Emirates Journal of Food and Agriculture. 2023. 35(1): 17-22
doi: 10.9755/ejfa.2023.v35.i1.2988
http://www.ejfa.me/

RESEARCH ARTICLE

Physicochemical properties of chickpea hull and corn bran gums

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ABSTRACT

Currently, there is increasing interest on natural hydrocolloids such as gums. In the present work, the solubility, zeta potential and rheological properties of gums from chickpea hull and corn bran were studied. Chickpea hull and corn bran gums were extracted from chickpea hulls and nejayote, respectively. The chickpea hull gum had 2.98% of protein (w/w) and corn bran gum 2.28% (w/w), an ash content of 2.25% (w/w) and 6.21% (w/w), respectively. Chickpea hull gum (CHG) had its highest solubility (above 50%) at 50 °C and 12 hours. Corn bran gum showed a solubility over 90% at 12 hours at 25 °C. The Zeta potential values for both gums were negative (from -0.33 mV to -20.0 mV) through the pH range studied (from 2.0 to 7.0). The dispersions of both gums showed a rheological behavior in which viscosity decreases when increasing the shear rate from 10^{-2} s^{-1} to 10^{3} s^{-1} for chickpea hull gum and corn bran gum at 2%; the rheological viscosity values of the dispersions was adjusted to the Carreau-Yasuda model.

Keywords: Gums; Solubility; Zeta Potential; Viscosity; Shear-thinning

INTRODUCTION

Gums are molecules hydrophilic or hydrophobic that form viscous solutions at low concentrations. Are defined as polysaccharides of plant and microbial origin (Barak et al., 2020). Polysaccharides are used for various application as drug delivery (Torres et al. 2019), packaging films (Liu et al 2020), acidified protein dispersions (Nomura et al. 2021) and backbones for the formation of nanoparticles (Moon et al. 2021). the use of polysaccharides isolated from watermelon rind and chickpea flour have been explored because they are an attractive alternative to be applied to food production (Romdhane et al., 2017; Ghribi et al., 2015; Shehata et al. 2020). In the other hand, the husk, pericarp or cover of cereals and legumes are normally destined as animal feed after grain processing; however, these wastes have the potential for technological exploitation, such is the case of chickpea husk and corn bran.

Chickpea hull is high in dietary fiber which is made up of cellulose, hemicellulose, pectin, lignin and gums. Chickpea hull polysaccharides have been shown to have antioxidant activity (Ye et al., 2016) and the ability to form viscous solutions. The chickpea hull composition has been reported by Akhtar et al. (2019), who reported the presence of mannose (2.16 %), rhamnose (2.96 %), galacturonic acid (42.17 %), glucose (9.87 %), galactose (23.15 %), xylose (6.29 %) and arabinose (13.38 %).

In Mexico, due to the increase in the production of white corn flour for the tortilla industry, the corn bran residues are a potential source of polysaccharides with functional properties for the food industry. During the nixtamalization process, a supernatant called nejayote is produced where all the components of the corn cell walls are dissolved. Non-cellulosic cell walls polysaccharides, which are in the corn pericarp, have functional properties as emulsifiers and gel formers. However, the nejayote is considered wastewater; therefore, it is considered an environmental pollutant.

Polysaccharide interactions, chemical or physical, are known to affect the rheological properties of suspensions (Tsatsaragkou et al., 2015; Shantilal and Bhattacharya 2015). These properties are used to create structures with

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Received: 11 July 2022; **Accepted:** 31 December 2022

reproducible physical properties (Kontogiorgos, 2015). Previous work has reported physicochemical properties of arabinoxylan gels of laccase-gelified nejayote, rheological properties of wheat arabinoxylan gels added with horseradish peroxidase and hydrogen peroxide (Niño-Medina et al., 2009; Skendi et al. 2011). In this work, the aim was to evaluate the solubility, zeta potential and rheological properties of the chickpea hull gum (CHG) and corn bran gum (CBG) at two concentrations.

