Study of the reaction of grafting acrylamide onto xanthan gum

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ABSTRACT

The present study aimed to study the reaction conditions of grafting of acrylamide on xanthan gum. It was analyzed the influence of reaction conditions, mainly type of initiator activation, initiator concentration and initiator/acrylamide ratio, on graft parameters and copolymer properties. Potassium persulfate was employed as an initiator and heating or N,N,N',N'-tetramethylethylenediamine was used to activate the initiator. Reaction time and initiator concentration were varied and final values for grafting percentage and grafting efficiency were the same for both methods, whereas speed in reaching these values differs from one technique to another. We found that reaction time was inversely proportional to intrinsic viscosity, likely due to main chain degradation promoted by potassium persulfate (KPS); furthermore, the increasing in the KPS concentration lowers grafting percentage, acrylamide conversion and chain degradation, possibly as a result of O_2 formation at high KPS concentrations.

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1. Introduction

Polysaccharides grafted with synthetic polymers, such as polyacrylamide, have attracted considerable attention from researchers in recent decades (Kutsevol, Guenet, Melnik, Sarazin, & Rochas, 2006; Rath & Singh, 1998; Stelter et al., 1999; Willett & Finkenstadt, 2003; Yuan et al., 2010). These polymers have the advantage of associating common properties of polysaccharides, including biocompatibility, biodegradability and higher thermal and shear stability, with polyacrylamide characteristics such as greater resistance to enzymes and good properties as flocculants (Adhikary & Singh, 2004; Biswal & Singh, 2004). Moreover, these materials present better control of their hydration when compared to the original polysaccharide (Kumar, Singh, & Ahuja, 2009; Mundargi, Patil, & Aminabhavi, 2007). As such, these polymers are considered potentially applicable in controlled drug release, flocculation of suspensions, water treatment and improved oil recovery (Biswal & Singh, 2004; Joshi & Sinha, 2007; Karmakar & Singh, 1998; Krishnamoorthi, Mal, & Singh, 2007; Kumar et al., 2009; Kutsevol et al., 2006; Mundargi et al., 2007; Yang, Li, He, Ren, & Wang, 2009). Xanthan gum-*g*-polyacrylamide copolymers in particular have been used in drug delivery systems (Kulkarni & Biswanath, 2009) and flocculants (Adhikary & Singh, 2004).

Different synthesis methods can be applied to obtain these materials (Behari, Pandey, Kumar, & Taunk, 2001; Kumar et al., 2009; Mundargi et al., 2007; Silva, Paula de & Feitosa, 2007; Singh, Tiwari, Tripathi, & Sanghi, 2006), among which, persulfate ion (Prashanth & Tharanathan, 2003; Silva et al., 2007; Yang et al., 2009) is somewhat popular. This oxidant can be activated in several ways to generate sulfate radicals, which allow the formation of active sites on the polysaccharide chain and react with monomers present in the reaction medium to produce the graft polymer (Criquet & Leitner, 2009; Hori et al., 2007; Huang, Couttenye, & Hoag, 2002; Oh, Kim, Park, Park, & Yoon, 2009; Reis, Cavalcanti, Rubira, & Muniz, 2003; Shi & Zhang, 2007). In accordance with the literature, the main drawback attributed to this type of reaction is the formation of a homopolymer, occurring parallel to grafting (Kumar et al., 2009; Singh, Tiwari, Tripathi, & Sanghi, 2004; Singh et al., 2006). However, there are few discussions regarding the influence of the type of initiator activation (Mostafa, Samarkandy, & El-Sanabary, 2011; Shi & Zhang, 2007) or polysaccharide degradation in these reactions (Hsu, Don, & Chiu, 2002; Meena, Chhatbar, Prasad, & Siddhanta, 2008; Mochalova et al., 2006; Pourjavadi, Sadeghi, & Hosseinzadeh, 2004).

