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Effect of lactic/glycolic acid side chains on the thermal degradation kinetics of chitosan derivatives

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Abstract

The thermal degradation properties of chitosan and lactic and/or glycolic acid grafted chitosan have been studied by differential scanning calorimetry (DSC) and thermogravimetric analyses (TG) in the range of 25–500°C. Both DSC and dynamic TG results show that the samples are thermal degraded easily after grafting the lactic and/or glycolic acid. From the isothermal TG experiments, the initial activation energy and the activation energy at different stages is obtained. The initial activation energy of all grafted samples is much lower than that of chitosan, especially for the sample GA/CS = 2 and it varies with degree of conversion. The FT–IR spectra of thermally degraded residues give an indication of the chitosan polyscaccharide ring degradation after 30 min in 280°C, while sample GA/CS = 2 will degrade only after 15 min.

Keywords: Chitosan; Chitosan derivative; Lactic acid

1. Introduction

Chitosan, (1,4)-2-amino-2-deoxy-β-D-glucan, is a natural polymer generally obtained by extensive deacetylation of chitin isolated from crustacean shells. Due to its special biological, chemical and physical properties, chitosan and its derivatives have applications in many industrial and agriculture activities [1–3]. In addition, Chitosan is a biocompatible material with a lethal dose, LD_{50}, as high as 16 g kg^{-1} in mice, after oral and intravenous administration, and shows mild antimicrobial activity arising from its cationic residue, which are important properties in view of its use as a biomedical material [4].

Apart from its biodegradable character in physiological conditions, chitosan has reactive amine side groups, which offer possibilities of modifications, graft reactions and ionic interactions. For instance, chitosan derivatives were synthesized in our group by grafting lactic and glycolic acid. The side chains could aggregate and form physical crosslinking, which results in pH-sensitive chitosan hydrogels [5–8]. These hydrogels have potential use in biomedical applications like wound dressings and drug release systems, since both polyester side chains and chitosan are biocompatible and biodegradable [1,2].

The thermal degradation behavior of chitosan [9], chitosan-metal ion complex [10], chitosan Schiff bases [11] and chitosan-poly(3-hydroxybutyric acid) blends [12] have been studied by thermal analysis techniques including pyrolysis-mass spectrometry, differential scanning calorimetry (DSC) and thermogravimetric analyses (TGA). However, no results have been reported concerning the effect of polyester side chains on the thermal degradation kinetics of chitosan. In this paper, both dynamic and isothermal conditions were used to study the thermal degradation. Weight loss, temperature and activation energy for the various decomposition stages were determined and compared. Further, FT–IR spectra of thermally degraded residues were obtained and the results were discussed.

2. Experimental

2.1. Materials

Chitosan (MW = 70, 000) from Fluka (Switzerland), D,L-lactic acid (LA) (99%) and glycolic acid (GA) (99%) from Lancaster (England) were used as received for the preparation of graft copolymers. The degree of deacetylation (DD = 88%) of chitosan was determined by the IR spectroscopy method [13].

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Table 1
Graft copolymerization of glycolic and D,L-lactic acid onto chitosan

Sample	CS[a] (g)	GA (g)	LA (g)	COOH/NH_2 (mol/mol)	Yield (g)	DP of side chains[b]	DS of side chains[c] (%)
GA/CS = 0.5	1.0	0.5	–	1.24	0.86	1.71	7
GA/CS = 2	1.0	2.0	–	4.96	0.94	3.85	16
GA/LA/CS = 1/1/1	1.0	1.0	1.0	4.58	0.95	2.91	13
LA/CS = 2	1.0	–	2.0	4.19	1.02	1.95	14
LA/CS = 0.5	1.0	–	0.5	1.05	0.86	0.99	6

[a] Water-soluble chitosan with 88% deacetylation was used.
[b] Degree of polymerization of side chains measured by elemental analysis.
[c] Degree of substitute measured by residual salicylaldehyde.

2.2. Preparation of chitosan hydrogels

The synthesis of hydrogel was carried out by direct grafting of D,L-lactic acid and/or glycolic acid onto chitosan in the absence of catalysts according to the method already reported [5]. In short, Chitosan powder was dissolved by adding lactic acid and/or glycolic acid with different feed ratios in water. The solutions were poured onto a Teflon dish with 15.0 cm diameter and dried at 80°C, followed by extraction with methanol in a Soxhlet apparatus for 24 h.