MATERIALS AND METHODS

Materials

Chickpea grains were obtained from a local market and nejayote (a wastewater product from the nixtamalization) obtained from a local tortilla shop, from Salvatierra, Guanajuato, México. Hydrochloric acid, sodium hydroxide (JT Baker, SA de CV) were bought in Celaya City, Mexico.

Extraction of chickpea hull and corn bran gums

The gums were obtained from the chickpea hull. The chickpea hull was ground and suspended in 0.5 N NaOH solution (50 g hull/1 L solution) at 70 °C for two hours, then filtered and centrifuged at 5000 rpm for 20 minutes. The supernatant was adjusted to pH 4.0 with 1 N of HCl, the acidified supernatant was centrifuged at 5000 rpm for 20 minutes, and the supernatant was recovered and precipitated with absolute ethanol in a ratio 1:2. The precipitate was recovered by centrifugation (5000 rpm, 10 min at 20 ºC) and dried (50 ºC, 1 h) to volatilize the ethanol. Concerning the corn bran gum, it was recovered from nejayote, a wastewater product from corn nixtamalization for tortillas, following the same procedure as the chickpea hull gum.

Proximate composition

The protein content was determined according to the Bradford method (Bradford, 1976) with some modification. Ash content was estimated gravimetrically by sample incineration in a muffle furnace (Felisa FE-340, EQUIPAR, Mexico City, Mexico) at 550 °C during 6 hours (AOAC, 1995). The sugar content in chickpea hull and corn bran gums was determined by the method reported by Niño-Medina et al., (2009). Hydrolysis was carried out with 2.0 N trifluoroacetic acid at 120 °C for 2 hours, it was cooled in an ice bath and the excess of trifluoroacetic acid was eliminated and the obtained extract was rinsed twice with 200 mL of water, subsequently it was solubilized in 500 mL of water. Sorbitol was used as standard. To analyze the samples by HPLC, the samples were filtered with a 0.45 membrane. A Supelcogel Pb column (300 x 7.8 mm; Supelco, Inc., Bellefont, PA) eluted with water (filtered with 0.2 μm membrane) at 0.6 ml/min and 80 °C. was used. A refractive index detector Star 9040 (Varian, St. Helens, Australia) was used.

Nuclear magnetic resonance (NMR) analysis

The nuclear magnetic resonance spectrum of gums samples was evaluated with the ^{13}C cross polarization/magic angle spin NMR method (CP/MAS) at 22 °C on Bruker Ascend III HD 400 NMR spectrometer. A zirconium dioxide (ZrO_2) rotor was used to place the solid samples and then centrifuged at 9 KHz. Chemical shifts were acquired relative to glycine (176.2 ppm), a $\pi/2$ pulse of 2.5 μs, 3.0 ms contact time and 5.0 s delay, and at least 512 accumulations were used.

Solubility

Samples of gums were prepared at a concentration of 0.1% w/w at a temperature of 25 ºC for 3, 6 and 12 hours under mechanical agitation. Other samples were prepared under the same conditions but at 50 °C. Each of the dispersions were centrifuged at 5000 rpm for 30 min, at 20 °C, then the supernatant was recovered and dried at 105 °C for 24 h to determine the percentage of solubility (Dakia, et al. 2008).

Zeta potential

The zeta potential of the gums dispersions was conducted using a Zetamaster (Malvern Instrument, Worcestershire, UK). The experiments were carried out at a pH interval of 2.0 to 7.0 at 25 °C. The dispersions were diluted using deionized water and placed in a measurement cell.

Rheological analysis

Gum samples (2% w/w and 4% w/w) were dispersed for 12 hours at 25 °C. The rheological behavior of the gum dispersions was measured using the method described by Yuliarti y col. (2015). Curves of apparent viscosity of the gums dispersions were obtained with a rheometer Physica MCR 301 (Physica Messtechnik, Stuttgart, Germany) using a double-spaced concentric cylinder geometry at room temperature applying a shear rates between 0.001 and 1000 s^{-1}.

