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Graft copolymerisation of acrylamide onto cashew gum

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Abstract

The synthesis of cashew gum-*g*-polyacrylamide was carried out at 60 °C by a radical polymerisation using potassium persulphate as the redox initiator under N_2 atmosphere. A series of graft copolymers, varying in acrylamide concentration and keeping the concentration of the initiator and polysaccharide constant, was prepared. These graft copolymers were characterised by elemental analysis, infrared and ^{13}C NMR spectroscopy, rheological studies, differential scanning calorimetry and thermogravimetric analysis. Comparisons amongst grafting parameters of the reaction of various natural polysaccharides with polyacrylamide (PAM) were carried out. High percentages of acrylamide conversion (%*C*) and grafting efficiency (%*E*) were obtained for cashew gum (CG), even with a low acrylamide/gum ratio. All copolymers had intrinsic viscosity and thus the hydrodynamic volume much higher than the CG value and closer to the PAM. The CG-*g*-PAM solution had an absolute viscosity at 2.5% concentration (wt./vol.) up to 33 and 3.3 times the CG and PAM values, respectively. Grafting of PAM chains onto the polysaccharide enhances its thermal stability.

Keywords: Graft copolymer; Acrylamide; *Anacardium occidentale* gum; Polysaccharide

1. Introduction

Natural polymers, mainly polysaccharides, are biodegradable, cheap, fairly shear stable and easily available from renewable agricultural resources. The biodegradability reduces their shelf-life and needs to be controlled. High molecular weight synthetic polymers, such as polyacrylamides (PAM), can be tailor made by controlling molecular weight and molecular weight distribution, and also other structural characteristics. However, they are less susceptible towards biodegradation and are unstable in shear fields and thus, lose some of their properties, such as flocculating effectiveness [1]. Many efforts have been made to combine the best properties of both by grafting polyacrylamide onto the backbone of polysaccharides. Natural polysaccharides like guar gum [2], xanthan gum [3–5], acacia gum [6], *Cassia tora* gum [7,8], *Tamarindus indica* mucilage [8] and Kundoor mucilage [9] have been grafted onto polyacrylamide in the past few years. Grafts of carboxymethyl cellulose [11], sodium alginate [12], amylopectin [13], amylose [14], starch [15,16], carboxymethyl starch [17], chitosan [18,19], and carrageenan [20] onto the same synthetic polymer have also been reported.

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These grafts have been synthesised in order to improve flocculation efficiency [4,8,10,12–14,19], decolorize textile dyes [21,22], increase the solution viscosity [23], enhance the drag reduction effectiveness and shear stability, impart resistance to biological degradation [24], prepare controlled drug delivery systems [5,6], and obtain superabsorbents [25–27].

Cashew gum (CG) is a polysaccharide extracted from a low cost source, the *Anacardium occidentale* tree, which is widely distributed all over the Brazilian Northeast. It is reported to contain galactose (72–73%), glucose (11–14%), arabinose (4.6–5%), rhamnose (3.2–4%) and glucuronic acid (4.7–6.3%) in wt.% [28,29]. CG is mainly composed of 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 [28].

In this study, the synthesis of graft copolymers of acrylamide onto cashew gum is reported. The materials prepared were characterised by FTIR, NMR, DSC, TGA, and rheological measurements. The authors intend to use the graft copolymer to prepare superabsorbent hydrogel with improved cost and biodegradability.

2. Experimental

2.1. Materials

Crude cashew gum samples (CG) were collected from early dwarf trees at Fortaleza, Ceará, Brazil, by the National Centre of Tropical Agribusiness Research – CNPAT-EMBRAPA in November, 2004. They were purified as a sodium salt using a previously described method [29]. Acrylamide and potassium persulphate (KPS) were supplied by Merck Corporation and were used without purification.

2.2. Graft copolymerisation

The graft copolymers of cashew gum and acrylamide were synthesised based on the work of Singh et al. [2] and Toti et al. [6] with some modifications, which are briefly described here. Grafts were obtained under a continuous flow of nitrogen gas using $K_2S_2O_8$ (KPS) as the initiator. An amount of 1.0 g of polysaccharide was dissolved in 30 ml of distilled water under N_2 and 0.1 g of KPS was added. The mixture was heated at 60 °C and stirred for 20 min. The monomer was then added and the system was continuously stirred for 3 h. Acetone was used as a non solvent to precipitate the polymeric material, which was washed with 30 vol.% aqueous methanol to remove the homopolymer of acrylamide. The product was dried at 40 °C. The amount of monomer varied from 0.3 to 1.5 g and the gum was kept constant at 1.0 g.

The polymerisation of homopolymer (PAM) was carried out using the same conditions of the graft reaction and the concentration of monomer 0.14 M but without the addition of the gum.