The grafting reaction of polyacrylamide chains onto xanthan gum probably occurs when a radical is formed in the alkoxy group of the polysaccharide by abstracting hydrogen atoms from the polysaccharide hydroxyls, which are then denominated macro-radicals (Silva et al., 2007; Singh et al., 2004). Grafting begins when acrylamide reacts with the active site of a macroradical. The initiator may also induce homopolymerization, beginning when acrylamide reacts directly with the initiator. In this study, the macroradical was formed by the reaction between sulfate radicals and hydroxyl groups of the polysaccharide. These radicals are

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Table 1
Copolymers codes, type of initiator activation, reaction time used and percentage of carbon, hydrogen and nitrogen in the samples.

Copolymer	Type of KPS activation	Time (h)	% C	% H	% N
CP-C2	Chemical (redox)	2	39.595	6.935	12.270
CP-C3	Chemical (redox)	3	36.610	6.533	11.590
CP-C4	Chemical (redox)	4	38.257	6.793	12.200
CP-T2	Thermal	2	39.100	6.925	12.410
CP-T3	Thermal	3	38.587	6.750	12.180
CP-T4	Thermal	4	39.830	6.900	12.770

known to be capable of abstracting hydrogen radicals (Criquet & Leitner, 2009), and our group has previously applied this technique to introduce acrylamide onto carboxymethylcellulose (Vidal, Balaban, & Borsali, 2008). Persulfate decomposition and, consequently, the formation of free radicals, takes place at ambient temperature, although it occurs slowly (Mano et al., 2004). As such, it generally requires an activator to accelerate fragmentation of the ion. The present study used N,N,N′,N′-tetramethylethylenediamine (TMEDA) or heating, widely employed for this purpose (Costa et al., 2009; Huang et al., 2002; Jones & Opella, 2004; Shi & Zhang, 2007), and aimed to determine the impact of the type of persulfate ion activation on graft parameters, analyzing the effect of initiator concentration, type of activation and reaction time on the final characteristics of polymers.

2. Materials and methods

Xanthan gum and acrylamide (AM) were kindly supplied by Petrobras and Oswaldo Cruz Química, respectively. Potassium persulfate (KPS) was obtained from Vetec and N,N,N′,N′-tetramethylethylenediamine (TMEDA) was purchased from Sigma–Aldrich.

2.1. Graft copolymerization

Each experiment was conducted under magnetic stirring, in a nitrogen atmosphere and at constant temperature. The reaction time was varied in 2, 3 and 4 h. To indentify the effect of type of KPS activation on graft parameters, reactions were carried out at two temperatures. Those at 35 °C were initiated with KPS activated by TMEDA at equimolar concentration, while for syntheses performed at 60 °C, KPS was activated by heating. The ratio between weights of acrylamide and xanthan gum feed into the reactor was constant and equal to 4.4. The influence of initiator concentration in the reactions was analyzed using 2×10^{-3} and 2×10^{-4} mol L^{-1} KPS solutions. In order to separate the homopolymer, reaction mixtures were poured into 7:3 methanol/water and NaCl was added. For syntheses conducted at 60 °C, reaction flasks were cooled before their contents were poured into methanol. Precipitates were filtered, dried in a vacuum oven at 40 °C, pulverized, weighed and stored in desiccators. The grafting parameters percentage of grafting, % G, (Eq. (1)) and grafting efficiency, % E, (Eq. (2)) were calculated according to Shi, Zhang, Ma, and Yi (2007):

$$\% \, G = \frac{100(w_g - w_p)}{w_p} \tag{1}$$

$$\% \, E = \frac{100(w_g - w_p)}{w_m} \tag{2}$$

where w_g, w_p and w_m denote the weights of pure graft copolymer, polysaccharide and vinyl monomer, respectively.

2.2. Elementary analysis (EA)

Copolymerization was verified by elementary analysis using a Perkin Elmer CHNS/O 2400 Series II, at a combustion column temperature of 925 °C and separation column temperature of 640 °C. Samples were analyzed in synthetic air using oxygen as the combustion gas and helium as the carrier gas. Analyses were performed in triplicate.

