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Interaction of Guar and Xanthan Gums with Starch in the Gels Obtained from Normal, Waxy and High-amylose Corn Starches

The objectives of the present study were to analyze the chemical interactions between guar and xanthan gums and starches. Gels were obtained from normal (NCS), waxy (WCS) and high-amylose (HACS) corn starches containing gums. The gels were evaluated according to their pasting properties and infra-red absorption. The guar (GG) and xanthan (XG) gums affected the properties of the NCS paste more significantly than those of the WCS paste. In the infra-red absorption spectra, no covalent bonds between the starches and gums were observed under the conditions studied, so probably the only interactions occurring between them were hydrogen bonds.

Keywords: Gums; Corn starch gels; Physical analyses

1 Introduction

The properties of starch-based formulations can be modified (increase in viscosity, reduction in retrogradation, reduction in syneresis and improvement in the texture characteristics) by incorporating small amounts of hydrocolloids. Guar gum (a galactomannan extracted from the seed kernel of the *Cyamopsis tetragonolobus* plant), alginates, carrageenan, and xanthan gum (extracellular polysaccharide produced by *Xanthomonas campestris*) are amongst the hydrocolloids most frequently used as stabilizers [1]. The positive effects of the use of hydrocolloids in reducing the hardness of corn starch gels have been observed in various studies [2–4].

Mali et al. [1] evaluated the stability of yam starch gels (*Dioscorea alata*) with added guar and xanthan gums, stored at refrigeration temperatures (4°C). The authors verified considerable modifications in the gel textures, and high degree of exudation in the gels without the addition of hydrocolloids. Syneresis occurred due to amylose retrogradation in those gels in which the texture was too firm. The incorporation of 0.5% xanthan gum retarded the occurrence of syneresis in these gels.

Tester and Somerville [5] evaluated the effect of hydrocolloids on gelatinization, water absorption and enzymatic hydrolysis. Hydrolysis by alpha-amylase and gelatinization were evaluated in the presence of different concentrations of five hydrocolloids (gum arabic, carra-

geenan, guar, pectin and xanthan). The main modification caused by the hydrocolloids was to decrease mobility of the water fraction in the system, thus limiting gelatinization. Less hydrolysis was also observed in the gels containing the hydrocolloids as compared to those prepared only with starch. This was due to the fact that the hydrocolloids decreased hydration in the amorphous regions, restraining attack by alpha-amylase.

The objectives of the present study were to analyze the chemical interactions between the gums and starches with high (71%), medium (27%) and minimal (1.8%) amylose contents.

2 Materials and Methods

2.1 Materials

The assays were performed using: (i) normal corn starch, Melojel® (M) (27.8% amylose); (ii) waxy corn starch, Amioca® (AP) (98.2% amylopectin); (iii) high-amylose corn starch, Hylon VII® (AM), (71.0% amylose), supplied by National Starch, Bridgewater, NJ, USA. The starches presented the following physicochemical specifications: color (white, slightly yellowish), form (fine powder), maximum moisture content of 14%, pH (20% solution) between 4.5 and 7.0.

The hydrocolloids used were: guar and xanthan gums supplied by Rhodia Paulínia, SP, Brazil. Xanthan gum (Rhodigel 200®) was obtained by fermentation by the bacteria *Xanthomonas campestris*. A 1% aqueous solution had a viscosity of 1,200 to 1,600 mPa s and a pH between 6.0 and 8.0. Guar gum (Higum 551®) was isolated from the kernel of the seed of the *Cyamopsis tetragonolobus* guar

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plant. A 1% aqueous solution had a viscosity of 5,300 to 5,500 mPa s and pH between 5.5 and 6.5.

2.2 Methods

2.2.1 Preparation of the corn starch-gum gels

The suspensions of normal and waxy corn starches containing gums (0.15, 0.50, 0.85, and 1%), with total solids concentrations of 10%, were gelatinized by heating at 100°C in a double-boiler (Dubnoff TE 053, Tecnal, Pinacaba, SP, Brazil), boiling for 15 min with mechanical agitation (Fisatom, 720, São Paulo, SP, Brazil) at 800 rpm. For the high-amylose corn starch, the suspensions with total solids concentrations of 10% were gelatinized in the Pressure Reaction Apparatus N° 4501 reactor (Parr Instrument Company, Moline, IL, USA), at 3.79 bar (55 psi) and 150°C. For all preparations, a blank without gum was prepared.

