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Research Article

Effect of Temperature, pH and Concentration of Soluble Solids on the Rheological Behavior and Molecular Mass of Pectin Obtained from Mango Vallenato Shell (*Mangífera indica l.*)

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Abstract: The aim of the study was evaluating the incidence of pectin concentration, soluble solids concentration, extraction temperature and pH in the rheological behavior and molecular mass of a mango vallenato pectin gel. Experimental design was in blocks (mango pectin and commercial) completely random, in factorial arrangement 2^4, for the factors, pectin concentration (0.5-0.25% w/w), temperature (50, 70°C), pH (2.2- 2.8) and solids concentration (55, 65°Brix), with three replicates. Storage modulus (G'), loss modulus (G") and loss tangent (tan δ), determined on the rheometer AR 1500 with parallel plate geometry, were determined. The data were adjusted to the Mark-Houwink-Sakurada model to determine the molecular weight of the pectin gel. Gels with 0.25% of mango pectin showed viscous behavior with little gelling property, the gels prepared with 50% of mango pectin at 55°Brix soluble solids concentration had a structured gel behavior, similar behavior to those of commercial pectin. The molecular mass of the gel prepared with mango pectin was in the range of 583.90 to 24.17 kDa, being significantly affected by the concentration of 0.25% of pectin, the extraction temperature and soluble solids concentration.

Keywords: Complex viscosity, gel, loss modulus, loss tangent, storage modulus, thickener, viscoelasticity

INTRODUCTION

Pectin is used in the food industry as a thickener, texturizer, emulsifier and stabilizer in jellies and marmalades, confectionery, dairy products, fruit preparation, bakery filling, glazed and frosted; fat substitutes in cream spreads, salad dressings, ice creams and emulsified for meat products. In general, commercial pectin solutions behave as pseudo-plastic, which is dependent on the raw material and the extraction conditions (Manohar *et al*., 1990). The viscous properties of pectin solutions are essential in food products, especially in fruit-based products such as fruit juice, jellies and marmalades of fruits because it increases the viscosity giving a better sensation in the mouth and a greater feeling of fruitiness and also sweetness in the final product. Jellies and marmalades, which include pectin in its formulation are viscoelastic solids when the ratio of viscosity to elasticity depends on the degree of esterification of the pectin; the pH condition and the type of pectin used in the process (Javanmard and Evand, 2010).

Pectin is added when looking for changes in the texture or behavior flow of the final product. Adding water to the pectin will give a viscous behavior that can be dispersed in syrups with high sugar content. To rapidly dissolve the pectin can be done under gentle heating (Gigli *et al*., 2009). The esterification degree influences the dissolution; pectins with low esterification dissolve better, where the temperature is one of the most critical parameters that affect the rheological behavior of the food (Rao and Steffe, 1992). The existence of pectin aggregates in solution has been recognized that under non-gelling conditions could be considered as precursors of gelation. The nature of these mixed could provide a basis for understanding if a particular pectin would or would not be an excellent gelling agent (Fishman *et al*., 2000).

Pectin is found in high concentrations in mango pulp, the yield, esterification degree and gel strength of the product depends on the type of material used (variety and process conditions) and the extraction process. Studies show that mango and papaya have a higher content of polyuronic acids than apple and citrus fruits (Iagher *et al*., 2002). Pectin is mainly composed of methyl esters of the galacturonic acid that containing neutral sugars on the sides of the rings distributed in several amounts along the polysaccharide column.

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Gelation mechanism of pectin depends on molecular weight, esterification degree and distribution of methoxy groups (Iagher *et al*., 2002). The molecular weight of the polymers is related to the intrinsic viscosity (η), defined as the measurement of a polymer molecule to increase the viscosity of a solvent in the absence of intermolecular interactions. It is related to the molecular weight equation proposed by Mark-Houwink-Sakurada (MHS) (Kasaai, 2007; Yamakawa, 2001; Rinaudo, 2006):

$$\eta = KM_v^a \qquad (1)$$

where,

Mv = The viscometric average molar mass
K and a = Viscometric constants

Which vary according to the nature of the solvent, temperature and chemical structure of the polymer (Costa *et al*., 2015; Matusinović *et al*., 2005; Moreira *et al*., 2004).

This work aimed to study the incidence of pectin concentration, soluble solids concentrations, extraction temperature and pH in the rheological behavior and molecular mass of a pectin gel of mango vallenato.

