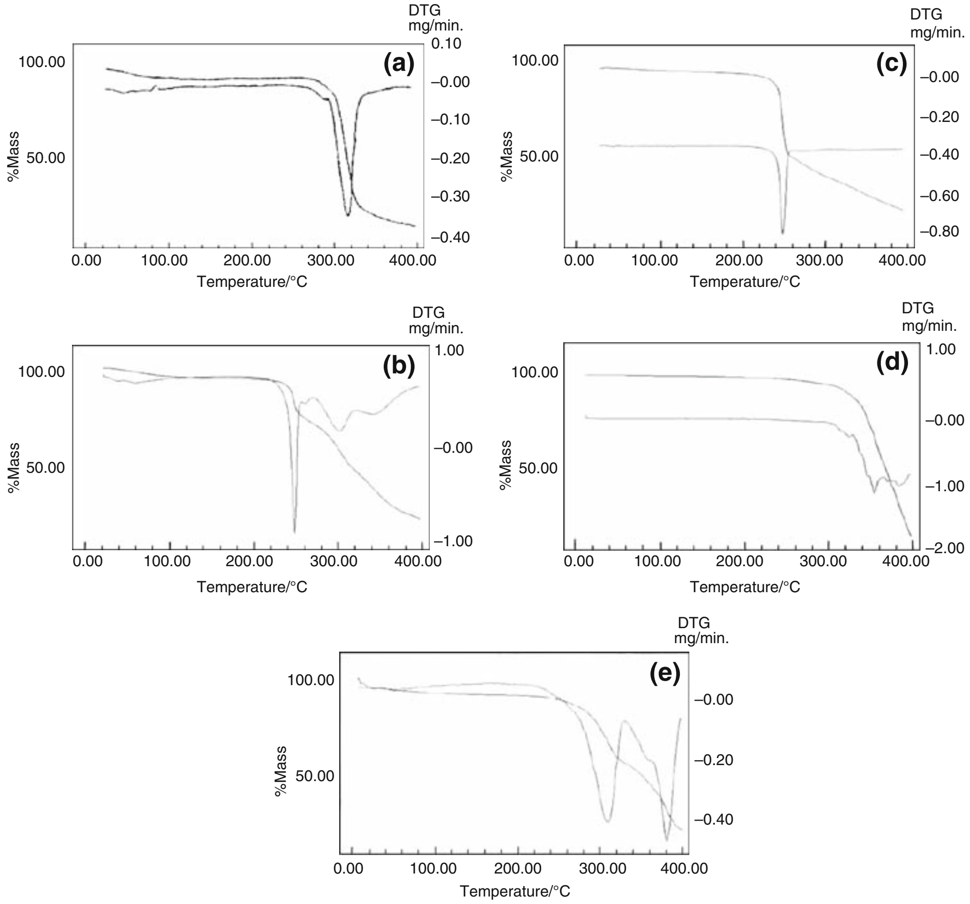

Fig. 1 TG curves for **a** pure starch, **b** pure poly(*tert*-BAC), **c** starch-g-(*tert*-BAC) (%GE = 80), **d** pure poly (*n*-BAC), and **e** starch-g-(*n*-BAC) (%GE = 88)

Table 1 Thermal decomposition data for different samples

Sample	$T_{max.}$ (°C)	% Mass loss
Pure starch	316	69
Pure poly(*tert*-BAC)	250	81.5
Starch-g-(*tert*-BAC) (%GE = 80)	316, 250	53, 22
Pure poly(*n*-BAC)	379	74
Starch-g-(*n*-BAC) (%GE = 88)	316, 379	42, 39

379 °C, whereas $T_{max.}$ for poly(*tert*-BAC) = 250 °C, with a difference of 129 °C. This large thermal stability difference was further noticed here in X-ray diffraction patterns. The increase in %crystallinity in starch-g-(*n*-BAC) over starch-g-(*tert*-BAC) was owed to structure of normal butyl groups which encourage crystallinity formation, and consequently inclines the thermal stability of poly(*n*-BAC). In contrary, tertiary-butyl groups not only cause decrease in thermal stability due to its three dimensional structure but also cause more destruction to the crystalline regions of starch macromolecules [21].