2.2.2. Pasting properties

The pasting properties were determined with a Rapid Visco Analyser (Newport Scientific Instruments, Warriewood, Australia). Guar and xanthan gums at concentrations of 0.15, 0.50, 0.85 and 1% were dissolved in water and the normal and waxy starches mixed directly into these solutions to give a total of 10% solids. Starch solutions without gums (controls) were also analyzed. The aluminum canister containing the sample was placed in the equipment and submitted to analysis according to Standard Method #1, as described in the equipment manual, with a 13 min test, equilibrating at 50°C for 1 min, heating to 95°C in 7.45 min and cooling to 50°C in 4.15 min.

2.2.3 Infra-red spectrometry

The starch and gum gels prepared as in section 2.2.1 and the retrograded gels (seven days at 10°C), were stored at –18°C and freeze-dried for the infra-red analyses. The infra-red spectra were obtained with the objective of characterizing the different starches and gums and their gels, and verifying possible chemical interactions occurring during the processes of gelatinization and retrogradation. Twenty-eight samples were prepared by mixing 100 mg of KBr and 10 mg of each material to be analyzed: (i) starch powders; (ii) gum powders; (iii) freeze-dried gelatinized starches, with and without added xanthan and guar gums; and (iv) freeze-dried retrograded gels, with and without added guar and xanthan gums. Each material was placed in a Carver hydraulic press and

submitted to a pressure of 8 t/cm² for 5 min. The infra-red spectra (from 4,000 to 400 cm⁻¹) of the samples were obtained using a Fourier transformed infra-red spectrophotometer (FTIR) (FTLA2000-100, Shimadzu, Kyoto, Japan), using the techniques of qualitative and differential analyses.

3 Results and Discussion

3.1 Pasting properties

Tab. 1 shows the effects of the guar and xanthan gums on the pasting properties of the normal (M) and waxy (AP) starches. It can be seen that the addition of 0.50, 0.85 and 1% guar gum significantly increased the maximum viscosity at 95°C, the final viscosity at 50°C and the minimal viscosity at 95°C of the normal corn starch. This gum significantly decreased retrogradation, presenting a significant difference between the samples containing the gum and the control, independent of the gum concentration used. The addition of 0.85 and 1% gum increased the gel viscosity breakdown, and the pasting temperature significantly increased with the incorporation of 0.15 and 1% of guar gum (Tab. 1).

The addition of xanthan gum to the normal starch gels significantly decreased the values of the maximum viscosity at 95°C and the final viscosity at 50°C. Xanthan depressed the *MV* but increased the V_m and paste viscosity, delaying granule swelling. Due to this delay, the mechanical breakdown of the swollen granules (at 95°C) had already started before the viscosity peak was attained, the result being a lower *MV* and reduced breakdown. This hypothesis was supported by the fact that XG increased peak time suppression and the delay in granule swelling could also account for the much reduced setback, i.e. less time for mobilization of the amylose. The maximum viscosity was decreased from 3,280 mPa s to 2,625 mPa s (reduction of 10.6%) by the addition of 1% gum, which significantly decreased retrogradation of the normal corn starch. The incorporation of xanthan gum significantly increased starch gel stability, and on being submitted to mechanical agitation at the cooking temperature, the value of the viscosity breakdown became significantly smaller with increasing concentration of added gum as compared to the control (Tab. 1). The addition of 0.15% xanthan gum to the normal corn starch increased the pasting temperature from 75°C to 76°C, reaching ~77°C at the maximum concentration of this gum.

In case of the waxy starch, guar gum had no effect on either the minimal viscosity at 95°C, breakdown or retrogradation, although it caused a significant increase in the

Tab. 1. Effect of the addition of guar (GG) and xanthan (GX) gums at concentrations of 0.15; 0.50; 0.85 and 1.0%, on the pasting properties of the normal (M) and waxy (AP) starches^{1,2}.

