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Characterization of crosslinked cashew gum derivatives

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Abstract

Crosslinked materials from cashew gum (CG) and carboxymethylated CG (CMCG) were synthesized using epichlorohydrin (E) as the crosslinking agent. The products were characterized by ^{13}C nuclear magnetic resonance, IR spectroscopy, swelling degree and thermal analysis. The reaction yield with CG increases with increasing of epichlorohydrin/gum molar ratio (E/G) up to 0.17 (CGgel3 sample) and then decreases. The swelling degree of CGgels decreases with increasing E/G ratio due to the increase of crosslinking density. Carboxymethylation of cashew gum crosslinked gel (CGgel3), denoted as CMCGgel3, increases the swelling degree by 23%. The thermal degradation of cashew gum, carboxymethylated cashew gum and crosslinked derivatives (CMCGgel3 and CGgel3) were evaluated by thermogravimetry and infrared spectroscopy. Activation energies follow the order: CGgel3 > CMCG > CMCGgel3 > CG, and stay in the range of 106–219 kJ mol^{-1}. Infrared analysis performed in residual products after heating at different temperature indicates that the mechanism of thermal degradation includes formation of carbonylic products, double bond and cyclic structures.

Keywords: Crosslinking; Cashew gum; *Anacardium occidentale*; Swelling; Thermal degradation

1. Introduction

Cashew tree gum, denoted also as cashew gum (CG), is an exudate from *Anacardium occidentale* trees. It is a branched acidic heteropolysaccharide of low viscosity, comparable in many aspects to arabic gum (de Paula & Rodrigues, 1995). The gum from Brazil is composed of β-D-galactose (72%), α-D-glucose (14%), arabinose (4.6%), rhamnose (3.2%) and glucuronic acid (4.7%) (de Paula, Heatley, & Budd, 1998). It has three types of galactan units within the core, linked by C-1 and C-3; C-1 and C-6 and C-1, C-3 and C-6. The glucose is present as a side chain, up to five units long (de Paula et al., 1998). Cashew tree culture is very important to some regions of countries like Brazil, India, Mozambique, Tanzania and Kenya. The average gum production per year could reach 120 kg/plant and makes the study of gum of potential industrial interest (de Paula & Rodrigues, 1995).

Many polysaccharides have been modified in order to improve their properties for application as matrix for controlled drug delivery (Enel & Mcclure, 2004), tissue reconstruction (Kim et al., 1999), pH and electrical sensitive hydrogels (Chen et al., 2004), matrix for lectin separations (Lima, Lima, de Salis, & Moreira, 2002) and also to remove heavy metal from effluents (Jeon & Höll, 2003).

Hydrogels can be formed by crosslinking. The covalent bonds between polymer chains permit the expansion of the matrix and the absorption of a large amount of water. Polysaccharides gels can be formed using epichlorohydrin as bifunctional molecules as was done with cashew gum to prepare bioaffinity ligand matrix for lectins (Lima et al., 2002).

The reaction of the polysaccharide with epichlorohydrin occurs, is started, with the formation of polysaccharide alcoxide by addition of NaOH. When epichlorohydrin is added to the system the epoxy ring is opened, resulting in

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a new macromolecular epoxy. In the last reaction stage, the macromolecular epoxy reacts with other polysaccharide alcoxyde forming a bridge between chains (Fig. 1A). Crosslinking drastically reduces segments mobility in the polymer and the formation of interchain linkages leads to the formation of a three-dimensional network (Crini, 2005).

Carboxymethylation is one of most used reaction for polysaccharide derivatization. The product obtained is usually a polyelectrolyte that can be applied in a wide variety of fields, e.g., in the chemical, food, pharmaceutical, and cosmetic industries. Other advantages of carboxymethylation reactions are the ease of processing, the low cost of the chemicals, and the non-toxicity of the products (Verraest, Peters, Kuzee, Batelaan, & Van Bekkum, 1995). Carboxymethylation of cashew gum has been recently studied in order to produce a new material (Silva et al., 2004).

Thermogravimetric analysis of some polysaccharides and derivatives has been reported and found to be a promising and sensitive technique for characterizing structural modifications of natural polymers, such as xanthan and Na-hyaluronate (Villetti et al., 2002), arabic and cashew gum (Mothe & Rao, 2000), guar gum (Patel, Patel, & Patel, 1988; Varma, Kokane, Pathak, & Pradhan, 1997), sesbania gum (Wang et al., 1997), cellulose (Li, Huang, & Bai, 1999; Varma & Chavan, 1995), starch (Bori, Kimura, Minami, & Yamada, 1998; Kapusniak, Ciesielski, Koziol, & Tomasik, 2001), chitosan (Penich-Covas, Argüelles-Monal, & Román, 1993; Qu, Wirsen, & Albertsson, 2000) chitosan/cashew gum polyelectrolyte complex (Maciel, Silva, Paula, & de Paula, 2005) and a galactoxyloglucan from *Hymenaea courbaril* seeds (Freitas, Martin, Paula, Feitosa, & Sierakowski, 2004). The technique has been also considered important to elucidate the effect of the crosslinker on the thermal stability of the modified polysaccharide (Glico-Kabir, Penhasi, & Rubinstein, 1999).

The present work reports on the synthesis and characterization of gels from cashew gum using epichlorohydrin (E) as crosslinking agent. Products are expected to behave as new hydrogel matrices.

2. Experimental

2.1. Origin and purification

Crude samples from cashew gum were collected from native trees at Fortaleza, Ceará, Brazil. They were purified as a sodium salt using the method previously described (de Paula, Santana, & Rodrigues, 2001). Nodules free of bark were selected and dissolved in distilled water at room temperature to give a 5% (w/v) solution. The solution pH was adjusted to approximately 7.0 by addition of diluted aqueous NaOH. The clear solution was successively filtered through sintered glass and the polysaccharide precipitated with ethanol.