Scanning electron microscopy (SEM)

Figure 4 shows the SEM micrographs of (a) pure starch (b) starch-g-(*tert*-BAC) copolymer (%GE = 80), at magnification of 2500, and (c) starch-g-(*n*-BAC copolymer (%GE = 88) at magnification of 500 (d) starch-g-(*n*-BAC copolymer (%GE = 88) at magnification of 2500.

The study of morphological changes, when accompanied with molecular level insight not only on the outer shells of the polymer but rather to inner sights. It could be seen from Fig. 4a that starch is formed from granules that are separate from each other, when grafted with poly(*tert*-BAC), those granules became more in contact and coherent with a more regular shape, and when grafted with poly(*n*-BAC), the coherency have increased to form a merged units which is more likely to be a solidified marine sponge. Thus the presence of normal butyl group, have caused the increase in crystallinity in starch-g-(*n*-BAC) over starch-g-(*tert*-BAC) as deduced from XRD patterns and further increased the thermal stability of starch-g-(*n*-BAC) over starch-g-(*tert*-BAC) as deduced from TG and eventually formed a merged units similar to solidified marine sponge (Fig. 4d).

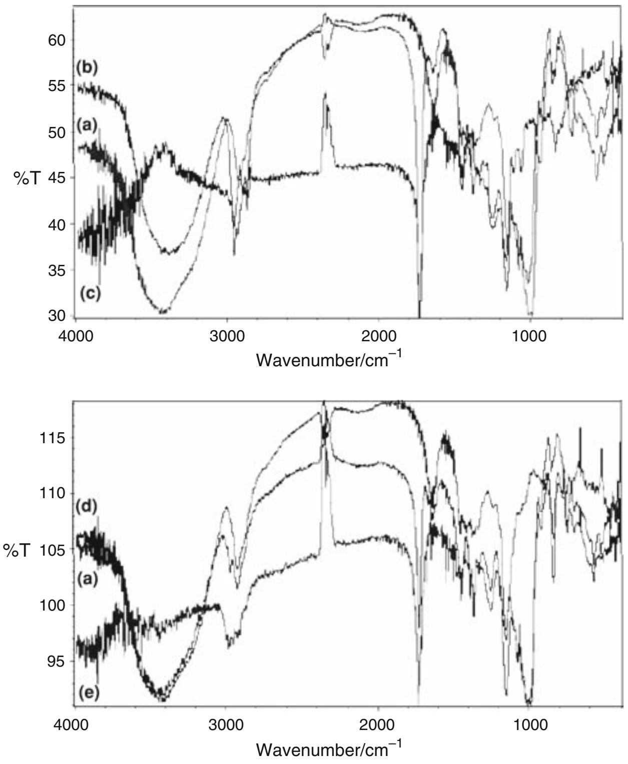

Fig. 2 FTIR spectra for **a** pure starch, **b** starch-g-(*tert*-BAC) (%GE = 80), **c** pure poly(*tert*-BAC), **d** starch-g-(*n*-BAC) (%GE = 88), and **e** pure poly(*n*-BAC)