The percentage of grafting (%*G*), grafting efficiency (%*E*) and percentage of conversion of acrylamide (%*C*) were calculated according to Toti and Aminabhavi [30]:

$$\%G = \frac{\text{mass of acrylamide in the graft polymer}}{\text{mass of original gum}} \times 100 \quad (1)$$

$$\%E = \frac{\text{mass of graft polymer}}{\text{mass of (polymer + acrylamide)}} \times 100 \quad (2)$$

$$\%C = \frac{\text{mass of acrylamide in the graft polymer}}{\text{mass of acrylamide taken}} \times 100 \quad (3)$$

where the mass of acrylamide in the graft was calculated as mass of graft minus the mass of gum taken.

2.3. Characterisation of graft cashew gum

2.3.1. Elemental analysis

The elemental analysis of the graft copolymers was performed using a Perkin Elmer CHN 2400 microanalyser to determine the carbon, hydrogen and nitrogen content.

2.3.2. Infrared spectral analysis

The IR spectra of gum, PAM and the graft copolymers were recorded in solid state using KBr pellets with a Shimadzu IR spectrophotometer (model 8300) between 400 and 4000 cm^{-1}.

2.3.3. NMR

^{13}C NMR and ^1H spectra of 6% (wt./vol.) solutions in D_2O of CG, PAM and CG-*g*-PAM 2 were recorded using a Bruker Model Avance DRX500 spectrometer.

2.3.4. Intrinsic and absolute viscosity

Viscosity measurements of all the grafted polysaccharide solutions were carried out with the use of an Ubbelohde viscometer with a capillary diameter of 0.5 mm. Flow time was measured at five different concentrations in the range of 0.5–1.0 g/dl, at least in triplicate. The intrinsic viscosity was calculated by plotting specific viscosity/concentration (η_{sp}/c) *versus* concentration and then taking the intercept at $c = 0$ of the fitted straight line. The viscosities were measured in a 0.1 M NaCl solution at 25.0 ± 0.1 °C.

The measurements of absolute viscosity of CG and graft aqueous solution at 2.5% concentration (wt./vol.) were performed using a Brookfield cone-plate rheometer, model LV-DVIII, at 25 °C. The effect of shear rate on the viscosity of sample solutions was evaluated.

2.3.5. Thermal analysis

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were carried out under N_2 flow (50 ml/min) using Shimadzu TGA-50 and DSC-50 instruments at a heating rate of 10 °C/min and sample mass of 10 and 5 mg, respectively. The recorded DSC curve is a second heating. The first curve was taken up to 110 °C, and this temperature being kept for 20 min followed by cooling up to ambient temperature.

3. Results and discussion

3.1. Grafting reaction

Graft copolymers based on cashew gum were synthesised by grafting acrylamide onto polysaccharide molecules by a radical polymerisation using KPS as the initiator. A series of graft copolymers, varying the acrylamide concentration and maintaining constant the concentration of the initiator and the polysaccharide, were synthesised. The grafting parameters are given in Table 1.

With the increase in the monomer concentration the %*G* increased continuously, as expected. This behaviour may be explained by the fact that an increase in monomer concentration leads to the accumulation of monomer molecules in close proximity to the polysaccharide backbone and a greater availability of grafting sites for the monomer [3].

There is no clear tendency of %*C* and %*E* values to change with acrylamide/cashew gum ratio. These percentages have been reported to increase with AM/P ratio in guar gum copolymerisation [30], but decrease in xanthan gum [3]. In acacia gum-*g*-PAM, %*C* decreased with AM/P, but %*E* increased. Even so, the acrylamide conversion reached a

Table 1
Comparison amongst grafting parameters of reaction between polysaccharides and acrylamides

Polysaccharide	Reaction condition				%*G*	%*E*	%*C*	Reference
	AM/P	Initiator	*T* (°C)	Time				
Cashew gum	0.3	KPS	60	3 h	25.2	84.0	96.2	This study
	0.5	KPS	60	3 h	39.9	79.8	93.3	This study
	1.0	KPS	60	3 h	67.6	67.6	83.8	This study
	1.5	KPS	60	3 h	144.4	96.3	97.8	This study
Guar gum	2.84	Microwave	63	20 s	120	57.3	42.1	[2]
	2.84	KPS/Ascorbic ac./$AgNO_3$	60	80 min	140	62.5	49.1	[2]
	2.84	Microwave/ KPS/Ascorbic ac./$AgNO_3$	60	13 s	190	75.5	66.7	[2]
	2.0	CAN	70	5 h	160	61.5	82	[30]
	3.5	CAN	70	5 h	304	75.3	87	[30]
	5.0	CAN	70	5 h	480	82.7	96	[30]
	5.0	CAN	30	24 h	350	58.3	50	[24]
Xanthan gum	1.1	BrO_3^-/Fe^{2+}	35	2 h	50.2	70.4	46	[3]
	2.2	BrO_3^-/Fe^{2+}	35	2 h	81.5	57.0	37	[3]
Acacia gum	1.0	APS	70	2 h	94.5	47.2	94.5	[6]
	3.0	APS	70	2 h	278	73.6	92.8	[6]
	5.0	APS	70	2 h	459	73.5	91.8	[6]
Cassia tora gum	1.2	CAN/HNO_3	30	5 h	111	58	25	[7]
Sodium alginate	3.4	CAN	27	24 h	785	94.1	92.4	[31]
Chitosan	2.84	Microwave	–	70 s	269	96.1	94.7	[18]
	2.84	KPS/Ascorbic ac.	35	1 h	82	47.4	28.8	[18]