2.2. Crosslinking reaction

Crosslinking of cashew gum was obtained by the method described by Appukuttan (Appukuttan, Surolia, & Bachhawat, 1977). The gum (1.00 g) was mixed with 1.2 ml of 5 M NaOH and distilled water (2.4–0.70 ml) until

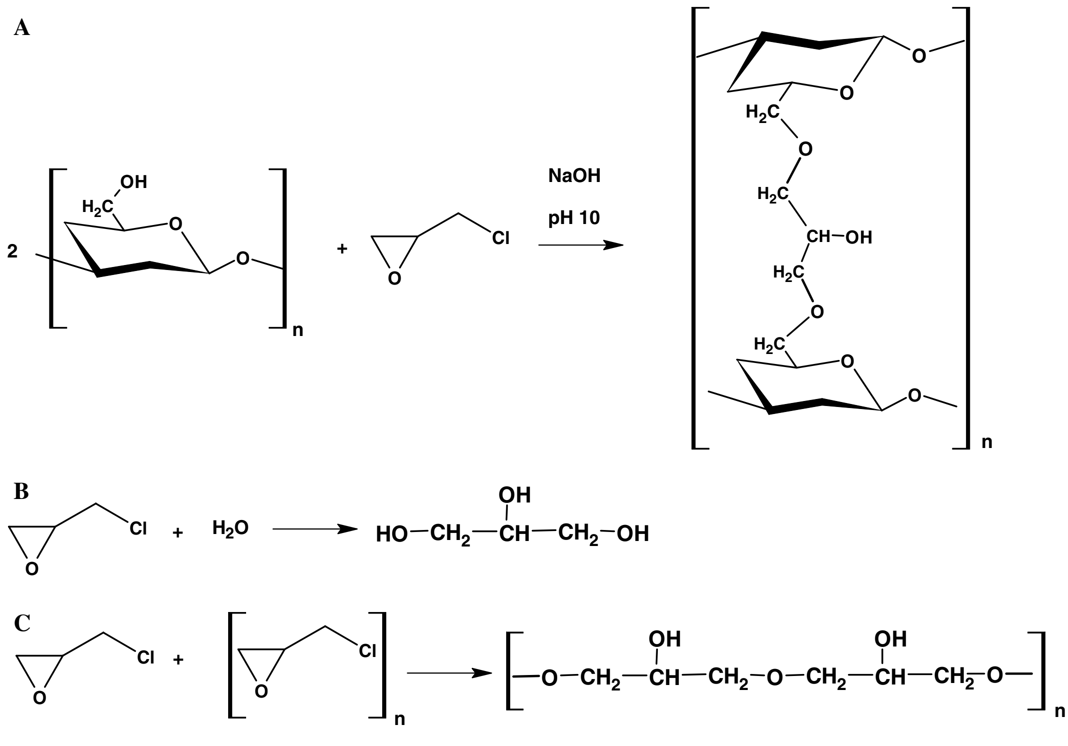

Fig. 1. Structure of cashew gum crosslinked with epichlorohydrin.

Table 1
Cashew gum crosslinking reaction conditions, swelling and yield data

Products	Reactional conditions				Yield (%)	Swelling degree ($g\ H_2O/g$ dry gel)
	Volume of 5 M NaOH (ml)	Volume of E[a] (ml)	Volume of water (ml)	E/G[b] molar ratio		
CGgel1	1.2	0.40	0.70	0.09	33.5	11.1
CGgel2	1.2	0.50	0.60	0.11	60.0	9.8
CGgel3	1.2	0.72	0.28	0.17	97.2	7.3
CGgel4	1.2	0.86	0.24	0.20	81.7	5.1
CMCG3	1.2	0.72	0.28	0.17	97.0	9.0

Mass of cashew gum was maintained in 1.00 g.

[a] Epichlorohydrin.

[b] E/G = Epichlorohydrin/gum.

a homogeneous paste was formed. The epichlorohydrin (volume in the range of 0.4–0.86 ml) was then added to the mixture and kneaded for homogenisation. The mixture was heated at 40 °C for 24 h, followed by a second heating time of 15 h at 70 °C. The crosslinked gel was washed with distilled water and dialysed for 72 h against distilled water and freeze-dried. The conditions applied to each sample are reported in Table 1. The yield was calculated by

$$\text{Yield} = (m_{\text{gel}}/m_{\text{gum}}) \times 100, \tag{1}$$

where m_{gel} is the mass of freeze dried gel and m_{gum} is the initial mass of gum.

2.3. Carboxymethylation of cashew gum crosslinked gel

The carboxymethylated gel was prepared as described by Kim and Lim (1999). Crosslinked gum (CGgel3 sample, 5.00 g) was immersed in 15 ml ethanol and allowed to swollen. Ten molar of NaOH (2.5 ml) was then added and mixed thoroughly with the swelled gel. After homogenisation, 2.43 g monochloroacetic acid (MCA) was added and the mixture was heated for 3 h at 50 °C with magnetic stirring. After this time the product was washed with distilled water, dialysed for 72 h and freeze-dried. This sample was denoted as CMCGgel3.

2.4. Carboxymethylation of cashew gum

Cashew tree gum was carboxymethylated in aqueous alkaline medium using monochloroacetic acid (MCA) as the etherifying agent (Silva et al., 2004). In order to provide a better comparison with a carboxymethylated hydrogel, a polysaccharide with a low degree of carboxymethylation (DS) was prepared. The reaction condition was as described by Silva et al. (2004) to obtain the product coded CMCG 1 and is briefly described here. The purified cashew gum (5.00 g) was mixed with 5 ml water until a homogeneous paste was formed. Ten molar of NaOH solution (volume of 2.7 ml) was added and the mixture was kneaded for 10 min. After that, monochloroacetic acid (2.62 g) was mixed thoroughly with the paste. The mixture was heated at 55 °C, during 3 h. The system was neutralised with 1 M HCl and dialysed against distilled water until all remained reagents and added salt were eliminated (4–5 days). The solid carboxymethylated products were recovered by freeze-drying and denoted as CMCG.

2.5. ^{13}C solid-state nuclear magnetic resonance spectroscopy (^{13}C-CP/MAS NMR)

^{13}C solid-state nuclear magnetic resonance spectroscopy of samples was carried out using a 300 BRUKER instrument, operating at 75 MHz. The cross-polarization pulse sequence was used for all samples, which were spun at the magic angle at 4.5 kHz. A contact time of 1 ms and a pulse repetition time of 3 s were used. An average of 1100 scans were accumulated for each sample.