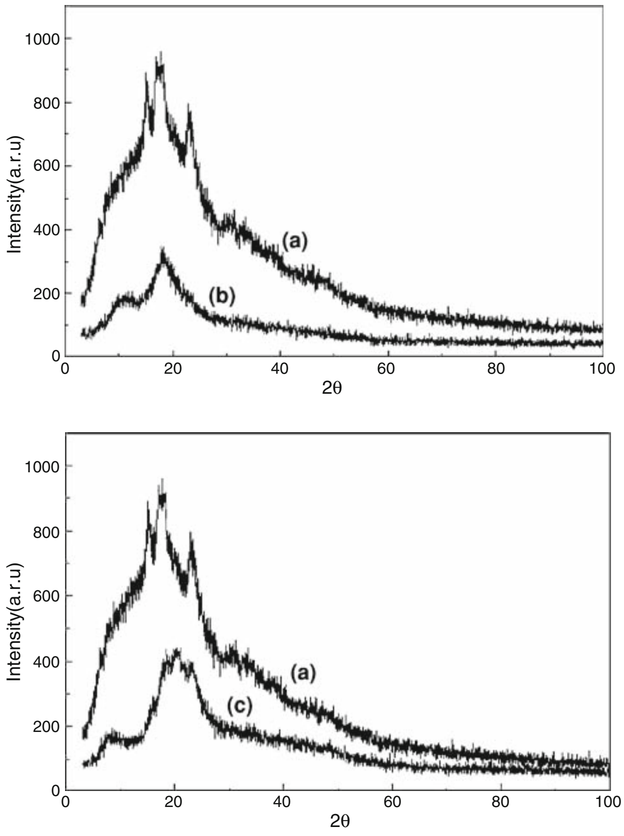

Fig. 3 XRD patterns for **a** pure starch, **b** starch-g-(*tert*-BAC) (%GE = 80), **c** starch-g-(*n*-BAC) (%GE = 88)

Properties of grafted starch

Monomer & initiator concentration optimizations

Table 2 shows the optimum values of monomer concentration for both *tert*-BAC and [*n*-BAC], which equals to 0.04 mol/L. Using larger concentrations (i.e. 0.06 mol/L) of monomers in the medium cause a decay in %GE values for both monomers, which was attributed to homopolymer formation. This was clear throughout the washing process of the grafted polymer, where larger homopolymer amounts were precipitated using methanol were observed. In Table 3 increasing the [CAN] for starch-g-(*tert*-BAC) increases the %GE until it reaches its maximum %GE = 80 using [CAN] = 9.0×10^{-4}, whereas the optimum [CAN] for starch-g-(*n*-BAC) was obtained at 4.0×10^{-3} mol/L, where further increase of [CAN] causes a decline in %GE. This could be ascribed to recombination of free radicals with each other, which dramatically inhibits the grafting process and lead to lower %GE.

Temperature optimization

Figures 5 and 6 illustrate the change of %GE with time at different temperatures, it could be noticed that the increase of temperature led to increase in %GE. This Arrhenius behavior continues up to 20 °C for starch-g-(*tert*-BAC), and to 30 °C for starch-g-(*n*-BAC) copolymers. Further increase in increase in temperature led to simultaneous decay in %GE values for both copolymers. This decay at elevated temperatures could be explained

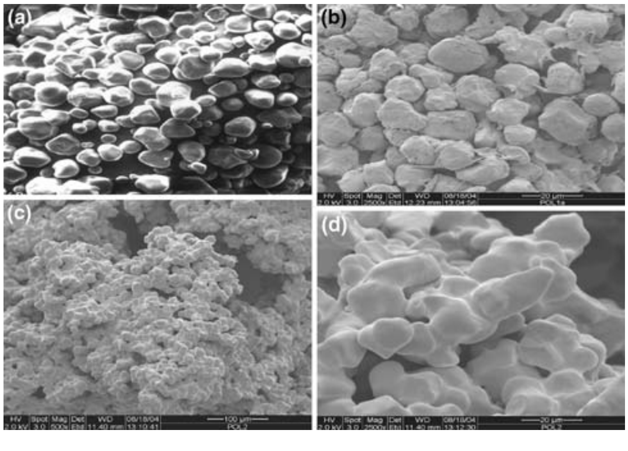

Fig. 4 SEM micrographs of **a** pure starch, **b** starch-g-(*tert*-BAC) (%GE = 80), **c** and **d** starch-g-(*n*-BAC) (%GE = 88)

