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Effects of drying conditions on the rheological properties of reconstituted mucilage solutions (*Opuntia ficus-indica*)

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ABSTRACT

The effects of spray drying conditions on reconstituted mucilage solutions were studied as a function of rheological properties (elastic and viscous properties) and particle size distribution (PSD). Rheological measurements were carried out at 25 °C and at concentrations of 1–6% (w/v) for spray dried and freeze dried samples.

Experimental results showed that the shear viscosity slightly decreased with the increasing of inlet air temperature and atomization speed, and increased with the increasing of the feed flow rate. The Cross model was found to be the most appropriate to fit the flow curves of reconstituted mucilage solutions at concentrations ≥ 3% in spray dried samples; for freeze dried samples the Ostwald-de Waele model was better. The viscous modulus G'' predominated over the elastic modulus G' for the spray dried samples, indicating a liquid-like material. The dynamic response and steady-shear measurements suggested a "random coil configuration". The majority of the powdered samples had a mean particle diameter > 100 µm with a multimodal particle size distribution (PSD).

1. Introduction

The mucilage from *Opuntia ficus-indica* (*Ofi*) is a hetero-polysaccharide of high molecular weight (2.3×10^4–3×10^6) with important functional properties: rheological, medicinal, and nutritional (Cárdenas, Higuera-Ciapara, & Goycoolea, 1997; León-Martínez, Méndez-Lagunas, & Rodríguez-Ramírez, 2010; Medina-Torres, Brito-De La Fuente, Torrestiana-Sánchez, & Katthain, 2000; Sáenz, Sepúlveda, & Matsuhiro, 2004). It is distributed in the different parts of plant, in the cladodes and the fruit (peel and pulp), therefore extraction and purification methods depend on the origin of the mucilage.

Physicochemical and rheological properties of mucilage gum extracted from *Opuntia* spp. have been studied by several research groups (Cárdenas et al., 1997; Majdoub et al., 2001; Medina-Torres et al., 2000; Trachtenberg & Mayer, 1982). In general, the carbohydrate composition in mucilage contains varying proportions of L-arabinose, D-galactose, L-rhamnose, and D-xylose as the major neutral sugar units as well as D-galacturonic acid.

Ofi mucilage can be considered as a potential source of industrial hydrocolloid (Sáenz et al., 2004). The hydrocolloids are widely used in the food industry as emulsifiers, stabilizers and thickeners. *Ofi* extract is also used in other applications, such as in the construction materials industry, where it is used as a natural viscosity modifier in mortars, and as an adhesive for lime [$Ca(OH)_2$] (Cárdenas et al., 1997; Torres-Acosta & Cano-Barrita, 2007). Others studies have used mucilage as a natural coagulant for water treatment (Miller, Fugate, Craver, Smith, & Zimmerman, 2008).

Fresh mucilage is susceptible to microbial attack due to its high water activity (>0.8) and composition, reducing its shelf life to a few days (2–3) at a temperature of 25 °C (León-Martínez et al., 2010). Therefore, it is necessary to extend the shelf life of this substance by multiple preservation process.

Dehydration by spray drying is a valuable technique for water evaporation, using hot air to stabilize liquid solutions and suspensions, with the objective of producing light and porous powders (Berk, 2009, chap. 22). Spray drying is a phenomenon of surface water evaporation maintained by the movement of capillary water from the interior to the surface of the droplet (Schuck, 2009). It is 30–50 times less expensive than freeze drying (Oomah & Mazza, 2001).

The rheological properties of spray dried biopolymers have been studied by some research groups. In general, the spray drying method produces significant changes in the rheological properties of the materials studied, in materials with carbohydrate composition (gum, mucilage, pectins, etc.). The apparent viscosity and

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Nomenclature

η	shear viscosity, Pa s
$\dot{\gamma}$	shear rate, s^{-1}
σ_{12}	shear stress, Pa
k	consistency index, Pa s^n
n	fluid behavior index in Ostwald de-Waele model, dimensionless
η_0	asymptotic viscosity at low shear rate, Pa s
η_∞	asymptotic viscosity at high shear rate, Pa s
K	Cross constant, s
m	flow index in Cross equation ($m = 1 - n$), dimensionless
N_1	primary normal stress difference, Pa
G'	storage modulus, Pa
G''	loss modulus, Pa
ω	angular frequency, rad/s
λ	characteristic relaxation time, s
G^*	complex modulus, Pa s
η'	dynamic viscosity, Pa s
η''	out of phase component of the complex viscosity, Pa s
η^*	complex viscosity, Pa s
R^2	coefficient of determination, dimensionless
SE	standard error
T_i	inlet air temperature, °C
S_a	atomizer speed, rpm
F	feed flow rate, L/h

shear-thinning behavior were less pronounced, this an inverse relationship (Abu-Jdayil, Banat, Jumah, Al-Asheh, & Hammad, 2004; Oomah & Mazza, 2001; Salvador, Sanz, & Fiszman, 2001; Wang, Wang, Li, Xue, & Mao, 2009; Wang, Li, Wang, Li, & Adhikari, 2010).