2.6. Infrared spectral analysis

The Fourier transform IR spectra (FT-IR) of the unheated and heated samples were recorded with a Shimadzu IR spectrophotometer (model 8300) between 400 and 4000 cm^{-1}. Samples were transformed to the acid form in order to improve the accuracy in the determination of degree of substitution. All other analyses were performed with salt form polysaccharides, as they were prepared. The samples were analysed as KBr pellets. To analyse decomposition products, small amount of samples (20–30 mg) were heated in an oven and ambient air, during 15 min at different constant temperatures (280, 320, 350, 450, 500 and 600 °C) and analysed by FT-IR.

2.7. Swelling degree

To measure the sample swelling degree, pre-weighed dry samples were immersed in distilled water until maximum swelling was reached. After excessive surface water had been removed with filter paper, the weights of swollen samples were measured. The swelling degree (Q) was determined by

$$Q = (W_s - W_d)/W_d, \tag{2}$$

where W_s and W_d represent the weight of swollen and dry samples. Experiments were run in triplicate.

2.8. Thermal analysis

Thermogravimetric analyses (TG) were carried out using a Shimadzu-TGA-50 thermobalance. All TG runs were performed with 10 ± 0.1 mg of finely powdered samples in a platinum crucible, under synthetic air, with gas flowing at 50 mL min^{-1}. Non-isothermal experiments were run at five heating rate of 5, 10, 15, 20 and 30 °C min^{-1}. In order to compare the effect of atmosphere on thermal stability, experiments were run in nitrogen atmosphere at a heating rate of 10 °C min^{-1}. Kinetic analysis of the TG data was carried out using a differential method (Kissinger) (Kissinger, 1957) and an integral method (Flynn–Wall–Osawa) (Flynn & Wall, 1966; Ozawa, 1965).

2.8.1. Kissinger differential method (Kissinger, 1957)

Analysis of the changes in thermogravimetric data, which are brought about by variation of heating rate, is the basis of the most powerful differential methods for the determination of kinetics parameters (Wang et al., 2004).

The Kissinger method has been used to determine the activation energy of solid state reactions, without the precise knowledge of the reaction mechanism, using the following equation:

$$\ln(\beta/T^2_{\max}) = \{\ln(AR/E_a) + \ln[n(1-\alpha_{\max})^{n-1}]\} - E_a/RT_{\max}, \quad (3)$$

where β is the heating rate in °C min^{-1}, $T_{\max}$ is the absolute temperature of maximum decomposition obtained by peak in DTG curve, A is the pre-exponential factor, n is the reaction order, $\alpha_{\max}$ is the maximum degree of conversion, E_a is the activation energy (J mol^{-1}), and R the universal gas constant (8.314 J mol^{-1} K^{-1}) (Wang et al., 2004). The activation energy can be calculated from the slope of the plot of $\ln(\beta/T^2_{\max})$ versus $1/T_{\max}$ and fitting to a straight line.

2.8.2. Flynn–Wall–Ozawa integral method (Flynn & Wall, 1966; Ozawa, 1965)

Flynn–Wall–Ozawa is one of the integral methods that can determine the E_a without the knowledge of reaction order. It is used to calculate the activation energy for a given degree of conversion, based on the following equation:

$$\log\beta = \log[AE_a/g(\alpha)R] - 2.315 - 0.457E_a/RT, \quad (4)$$

where β, E_a, R, have the known meanings. T is the absolute temperature, α is the degree of conversion and $g(\alpha)$ is the integral function of conversion (Wang et al., 2004). The activation energy in J mol^{-1} for different α values can be calculated from the plot of $\log\beta$ versus $1/T$.

3. Results and discussion

3.1. Swelling and yield of crosslinked cashew gum derivatives

Table 1 shows the product yield and swelling degree of cashew gum gels. For the crosslinked cashew gum (CG) the reaction yield increases with increasing E/G molar ratio up to 0.17 and then decreases. This decrease (for E/G = 0.20, CGgel4 sample) may be due to side chain reactions when excess of epichlorohydrin is present (Figs. 1B and C) which ultimately resulted in less of the gum molecule been crosslinked. The swelling degree decreases with increasing E/G ratio, for crosslinked cashew gum (Table 1). This can be explained by the increasing of crosslinking density which provokes the formation of rigid networks leading to less expanded structures and less water absorption. Carboxymethylated CGgel3 (CMCGgel3) has higher Q value (9.0 g H_2O/g gel) than CGgel3 (7.3 g H_2O/g gel). The increase of swelling degree for carboxymethylated gel (23% in relation to CGgel3) is likely to be due to insertion of hydrophilic groups ($-CH_2COO^-$) in CMCGgel3.

3.2. Spectroscopy characterisation

Fig. 2 shows the C-13 CP/MAS spectra for CG and crosslinked samples (CGgel3 and CMCGgel3). Peak assignments are based on literature data (de Paula et al., 1998). Although a fairly good resolution can be achieved for CG in solution that is not the case for solid samples. In powder CG spectrum (Fig. 2A) there is a broad overlapped region at 70.6 ppm which is assigned to C-2, C-4 and C-5 carbons of the pyranosic ring. The peaks at 62.3 and 81.0 ppm can be assigned to C-6 and C-3 of galactose in CG. Anomeric carbon resonance was observed at 104.0 ppm. A low intensity peak at 17.3 ppm is due to the CH_3 of rhamnose. The resonance due to C=O of glucuronic acid residues also present in CG was not detected in the solid ^{13}C-NMR. CGgel3 spectrum (Fig. 2C) was found to be similar to the CG spectrum. Carboxymethylation of CGgel3 was confirmed by the presence of signal at 178.8 ppm in CMCGgel3 spectrum (Fig. 2C) which was attributed to C=O resonance of $-H_2CCOONa$ group inserted in CGgel3.

Figs. 3(A–D) show the FT-IR spectra of cashew gum and its derivatives. The presence of band around 1730 cm^{-1} in Fig. 3A is characteristic of C=O stretching vibration of glucuronic acid present in the starting polysaccharide (CG). A decrease in peak resolution is observed after the CG crosslinking reaction (Fig. 3B). The carboxymethylation reaction led to insertion of new carboxylic groups per macromolecule. The observation of a substantial increase in the absorbance of C=O vibration was expected (Figs. 3C and D) for CMCG and CMCGgel3 samples.