Table 2 The influence of [*tert*-BAC] and [*n*-BAC] monomers on the grafting efficiency (%GE) values

Time/h	[*tert*-BAC]	%GE$_{(tert\text{-BAC})}$	[*n*-BAC]	%GE$_{(n\text{-BAC})}$
1.0	0.020	20	0.012	12
2.0	0.020	29	0.012	26
3.0	0.020	38	0.012	41
1.0	0.040	20	0.040	42
2.0	0.040	58	0.040	61
3.0	0.040	80	0.040	88
1.0	0.060	24	0.060	41
2.0	0.060	52	0.060	45
3.0	0.060	73	0.060	62

Reaction conditions: starch = 1.0 g, T = 30 °C, $V_{\text{sol'n}}$ = 100 mL

Table 3 The influence of initiator concentration on the grafting efficiency (%GE) values

[CAN]$_{(tert\text{-BAC})}$	%GE$_{(tert\text{-BAC})}$	[CAN]$_{(n\text{-BAC})}$	%GE$_{(n\text{-BAC})}$
1.0×10^{-4}	52	1.0×10^{-3}	60
2.0×10^{-4}	60	2.0×10^{-3}	72
4.0×10^{-4}	62	4.0×10^{-3}	88
7.5×10^{-4}	64	7.5×10^{-3}	65
9.0×10^{-4}	80	9.0×10^{-3}	39

Reaction conditions: starch = 1.0 g, [*tert*-BAC] = 0.04 mol/L, [*n*-BAC] = 0.04 mol/L, T = 30 °C, and $V_{\text{sol'n}}$ = 100 mL)

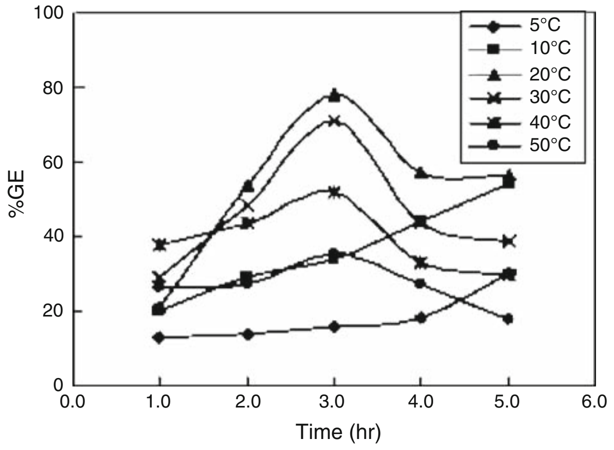

Fig. 5 Change of %GE with time at different temperatures for Starch-g-(*tert*-BAC) copolymers. Reaction conditions: starch = 1.0 g, [*tert*-BAC] = 0.04 mol/L, [CAN] = 9.0×10^{-3} mol/L)

by the violent and rapid motion of starch macroradicals in solution, and as a result consequent radical scavenging probability and/or radical re-combination, which eventually led to lower %GE values. Furthermore, the decay of %GE after 4 and 5 h of copolymerization was ascribed to expected partial hydrolysis, which could cleave many COC bonds, which then were removed by washing leaving lower weight of copolymer and consequent lower %GE values.

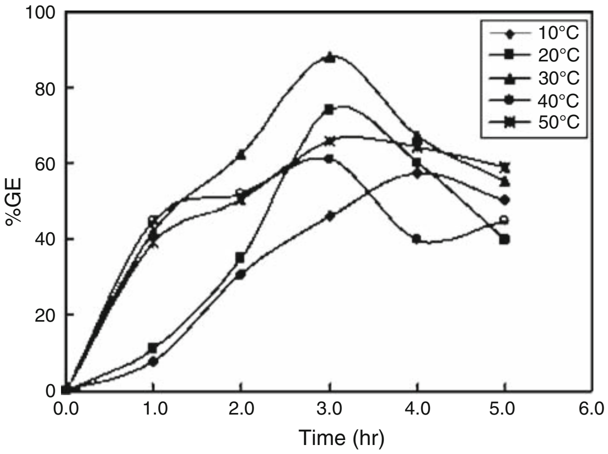

Fig. 6 Change of %GE with time at different temperatures for starch-g-(*tert*-BAC) copolymers. Reaction conditions: starch = 1.0 g, [*n*-BAC] = 0.04 mol/L, [CAN] = 4.0×10^{-3} mol/L)