MATERIALS AND METHODS

Obtaining pectin and preparation of gel: Pectin was extracted from the mango shells (*Mangífera indica* L.) under standardized conditions (86.5°C, 87.7 min and a pH of 1.9 with HCl) following the methodology of Durán and Villa (2012). The gel samples were prepared at concentrations of mango pectin and commercial pectin according to the experimental design, modifying the pH with citric acid, is heated at a constant temperature for 15 min and adding saccharose until to obtain the desired soluble solids concentration. The soluble solids content was determined by an RX-1000 digital refractometer and the pH with pH-meter digital Crisson Micro-pH 2000.

Rheological measurements: Viscoelastic measurements were performed using the methodology proposed by Tirado *et al*. (2015). Each sample was subjected to an effort sweep test and deformation, the latter was determined in the linear viscoelastic range. The frequency sweep was performed in a variety of 0.1 Hz and 100 Hz. The temperature of the sample was kept at 25±0.1°C. The tests were performed on a rheometer TA AR 1500® TA Instruments LTDA., using a 40 mm plate, controlled by TA Universal Analysis Version 5.2® software, installed in a computer connected to the rheometer. With the oscillatory tests the storage modulus (G '), loss modulus (G ") and loss tangent (tan δ) were determined, as a function of the deformation frequency. All samples were left to stand for 15 min to allow relaxation of the sample, before performing the assay. Rheological data analysis was performed using Rheology Advantage Data Analysis Version 5.7® software.

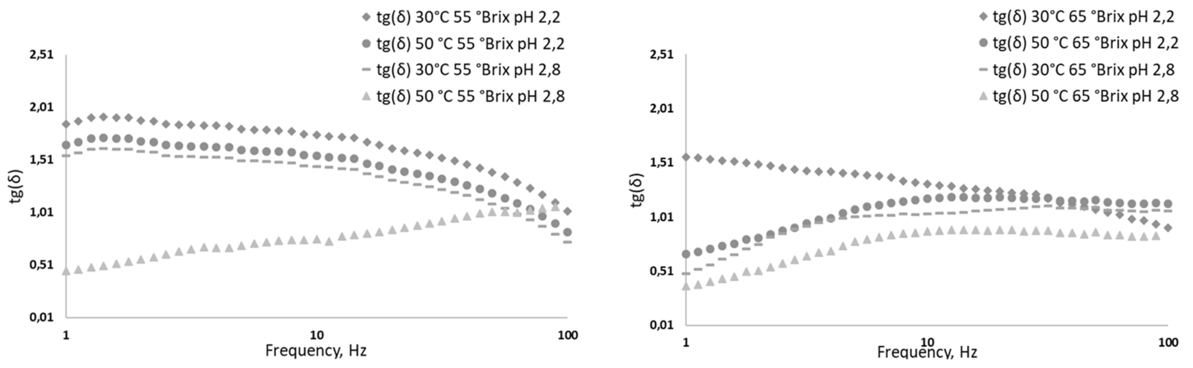
The molecular mass of the gel was determined by the rheological measurements, with the data from storage modulus (G') and loss modulus (G") using Eq. (1), in Rheology Advantage Data Analysis V 5.7® software.

Experimental design and statistical analysis: The experiment was conducted under a completely randomized block experimental design (DBCA) blocking pectin types (mango and commercial), with factorial arrangement of 2^4, for factors, pectin concentration (0.5-0.25% w/w), temperature (50, 70°C), pH (2.2-2.8) and solid concentration (55, 65°Brix), with three replicates. The response variables were storage modulus (G'), loss (G") and loss factor (tan δ). Experimental data of the G' and G" modules were fitted to the Mark-Houwink-Sakurada model to determine the molecular weight of the pectin gel Eq. (1). Statistical criteria of the Standard Error (S.E.) determination coefficient were used for model validation. The molecular mass obtained by equation one were analyzed by an Analysis of Variance (ANOVA) and a Tukey test with a significance level of 5% to determine the influence of pectin concentration, concentrations insoluble solids, extraction temperature and pH in the rheological behavior and molecular mass of a mango vallenato pectin gel. Data processing was performed in the STATGRAPHICS® Centurion XV software.