2.3. Methods

DSC curves were recorded in a Mettler Toledo DSC 820 Calorimeter fitted with a cooling accessory. The samples were cut into small pieces and put into aluminum vessels. The sample vessels were heated from room temperature to 500°C at a heating rate of 10°C min^{-1}.

Dynamic and isothermal TGA were carried out with a METTLER TGA/SDTG 851[e] system. All the TGA were performed with 4–5 mg of finely cut sample pieces in an Al_2O_3 crucible (70 μl) under a dynamic nitrogen atmosphere flowing at 50 ml min^{-1}. Dynamic experiments were run at a scanning rate of 10°C min^{-1}. In isothermal experiments samples were dried in the oven at 150°C for 20 min and then heated to the experimental temperature, taking as zero time the moment at which the temperature of the system was stabilized automatically.

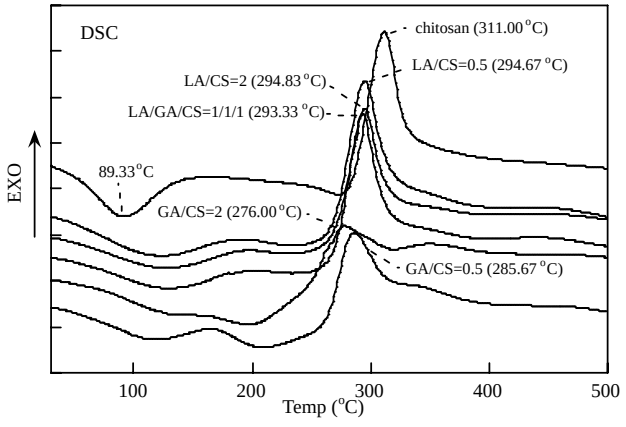

Fig. 1. DSC thermograms of chitosan and its derivatives.

The FT–IR spectra were obtained from the film samples on a Perkin–Elmer FT–IR 1725X spectrometer.

The degree of substitution of the chitosan amino groups was determined by formation of *N*-salicylidene chitosan [3] for methanol extracted samples. An accurately weighed dry sample was immersed for 24 h in 100 ml 0.02 M solution of salicylaldehyde in methanol/1% acetic acid aqueous solution (80/20 v/v). After 24 h the mixture was filtered, a portion of the filtrate diluted 400 times and the UV absorbance at 255 nm measured to determine the residual concentration of salicylaldehyde (SA) by comparing to the blank SA solutions.

2.4. Elemental analysis

The content of C, H and N was determined for virgin and methanol extracted grafted chitosan samples. The total nitrogen content was determined according to Dumas with a Carlo Erba NA 1500 instrument. All analyses were performed by Mikro Kemi AB, Uppsala Sweden.

3. Results and discussion

The pH-dependent swelling behavior and kinetics of hydrogels based on D,L-lactic acid, glycolic acid and chitosan are already reported in our previous articles [5–8]. Table 1 gives the monomers to chitosan feed ratios, yields and grafted side chains data for the chitosan hydrogels. The average side chain length (DP) and degree of substitution (DS) were calculated from the results of the elemental analysis and the residual salicylaldehyde method [3]. With the increase of the monomer feed ratios, both DP and DS of the side chains increase. Compared to lactic acid, grafting glycolic acid will give higher values of the side chain length.

3.1. Dynamic studies by differential scanning calorimetry and thermogravimetry

DSC curves of chitosan and its derivatives recorded in nitrogen from ambient temperature to 500°C are shown in Fig. 1. The temperatures for various thermal effects are

Table 2
Peak temperatures and weight loss in DSC and TG during the thermal degradation of chitosan and its derivatives