Starches	MV 95°C [mPa s]	FV 50°C [mPa s]	V _m 95°C [mPa s]	Breakdown [mPa s]	Retrogradation [mPa s]	T _p [°C]	pt [min]
M + 0.00% GG	2,937 ^d	3,153 ^{bc}	1,934 ^c	1,002 ^b	1,218 ^a	75.02 ^b	5.03 ^a
M + 0.15% GG	2,922 ^d	3,094 ^c	1,927 ^c	994 ^b	1,167 ^b	75.43 ^a	5.07 ^a
M + 0.50% GG	3,022 ^c	3,157 ^b	2,004 ^b	1,017 ^b	1,153 ^b	75.21 ^{ab}	5.18 ^b
M + 0.85% GG	3,208 ^b	3,269 ^a	2,127 ^a	1,080 ^a	1,141 ^b	75.34 ^{ab}	5.21 ^b
M + 1.0% GG	3,280 ^a	3,301 ^a	2,161 ^a	1,119 ^a	1,140 ^b	75.49 ^a	5.23 ^b
M + 0.00% GX	2,937 ^a	3,153 ^a	1,934 ^c	1,002 ^a	1,218 ^a	75.02 ^c	5.03 ^d
M + 0.15% GX	2,822 ^b	2,926 ^b	1,873 ^c	948 ^b	1,053 ^b	76.12 ^b	5.17 ^c
M + 0.50% GX	2,762 ^b	2,935 ^b	2,053 ^b	709 ^c	882 ^c	76.82 ^a	5.35 ^b
M + 0.85% GX	2,604 ^c	2,895 ^b	2,053 ^b	551 ^d	842 ^{cd}	76.70 ^a	5.40 ^a
M + 1.0% GX	2,625 ^c	2,952 ^b	2,128 ^a	497 ^e	823 ^d	76.87 ^a	5.49 ^a
AP + 0.00% GG	3,950 ^b	2,056 ^b	1,667 ^a	2,282 ^a	389 ^a	71.18 ^d	3.47 ^b
AP + 0.15% GG	3,963 ^b	2,105 ^{ab}	1,689 ^a	2,274 ^a	416 ^a	71.34 ^{cd}	3.52 ^b
AP + 0.50% GG	4,094 ^{ab}	2,127 ^{ab}	1,724 ^a	2,370 ^a	403 ^a	71.64 ^{bc}	3.59 ^a
AP + 0.85% GG	4,129 ^a	2,148 ^{ab}	1,725 ^a	2,403 ^a	422 ^a	72.00 ^{ab}	3.62 ^a
AP + 1.0% GG	4,185 ^a	2,188 ^a	1,765 ^a	2,420 ^a	422 ^a	72.10 ^a	3.64 ^a
AP + 0.00% GX	3,950 ^a	2,056 ^a	1,667 ^a	2,282 ^a	389 ^a	71.18 ^c	3.47 ^d
AP + 0.15% GX	3,963 ^a	2,093 ^a	1,663 ^a	2,299 ^a	430 ^a	72.37 ^b	3.64 ^c
AP + 0.50% GX	3,975 ^a	2,078 ^a	1,644 ^a	2,330 ^a	433 ^a	73.56 ^a	3.76 ^b
AP + 0.85% GX	3,896 ^a	2,044 ^a	1,585 ^a	2,310 ^a	463 ^a	73.50 ^a	3.80 ^{ab}
AP + 1.0% GX	4,008 ^a	2,104 ^a	1,640 ^a	2,365 ^a	456 ^a	73.87 ^a	3.83 ^a

¹ MV 95°C = maximum viscosity at 95°C; FV 50°C = final viscosity at 50°C; V_m 95°C = minimal viscosity at 95°C; T_p = pasting temperature; pt = peak time.

² Means followed by the same letter in a vertical column do not differ statistically according to the Tukey test, at a 5% level of probability.

maximum viscosity at 95°C at concentrations of 0.85 and 1%, and in the final viscosity at 50°C at a concentration of 1%. Guar gum significantly increased the peak time at a concentration $\geq 0.50\%$.

The incorporation of xanthan gum into the waxy corn starch did not influence the maximum viscosity at 95°C, the final viscosity at 50°C or the minimal viscosity at 95°C, no significant differences being detected between the samples with added gums and the controls. On the other hand, the peak time and pasting temperature were significantly increased by this gum. The pasting temperature increased from 71°C to 72°C, reaching ~74°C with the addition of 1% xanthan gum.