Miyamoto, Tsuji, Nakamura, Tokita, and Komai (1996) suggested a method to quantify the carboxymethyl group for CM-Gellan based on IR spectra. The degree of substitution, denoted as relative DS (DS_{rel}), could be calculated, in the present case, by the following formula:

$$DS_{rel} = A_{1730}/A_{2920} - B, \quad (5)$$

where A_{1730} and A_{2920} are, respectively, the absorbance of C=O (1730 cm^{-1}) and C–H (2920 cm^{-1}) stretching vibrations of the carboxymethylated products. B is a numerical constant correspondent to A_{1730}/A_{2920} ratio of the starting

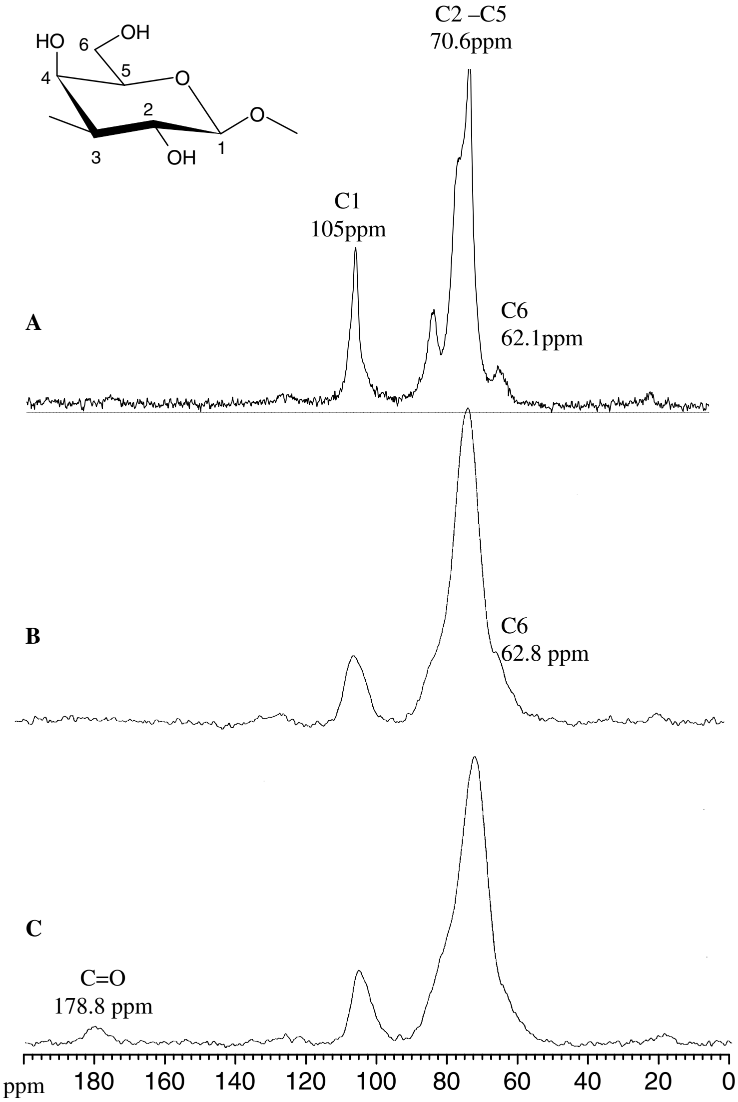

Fig. 2. ^{13}C solid-state nuclear magnetic resonance spectra: (A) cashew gum; (B) crosslinked cashew gum; sample CGgel3; (C) carboxymethylated crosslinked cashew gum (CMCGgel3).

cashew gum material. *B* value of 0.23 was determined from Fig. 3A.

Silva et al. (2004) found a linear correlation between DS_{abs} determined by potentiometric titration and DS_{rel} obtained by FT-IR ($DS_{abs} = 0.12\ DS_{rel}$) for low degree of substitution. The DS_{rel} and DS_{abs} values for carboxymethylated cashew gum gel (CMCGgel3) were 0.75 and 0.09, respectively. The calculated values for CMCG, based on Fig. 3C were 0.83 and 0.1, respectively, as determined by Silva et al. (2004).

3.3. *Thermogravimetric analysis*

Figs. 4 and 5 exhibit the thermogravimetric curves (TG and DTG) of cashew gum and its derivatives in N_2 and in air. The event in the region of 25–200 °C is due to water evaporation. When compared to crosslinked samples (CGgel3 and CMCGgel3), cashew gum and carboxymethylated gum samples have higher moisture contents. 12.9%, 14.6%, 11.0% and 9.0% of water was released from CG, CMCG, CGgel3 and CMCGgel3, respectively (Fig. 5).

Decomposition process in N_2 occurs in two stages for CG and CMCG and in one stage for CGgel3 and CMCgels (Fig. 4). Zohuriaan and Shokrolahi (2004) observed that nearly all seven gums studied, included arabic gum, exhibited a double stage decomposition pattern. The main decomposition of the studied polysaccharides starts above 200 °C (Zohuriaan & Shokrolahi, 2004).

Table 2 shows thermal stability data of cashew gum and its derivatives in N_2. The initial decomposition temperature (T_{initial}) is above 200 °C, as verified for some others polysaccharides (Zohuriaan & Shokrolahi, 2004). T_{initial} decreases after carboxymethylation. The decomposition of derivatives of some polysaccharides, such as guar gum (Varma et al., 1997) and galactoxyloglucan (Freitas et al., 2004) also starts in lower temperature than that of original polymer. Cashew gum gels (CGgel3 and CMCGgel3) initiate their decomposition in higher