2.3. Viscometric measurements

Copolymers stoke solutions with concentration of 9 g L^{-1} were prepared by dissolution of a known amount of polymer in 0.1 mol L^{-1} NaCl aqueous solution and filtration through 0.45 μm cellulose acetate Millipore membrane filters. After each dilution, samples were kept under stirring for 2 min and temperature was stabilized at 25 °C for 10 min before starting the measurements. Flow time of each concentration was performed in triplicate, using a capillary with an inner diameter of 0.46 mm, and an AVS-360 Schott-Geräte automatic counter. A fixed volume of the final solution was dried in a ThermoSanvant freeze-drier, model ModulyoD. Polymer weight was determined and concentrations were corrected due to solvent evaporation during filtration.

2.4. Infrared spectroscopy (IR)

IR spectra were measured on a Thermo Nicolet Nexus 470 FT-IR using KBr pellets in a range of 400–4000 cm^{-1}.

2.5. Differential scanning calorimetry (DSC)

DSC analyses were performed using Shimadzu DSC-50 equipment. Experimental parameters employed in these analyses were: average weight of 2.229 mg samples, alumina sealed pans, 50 mL min^{-1} nitrogen atmosphere, heating rate of 10 °C min^{-1} and temperature range between ambient and 450 °C.

2.6. Rheological measurements

Steady shear rheological properties of polymer solutions were measured in distilled water, at a polymer concentration of 2.5 g L^{-1}, using a RheoStress RS 150 rheometer from Haake, equipped with a concentric cylinder system and a DC 50 thermostatic bath. Measurements were performed at 25 °C and curves were recorded in the controlled-shear mode.

3. Results and discussion

EA were conducted to confirm the graft procedure was effective and findings are displayed in Table 1. The results obtained show that all samples contain nitrogen. Since xanthan gum does not have nitrogen in its composition, identification of this element confirms the grafting.

3.1. Influence of reaction time and persulfate activator

Grafting parameters are defined in several different ways in the literature, as exemplified by Mundargi et al. (2007) and by Silva et al. (2007). According to the definition adopted in this study, % G indicates the weight of polyacrylamide chains grafted onto 100 g
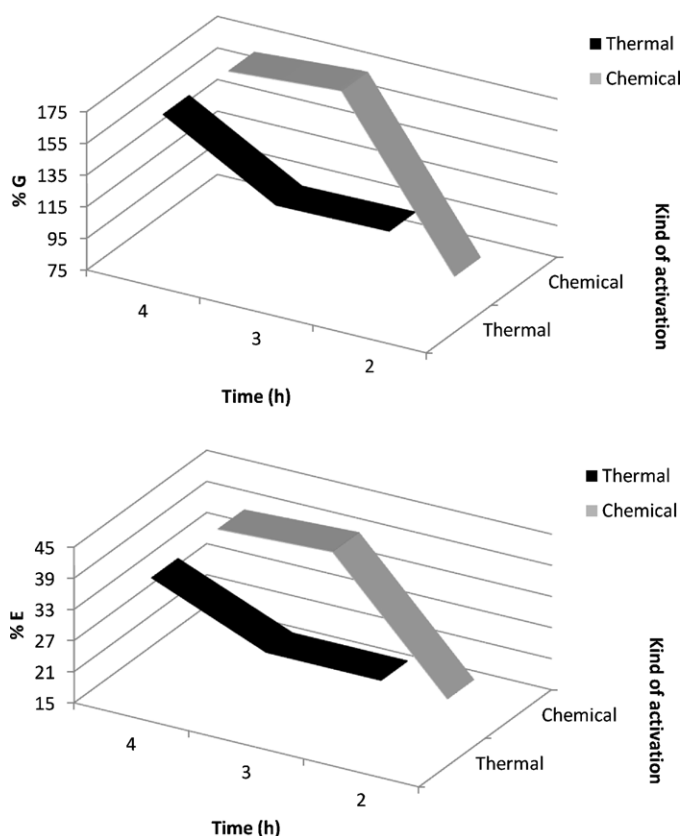
Fig. 2. Comparison of the percentage of grafting (% G) of the copolymer obtained in this work with the results from literature (Behari et al., 2001; Kumar et al., 2009).