Sample	First range (30–200°C)			Second range (200–400°C)		
	DTG_{max} (°C)	DSC_{min} (°C)	Weight loss (%)	DTG_{max} (°C)	DSC_{max} (°C)	Weight loss (%)
Chitosan	61.36	89.33	7.09	304.17	311.00	47.39
LA/CS = 0.5	95.28	116.17	6.40	287.33	294.67	45.15
LA/CS = 2	109.75	122.33	7.28	286.62	294.83	44.23
LA/GA/CS = 1/1/1	119.96	123.83	8.17	283.14	293.33	43.78
GA/CS = 2	109.79	128.33	8.59	279.34	276.00	45.17
GA/CS = 0.5	80.30	110.33	7.55	279.56	285.67	44.56
Interpretation	Water evaporation			Thermal degradation		

given in Table 2. For chitosan, the endothermic peak at 89.33°C in the first range (30–200°C) is associated with loss of water, whereas the exothermic peak at 311°C in the second range (200–400°C) corresponds to the degradation and deacetylation of chitosan. As for the derivatives, the endothermic peaks shift to a higher temperature range (110–130°C) depending on the type and length of the side chains. This could be attributed to the much stronger interactions between water and the grafted chitosan chains, since the crystallinity of chitosan has been largely decreased after grafting as we reported in previous papers [5–8]. Meanwhile, the chitosan derivatives have lower thermal stability than chitosan. Their decomposition peaks vary from 276 to 295°C depending on the type and length of side chains, and are lower than that of chitosan (311°C). Among the samples investigated, GA/CS = 2 has the lowest value (276°C) due to the low thermal stability of glycolic acid side chains. It will be further explained by the activation energy (E_a) change in the following paragraphs. These results are anticipated since both the lactic acid and glycolic acid oligomers are easily thermally degraded [14,15], and the degradation of the side chains may further induce the degradation of the whole material as we will discuss below. All samples are considered to be homogeneous during the thermal degradation, since only one exothermic peak has been found in the DSC curves.

TG and differential thermogravimetric (DTG) curves for chitosan and its derivatives recorded in nitrogen are shown in Figs. 2 and 3. The temperatures and the weight losses (%) are also given in Table 2. When compared to its derivatives, chitosan has lower water evaporation and higher thermal degradation temperatures. The weight loss of all samples is similar in both the first and second ranges. These results are correlated well with the results of DSC.

The apparent activation energy for the thermal degradation of chitosan and its derivatives were determined from the TG curves using the method described by Broido [16]. The equation used can be written in the form:

$$\ln[\ln[1/(1-\alpha)]] = -E_a/RT + \ln[(R/E_a)(Z/U)T_m^2] \quad (1)$$

α is the extent of conversion and is given by:

$$\alpha = W_e/W_0$$

where W_e is the mass of polymer evolved as volatile fragments and W_0 is the initial mass, R the gas constant, Z the constant, T_m the temperature of the maximum reaction velocity and U the rate of heating.

Plots of $\ln[\ln[1/(1-\alpha)]]$ versus $1/T$ for the temperature range 225–330°C, which is in the second temperature range 200–400°C as mentioned earlier, are shown in Fig. 4. Linear plots are obtained but with different slopes indicating three

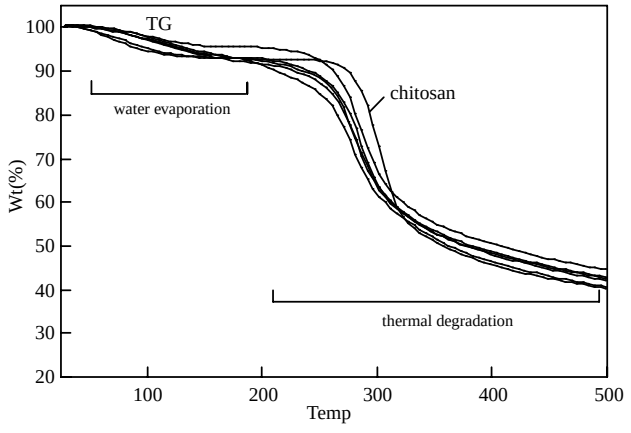

Fig. 2. TG curves of chitosan and its derivatives.