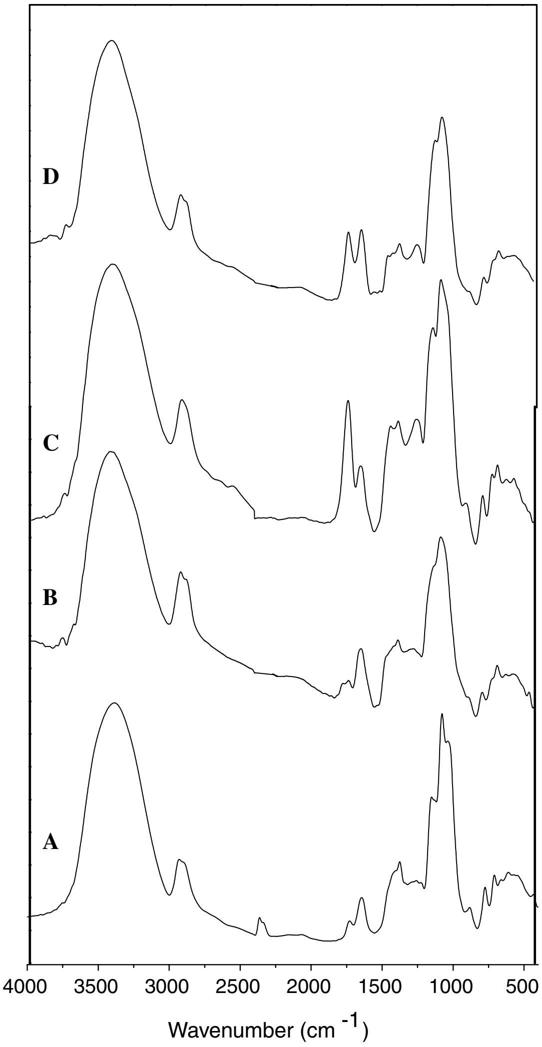

Fig. 3. FT-IR spectra of cashew gum and derivatives in acid form. (A) CG; (B) CGgel; (C) CMCG; (D) CMCgel.

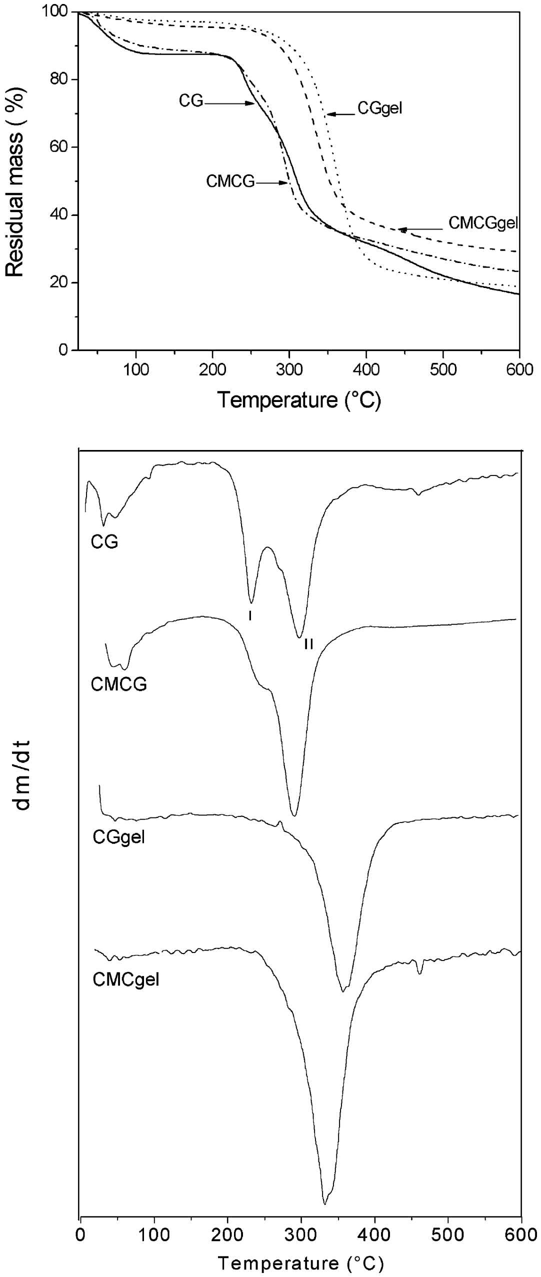

Fig. 4. Thermogravimetric curves (TG and DTG) for cashew gum and derivative in nitrogen at heating rate of 10 °C/min.

temperatures than the uncrosslinked ones (CG and CMCG).

Mothe and Rao (2000) investigated the effect of water on thermal decomposition behaviour of cashew gum. For dry cashew gum, TG curves in N_2 show only one decomposition step with $T_{\max}$ around 300 °C. This behaviour is different from the results observed in this work, with the two step decomposition pattern, not included water release event. However, the $T_{\max}$ of the second event (307 °C) is similar to that previously reported for cashew gum (Mothe & Rao, 2000). The maximum degradation temperature in the range of 270–320 °C has been determined for other polysaccharides: arabic gum (316 °C) (Zohuriaan & Shokrolahi, 2004), chitosan (300 °C) (Penich-Covas et al., 1993), guar gum (306 °C) (Varma et al., 1997), xanthan and sodium hyaluronate (298 and 276 °C) (Villetti et al., 2002). When compared to its carboxymethylated product, cashew gum has higher decomposition temperature of the main event (around 300 °C). Similar behaviour was reported for chitosan (Qu et al., 2000) and galactoxyloglucan (Freitas et al., 2004) derivatives.

The residual mass at 600 °C in nitrogen atmosphere (16.6–29.2%) is in the range verified for some polysaccharide (8.0–34.9%) (Zohuriaan & Shokrolahi, 2004). A larger residue was observed in gel decompositions when compared to their related starting materials. The increase in residual mass after derivatization was also noticed in thermal decomposition of galactoxyloglucan (Freitas et al., 2004).

In a synthetic air atmosphere the initial decomposition temperatures for CMCG, CGgel3 and CMCGgel3 were lower than those observed in N_2 atmosphere (Table 3).