RESULTS AND DISCUSSION

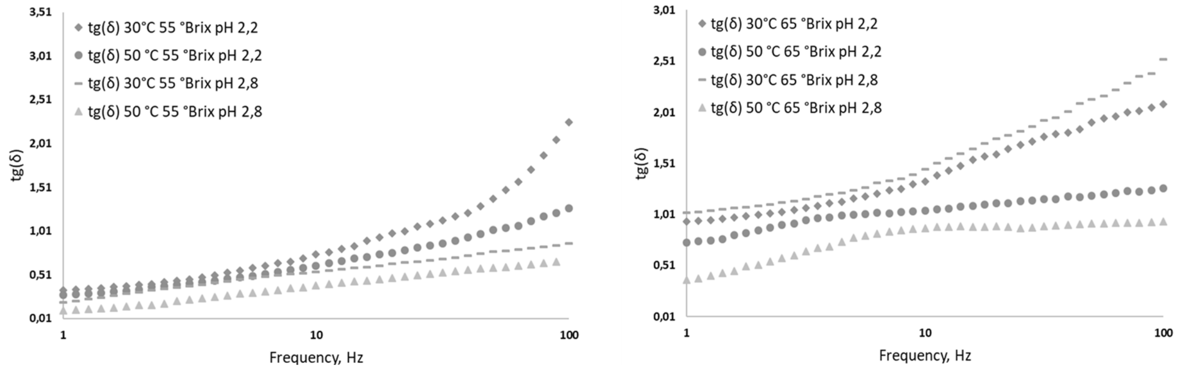
The content of soluble solids significantly affects the rheological behavior of the gel. Gels prepared at pH 2.8 showed a weak gel behavior (Fig. 1a and 1b). The dominant performance in gels made at 0.25% of mango pectin, was viscous (loss factor tan δ greater than 0.9) at different temperatures and pH (Fig. 1a and 1b). However, the concentration of soluble solids of 65°Brix, pH 2.8 and gel extraction temperature of 50°C the elastic behavior is favored (loss factor tan δ less 0.7), although it is negatively affected by the increase in frequency. Similar behavior was reported by Iagher *et al*. (2002).

Gels prepared with 0.25% commercial pectin (Fig. 2) show similar behavior concerning the solids concentration since gels with 65°Brix had a higher elastic modulus than those with 55°Brix. However, the level of soluble solids affected the behavior of the gel differently, because at 55°Brix concentrations the elastic behavior was favored (loss factor tan δ less 0.7). Furthermore, at pH of 2.8, the gel at different temperatures presented a more structured behavior than



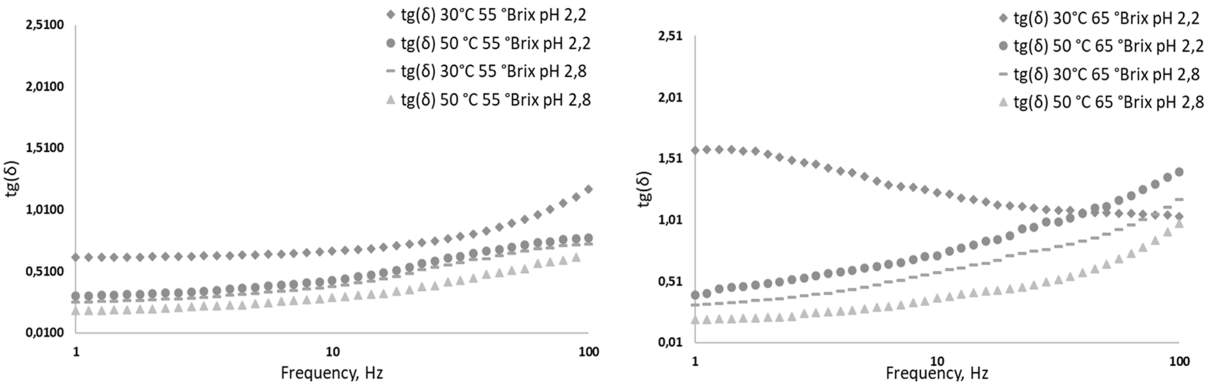
(a) (b)

Fig. 1: Loss factor (tan δ) for gels prepared with 0.25% mango pectin (a) Soluble solids concentration at 55° Brix, (b) Soluble solids concentration at 65° Brix at different pH and temperatures



(a) (b)

Fig. 2: Loss factor (tan δ) for gels prepared with 0.25% commercial pectin (a) Soluble solids concentration at 55° Brix, (b) Soluble solids concentration at 65 ° Brix at different pH and temperatures