All data were adjusted to the Carreau-Yasuda model:

$$\eta_a = \eta_\infty + \frac{(\eta_0 - \eta_\infty)}{\left[1 + \left(\lambda \dot{\gamma}\right)^2\right]^N}$$

Where γ is the shear rate (s^{-1}), η_a is the apparent viscosity (Pa.s), η_0 is the initial viscosity (Pa.s), η_∞ is the infinite viscosity (Pa.s), λ is a constant related to the viscose relaxation time (s) and N is the consistency index (dimensionless).

Statistical analysis

To analyze the data from all the experiments, a one-way analysis of variance was carried out and the means of the treatments were compared using the Tukey test ($p \leq 0.05$). For the analysis, the statiscal package Statgraphics Centurion XVI.I (Statistical Graphics Corp., Manugistics, Inc., Cambridge, MA, USA) was used.

RESULTS AND DISCUSSION

Proximate composition analysis

Corn bran gum presented protein and ash values of 2.28 g/100 grams and 6.21 g/100 grams respectively, these values were different from those found in chickpea hull gums (2.98 g/100 grams of protein and 2.25 g/100 grams of ash respectively). Carvajal-Millan et al. (2007) reported the proximate composition of the corn bran gum. They found 2.50 g/100 grams of protein, similar with the reported in this work and 4.10 g/100 grams of ash in corn bran gum. On the other hand, the protein content in corn bran gum was significantly lower than those reported by Niño-Medina et al. (2009), they reported 4.50 g/100 grams of protein, this could present due to the precipitation of proteins at pH 4.0 during the extraction of the gums (near the isoelectric point of the protein).

Table 1 shows the composition of sugars in chickpea hull gum and corn bran gum, it can be seen that the sugars present mostly in chickpea hull gum were galactose and arabinose (19.20% and 14.52, respectively). In the case of CBG the dominant monosaccharide units were xylose and arabinose (46.31 and 32.2% respectively).

Table 1: Physicochemical characteristics of gums from chickpea hull and corn bran

Parameters	CHG	CBG
Protein (%)	2.98	2.28
Fat (%)	2.56	1.98
Ash (%)	2.25	6.21
Moisture (%)	6.5	6.3
Arabinose (%)	14.52	32.2
Xylose (%)	5.29	46.31
Glucose (%)	9.15	5.10
Mannose (%)	2.02	0.7
Galactose (%)	19.20	3.42

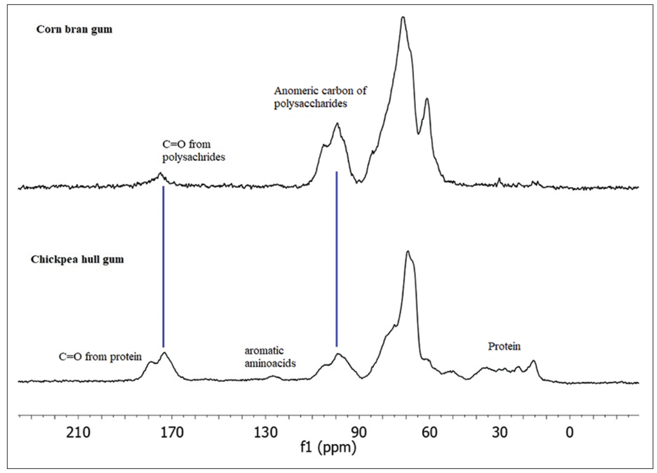

Fig 1. ^{13}C CP/MAS NMR powder profile of chickpea hull and corn bran gums.

NMR analysis is a powerful tool to identify the structure of polysaccharides (Wang et al., 2018). Fig. 1 shows the spectrum which suggests that CHG and CBG are heteropolysaccharides. At 100 ppm, both gums presented anomeric carbon of polysaccharides which indicates that the sugar chain of CHG has 1,4-D-galacturonan with methyl-esterified carboxyl group, Akhtar et al. (2019) reported similar values in chickpea hulls polysaccharides. Corn bran gum showed a prominent signal at 71.2 ppm and chickpea hull at 70.0 ppm, according to Popov et al., (2011) and Akhtar et al. (2019) this is related to C4 of 1,4-D-galactopyranosylurona, and the signal at 61.50 ppm in corn bran gum is related to the methyl carbons of the methyl ester (COOCH3).