Fig. 1. Percentage of grafting (% G) and percentage of grafting efficiency (% E) of copolymers, as a function of time, when using thermal or chemical activation of the initiator.

of xanthan gum and % E shows how much of the acrylamide used was actually grafted onto xanthan gum.

$$[\eta]_{\text{copolymer AB}} = \frac{([\eta]_{\text{polymer A}} \times \text{molar fraction}_{\text{polymer A}}) + ([\eta]_{\text{polymer B}} \times \text{molar fraction}_{\text{polymer B}})}{100} \quad (3)$$

Results shown in Fig. 1 demonstrate that, for the time interval analyzed, both thermal activation and chemical activation of the initiator yield the same final values for % G and % E. However, when chemical activation is employed, graft parameters reach maximum values faster than when thermal activation of the initiator is used. TMEDA radicals not only activate KPS, but also work as an initiator for the vinyl monomer. This justifies the lower graft parameters for chemical activation in the beginning of reaction, which reach maximum values in a shorter time period than in thermal activation (Feng, Guo, & Qiu, 1988). Although 4.4 times more acrylamide (in weight) was used in relation to xanthan gum, maximum grafted polyacrylamide obtained in relation to the polysaccharide was around 1.7 times, and for the most favorable condition, only 40% of the acrylamide employed was grafted.

When comparing the results of this investigation with those in the literature, it was found that when ceric ammonium nitrate (CAN) was used as a redox initiator at 60 °C and 4 h, with the same acrylamide/xanthan gum ratio, the % G achieved was only 60% (Kumar et al., 2009), as per Fig. 2. If the redox system Fe^{2+}/BrO_3^- is used as initiator (Behari et al., 2001) applying the same acrylamide/xanthan gum ratio, outcomes are similar to those from the present study. It is important to point out that, in addition to using different types of initiator systems, the molar ratio between the vinyl monomer and initiator also changed. The acrylamide/KPS molar ratio applied to obtain our results was 200, indicating significantly more acrylamide was used. However, in Kumar et al. (2009),
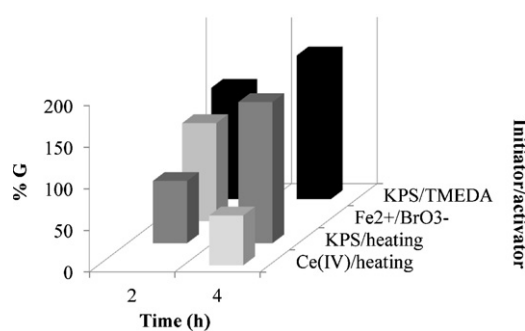
a larger amount of initiator was used, with an AM/Ce(IV) molar ratio of 0.312. Excess acrylamide was also employed for Behari et al. (2001), in relation to the initiator system, and although this excess was only 8, percentage of grafting is higher than 100%. These findings demonstrate that, in addition to studying type of initiator, the ratio between initiator and vinyl monomer concentrations in feeding is also important and has a significant influence on results.

The influence of time and type of activator used on intrinsic viscosity of the copolymers were evaluated (see Fig. S1 in the supplementary data). From these analyses, it was observed that the intrinsic viscosity values decline as reaction time increases, when both thermal activation (60 °C) and the chemical activation (TMEDA) are used for the formation of free radicals from the KPS. And it is possible to observe in Fig. S1 that the final value of intrinsic viscosity is the same, and this result does not depend on the kind of initiator activation. These initial findings establish an inverse tendency between graft parameters and intrinsic viscosity, which is related to the hydrodynamic volume of the macromolecule. Bokias, Mylonas, Staikos, Bumbu, & Vasile, 2001 found that intrinsic viscosity of copolymers is due to the contribution of intrinsic viscosity by the parent homopolymers. These results enable the formulation of Eq. (3).