Acid hydrolysis and MW measurements

Acid hydrolysis using 0.5 M HCl of the grafted copolymers leads to decomposition of repeating units of starch into glucosidic units which in turn does not precipitate upon addition of non-solvent such as methanol, and only precipitate grafted poly(*tert*-BAC) or poly(*n*-BAC) chains that resist acid hydrolysis. Consequently, the viscosity average molecular weight of these samples can be determined. Table 3 shows the change of average molecular weight as temperature changes and as [CAN] changes. Through Figs. 5 and 6, it were shown that at fixed [monomer], and fixed [CAN], %GE decreases as temperature increases above 30 °C due to homopolymerization, three arbitrary samples of both starch-g-(*tert*-BAC) and starch-g-(*n*-BAC) at elevated temperatures as Table 4 shows were exposed to acid hydrolysis and later their average molecular weight (M_v) were calculated, the results concluded that the M_v decreases as temperature increases, which came in accordance with %GE decrease as deduced from Figs. 5 and 6. Furthermore, as [CAN] increase it was found that M_v first increased then decreased, which was in accordance with data of %GE [21].

Water absorbency

Figure 7 shows the water absorbency versus monomer/starch ratio using different volumes of solutions. In both copolymers, both water uptake and moisture uptake shown a maximum absorbency at *tert*-BAC/starch = 0.5, whereas *n*-BAC/starch = 1.0. Furthermore, the starch-g-(*n*-BAC)

Table 4 Change of viscosity average molecular weight (M_v) and %GE with temperature and [CAN]

Experimental conditions	$\%GE_{(tert\text{-BAC})}$	$\overline{M}_{v(tert-\text{BAC})}$	$\%GE_{(n\text{-BAC})}$	$\overline{M}_{v(n-\text{BAC})}$
30 °C	64.9	2.30×10^6	74.0	2.14×10^6
40 °C	48.0	2.26×10^6	66.0	1.65×10^6
50 °C	39.0	1.91×10^6	61.0	1.58×10^6
$[CAN] = 1.8 \times 10^{-3}$	32.0	1.45×10^6	72.1	2.44×10^6
$[CAN] = 3.7 \times 10^{-3}$	72.3	2.40×10^6	88.2	2.97×10^6
$[CAN] = 9.1 \times 10^{-3}$	50.0	1.85×10^6	66.4	2.08×10^6

seems to absorb water more than five folds of its weight whereas starch-g-(*tert*-BAC) could only absorb 0.6 folds of its weight. Furthermore it clearly shows that starch-g-(*n*-BAC) hydrogel could absorb water ten times more than that of starch-g-(*tert*-BAC) hydrogel. Thus, by referring to Fig. 4d of starch-g-(*n*-BAC), it would be clearly seen that outer shell of this copolymer which is similar to marine sponge as well as its larger crystallinity (Fig. 3c) and larger thermal stability, adapt the copolymer to form pores that can hold water molecules ten times more than of starch-g-(*tert*-BAC) copolymer and consequently absorb large amounts of water and act as hydrogel.