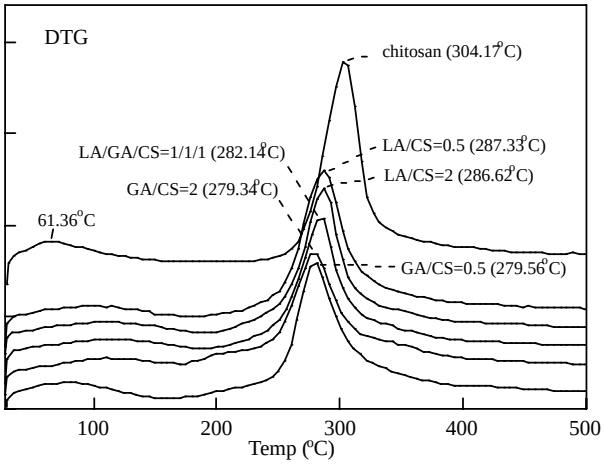

Fig. 3. DTG curves of chitosan and its derivatives.

Table 3
Activation energies and weight loss in dynamic TG analysis during the thermal degradation of chitosan and its derivatives (Broido method)

Sample	Period I (225–256°C)		Period II (256–322°C)	
	E_a (kJ mol^{-1})	Weight loss (%)	E_a (kJ mol^{-1})	Weight loss (%)
Chitosan	5.3	0.54	113.4	35.46
LA/CS = 0.5	34.2	3.04	99.0	31.64
LA/CS = 2	29.3	3.86	79.6	29.89
LA/GA/CS = 1/1/1	27.3	4.11	74.0	28.63
GA/CS = 2	29.0	5.10	64.6	27.04
GA/CS = 0.5	24.5	3.42	81.5	29.66
Interpretation	Degradation of side chains		Degradation of chitosan chains	

temperature regions of degradation. The values of the apparent activation energies, E_a, were determined from the slopes of these plots. The E_a and weight loss data obtained for the two degradation periods are reported in Table 3. Chitosan is almost not degraded in region I (225–256°C), since only 0.54% weight was lost with an E_a value of 5.3 kJ mol^{-1}. E_a as well as weight loss of the chitosan derivatives increased in the same range, suggesting the thermal degradation of polyester side chains. In region II (256–322°C), the chitosan main chains start to degrade with an E_a value of 113.4, which could be dramatically decreased by grafting various side chains. Worth noting is that the total amounts of weight loss during both periods are of similar magnitudes for all samples. Above region II, a third temperature region (>322°C) is indicated in Fig. 4 where all samples seem to have lower E_a values (lower slopes) than in region II.

3.2. Isothermal studies by thermogravimetry

The kinetics of thermal decomposition was also studied for all samples in isothermal experiments. Typical curves for chitosan and sample GA/CS = 2 expressing the change of the degree of conversion (α) with time at different temperatures are shown in Figs. 5 and 6. At the same temperature, the thermal degradation rate of GA/CS = 2 is much higher than that of chitosan for the first several minutes, especially at low temperature like 220°C. From the initial slopes of the TG curves, initial rates of degradation have been obtained and the initial apparent activation energy for the beginning of the degradation was evaluated by means of an Arrhenius plot. The straight lines obtained are shown in Fig. 7, and the initial apparent activation energy values obtained are reported in Table 4.

The apparent activation energies at different degrees of conversion were also evaluated according to MacCallum [17]. If the rate of the decomposition process, $d(1-\alpha)/dt$, can be expressed as a function of the degree of conversion, α, using the general formulation:

$$-d(1-\alpha)/dt = kf(1-\alpha) \quad (2)$$

where k is described as a rate constant, f constant, and the integrated form of Eq. (2) is

$$F(1-\alpha) = kt \quad (3)$$

Provided that the value of $F(1-\alpha)$ for a given value of α does not depend on temperature, while k depends on temperature according to the Arrhenius relationship, Eq.

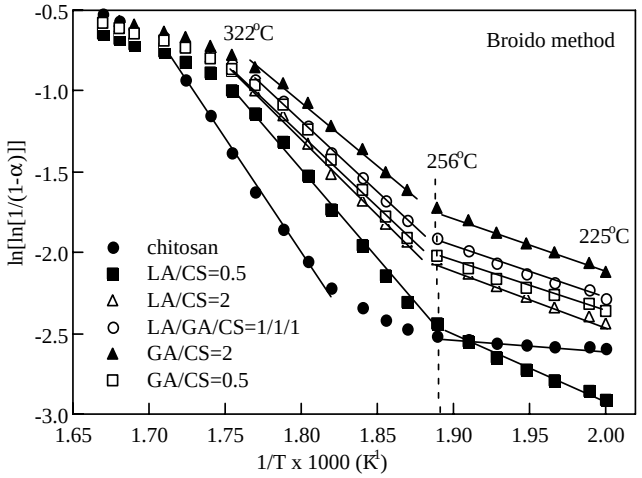

Fig. 4. Plots of $\ln[\ln[1/(1-\alpha)]]$ vs. $10^3 T^{-1}(K^{-1})$ using Broido's equation for chitosan and its derivatives during the thermal degradation.