Intrinsic viscosity of the graft chains can be calculated by Eq. (3), based on intrinsic viscosity of the copolymer and xanthan. This outcome can be used to calculate the molecular weight of graft chains. If this logic is applied to determine the molecular weight of polyacrylamide graft chains, considering the molecular weight of the xanthan gum main chain remains unchanged during the reaction, the molecular weight of graft chains for copolymers CP-T2 and CP-T4, differing only in reaction time, would be 6×10^5 g mol^{-1} and 3×10^5 g mol^{-1}, respectively. Given that a reduction in polyacrylamide chain length with increased reaction time is unlikely, this can be considered evidence of xanthan gum degradation. KPS is known to be capable of degrading polysaccharide chains (Pourjavadi et al., 2004), this behavior is related with the formation of free radicals and is independent of the way in which the KPS is activated (chemically or thermally) to form these free radicals. This could contribute to the decrease in hydrodynamic volume and intrinsic viscosity. Copolymers obtained in this work have a higher proportion of grafted polyacrylamide, and the xanthan gum backbone has a lower molecular weight than the xanthan gum parent.

3.2. Influence of initiator concentration

The influence of KPS concentration on grafting parameters and viscosity is shown in Figs. 3 and 4, respectively, which indicates an increase in the grafting parameters when the initiator concentration decreases. Other authors have recorded similar results for
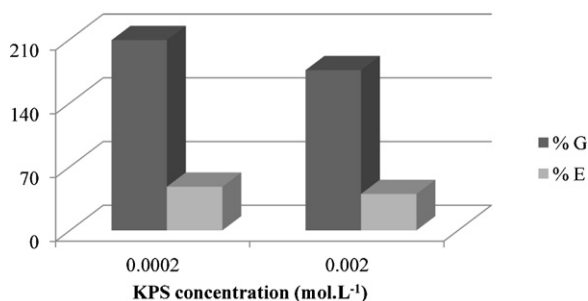
Fig. 3. Percentage of grafting (% G) and percentage of grafting efficiency (% E), as a function of KPS concentration, for copolymers CP-C3.
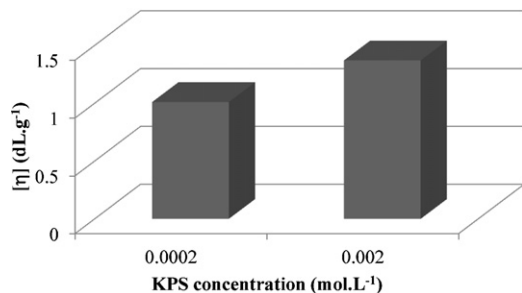

Fig. 4. Intrinsic viscosity as a function of KPS concentration, for copolymers CP-C3.

the graft reaction of methacrylic acid onto starch, attributing this reaction to the formation of HSO_4^- and molecular oxygen (O_2) at higher KPS concentrations (Mostafa et al., 2011; Shi & Zhang, 2007). As expected, intrinsic viscosity is greater for the sample with lower % G and % E, due to the proportional contribution of the parent homopolymers and/or polysaccharide degradation.

3.3. Characterization of the graft copolymer

The infrared spectra of xanthan gum, polyacrylamide and CP-C3 are shown in Fig. 5. These spectra are consistent with those presented in the literature (Kumar et al., 2009). The spectrum of xanthan gum displays a broad band at $3404\,cm^{-1}$, a typical stretch for the OH group. A band corresponding to stretching of the CH group appears at $2917\,cm^{-1}$. Bands at 1732 and
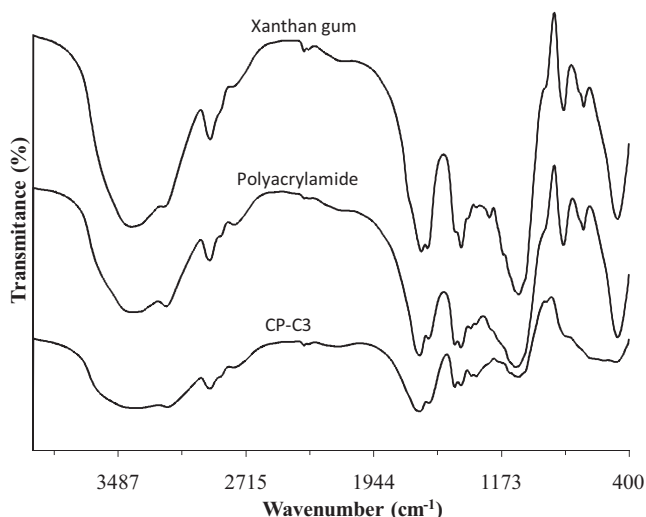