Solubility

Fig. 2 shows the solubility of both gums at different time and temperature. Chickpea hull gum (CHG) had its highest solubility (above 50%) at 50 °C and 12 hours of solubility. Corn bran gum showed a solubility over 80% at 3 hours and over 90% at 12 hours at 25 °C and at 50 °C the solubility was above 90% after 6 hours. CBG had a higher solubility percentage with no greater effect of temperature and exposure time. The solubility of arabinoxylan polysaccharides is related to the presence of arabinose throughout the xylan skeleton and according to Niño-Medina et al., (2009), CBG contains 32% of arabinose compared to 13.38% contained in the chickpea hull, which possibly makes CBG more soluble than CHG.

Zeta potential of gums dispersions

According to Dai et al. (2017) the surface charge of the particles determines the forces of attraction and repulsion and plays an important role in the aggregation of the particles. On the other hand, Crispín-Isidro et al. (2019) mention that if the particles in a suspension have a high positive or negative zeta potential, they tend to repel each other and therefore can be considered stable. The Zeta potential values for CBG and CHG dispersions were negative through the studied pH interval. Kamboj and Rana (2014), found that aqueous dispersion of corn fiber gum exhibited negative zeta potential due the presence of -OH and $–COO^{-}$ group. In our work the zeta-potential of the dispersion at pH 2.0 showed values of -0.98 mV

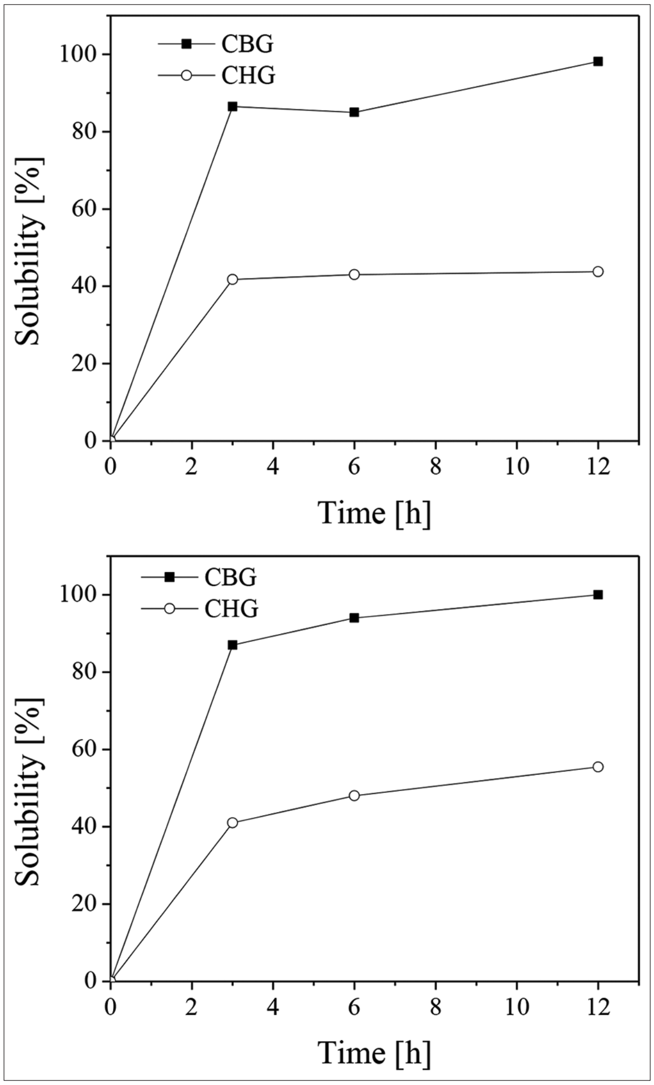

Fig 2. Solubility kinetics of chickpea hull gums (CHG) and corn bran gum (CBG) (a) 25 ° C and (b) 50 ° C.