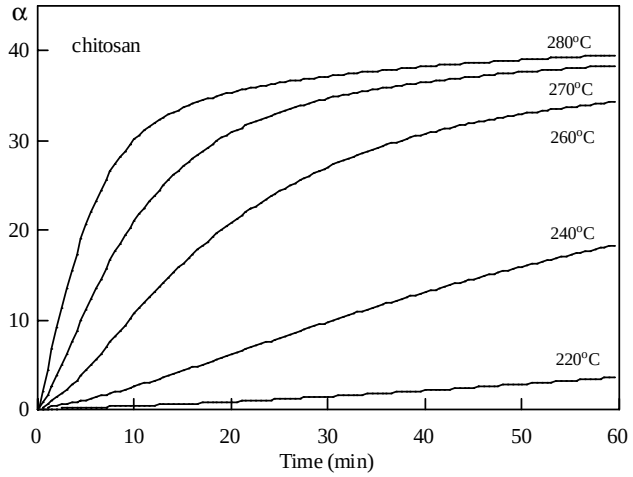

Fig. 5. Isothermal TGA of chitosan with degree of conversion (α) vs. time at various temperature.

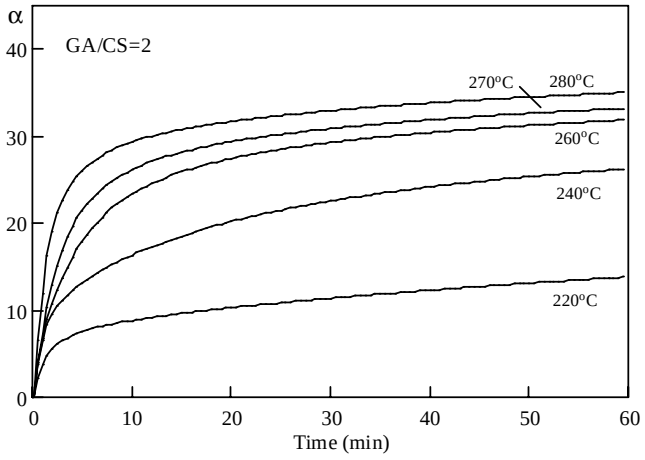

Fig. 6. Isothermal TGA of sample GA/CS = 2 with degree of conversion (α) vs. time at various temperatures.

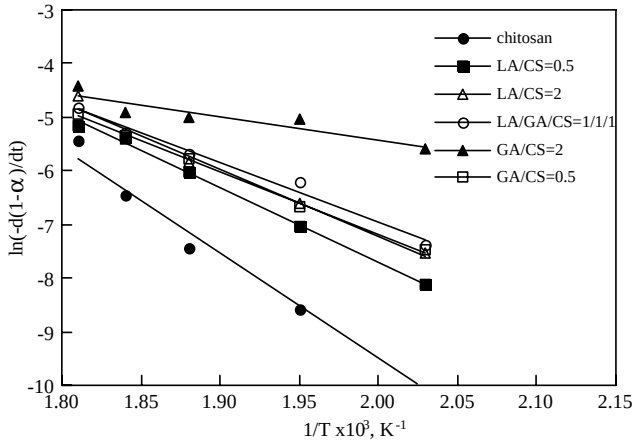

Fig. 7. Arrhenius plots of initial thermal degradation of chitosan and its derivatives under isothermal conditions.

(3) can be rewritten in the form:

$$F(1-\alpha) = A\,\mathrm{e}^{-E_a/RT}t \tag{4}$$

or

$$\mathrm{e}^{E_a/RT}F(1-\alpha)/A = t \tag{5}$$

and therefore

$$E_a/RT + \ln[F(1-\alpha)] - \ln A = \ln t \tag{6}$$

where E_a is the apparent activation energy, A the pre-exponential factor and R the gas constant.