AM/P = mass ratio of acrylamide and polysaccharide; KPS = potassium persulphate, APS = ammonium persulphate; CAN = ceric ammonium nitrate.

promising value, in the range of 83.8– 97.8%, higher than most %*C* values shown in Table 1, varying between 25% and 96%. The %*E* for CG-*g*-PAM ranges from 67.6 to 96.3, also higher than values reported for other grafts with polysaccharides (47.2–96.1%).

Based on Table 1 it is not possible to ascribe a general trend of grafting efficiency (%*E*) or percentage of acrylamide conversion (%*C*) to an increase in AM/P ratio, particularly for low ratios. Other reaction parameters, such as temperature and time are more important conditions in terms of obtaining a high %*C* and %*E*.

3.2. Elemental analysis

The most significant data in Table 2 is the percentage of nitrogen. Cashew gum polysaccharide does not contain nitrogenated groups in its structure. The reduced amount observed was due to trace quantities of proteins, sometimes aggregated to the polysaccharide [28]. The %*N* observed for PAM was lower than expected. This could be due to hydrolysis of polyacrylamide, which changes some of the –CONH$_2$ groups into –COO$^-$ groups. The %*N* in grafts is considerable and increases with AM/P ratio. This tendency corroborates the results of increasing grafting efficiency with concentration of acrylamide (Table 1). The difference between experimental values and those calculated using the data shown in Table 1 is around 8%. The content of PAM in grafts was calculated based on %*N* and taking into account the moisture content of gum and copolymers. CG-*g*-PAM 1, 2, 3 and 4 contain 21%, 33%, 47% and 56% of PAM, respectively.

3.3. Infrared spectral analysis

The IR spectra of the CG, PAM and graft copolymers are shown in Fig. 1. The gum had a broad peak at 3379 cm^{-1} due to stretching vibrations of O–H, a small peak at 2933 cm^{-1}, attributed to C–H stretching vibrations, and absorption at 1649 cm^{-1} due to O–H scissor vibrations from bonded water molecules [32]. Strong peaks at 1150, 1080 and 1030 cm^{-1} are due to stretching vibrations of C–O–C from glucosidic bonds and O–H bending from alcohols. In the PAM spectrum the strong absorption at 3435 cm^{-1} and the shoulder at around 3200 cm^{-1} are attributed to the N–H stretching vibrations of the primary amide. The two bands at 1683 and 1653 cm^{-1} are due to amide-I ($\nu_{C=O}$) and amide-II (δ_{NH}), respectively. The existence of shoulders at 1562 and 1414 cm^{-1} may be attributed to asymmetrical and symmetrical –COO$^-$ vibrations and is indicative of polyacrylamide hydrolysis [33], as suggested by the elemental analysis.

Table 2
Elemental analysis of CG, PAM and graft copolymers

Sample	Experimental			Calculated
	C (%)	H (%)	N (%)	N (%)
CG	37.47	6.32	0.12	–
CG-*g*-PAM 1	41.68	6.69	4.15	4.78
CG-*g*-PAM 2	40.25	6.83	6.41	6.00
CG-*g*-PAM 3	41.08	6.67	9.31	8.60
CG-*g*-PAM 4	43.10	6.79	11.1	11.9
PAM	42.40	7.22	16.3	19.7