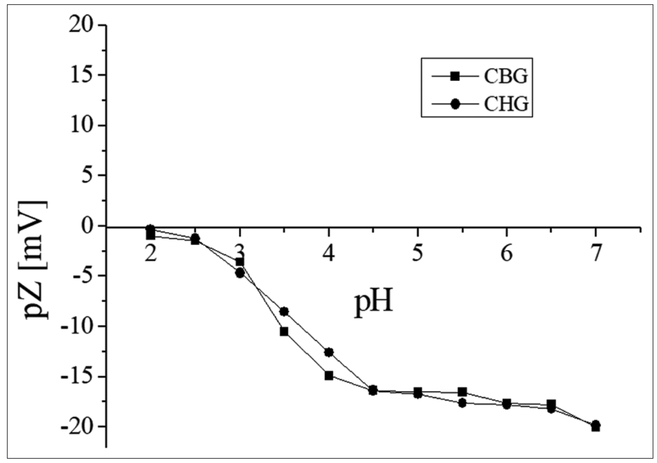

Fig 3. Zeta potential at a different pH (2.0-7.0 in 0.5 of increase) for solutions of 1.0 mg mL^{-1} of corn bran gum (CBG) and chickpea hulls gum (CHG).

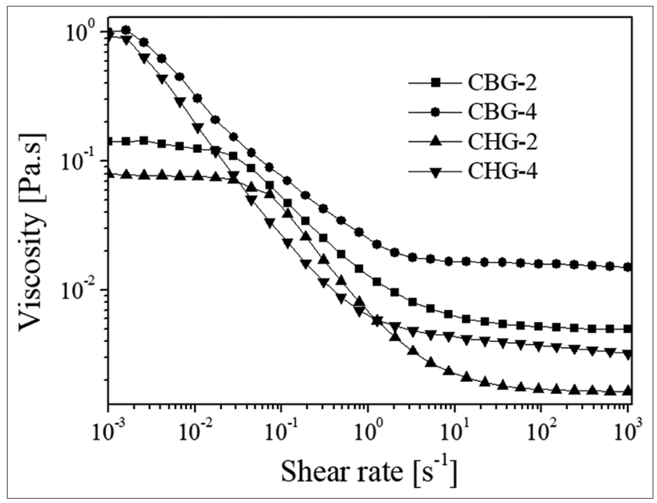

Fig 4. Apparent viscosity pattern for the different gums dispersions.

and -0.33 mV for CBG and CHG respectively, at this pH the dispersions can be considered unstable and could presented a lot of aggregation, at pH 7.0 both, CBG and CHG showed values of -20.0 mV of Z potential (Fig. 3).

Rheological analysis

The apparent viscosity of the corn bran gum (CBG) and the chickpea hull gum (CHG) at concentrations of 2 and 4% is shown in Fig. 4. The samples at 4% showed shear thinning behavior at low shear rates; however, by increasing the shear rate, the samples showed a Newtonian behavior. On the other hand, as can be seen in Fig. 4, the samples at 2% showed Newtonian behavior at very low shear rates, but when the shear rate increased from 10^{-1} s^{-1} to 10^{1} s^{-1} the samples showed a shear thinning behavior followed by Newtonian behavior at shear rates above 10^{1} s^{-1}. Both CBG and CHG at 4% revealed higher solution viscosity than at 2%, indicating that increase the concentration of CBG and CHG samples increased viscosity. The marked thinning behavior at higher concentrations is related to a greater molecular disentanglement with the shear rate.

CBG-2: corn bran gum dispersion 2% (p/p); CBG-4: corn bran gum dispersion 4% (p/p); CHG-2: chickpea hulls gum dispersion 2% (p/p); CHG-4: chickpea hulls gum dispersion 4% (p/p). Different superscripts within the same column indicate that the means differ significantly ($p \leq 0.05$).