By using Eq. (6), plots were made of the time necessary to reach a certain degree of conversion versus the inverse of temperature. Typical results for chitosan and the sample GA/CS = 2 are shown in Figs. 8 and 9, respectively. For a given value of α, the slope of the line is found to be generally higher in the higher temperature range. The apparent activation energy (E_a) values calculated from these slopes are shown also in Table 4. It is seen in Fig. 8 that the E_a value of chitosan is almost constant with temperature and the degree of conversion (α), while as seen in Fig. 9 and Table 4 the E_a values of its derivatives is lower compared to that of chitosan and increase with α.

Table 4
Activation energies in isothermal TG analysis during the thermal degradation of chitosan and its derivatives (MacCallum method)

Sample	Initial activation energy (kJ mol^{-1})	Activation energy (kJ mol^{-1})		
		$\alpha = 0.05$	$\alpha = 0.15$	$\alpha = 0.25$
Chitosan	162.4	156.7	153.1	160.6
LA/CS = 0.5	115.3	134.4	152.1	241.2
LA/CS = 2	104.3	146.0	168.1	201.6
LA/GA/CS = 1/1/1	92.1	134.2	138.8	140.0
GA/CS = 2	35.8	46.5	93.3	139.1
GA/CS = 0.5	95.7	133.7	144.6	149.2

For the chitosan derivatives, these results indicate that the apparent activation energy increases as the reaction progresses, implying involvement of further degradations of chitosan chains at advanced decomposition. The side chains could effectively reduce the activation energy of chitosan in some cases, and decrease the starting temperature for thermal degradation simultaneously. Furthermore, it is not surprising that the sample GA/CS = 2 has the lowest E_a value (36–139 kJ mol^{-1}) among all samples due to the low thermal stability of the glycolic acid side chains. The E_a value of poly (glycolic acid) has been reported to be 88 kJ mol^{-1}, that of poly (lactic acid) 120 kJ mol^{-1} and chitosan 150 kJ mol^{-1} in the literature [14,19]. The values of initial apparent activation energy from the isothermal TG curves are also given in Table 4. They are generally lower than the E_a values obtained by the MacCallum method, but follow the same trend.

3.3. Infrared spectra of residual products

The IR spectra of the residues from the isothermal

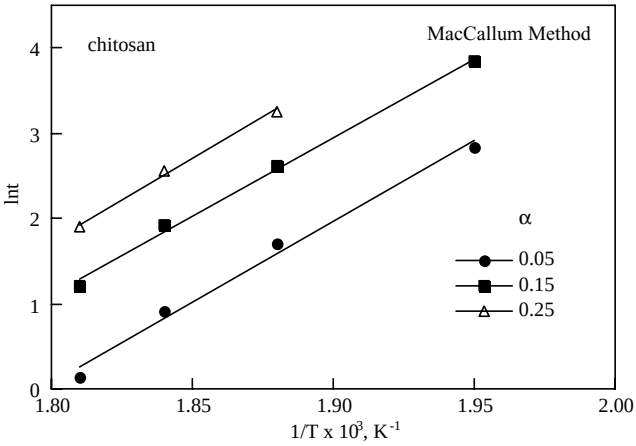

Fig. 8. Plots of ln(time to fixed conversion) versus 1/T according to the MacCallum method for chitosan.

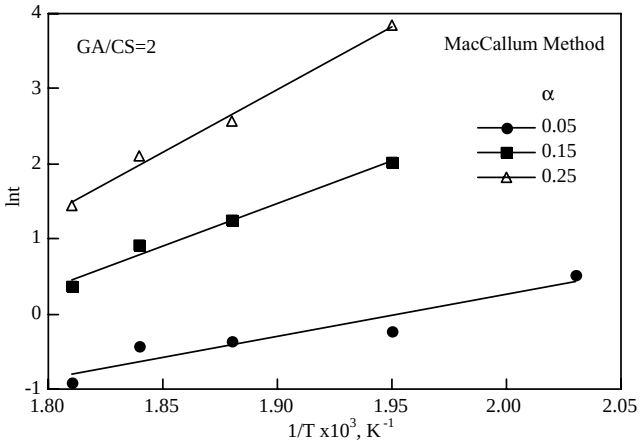

Fig. 9. Plots of ln(time to fixed conversion) versus $1/T$ according to the MacCallum method for sample GA/CS = 2.