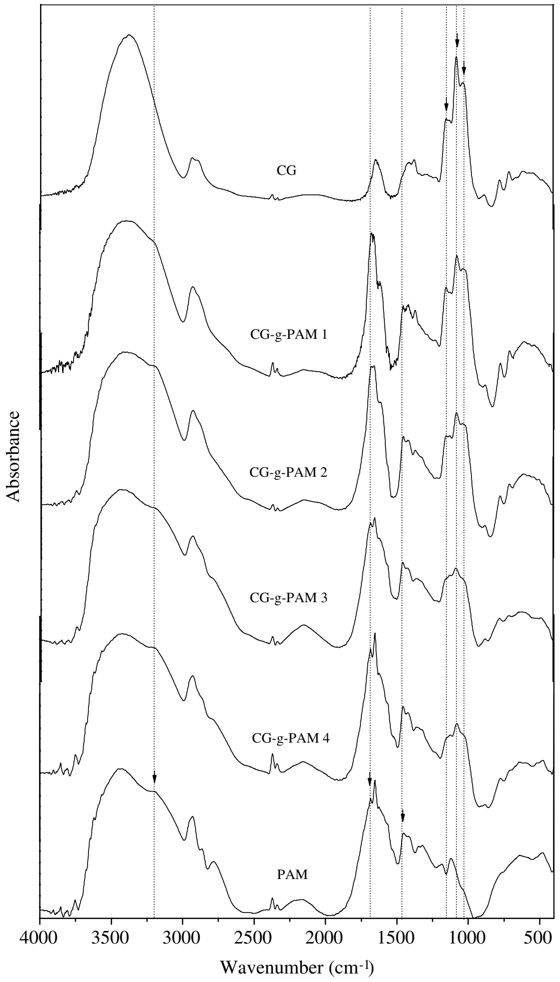

Fig. 1. Infrared spectra of cashew gum, PAM, and graft copolymers of PAM onto cashew gum.

Some differences were observed in the spectra of the graft products compared with cashew gum (Fig. 1). The appearance of a shoulder at 3200–3224 cm^{-1}, and a sharp peak at 1673–1684 cm^{-1} is attributed to NH and C=O stretching of PAM, respectively. A new peak at 1454–1458 cm^{-1} is due to CN bending vibrations.

The effect of the acrylamide/gum ratio can also be seen in Fig. 1. With an increase in the amount of acrylamide (from CG-*g*-PAM 1 to 4) a decrease in the absorbance of bands at around 1080, 1030 and 1150 cm^{-1} is observed, characteristics of the polysaccharide. The intensification of absorbance at 1673–1684 cm^{-1}, from amide-I of the PAM is also observed. The shoulder at 3435 cm^{-1} in PAM is gradually shifted to higher wavenumbers as acrylamide content increases. The N–H stretching in CG-*g*-PAM 1 and 4 appears at 3392 and 3422 cm^{-1}, respectively.

A physical blend of gum and PAM was prepared, by mixing only CG (1 g) and PAM (0.5 g). It was washed in the same way as in the preparation of grafts in order to remove the homopolymer. Spectra of the blend before and after washing were obtained and analysed (data not shown). Before washing the blend spectrum showed bands from both polymers. After washing, the spectrum is similar to that of cashew gum. This indicates that the washing is an efficient way to remove the homopolymer. Therefore, the new peaks for the grafts, observed in Fig. 1, in comparison with that for the gum, provide strong evidence of the grafting reaction of acrylamide onto the cashew gum.

3.4. Nuclear magnetic resonance (NMR)

The ^{13}C nuclear magnetic resonance spectra of the gum, PAM and CG-*g*-PAM 2 are shown in Fig. 2. The gum spectrum is very similar to that obtained by Paula et al. [29]. It has overlapping peaks in the region of 69–85 ppm which were assigned to carbons (C-2–C-5) of the pyranose ring. The peaks at 62–63 ppm can be assigned as primary carbons of sugar units. Anomeric carbon resonance was observed at 90–110 ppm. A low intensity peak at 17.3 ppm is due to the CH_3 of rhamnose. The PAM ^{13}C NMR spectrum has peaks at 35.0; 41.0 and 179 ppm assigned to the CH_2, CH and C=O groups of polyacrylamide. In the ^{13}C spectra of the grafts, peaks related to the gum and to the

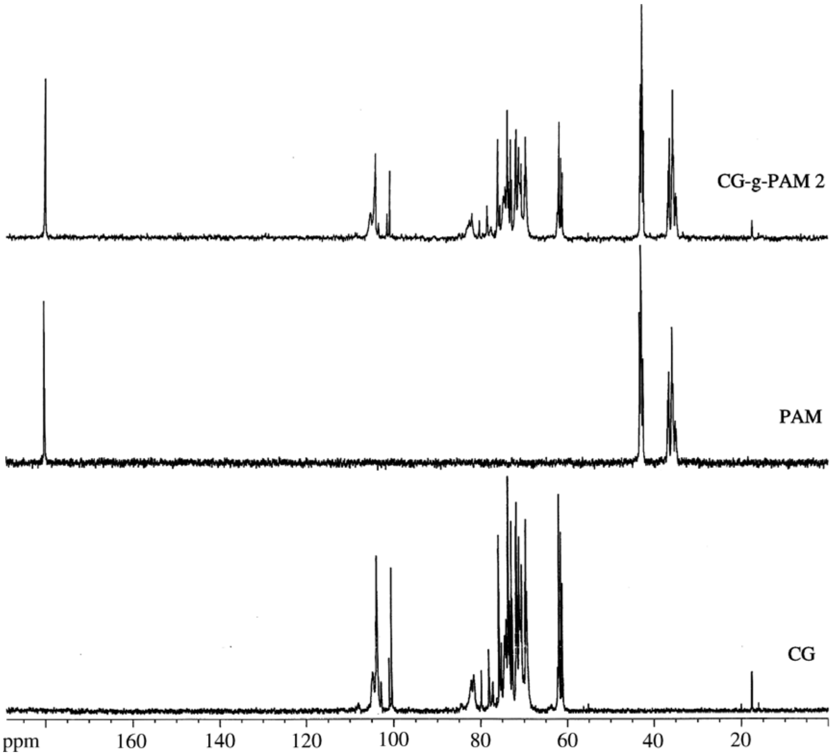

Fig. 2. ^{13}C NMR of PAM, CG and CG-*g*-PAM 2 in D_2O.