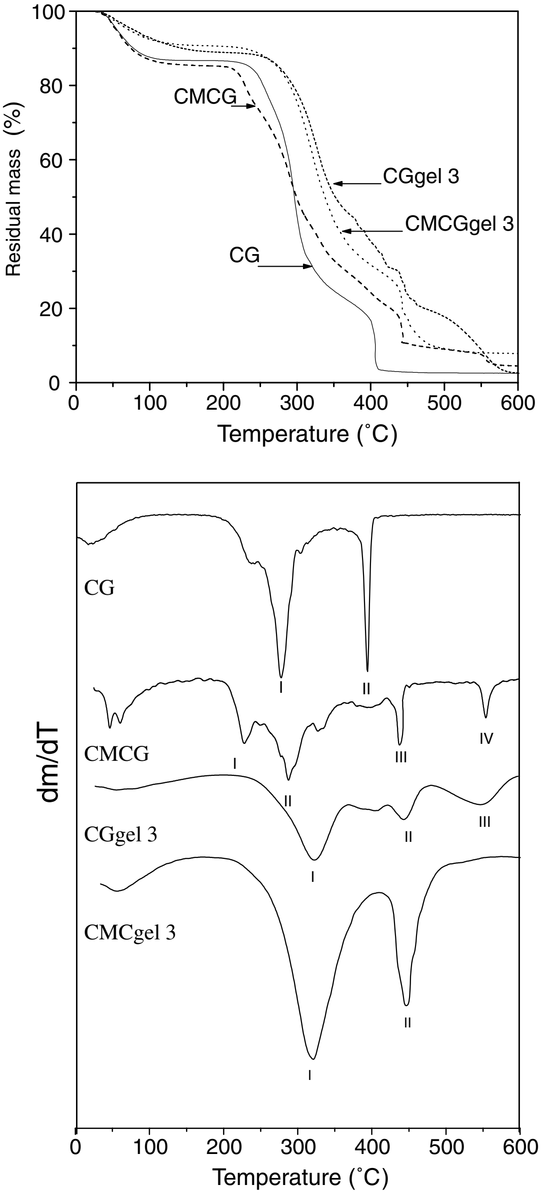

Fig. 5. Thermogravimetric curves (TG and DTG) for cashew gum and derivative in air at heating rate of 10 °C/min.

Table 2
Thermal analysis data of cashew gum and its derivatives in N_2 atmosphere

Data	CG	CMCG	CGgel3	CMCGgel3
$T_{initial}$[a] (°C)	235	225	309	286
T_{final}[b] (°C)	>600	>600	>600	>600
T_{max} (°C) in the range				
200–260	241	245 (sh)	–	–
260–400	307	296	361	338
Residual mass at 600 °C (%)	16.6	23.3	19.1	29.2

sh, shoulder.

[a] Initial decomposition temperature (TGA curve onset).

[b] Final decomposition temperature not detected.

Table 3
Thermal analysis data of cashew gum and its derivatives in air

Data	CG	CMCG	CGgel3	CMCGgel3
$T_{initial}$[a] (°C)	238	216	271	262
T_{final}[b] (°C)	415	445	475	576
T_{max} (°C) in the range				
220–260	243 (sh)	229 (I)	–	–
260–350	295 (I)	290 (II)	325 (I)	319 (I)
400–450	406 (II)	440 (III)	446 (II)	443 (II)
450–600	–	555 (IV)	550 (III)	
Residual mass at 600 °C (%)	2.2	4.5	2.6	7.8

sh, shoulder.

[a] Initial decomposition temperature (TGA curve onset).

[b] Final decomposition temperature.

No difference was observed for cashew gum. CG starts the oxidative decomposition in the same range of dextran (244 °C) (Bumbu, Vasile, Chitanu, & Carpov, 2001), guar gum (235 °C) (Patel et al., 1988) and chitosan (230 °C) (Penich-Covas et al., 1993). A shift of $T_{initial}$ to lower values for derivatives was reported for guar gum (Patel et al., 1988; Wang et al., 1997) and chitosan ((Penich-Covas et al., 1993), as was observed for CMCG. The crosslinked samples start the oxidative decomposition in higher temperature than non crosslinked ones, as verified in nitrogen atmosphere. The opposite behaviour was reported to guar gum crosslinked with glutaraldehyde (Glico-Kabir et al., 1999).

The decomposition pattern becomes more complex in oxidative atmosphere, as was observed for many other organic substances, e.g., guar gum (Varma et al., 1997). The major weight losses occur around 300 °C for all samples, as reported for guar gum and derivatives with low degree of oxidation (Varma et al., 1997). For CG, CMCG, CGgel3 and CMCGgel3 these weight losses were 52.2%, 30.7%, 33.7% and 60.2%, respectively. The final degradation temperature under air atmosphere is in the region of 400–600 °C, while under nitrogen it is higher than 600 °C. As a consequence, almost all polysaccharide have been found to degrade in air at 600 °C, with residual mass of 2.2–7.8%, much lower than the average residue obtained under nitrogen, 22%. The final mass of CG (2.2%) is in the usual range (1–6%) (Patel et al., 1988; Varma et al., 1997). Higher residues in carboxymethylated samples (4.5 and 7.8, for CMCG and CMCGgel3, respectively) could be due to higher Na content of carboxylated polysaccharide which was increased by the carboxymethylation. An increase in residue has also been observed after derivatization of guar gum (Patel et al., 1988; Varma et al., 1997). Gels of guar gum showed less weight loss at 600 °C than native gum (Glico-Kabir et al., 1999), a behaviour that was also verified for cashew gum gels.

Activation energy (E_a) in synthetic air was investigated using Kissinger and Flynn–Wall–Ozawa methods. Fig. 6 shows the Kissinger plots of $\ln(\beta/T_{max}^2)$ versus $1/T_{max}$ related to the main event (around 300 °C) for CG and its derivatives. In Table 4, the calculated values for all samples were summarised. The Flynn–Wall–Ozawa plots for the CG sample were depicted in Fig. 7. Similar mathematical procedures were used for the CG derivatives. The activation

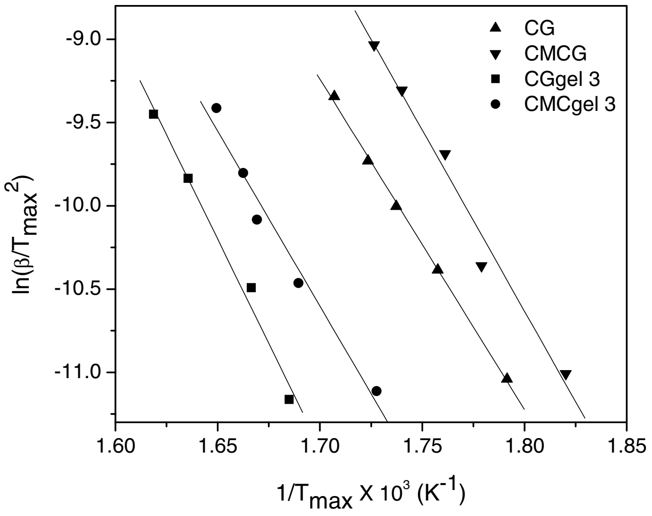

Fig. 6. Kissinger method applied to cashew gum and derivatives related to main event in cashew gum and derivative.