degradation of chitosan at 280°C for different degradation times are shown in Fig. 10. The IR spectrum of chitosan before degradation [5–8] shows peaks assigned to the saccharide structure at 897 and 1153 cm^{-1} and a strong amino characteristic peak at around 1591 cm^{-1}. The absorption bands at 1655 and 1325 cm^{-1} are characteristic of *N*-acetylated chitin and have been reported to be the amide I and III bands, respectively. The sharp band at 1377 cm^{-1} has been assigned to the CH_3 symmetrical deformation mode [18]. After 15 min at 280°C, the peaks at 1655 and 1550 cm^{-1} increase and all peaks become wider than that of the original chitosan. These changes indicate that the degradation of chitosan is due to the formation of the unsaturated structures during the

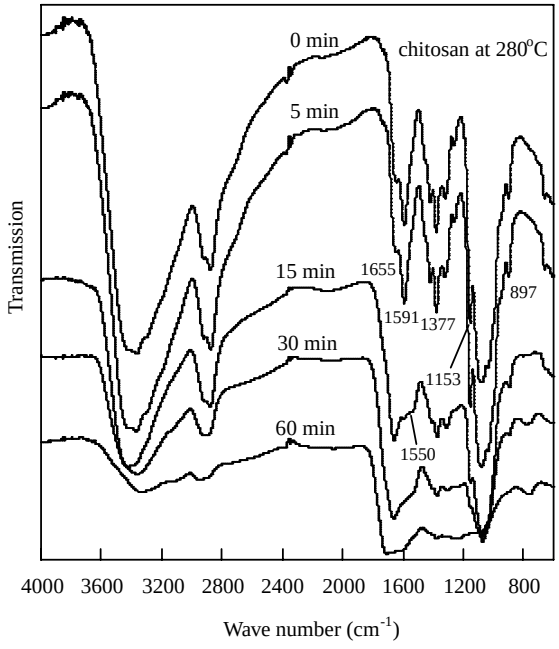

Fig. 10. Infrared spectra of chitosan heated at 280°C for different periods of time.

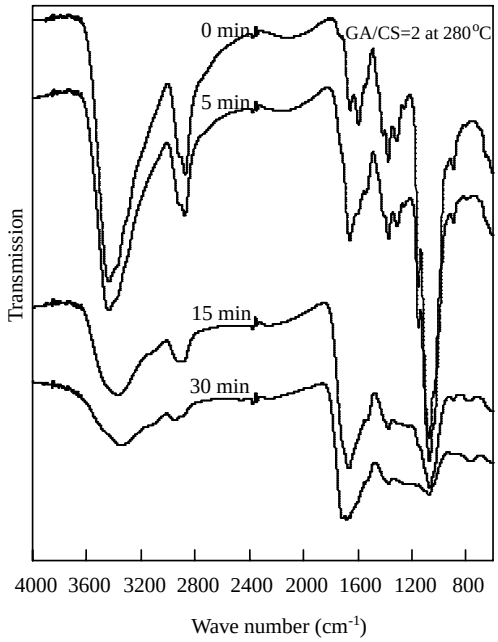

Fig. 11. Infrared spectra of sample GA/CS = 2 heated at 280°C for different periods of time.

degradation. The peaks of the saccharide structure at 897 and 1153 cm^{-1} become wider after 30 min degradation, which indicates the rupture of the β-glycosidic linkages between the glucosamine and *N*-acetylglucoamine moieties [19]. Sample GA/CS = 2 is much easier to degrade than chitosan due to its glycolic acid side chains. It starts to decompose at 280°C after only 5 min as shown in Fig. 11. For longer times, the degradation behavior is similar to that of chitosan. For other samples, the changes in IR spectrum follow the same trend during the thermal degradation.

4. Conclusion

The thermal degradation kinetics of chitosan and chitosan derivatives were studied by DSC and TG. The results show that a stronger interaction existed between water and chitosan chains after grafting lactic and/or glycolic acid. Both initial apparent activation energy and the starting degradation temperature decrease for grafted chitosan samples. It is due to the low thermal stability of the lactic acid and/or glycolic acid side chains, which may further induce the degradation of chitosan chains.

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