The high swelling power of AP starch is connected to (a) a high and early viscosity peak and (b) high breakdown, because high swelling indicates a low degree of physical cross-linking within the swollen granules and hence a weak swollen granule structure. The small setback is due to the lack of amylose.

An increase in the maximum viscosity of starches containing added hydrocolloids was previously reported by other authors [6–8]. *Christianson et al.* [9] attributed the increase in viscosity to the interaction of the soluble part (dissolved amylose and low-molecular mass amylopectins) of the starch granule and the gums. An alternative explanation was that the added gums interacted with the starch granules, forming more viscous suspensions than the starch-water suspension made with the same concentration of starch alone.

Lee et al. [10] obtained similar results to those obtained in the present study when evaluating the pasting properties of sweet potato starch with added hydrocolloids, giving a total solids concentration of 7%, concluding that the addition of 0.6% xanthan gum reduced the maximum viscosity of the starch by 17.07%, whilst guar gum increased the viscosity by 122%.

Shi and BeMiller [11] also verified that the addition of 0.4% xanthan gum to a 7.5% suspension of potato starch

decreased the maximum viscosity from 11,200 mPa s to 2,810 mPa s. Apart from xanthan gum, other anionic gums (sodium alginate, carboxymethyl cellulose, pectin and κ -carrageenan) also decreased the maximum viscosity. *Shi et al.* [12], showed that corn starch granules heated in a xanthan gum solution did not disintegrate on heating, and the resulting mixture behaved as a suspension of granules swollen within a continuous phase formed by the xanthan solution. Addition of the gum caused a decrease in hydration of the starch granules, which could have been the cause of the reduction in the maximum viscosity of the starch-xanthan gum-water system. *Lai et al.* [4], also showed a reduction in viscosity of pastes made with normal corn starch and wheat starch with added HG (hsian-tsaio) gum, which they attributed to a restriction in the exit of amylose.

Funami et al. [13], elaborated starch-containing systems with 50, 26 and 14% amylose plus different molecular

weight guar gums (G3: 20.1; G6: 10.1; and G8: 0.02×10^{-5} g/mol). The suspensions were prepared with 15% starch and 0.5% guar gum and their pasting properties determined. The addition of G3 increased the pasting temperature of the starches with 26% and 14% of amylose, but the opposite occurred with starch containing 50% amylose, where the addition of G3 and G6 decreased the pasting temperature.

Bahnassey et al. [14] used RVA to study the effects of using different concentrations of konjac, guar, gellan, xanthan and locust bean gums on the pasting properties of wheat, corn, waxy corn, cassava and amaranth starches. They observed that the maximum viscosity increased with the maximum gum concentrations, especially with 0.4% locust bean gum. The xanthan and gellan gums caused the lowest increases. The increase in the maximum viscosity caused by the gums was more pro-