Fig. 5. Infrared spectra for xanthan gum, polyacrylamide and copolymer CP-C3.
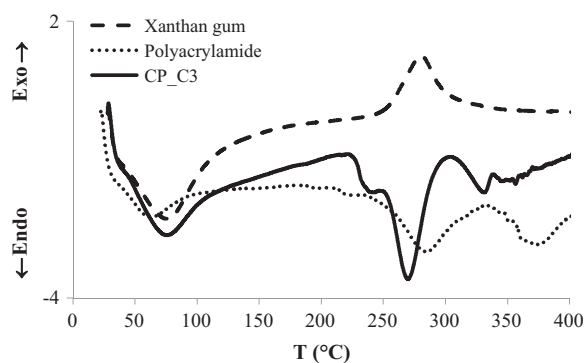

Fig. 6. DSC of xanthan gum (--), polyacrylamide (···) and copolymer CP-C3 (–).

$1620\,cm^{-1}$ represent stretching of the carbonyl (C=O) ester of acetyl groups and asymmetrical stretching of C=O for the carboxylate group, respectively. The polysaccharide also exhibited a band at $1410\,cm^{-1}$, attributed to angular deformation of CH_3 groups, and another at $1061\,cm^{-1}$, due to stretching of the CO bond. Polyacrylamide presented bands at 3410 and $3199\,cm^{-1}$, associated with asymmetrical and symmetrical stretching of the NH bond, respectively. The band shown at $2937\,cm^{-1}$ represents typical stretching of CH bonds. Typical bands of amide are seen at 1666 and $1610\,cm^{-1}$, the first corresponding to stretching of the C=O group (amide I) and the second to angular deformity of the NH_2 group (amide II). The band at $1411\,cm^{-1}$ was attributed to CN bond stretching. The copolymer spectrum presented a combination of the bands found in spectra of xanthan gum and polyacrylamide, indicating grafting was successful. A broad band is recorded at $3365\,cm^{-1}$, corresponding to the overlapping of asymmetrical OH and NH stretches. The signal depicted at $3186\,cm^{-1}$ is related to symmetric stretching of the NH bond. A peak representing CH bond stretching is seen at $2929\,cm^{-1}$, while an intense peak, associated with superposition of the amide I band of polyacrylamide and asymmetrical stretching of carboxylate C=O appears at $1664\,cm^{-1}$. The signal observed at $1608\,cm^{-1}$ corresponds to amide II. Bands at 1454 and $1415\,cm^{-1}$ represent CN stretching and angular deformation of CH, respectively.

To evaluate the effect of polyacrylamide grafting on the thermal properties of xanthan gum, the DSC curve of the CP-C3 copolymer was compared to curves of the xanthan gum precursor and polyacrylamide formed during the graft reaction. Fig. 6 demonstrates that the three samples showed broad endothermic peaks below 100 °C, attributed to loss of moisture in the samples. The xanthan gum precursor displayed an exothermic peak at 275 °C, attributed in the literature to polysaccharide degradation (Wang et al., 2010). This stage of degradation is probably exothermic, since the formed products (CO, CO_2, CH_4) are more stable than the polysaccharide chain (Zohuriaan & Shokrolahi, 2004). The polyacrylamide has an endothermic peak (around 280 °C) related to the first stage of polymer degradation, resulting from ammonia loss and formation of imine (Silva, Dutra, Mano, & Machado, 2000), and another at 370 °C, corresponding to the second stage of polymer decomposition with imine group degradation (Silva et al., 2007). The profile of copolymer thermal decomposition, exemplified by CP-C3, is similar to that of the polyacrylamide; however, endothermic peaks related to the two stages of polyacrylamide degradation were displaced to lower temperatures of 266 and 325 °C, respectively.

