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Dynamic rheological study of *Sterculia striata* and karaya polysaccharides in aqueous solution

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Abstract

Chichá polysaccharide is the dry exudate from *Sterculia striata*, which belongs to the same family of karaya polysaccharide. *S. striata* polysaccharide (SSP) contains (mol%) rhamnose (23.8), galactose (19.3), xylose (7.7), uronic acid (49.2), and acetyl groups (9.6). Dynamic rheological analysis of SSP, deacetylated SSP (DSSP), and karaya polysaccharide (KP) in aqueous solution has been carried out. SSP behaves as a weak gel in the concentration range of 2–4% and as a true gel at higher concentrations. Karaya polysaccharide behaves as a true gel at concentrations higher than 2%, and forms a gel than stronger than that of SSP at the same polysaccharide concentration. The addition of 0.1 M NaCl to both polysaccharides decreases their gel strength, however, more pronouncedly that of the SSP solution. The presence of acetyl groups is necessary to promote interactions between polysaccharide chains, which make gels strong. No sharp conformational transition has been observed for either SSP or KP samples by thermal rheological analysis.

Keywords: *Sterculia striata* polysaccharide; Karaya polysaccharide; Gel; Dynamic rheology; Dynamic viscoelastic measurements

1. Introduction

Polysaccharide hydrocolloids (e.g., carrageenan, alginate, agar–agar, starches, pectins, guar, and karaya polysaccharides) are high molecular weight macromolecules that are easily dissolved and dispersed in water, and under appropriate conditions they can modulate rheological properties. Due to these properties, they are used as food thickeners, stabilizers and emulsifiers (Salazar-Montoya, Ramos-Ramírez, & Delgado-Reyes, 2002).

Karaya polysaccharide is used as a food additive. The Food and Drug Administration of the USA (FDA, 1974) lists 18 acceptable contributing *Sterculia* sp., denoted as karaya polysaccharide. The Food and Agriculture Organisation (FAO, 1991) included *Cochlospermum gossypium* and other species of *Cochlospermum* in this list. Native karaya polysaccharide is a complex, partly acetylated polysaccharide of the substituted rhamnogalacturonoglycan (pectic) type. Its primary structure has been shown to be made up of D-glucuronic acid, D-galacturonic acid, D-galactose, and L-rhamnose in different proportions according to the quality, type, and origin of the polysaccharide (le Cerf, Irinei, & Muller, 1990). The average composition of acetyl-free samples is 60% neutral sugar (rhamnose and galactose) and 40% acidic sugar residues (galacturonic and glucuronic acid) (Stephen & Churms, 1995). Native polysaccharide contains approximately 8% acetyl groups (Meer, 1980).

Chicha polysaccharide is an exudate from *Sterculia striata* trees. HPLC analysis shows that the deacetylated sample contains (mol%) 57.8% neutral sugar (23.4% galactose; 28.8% rhamnose, and 5.6% xylose) and 42.2% uronic acid residues. Acetyl groups account for 10.7% (Brito, Silva, de Paula, & Feitosa, 2004).

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The effect of polysaccharide deacetylation and of the presence of metal ions on melting transition temperature (T_m) obtained by visual observation of gel fluidity onset on heating was investigated by Silva, Brito, de Paula, Feitosa, & Paula, 2003. The presence of acetyl groups in both polysaccharides seems to stabilize the gel. T_m decreases, while the critical gelation concentration (CGC) increases after deacetylation. The authors (Silva et al., 2003) have proposed a gelation model elsewhere. The intermolecular junction zones could occur predominantly through ionic interaction between counterions and either two galacturonic acid residue segments on different main chains or glucuronic acid branching residues. Hydrogen bonding between rhamnose segments may also form junction zones in hydrophobic areas. The interaction between homogalacturonic segments of different chains, such as in the 'egg-box model', is likely to occur, but to a small extent (Silva et al., 2003).