CG-*g*-PAM can be observed. The presence of a very intense peak at 179 ppm due to the carbonyl groups, along with two additional groups of peaks due to the methylene group at 35 ppm and the carbon connected to carbonyl group at 41 ppm, confirm the IR results.

The H^1 NMR spectra of the CG-*g*-PAM 2 compared with the unmodified gum show two additional peaks at 1.5–1.6 ppm and 2.2–2.4 ppm due to protons of the PAM chains grafted on the gum backbone (data not shown).

3.5. Grafting mechanism

The copolymerisation mechanism of acrylamide grafting onto polysaccharides, using persulphate as the initiator, has been well studied [7,25]. The persulphate initiator is decomposed under heating to generate sulphate ion radicals, which are well known as chain carriers [18]. The hydrogen radical is abstracted from the hydroxyl group of the polysaccharide to form alkoxy radicals on the substrate. Therefore, this persulphate saccharide redox system results in active centres on the substrate, which initiates a radical polymerisation of acrylamide and leads to a graft copolymer.

3.6. Intrinsic and absolute viscosity

3.6.1. Intrinsic viscosity

The intrinsic viscosity of a polymer is a measure of its hydrodynamic volume in solution, which, in turn, depends on its molar mass and structure, the nature of the solvent and the temperature of the medium. The intrinsic viscosity (0.084 dl/g) and the hydrodynamic volume of cashew gum are very low (Table 3). Its molar mass is around 1.1×10^5 g/mol [29]. The $[\eta]$ of the PAM synthesised in this study was found to be 1.90 dl/g. The viscosity average molar mass of PAM calculated through the use of the Mark–Houwink equation ($[\eta] = 5.31 \times 10^{-5} M_v^{0.79}$) [34] is 5.7×10^5 g/mol. PAM and CG have molar masses in the same order of magnitude, but the intrinsic viscosity of polyacrylamide is twenty times higher. PAM is a linear polymer and CG is a highly branched polysaccharide [35].

Table 3
Intrinsic viscosity and Huggins constant for CG, PAM and graft copolymers in 0.1 M NaCl

Sample	PAM (wt.%)	$[\eta]$ (dl/g)	k_H
CG	0	0.084	1.62
CG-*g*-PAM 1	21	0.47	0.42
CG-*g*-PAM 2	33	0.77	0.43
CG-*g*-PAM 3	47	2.29	0.47
CG-*g*-PAM 4	56	2.06	0.71
PAM	100	1.90	1.23

The $[\eta]$ of all grafts in comparison with values for CG and PAM are also reported in Table 3. All copolymers had values for $[\eta]$ and hydrodynamic volume much higher than those for CG and close to those of PAM. The results suggest that the grafted PAM chains contribute more to the graft conformations in solution than CG. This is due to the presence of the longer dangling grafted PAM chain.

The average number of grafting sites per polysaccharide molecule depends on the ratio of initiator concentration to polysaccharide [13,24,31]. As the ratio increases, the number of grafting sites increases, caused by the induction of a larger number of free radical sites onto the polysaccharide [13]. The length of the polyacrylamide graft chains, on the other hand, depends on the ratio of the concentration of acrylamide monomer to initiator [24]. As the ratio decreases the length of the PAM graft chains also decreases. The values for intrinsic viscosity and length of CG-*g*-PAM chains are higher at lower initiator concentrations and higher acrylamide concentrations [11,13,24,31].

In this study, the AM/P ratio was the only reaction parameter that was varied. The initiator/gum ratio, time and temperature of the reaction were kept constant. In the series of CG grafted copolymers, the intrinsic viscosity increased with increasing acrylamide concentration up to CG-*g*-PAM 3, following a regular behaviour. Therefore, the length of the PAM chain increases from CG-*g*-PAM 1 to 3.