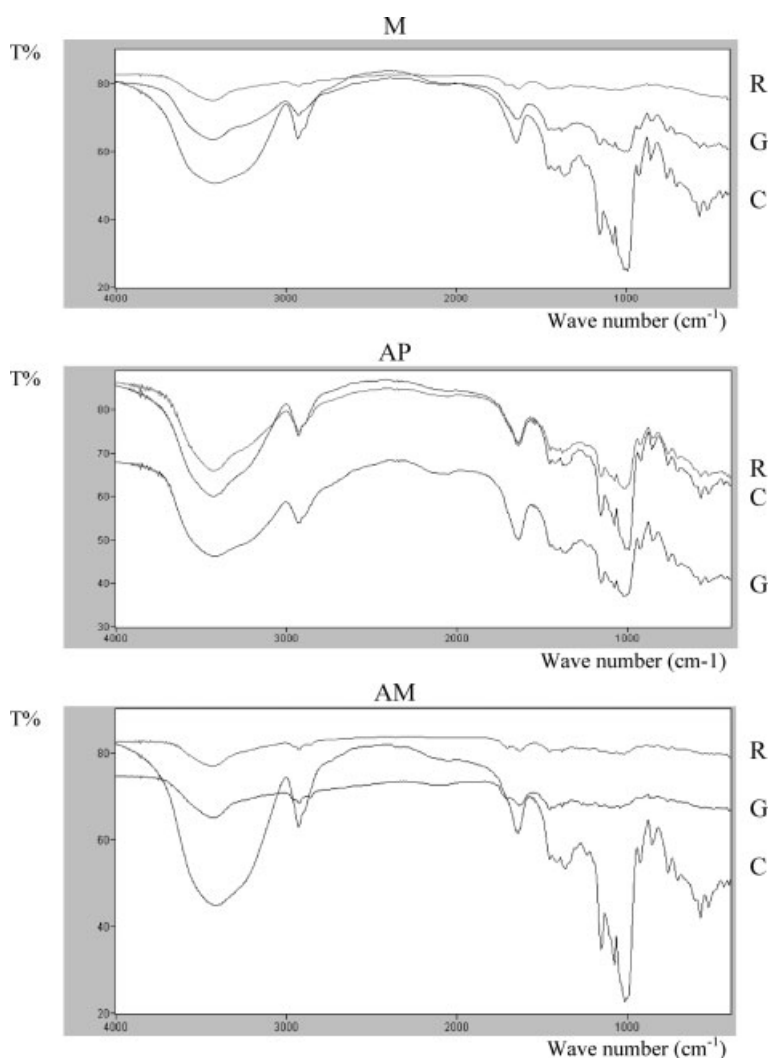


Fig. 1. Infrared absorption spectra of gelatinized and retrograded normal, waxy and high-amylose corn starch powders. Where: M= normal corn starch; AP = waxy corn starch; AM = high-amylose corn starch; C = crude powder; G = gelatinized and R = retrograded.

nounced with normal corn starch than with waxy corn starch. The amaranth starch showed a much smaller increase in viscosity than all the other starches. This is probably due to the higher amylose content of ~27% of the normal starch. Retrogradation was also significantly reduced by the gums.

Two possible explanations can be given for the modifications caused by the gums in the starch pasting properties: (i) an association of the gum with the swollen starch or with the soluble amylose and low molecular weight amylopectin fractions of the paste, and (ii) competition of the gum with the starch for the free water in the system.