Dynamic rheology is one of the methods most extensively used to study polysaccharide gel viscoelasticity. Chronakis, Doublier, and Piculell (2000) investigated the liquid-like and solid-like behaviour of κ- and ι-carrageenan in NaI. Tako, Tohma, Taira, and Ishihara (2003) reported on the gelation mechanism of deacetylated rhamsan polysaccharide. The effect of saccharose and polysaccharide concentration on viscoelastic properties of tamarind gel has been investigated by Salazar-Montoya et al. (2002). The effects of salt, temperature, molecular structure and acetyl content on the rheological transitions of gellan were reported by several research groups (Mazen, Milas, & Rinaudo, 1999; Morris, Gothard, Hember, Manning, & Robinson, 1996; Rinaudo, 2001; Yuguchi, Urakawa, & Kajiwara, 2002). Iglesias and Lozano (2004) reported on sunflower pectin extraction and gelling mechanism. Rheological features of mango pulp pectin were analyzed by Iagher, Reicher, and Ganter (2002). The influences of pH, calcium ion, temperature, and amidation on the gelation of low-methoxy pectin has been studied recently (Lootens, Capel, Durand, Nicolai, Boulenguer, & Langendorff, 2003; Dobies, Kozak, & Jurga, 2004). le Cerf and Muller (1994) studied the viscoelastic behaviour of a karaya polysaccharide solution and the dependence of gel-like properties on sample age.

This paper reports on the dynamic rheological characterization of aqueous solutions of purified and deacetylated *S. striata* and karaya polysaccharides.

2. Experimental

2.1. Purification method

Crude *S. striata* polysaccharide specimens were collected in February, 2001 from native trees in Fortaleza, Ceará, Brazil. The species was identified by the Prisco Bezerra Herbarium, Fortaleza, Ceará, Brazil, where a voucher sample is kept. The polysaccharide was purified as its sodium salt as previously described (Costa, Rodrigues, & de Paula, 1996). Bark-free nodules were selected and dissolved in distilled water at room temperature to give a 1% (w/v) solution. After adjusting to pH ~ 7.0, the solution was successively filtered with fine and medium sintered glass filters. The polysaccharide precipitated with ethanol (2:1, v/v), was considered to be 'native'. The preparation of Na-purified *S. striata* polysaccharide (SSP) was carried out in two stages. Initially, the native sample (1 g) was dissolved in distilled water (100 ml) at room temperature. Next, pH was adjusted to 7.0, and NaCl (1 g) was added in sequence. The polysaccharide was precipitated with ethanol (200 ml), washed with acetone, and dried with hot air. In order to eliminate excess Na^+, the polymer was finally redissolved in distilled water without the addition of NaCl and precipitated as described above.

Deacetylated *S. striata* polysaccharide (DSSP) was obtained according to the method of Lee, Ashby, and Day (1996). Deacetylation was carried out in 1 M NaOH solution for 20 min at room temperature (~28 °C). The solution pH was adjusted with diluted HCl to slightly above 7.0 before dialysis against deionized water. Deacetylation was monitored by infrared spectroscopy.

Karaya polysaccharide (KP) was obtained from Sigma Co. (specified as *Sterculia* sp.) and purified in Na-form as described for SSP.

2.2. Composition

Total hydrolysis of *S. striata* polysaccharide samples was performed using H_2SO_4 2 M at 100 °C for 8 h. After cooling, the solution was neutralized with $BaCO_3$ and the residue was converted to alditol acetate by successive reduction with $NaBH_4$ and acetylation with Ac_2O-pyridine at room temperature for 12 h. The product was examined by gas liquid chromatography (GLC) using a Varian model 3300 gas chromatograph with a DB-210 capillary column. The total uronic acid content of deacetylated *S. striata* and karaya polysaccharides was determined by conductimetric titration with 0.0221 M NaOH after conversion of carboxylate groups into carboxylic acid by passing the solution through an Amberlite-120 H^+ exchanger column as described by Costa, Rodrigues, & de Paula (1996).

Acetyl content was determined using the methodology described by Bédouet, Courtois, and Courtois (2003) based on ^1H nuclear magnetic resonance. First, ^1H NMR spectrum of *S. striata* polysaccharide solution (10 mg/ml) in D_2O was recorded at 80 °C. To this solution, 0.001 mol of NaOH was added and 256 scans were recorded after dissolution.

2.3. Preparation of dynamic rheological samples

S. striata polysaccharide solutions were prepared in concentrations ranging from 2 to 6% (w/v) for SSP, and from 4 to 5% (w/v) for DSSP by stirring for 2 h at 70 °C and then left to cool to room temperature. All aqueous solutions