Table 2 presents the parameters of the Careeau-Yasuda model that describes the flow behavior of the gums as a function of the shear rate. The viscose relaxation time (λ), is related to the transition point of shear-thickening and shear-thinning, whose reciprocal represents the shear rate at which the transition occurs between the Newtonian and shear-thinning behavior (Anidiobu, 2014), increased according to the concentration of the gum in solution. The increase in the λ values indicates the decrease in the speed of entangling configuration at a higher shear rate, with respect to the consistency index (*N*), if its value is high, the fluid is more viscous. CBG-4 and CHG-4 presented the highest values of consistency index (*N*), indicating that these dispersions were more viscous.

Fig. 5 shows the shear stress-shear rate flow curves of the corn bran gum and the chickpea hull gum at 2 and 4%, respectively. The results of Fig. 4 and 5 show the behavior of the shear stress and the viscosity of the dispersions of the chickpea hull gums and corn bran gums. It can be seen that both the viscosity and the shear stress depend on the shear rate, this dependence is characteristic of a pseudoplastic fluid. The pseudoplastic behavior of chickpea hull and corn bran gums is related to modifications in the organization of the macromolecular structure in the dispersion as the shear rate changes. The rupture of the network due to the applied shear stress causes the molecules to organize in the flow direction and the viscosity decreases when increasing the shear rate.

Dispersions at concentrations of 4% showed higher initial shear stress values than those at low concentrations (2%), indicating that the corn bran and chickpea gum dispersions at 4% formed stronger gel structures with greater resistance to shear forces.

Table 2: Parameters of rheological behavior obtained by the Carreu-Yasuda model

Treatments	λ (S)	N	η0 (Pa.S)
CBG-2	35.2137±3.48[a]	0.2379±0.02[a]	0.1261±0.00[a]
CBG-4	47.4540±0.00[b]	0.3595±0.05[b]	0.7861±0.02[b]
CHG-2	9.6325±0.11[c]	0.2306±0.00[a]	0.0633±0.00[c]
CHG-4	47.4540±0.00[b]	0.3454±0.00[b]	0.7601±0.00[b]

CBG-2: corn bran gum dispersion 2% (p/p); CBG-4: corn bran gum dispersion 4% (p/p); CHG-2: chickpea hulls gum dispersion 2% (p/p); CHG-4: chickpea hulls gum dispersion 4% (p/p). Different superscripts within the same column indicate that the means differ significantly ($p \leq 0.05$).

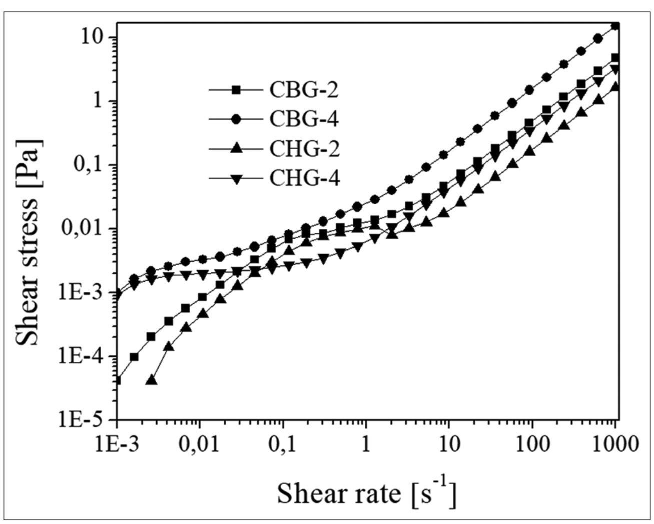

Fig 5. Shear Stress-Shear rate relationship of the gums dispersions at different concentrations.

CONCLUSION

The gums showed differences in the content of protein and ash, being the gum of chickpea hull the one that presented the highest amount of protein and the lowest ash content; however, the gum that presented the best solubility property was corn bran gum. Regarding the behavior of the Z potential of the gums, they presented the same behavior throughout the pH range studied. The rheological behavior of the gum dispersions was affected by the increase in concentration, the concentration being 4% which presented better values of consistency index due to the formation of better structured and stronger gels, presenting greater resistance to shear forces.

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