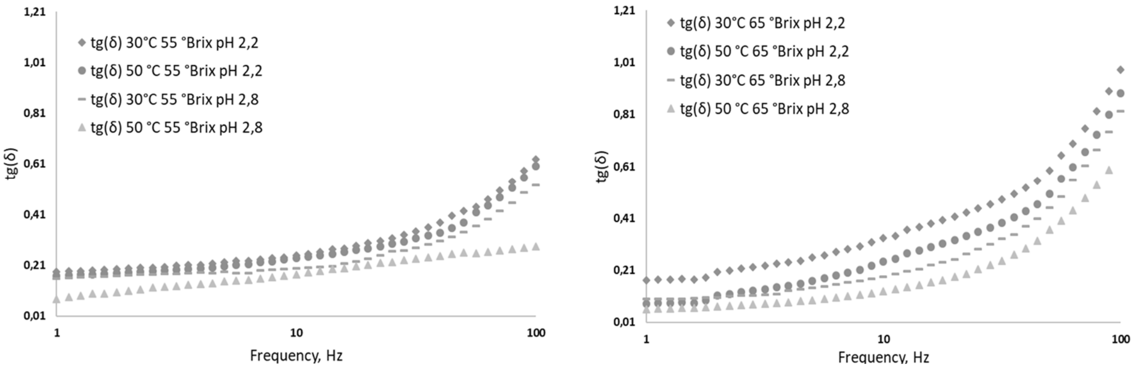


(a) (b)

Fig. 3: Loss factor (tan δ) for gels prepared with 0.50% mango pectin (a) Soluble solids concentration at 55°Brix, (b) Soluble solids concentration at 65°Brix at different pH and temperatures

the mango pectin gel (Fig. 2a and 2b), having the gels prepared with 55% pectin a structure that favors the physical stability of the system. The same behavior was reported by Trujillo-Cayado *et al*. (2013).

Gels prepared with 0.50% mango pectin at pH of 2.8 had a structured gel performance (loss factor tan δ less than 0.5) at frequencies below 70 Hz (Fig. 3a and 3b). Being more elastic the behavior of soluble solids of



(a) (b)

Fig. 4: Loss factor (tan δ) for gels prepared with 0.50% commercial pectin (a) Soluble solids concentration at 55°Brix, (b) Soluble solids concentration at 65°Brix at different pH and temperatures

Table 1: Molecular weight (M) of mango pectin gel at different concentrations, pH and temperature

Conditions	(M, g/mol)
0.25% pectin/55°Brix/2.2pH/30°C	34903
0.25% pectin/55°Brix/2.2pH/30°C	36113
0.25% pectin/55°Brix/2.8pH/30°C	90583
0.25% pectin/55°Brix/2.8pH/50°C	142833
0.25% pectin/65°Brix/2.2pH/30°C	24980
0.25% pectin/65°Brix/2.2pH/50°C	34513
0.25% pectin/65°Brix/2.8pH/30°C	24877
0.25% pectin/65°Brix/2.8pH/50°C	35883
0.50% pectin/55°Brix/2.2pH/30°C	34347
0.50% pectin/55°Brix/2.2pH/50°C	337733
0.50% pectin/55°Brix/2.8pH/30°C	338200
0.50% pectin/55°Brix/2.8pH/50°C	434200
0.50% pectin/65°Brix/2.2pH/30°C	43333
0.50% pectin/65°Brix/2.2pH/50°C	541633
0.50% pectin/65°Brix/2.8pH/30°C	33427
0.50% pectin/65°Brix/2.8pH/50°C	456167

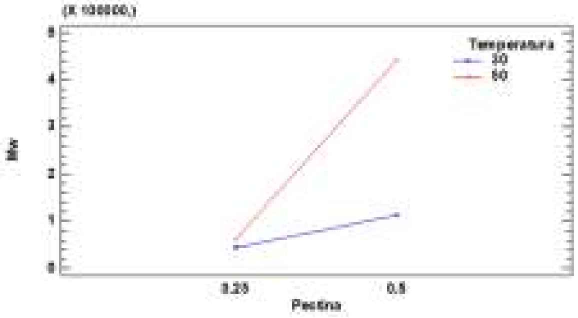


Fig. 5: Interaction of pectin concentration: extraction temperature (significance of 5%) for gels prepared with mango pectin (Tukey's tests for Mw)

55°Brix and an extraction temperature of 50°C (Fig. 3a). However, to this concentration when the temperature is 30°C, the behavior is a weak gel. The level of soluble solids of 65°Brix and pH of 2.2 (Fig. 2b) favored the viscous behavior (loss factor tan δ less than 1.0). This behavior is similar to reported by Lofgren and Hermansson (2007) and is explained by Pagan (1999), who maintains that when the pectin is extracted at a lower pH, the degrees of methoxylation decrease, indicating low gelation. The effect of low pH on the increase in elasticity by improving gelation could be due to the complete ionization of carboxylic groups of galacturonic acid from the opening of the pectin chains which offer better conditions for the interaction of functional groups. Lower pH values could lead to the formation of some non-permanent electrostatic bonds that affect the elastic property in the gel (Mesbahi *et al*., 2005).