Rheological behavior of the copolymer CP-C3 was compared with that of the parent xanthan gum and the polyacrylamide, which was isolated from de reaction medium during the copolymer purification, as per Fig. 7a, and studied using the model of power
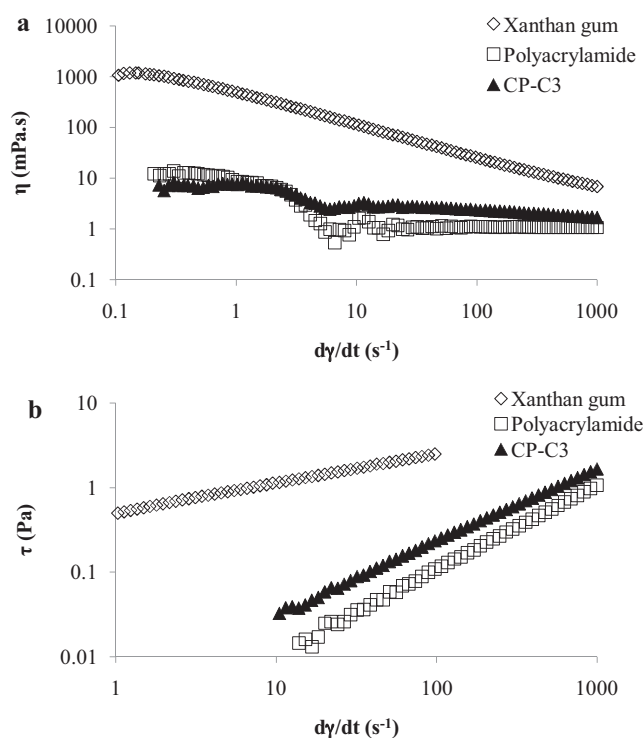
a

b

Fig. 7. Apparent viscosity (a) and stress (b) as a function of the shear rate for xanthan gum (◇), polyacrylamide (□) and CP-C3 (▲) in distilled water, at 25 °C.

law (Fig. 7b) (Martínez-Padilla, López-Araiza, & Tecante, 2004; Song, Kim, & Chang, 2006; Wyatt & Liberatore, 2009). As expected, the apparent viscosity of the copolymer is lower than that of the xanthan gum precursor. The plot also shows substantially low viscosity for the homopolyacrylamide obtained in the synthesis. Consistency and flow indices for xanthan gum, polyacrylamide and CP-C3 were calculated (Supplementary Table S1), indicating an adequate fit for the three polymers to the power model, yielding acceptable R^2 values. The flow index for CP-C3 is between those of xanthan gum and polyacrylamide, with values indicating that the xanthan gum and the copolymer exhibit pseudoplastic character ($0 < n <1$), whereas polyacrylamide has almost a Newtonian character ($n \cong 1$). The results obtained for the polyacrylamide may be attributed to formation of a homopolymer of low molecular weight as byproduct of the graft reaction. These results also indicate that xanthan gum showed a consistence index higher than the other two polymers, in agreement with its greater viscosity.

4. Conclusions

The graft procedure was performed using thermal and chemical activation. Final values of graft percentage and graft efficiency were the same for both methods, although the speed in reaching these values varies from one technique to another. The graft/reaction time percentage was found to be inversely proportional to intrinsic viscosity/molecular weight, likely due to main chain degradation promoted by KPS. Increased KPS concentration decreases the graft percentage, acrylamide conversion and chain degradation, probably as a result of O_2 formation at high KPS concentrations. The copolymers obtained have intermediary properties between those of the parent polymers. Further study is needed regarding the relationship between type of initiator and its ratio with the vinyl monomer.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2012.05.059.

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