The Huggins constant (k_H) measures the interaction of the polymer molecules with the solvent and with each other. Its value usually ranges between 0.33 and 0.8 [36]. In general, a low value of k_H indicates good solvent and low intermolecular interaction. On the other hand, high values are characteristics of poor solvent and high intermolecular interaction. The Huggins constant for CG-*g*-PAM 1, 2 and 3 is similar and in the range of 0.42 to 0.47, lower than the k_H values for PAM and CG, 1.2 and 1.6, respectively (Table 3). The molecules of CG-*g*-PAM 1, 2 and 3 interact more with the solvent than with each other, probably due to a mixture of groups (OH from gum and $CONH_2$ from PAM) that interact better between each other (gum–gum and PAM–PAM) than between OH

Table 4
Comparisons amongst enhancement factors of intrinsic viscosity of CG and other polysaccharides due to grafting with PAM

Polysaccharide	AM/P	$[\eta]_g/[\eta]_P$	Structure		Reference
			Polysaccharide	Graft	
Starch	4.0	1.07	Branched	Semi-rigid	[15]
Sodium alginate	4.0	0.56	Linear, ionic	Semi-rigid	[15]
Guar gum	10	2.20	Linear, flexible	Semi-rigid	[15]
Sodium CMC	7.5	8.21	Linear, ionic	Semi-rigid	[15]
Cashew gum	1.0	27.3	Branched [35]	Semi-rigid	This study

$[\eta]_g/[\eta]_P$ = enhancement factor of intrinsic viscosity; $[\eta]_g$ = intrinsic viscosity of polysaccharide-*g*-PAM; $[\eta]_P$ = intrinsic viscosity of polysaccharide.

and $CONH_2$ groups. In CG-*g*-PAM 4 the intrinsic viscosity decreases slightly and the Huggins constant increases.

In general, the grafting increases the intrinsic viscosity of polysaccharide. This behaviour has been observed for starch, carboxymethylcellulose and guar gum [15] (Table 4). The opposite effect was reported for xanthan [4] and sodium alginate [15]. The enhancement factor ($[\eta]_g/[\eta]_P$) is defined here as the ratio between the intrinsic viscosity of the graft and the polysaccharide, which the acrylamide was copolymerised into. The enhancement factor shown in Table 4 ranges from 1.07 to 8.21 [15]. The intrinsic viscosity of CG-*g*-PAM increases 27.3 times, the highest enhancement factor, even with the lowest amount of acrylamide per mass of polysaccharide.

3.6.2. Absolute viscosity

The rheological studies of aqueous solutions were carried out at the concentration of 2.5%. Fig. 3 shows the relationship between viscosity and shear rate. The CG-*g*-PAM 1 and 2, CG and PAM samples showed Newtonian behaviours, with absolute viscosities of 2.3, 3.6, 1.4 and 15.4 MPa s, respectively. The aqueous solutions of CG-*g*-PAM 3 and 4 had a pseudoplastic behaviour and high values of absolute viscosity, 24.5 and 34.9 MPa s, respectively. Pseudoplastic behaviour has also been observed for sodium alginate [23] and guar gum [15] grafted with PAM.

The effect of PAM content on the CG-*g*-PAM absolute viscosity at shear rate 190 s^{-1} and 2.5% concentration (wt./vol.) is shown in Fig. 4. The data fit the curve closely, and indicate that a maximum is to be expected at a PAM content of around 70%. A new graft (CG-*g*-PAM 5) was prepared using 1.0 g of CG and 2.5 g of AM, keeping constant all other reaction conditions. The viscosity of the CG-*g*-PAM 5 solution was 51.5 MPa s. Taking the nominal PAM content as 71.4%, a new curve fit was obtained. The two curves are very similar, with maximum values around 70%. The CG-*g*-PAM 5

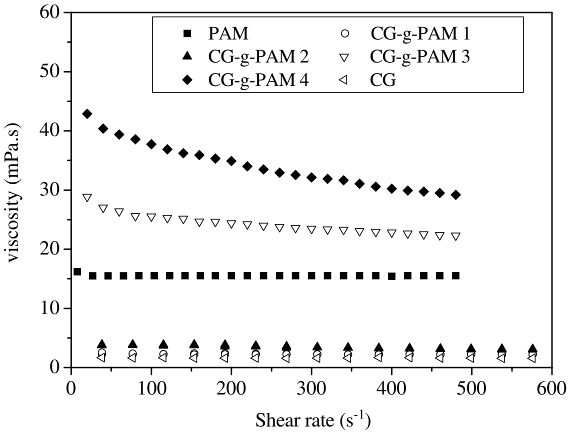

Fig. 3. Effects of shear rate on the absolute viscosity of CG and graft aqueous solutions at 25 °C.