Gels prepared with 50% commercial pectin and at 55°Brix soluble solids concentration (Fig. 4a and 4b) show similar behavior to the soluble solids concentration than pectin gels of mango at the same concentration (Fig. 3a). With both pectins structured gels were obtained at pH of 2.2 and extraction temperature of 55°C, however, with the commercial pectin, a gel with greater elastic behavior was obtained, since the gels with 55°Brix had greater elastic modulus (factor of loss tan δ<0.3). The extraction temperature of 65°Brix did not affect the viscoelastic behavior of the gels at pH 2.8, however, if affected when the pH is 2.2.

The molecular mass of the mango pectin was in the range of 583.90 to 24.17 kDa (Table 1). These values are similar to those reported by Kasaai (2008) for Hydroxyethylcellulose Chitosan hydroxypropyl cellulose and Pagan *et al*. (2001) for pectin of the bagasse of peach. The analysis of variance (significance of 5%) to determine the incidence of pectin concentration, temperature of extraction, pH and, level of the soluble solids of the gel on the behavior of the molecular weight; showed that the interactions of these factors have a statistically significant effect on molecular weight of the mango pectin gel (Mw). Also, it can be seen the correlation between molecular weight values and intrinsic viscosities. At higher molecular weight value, higher inherent viscosity value.

In Fig. 5 it can be observed that the gel prepared with 0.5% of mango pectin at an extraction temperature

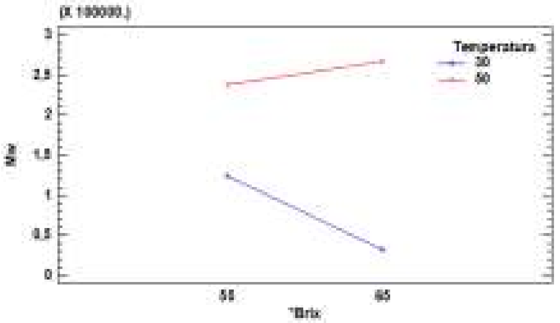


Fig. 6: Soluble solids concentration interaction: extraction temperature (significance of 5%) for gels prepared with mango pectin (Tukey's tests for Mw)

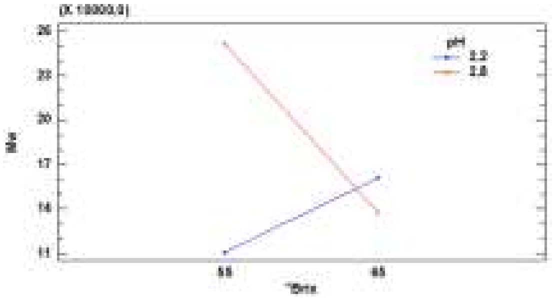


Fig. 7: Soluble solids concentration interaction: pH (significance of 5%) for gels prepared with mango pectin (Tukey's tests for Mw)

of 50°C have higher molecular weight, this agrees with the rheological results, where for these conditions a more top elastic behavior is obtained. However, the extraction temperature does not significantly affect when the gel is made with 0.25% mango pectin. The same behavior is observed with the interaction of soluble solids concentration: Extraction temperature, although at 55°Brix the temperature does significantly affect the molecular weight of the gel (Fig. 6). On the other hand, the molecular weight is influenced by the pH of the gel with 55°Brix of soluble solids (Fig. 7), presenting a higher molecular weight at a pH of 2.8. However, at concentrations of soluble solids of 65°Brix molecular weight is lower for gel prepared at the same pH.

CONCLUSION

Mango pectins showed a viscous behavior with little gelling property when is prepared at a concentration of 0.25% pectin, however, at a pH of 2.8, a weak gel can be obtained at extraction temperatures. That can be used as a thickening agent. Gels prepared with 50% mango pectin at 55°Brix soluble solids concentration presented a behavior of structured gel a similar action that the commercial pectin, at the same soluble solids concentration, favoring the elastic behavior at high pH and high extraction temperatures. The molecular mass of the gel prepared with mango pectin was in the range of 583.90 to 24.17 kDa, being significantly affected by the concentration of 0.25% pectin, extraction temperature and soluble solids concentration.

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