Table 4
The activation energy for the thermal degradation of cashew gum and its derivatives by Kissinger method

Samples	Event	Activation energy (kJ mol^{-1})	*R*
CG	I	165	0.999
CMCG	II	181	0.999
CGgel	I	208	0.993
CMCGgel	I	175	0.987

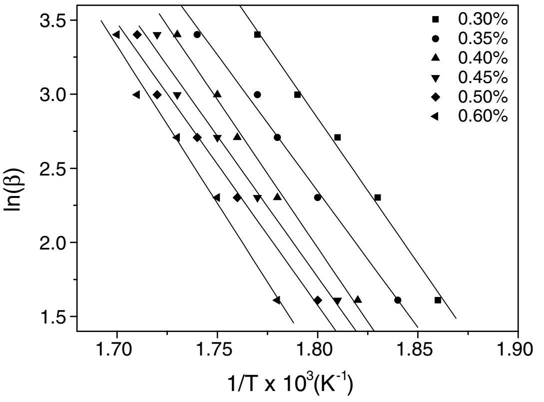

Fig. 7. Flynn-Wall–Ozawa method applied to cashew gum and derivative at different degree of conversion.

energy at a given degree of conversion can be calculated by the curve slop from Fig. 7 and from data not shown. The obtained results are exhibited in Fig. 8. The linear correlation coefficient for all determination was between 0.991 and 0.998. It is observed that the activation energy increases with increasing of the conversion degree, probably related to the changes in the mechanism of degradation and the occurrence of more than one stage of degradation in the system (Kanis et al., 2000).

From Table 5, it is found that the activation energy (E_a) obtained using Kissinger method is an intermediate value

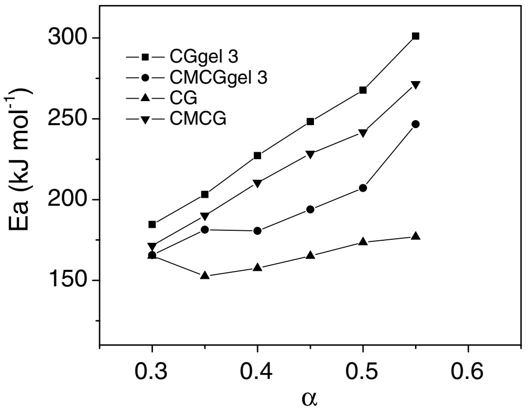

Fig. 8. Plots of activation energy vs. degree of conversion for cashew gum and derivatives obtained by Flynn-Wall–Ozawa method.

Table 5
Comparison of activation energy obtained by Kissinger and Flynn-Wall–Ozawa methods

Samples	Activation energy (kJ mol^{-1})		
	Kissinger[a]	Flynn-Wall–Ozawa in α	
		0.3	0.4
CG	165	166	158
CMCG	181	166	205
CGgel3	208	185	228
CMCGgel3	175	171	181

[a] Event with higher weight loss.

between E_a values obtained by Flynn–Wall–Ozawa at the same temperature range ($\alpha = 0.3$ and 0.4). The activation energies for cashew gum and derivatives are in good agreement with those values (106–219 kJ mol^{-1}) determined for polysaccharides and derivatives shown in Table 6.

Based on E_a values, the thermal stability of cashew gum and derivatives follows the order:

CGgel3 > CMCG > CMCGgel3 > CG.

This order is different from that obtained using the initial decomposition temperature (CGgel3 > CMCGgel3 ≫ CG > CMCG). The difference in thermal stability based on T_{initial}, E_a or IPDT was also investigated for many polysaccharides (Patel et al., 1988; Zohuriaan & Shokrolahi, 2004). CGgel3 is the most stable material, independent of parameter employed in the calculation. CMCG has the lowest initial decomposition temperature, but decomposes slowly as soon this temperature is reached. Carboxymethylation of hydroxypropyl Sesbania gum (Wang et al., 1997) and potato starch (Bori et al., 1998) also improved thermal stability of related polysaccharide, as was verified in the present work, if Ea order was used as tool for assignment of stability. Crosslinked guar gum was recognised to be more thermally stable than the corresponding native material (Glico-Kabir et al., 1999).

Figs. 9(A and B) show FT-IR spectra for the residual products corresponding to the degradation reaction of CG and CMCGgel3 heated in air at different temperatures

Table 6
Activation energy for thermal degradation of polysaccharide and derivatives under air related to main event

Polysaccharide	Temperature range (°C)	E_a (kJ mol^{-1})	Method	Ref.
Chitosan	230–310	160	Broido	Penich-Covas et al. (1993)
HMPchitosan[a]	210–250	106	Broido	Penich-Covas et al. (1993)
Guar gum	Not specified	219	Not specified	Patel et al. (1988)
Dextran	244–387	200	Coats–Redfern	Bumbu et al. (2001)
Dextran	244–387	180	Swaminathan–Madhavan	Bumbu et al. (2001)
Ethyl cellulose	Not specified	123	Not specified	Li et al. (1999)
Methyl cellulose	Not specified	144	Not specified	Li et al. (1999)

[a] *N*-(2-Hydroxy-3-mercaptopropyl)-chitosan.