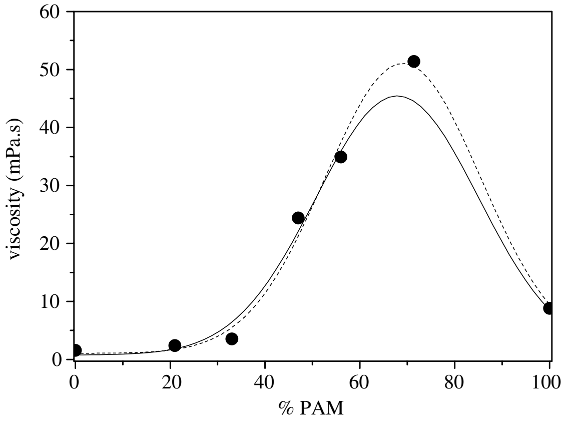

Fig. 4. Effects of PAM content on the absolute viscosity of graft aqueous solutions, with concentration 2.5% at 25 °C and shear rate 190 s^{-1}.

has a viscosity 33 and 3.3 times that of CG and PAM, respectively. The increase in viscosity is attributed to an increase in the molar mass of the polymer and additional entanglement of the graft copolymeric chains acting as temporary cross-linkers [6]. The entanglement and intermolecular interaction was indicated by the Huggins constant of CG-*g*-PAM 4.

3.7. Thermal analysis

Thermogravimetric curves of CG, PAM and CG-*g*-PAM 3 in a nitrogen atmosphere are displayed in Fig. 5. In the case of PAM, a continuous weight loss starting at the beginning of the heating was observed, and at least four thermal events, the main event having a T_{max} (from DTG curve) at 372 °C [37]. Above 240 °C the degradation of PAM is due to loss of ammonia with the formation of imide group via cyclisation [38]. Ammonia and water are the only volatile products below 340 °C in PAM [37]. Decomposition of the cyclised product was observed starting from 380 °C [38].

In general, the main decomposition of the polysaccharides starts above 200 °C. The decomposition process in N_2 for the gum occurs in three stages, as observed by Zohuriaan and Shokrolahi [39]. The first was attributed to desorption of moisture as hydrogen bound water to the polysaccharide structure. The second and third stages of decomposition take place at 241 and 307 °C, respectively, probably due to depolymerisation with formation of water, CO, and CH_4 [39].

The pattern of copolymer thermal decomposition, exemplified by CG-*g*-PAM 3, is different from those for the starting materials (CG and PAM). The graft decomposition is observed in at least five stages. The main events were observed at T_{max} values 278, 321, 378 and 666 °C. The first three events of graft decomposition occurred at higher temperatures than those for gum and PAM (241, 307, 372 °C). The event at T_{max} 666 °C is absent in the starting materials.

All graft copolymers had at least four thermal decomposition events (data not shown). The water loss was observed in the range of 60–76 °C. A new event was observed in the thermal decomposition of all grafts in the range of 600–670 °C. The presence of PAM chains grafted onto cashew gum provoked a reduction in residue at 850 °C, from 17.5% (CG) to 2.2–4.0% (grafts). An even greater reduction has been reported for PAM grafted onto sodium alginate. The residue of gum (around 40%) decreased to about 4% for the grafted copolymer, as reported in the literature for sodium alginate copolymers [31].

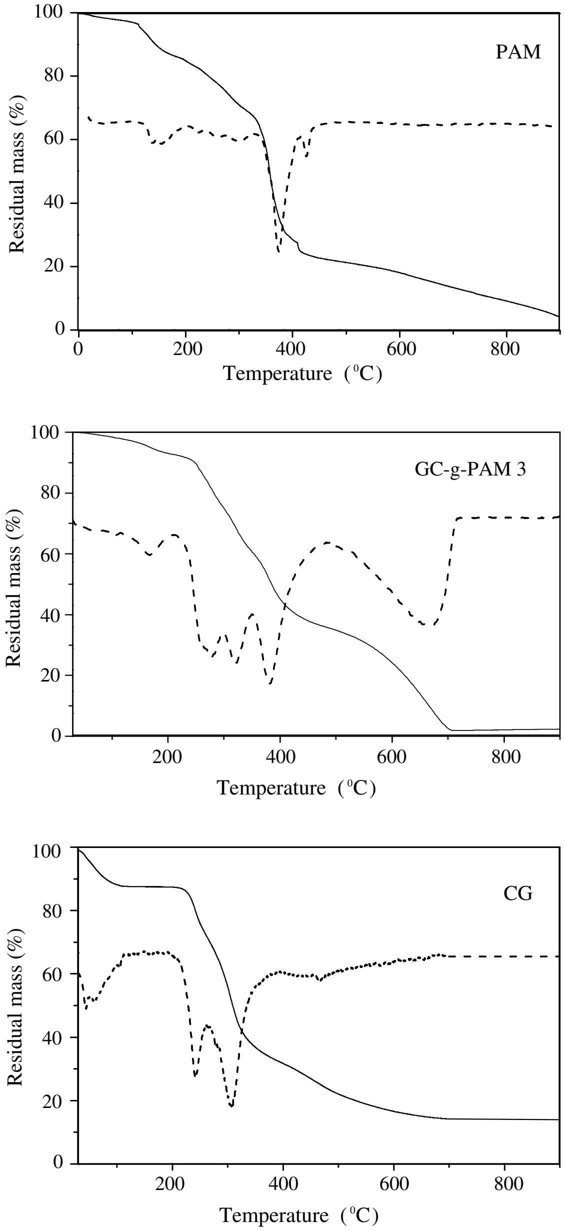

Fig. 5. TGA and DTG curves obtained under N_2 atmosphere of PAM, CG and CG-*g*-PAM 3.