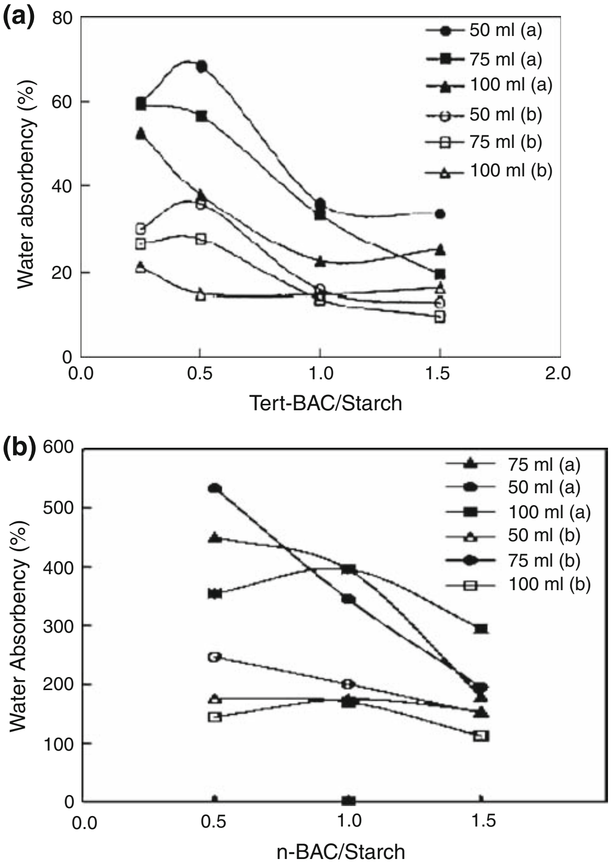

Fig. 7 Change of water absorbency versus monomer/starch ratio represented in the legends as **a** water uptake and **b** moisture uptake

Conclusions

Several conclusive remarks deduced from grafting of *tert*-butylacrylate and *n*-butylacrylate onto starch at different monomer, initiator concentrations and temperature, which were as follows:

- The optimum conditions for the grafting process of *tert*-butylacrylate into 1.0 g of starch are as follows: temperature = 20 °C, [*tert*-BAC] = 0.04 mol/L, $[CAN] = 9.0 \times 10^{-4}$ mol/L, in 100 mL solution, whereas the results using *n*-butylacrylate monomer are as follows: temperature = 30 °C, [*n*-BAC] = 0.04 mol/L, $[CAN] = 4.0 \times 10^{-3}$ mol/L in 100 mL solution.
- At elevated temperature of copolymerization, the %GE first increase to a maximum value and then it decays simultaneously. This decay could be explained by the violent and rapid motion of starch macroradicals in solution, and as a result consequent radical scavenging and/or radical re-combination, which eventually led to lower %GE values. Furthermore, the decay of %GE after four and five hours of copolymerization was ascribed to expected partial hydrolysis, which could cleave many COC bonds, that were removed by washing leaving lower weight of copolymer and consequent lower %GE values.
- DTG technique showed that the starch-g-(*n*-BAC) gives two peaks one at 316 °C referring to starch, and at 379 °C referring to poly(*n*-BAC), whereas the two peaks in starch-g-(*tert*-BAC) at 250 and 316 °C referred to poly(*tert*-BAC) and starch, respectively. X-ray technique showed larger crystallinity of starch-g-(*n*-BAC) over starch-g-(*tert*-BAC) with about 120–150 accounts which could be explained by the alignment of normal butyl groups over each other in poly(*n*-BAC) over that of tertiary butyl groups in poly(*tert*-BAC).
- Acid hydrolysis method in grafted natural polymers is a useful method to determine the exact molecular weight

of grafted polymer into the natural polymer (i.e. starch). Furthermore, it can be an absolute method to determine the real grafting efficiency namely %grafting yield (%GY).

- The water absorbency of starch-g-(*n*-BAC) hydrogel was found to be 10 times more than that of starch-g-(*tert*-BAC) hydrogel, which could be deduced from the increase in crystallinity, the increase in thermal stability, and the marine-sponge like structure as Figs. 1, 3 and 4 suggest.

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