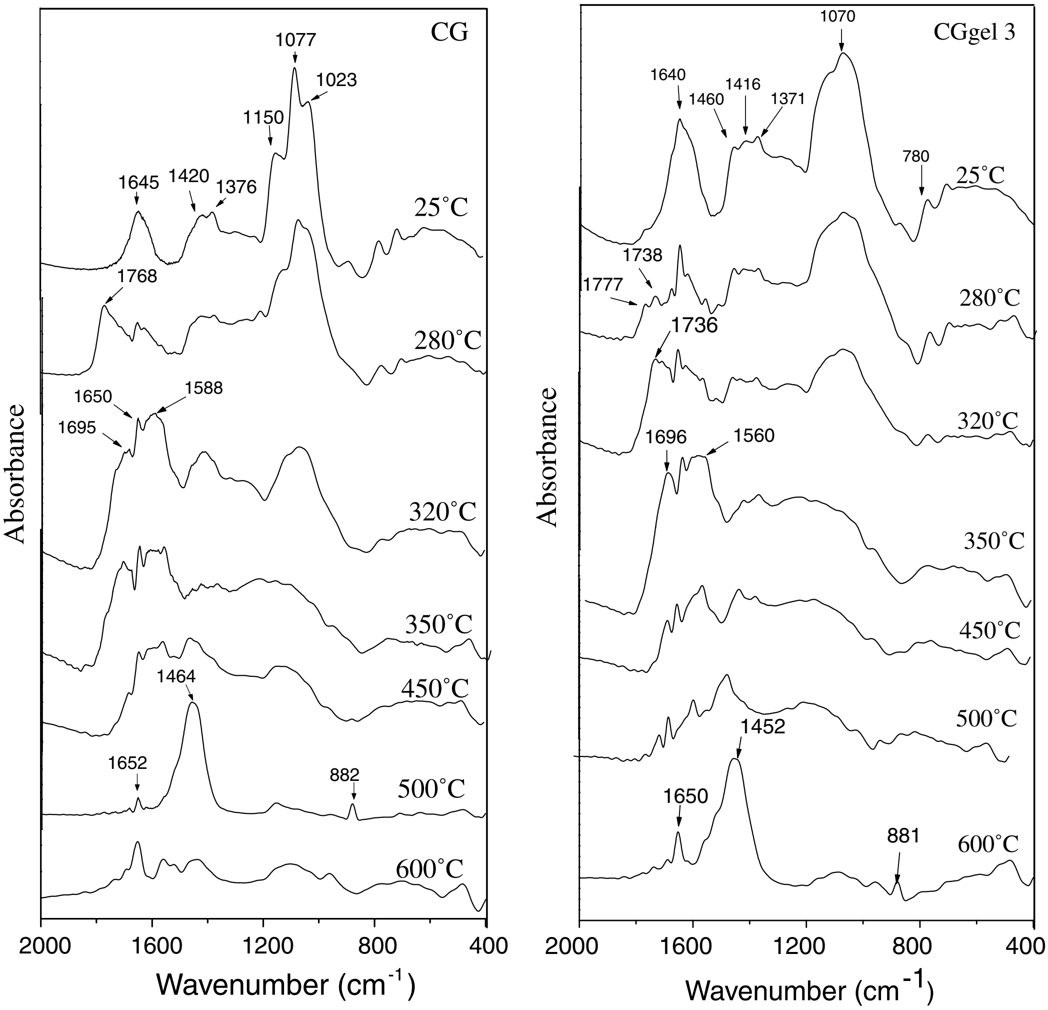

Fig. 9. FT-IR spectra of CG and CGgel during thermal degradation at different temperatures.

during 15 min. The spectra of unheated samples are very similar, but with less definition to that related to CMCG-gel3. The absence of band at 1730 cm^{-1}, observed in Fig. 3, confirms that now the samples are in Na-carboxylate form, and not in acid form. At 25 °C, the main bands are assigned to C=O from COO$^-$ at 1640–1645 cm^{-1}, C—O—C group at 1150 cm^{-1} (O-bridge), the C—O (exocyclic) and C—C groups at 1070–1077 cm^{-1}, and C–OH groups at 1023 cm^{-1} (Villetti et al., 2002). The bands at 1420 cm^{-1} are assigned to —CH symmetric bending and C—O stretching from carboxylate, and that at 1371 cm^{-1} to —CH$_2$ bending (Qu et al., 2000).

In the spectra of samples heated at 280 °C, the intensity of bands corresponding to OH stretching (3450 cm^{-1}) and the exocyclic groups (1150, 1077 and 1023 cm^{-1}) decreases, as a consequence of the glycosidic bond cleavage in the backbone and the release of water. New bands in the region of 1700–1777 cm^{-1} appear, corresponding to C—O stretching vibration of carbonylic products of different nature. The changes in CG heated at 280 °C are more significant than in CGgel3, corroborating with the higher thermal stability of this gel found by thermogravimetric trials. Bands at 1695–1696 cm^{-1} and 1560–1588 cm^{-1}, well characterised in CG spectra at 320 °C, could be attributed to unsaturation of residual products, as verified for chitosan decomposition at 270–280 °C (Qu et al., 2000). CGgel3 needs a higher temperature (350 °C) to reach the same spectral pattern in this region. At 350 °C, the glycosidic bond in CG and CGgel3 backbone totally disappears. A sharp decrease in the intensity of band attributed to CH group stretching (2860–2872, and 2920–2937 cm^{-1}) could also be observed, an indication that the strong links are mainly broken at this or a higher temperature. At 500 °C, the CG spectrum shows bands at 1452–1464 and 882 cm^{-1}, which are associated with the formation of cyclic structures, as was reported for Na-hyaluronate and xanthan (Villetti et al., 2002). In CGgel3 heating, the same bands appear only at 600 °C, indicating once more the higher stability of the gel. New bands at 1650–1652 cm^{-1} in the final decomposition stage could indicate the formation of unsaturated structures, as observed for methyl cellulose at 500 °C (Villetti et al., 2002). At 280, 350, 500 and 600 °C, the behaviour of CMCG and CG are very similar. At 320 °C, CMCG seems to be less decomposed. At 450 °C, occurs the opposite. The FT-IR spectra of CMCGgel3 after heating show the same pattern of CGgel3, but with a more intense decomposition degree.

4. Conclusions

The yield of crosslinking cashew gum gel reaction increases with increasing crosslinking agent/gum (E/G) molar ratio up to 0.17 and then decreases. The swelling degree decreases with increasing E/G ratio due to the augmentation of crosslinking density. Carboxymethylation of cashew gum crosslinked gel increases the swelling degree by 23%. Crosslinked cashew gum samples start oxidative decomposition at higher temperature than non crosslinked ones. The main thermal degradation event of native polysaccharide and derivatives are observed around 300 °C. Decomposition patterns of gels were found to be more complex. The activation energy obtained using Kissinger method is an intermediate value between E_a values determined by the use of Flynn–Wall–Ozawa at the same temperature range ($\alpha = 0.3$ and 0.4). Values in the range of 106–219 kJ mol^{-1} were obtained. Based on E_a values, the thermal stability of cashew gum and derivatives follows the order: CGgel3 > CMCG > CMCGgel3 > CG.

The cleavage of the glycosidic bond in the backbone and the formation of carbonylic products of different nature occur at 280 °C. At 320 and 350 °C unsaturated products formation are seen for CG and CGgel3, respectively. At 350 °C, the glycosidic bond totally disappears in all samples. Stronger linkages are mainly broken at this or at higher temperature. Cyclic structures are formed at 500 °C, for CG and at 600 °C, for CGgel3. The behaviour of CMCG and CG are very similar. The FT-IR spectra of CMCGgel3 after heating show the same pattern of CGgel3, but with a more intense degree of decomposition.

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