The thermal stability of the copolymers and starting materials was evaluated by IPDT (integral procedural decomposition temperature). The IPDT value for gum (350 °C) is in the same range as those for most polysaccharides [39]. The values for all

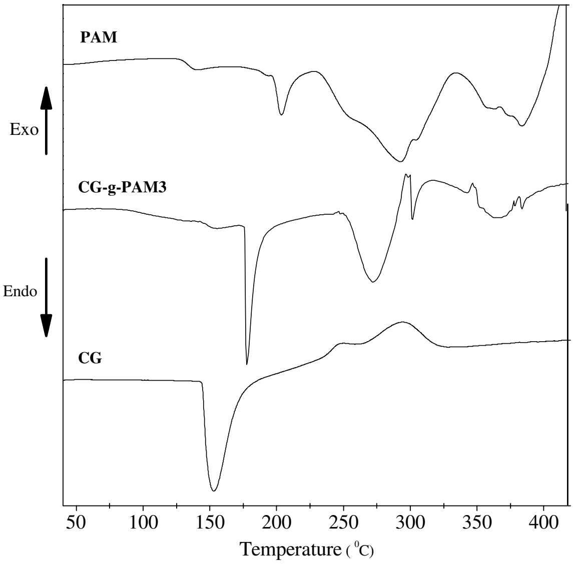

Fig. 6. DSC curves of PAM, CG and CG-*g*-PAM 3.

graft copolymers were in the same range as those for CG, but higher than the value for PAM (288 °C). The grafting of PAM chains onto the polysaccharide did not cause a significant change in the gum thermal stability, but enhanced the PAM resistance to heat.

The DSC curves for the second run of CG, PAM and CG-*g*-PAM 3 are shown in Fig. 6. PAM shows three main endothermic peaks. The peak at around 70 °C, due to the loss of absorbed moisture in the sample, usually observed in polyacrylamide [11], is absent. The moisture was eliminated during the first heating. The peak at 205 °C is for crystalline melting of PAM. Biswal and Singh observed this event at 203 °C [11]. The shoulder at 258 °C is probably due to loss of ammonia [11]. The peak at 297 °C is due to imide group formation via cyclisation. The last peak (384 °C) represents the decomposition of cyclized imide groups. This event has been reported to occur at 361 °C [11]. The glass transition may lie at a temperature of 193 °C. The value reported in the literature is 195–199 °C [37].

An endothermic peak (at 152 °C) and two exothermic peaks (at 246 and 301 °C) are recorded in the DSC curve of the cashew gum. The exothermic peaks are probably due to depolymerisation with formation of water, CO, and CH_4 [39]. Corresponding events are observed at similar temperatures in the DTG curves, at 241 and 307 °C, respectively.

The graft copolymer shows a distinct feature in the DSC curve (Fig. 6) having four endothermic peaks, at 178, 274, 302 and 369 °C. A transition at 148 °C may be due to the T_g of PAM chain. The decrease in the glass transition of PAM is to be expected because the amine group in the polyacrylamide chains grafted onto CG has more difficulty to interact. The CG-*g*- PAM 3 is expected to have longer PAM chains than CG-*g*-PAM 1 and 2. In these two copolymers the T_g is not evident. The T_g value for CG-*g*-PAM 4 is observed at 65 °C (data not shown). The PAM chains in CG-*g*-PAM 4, according to rheological results, seem to be shorter and more distributed than in CG-*g*-PAM 3. The decrease in glass transition value corroborates this assumption.

4. Conclusions

Graft copolymers of cashew gum and acrylamide were successfully synthesised at 60 °C using $K_2S_2O_8$ as the redox initiator under N_2 atmosphere. High percentages of acrylamide conversion (%*C*) and grafting efficiency (%*E*) were obtained, even with a low acrylamide/gum ratio. All copolymers had intrinsic viscosity and thus the hydrodynamic volume much higher than that of CG and close to that of PAM. This viscosity of CG-*g*-PAM increased up to 27.3 times, compared to the gum. This enhancement factor is higher than those reported for many polysaccharides, even with a lower amount of acrylamide (56%) grafted onto cashew gum. The CG-*g*-PAM solution has absolute viscosity up to 33 and 3.3 times the CG and PAM values, respectively. The possibility of increases in the viscosity of the gum is very important for new applications of this natural product. Grafting of PAM chains onto the polysaccharide enhances its thermal stability.

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