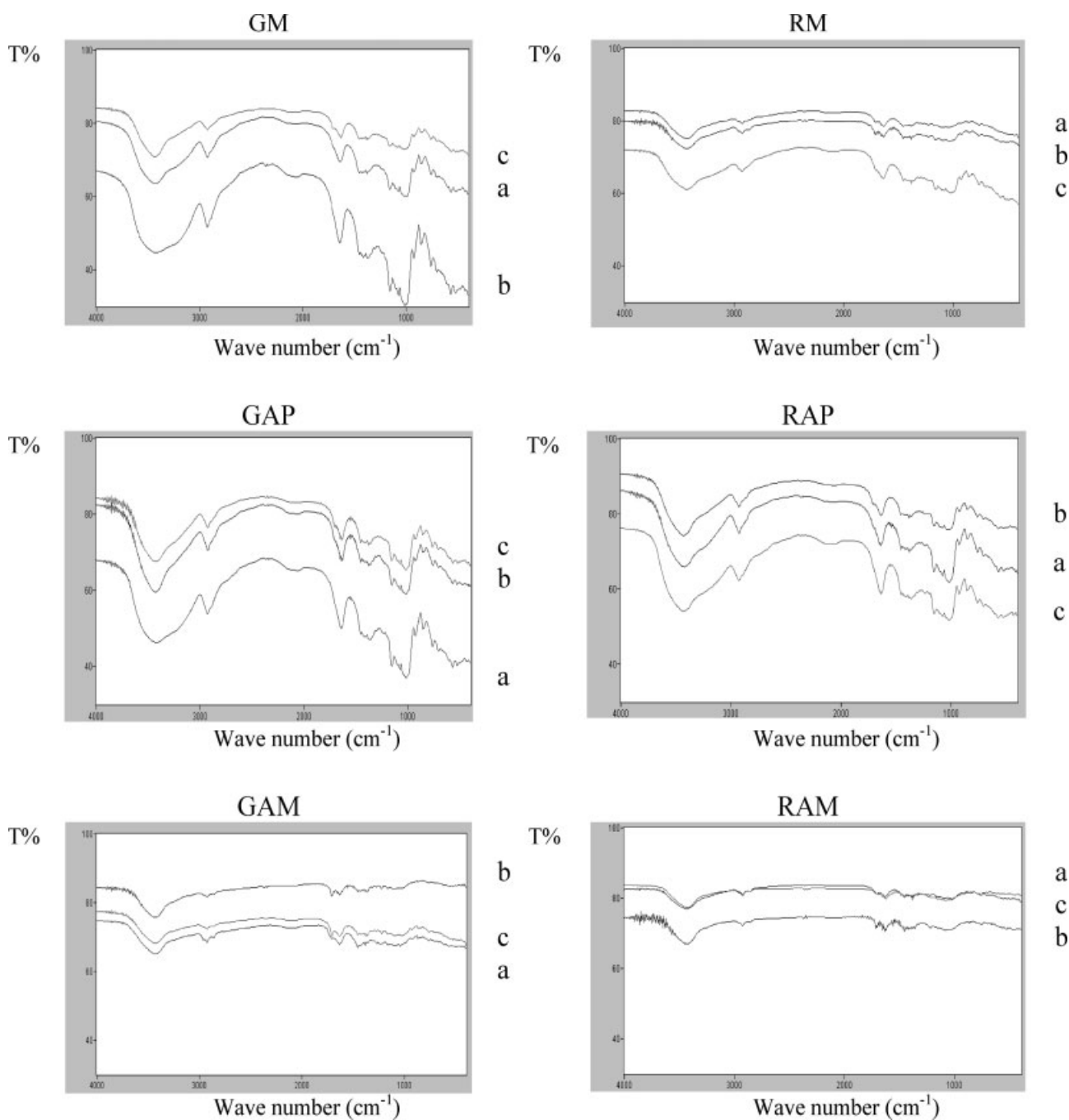


Fig. 2. Infrared absorption spectra of gelatinized (A) and retrograded (B) normal, waxy and high-amylose corn starches with 1% added guar and xanthan gums. Where GM = gelatinized normal corn starch, GAP = gelatinized waxy corn starch, GAM = gelatinized high-amylose corn starch; RM = retrograded normal corn starch, RAP = retrograded waxy corn starch, RAM = retrograded high-amylose corn starch; a = starch, b = starch + guar gum, c = starch + xanthan gum.

3.2 Infrared spectrometry

In the infrared absorption spectra of normal, waxy and high-amylose corn starches shown in Fig. 1 all starches presented the same bands, characteristic of their chemical structures, in the fingerprint region from 1,350 to 910 cm^{-1} [15].

As only peaks with an intensity greater than 20% are usually analyzed, some peaks, despite being present in the three types of starch, were not recorded by the software used. Differences in the absorption intensity of some functional groups between the starches became evident, such as, for example, the decrease in intensity of the hydroxyl groups, corresponding to the primary and secondary alcohol functions (1,241 cm^{-1} , 1,367 cm^{-1}).

During the retrogradation process of the starch gels stored at 10°C, structural changes, which can be monitored by infrared absorption, occurred, and a decrease in intensity of some bands, especially those appearing in the region from 1,300 to 800 cm^{-1} [21] can be observed (Fig. 1). A very high peak intensity can be seen in this region in the starch powder sample, the intensity these peaks decreased after gelatinization, and were even more reduced after retrogradation. A similar behavior was also found for the waxy and high-amylose starches.

Fig. 2 shows the infrared absorption spectra of normal corn, waxy corn and high-amylose starch gels and of those with added 1% guar and xanthan gums. From a comparison of the spectra shown in Fig. 1 with those shown in Fig. 2, it can be seen that no new covalent bonds had formed between the starches studied and the gums. Thus in the processes studied, the bonding between the gums and the starches must have been of the hydrogen bond type, since in the spectra the same characteristics were visible as in those of the pure starches, varying only with respect to the intensity of the bands.

4 Conclusions

Guar and xanthan gums affected the pasting properties of normal corn starch more than those of waxy corn starch. Guar gum caused a small overall increase (ca 10%) in the viscosity of normal starch, leading to small changes in breakdown and setback. Gums modify the rheology of starch pastes by contributing the gum viscosity to the system viscosity, and by their effect on granule swelling during and after gelatinization.

As concluded from the infrared spectra, no new covalent bonds were formed between the guar and xanthan gums and the starches (normal, waxy and high-amylose), and

thus the gum-starch interaction under the conditions studied occurred probably via hydrogen bonding.

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