The rheological and physicochemical properties of hydrocolloid gums are sensitive to preparation methods and may be significantly altered by the drying processes (Wang et al., 2010). Rheological properties are sensitive to variations in molecular structure, and are useful in developing structure–function relationships for systems of polysaccharide solutions and intermolecular interactions, as the gelling property of the gum polysaccharide depends upon the rheology of its solution (Vinod, Sashidhar, Sarma, & Vijaya-Saradhi, 2008). Rheological properties are also important in quality control, storage and processing of foods, stability measurements, and in predicting texture (Abu-Jdayil et al., 2004).

These characteristics depend on drying parameters (type of tower spray drier, nozzles/wheels, pressure, agglomeration and thermodynamic conditions of the air, such as temperature, relative humidity and velocity) and the characteristics of the concentrate before spraying (composition/physicochemical characteristics, viscosity, thermo-sensitivity and availability of water) (Schuck, 2009). The effects of the drying conditions on some physicochemical properties (apparent viscosity, bulk density, yield, moisture content, glass transition temperature, and particle morphology) have been investigated for spray dried *Ofi* mucilage (León-Martínez et al., 2010; Orozco, Díaz, & García, 2007).

However, the rheological properties of reconstituted solutions from *Ofi* mucilage have not been sufficiently examined and the effects of drying parameters on these properties are unknown. Consequently, the objectives of this study were to evaluate the effect of processing parameters, specifically inlet air temperature, atomizer speed, and feed flow rate, on the rheological properties (elastic and viscous) of reconstituted powders. Additionally, the particle size distribution (PSD) of the powders was considered. A lyophilized sample was used as control.

Table 1
Factorial design with three central points.

Treatment	T_i (°C)	S_a (rpm)	F (L/h)
1	130	21,000	2.30
2	170	21,000	2.30
3	130	24,000	2.30
4	170	24,000	2.30
5	130	21,000	3.30
6	170	21,000	3.30
7	130	24,000	3.30
8	170	24,000	3.30
9	150	22,500	2.80
10	150	22,500	2.80
11	150	22,500	2.80

An in-depth and complete understanding of the rheological properties of this powder is essential in optimizing the drying process in terms of functionality and cost (Kurozawa, Morassi, Park, & Hubinger, 2009). Studying the effect of operating parameters on the rheological properties of powder helps identify the optimum operating conditions of spray dryers and their effect on powder characteristics.

2. Materials and methods

2.1. Plant material

Cladodes with a mean age of 13 months were harvested from a local farm ("Rancho Tlapanochestli" Santa María Coyotepec, Oaxaca, Mexico). Cladodes with a moisture content of 91% wet basis were washed with water to eliminate spines from the skin. The isolation and purification techniques of the mucilage solution have been reported previously by León-Martínez et al. (2010).

2.2. Spray drying

A Mobile Minor concurrent flow spray dryer (Niro, Copenhagen, Denmark), equipped with a rotating atomizer nozzle (TS-Minor, M02/A) was used to dry the mucilage solution. A 2^3 factorial design with three central points was used to evaluate the effect of the following independent variables on the rheological properties of the reconstituted powders: inlet air temperature (130–170 °C), feed flow rate (2.3–3.3 L/h) and atomizer speed (21,000–24,000 rpm). This design had already been used in previous works; the treatments presented in Table 1 were selected based on the results of those works (León-Martínez et al., 2010).

2.3. Freeze drying

1000 mL of a mucilage solution with 3° Brix was frozen at −50 °C and freeze dried (LABCONCO-FreeZone, U.S.A.). The drying was conducted at 0.04 mbar of vacuum with a drying temperature programmed from −30 to 25 °C. The total time taken to dry the material was 72 h.

2.4. Reconstituted mucilage solutions

The mucilage powders (spray dried mucilage ⟨SDM⟩ and freeze dried mucilage ⟨FDM⟩) were scattered using a magnetic stirrer (Thermo Scientific, Telesystem 15) at 500 rpm and at 24 ± 1 °C during 90 min. Deionized water (pH ∼ 6–7) was used to dissolve the powders in order to achieve the required concentrations of 1%, 3%, and 6% (w/v). The pH of the mucilage reconstituted solution was determined directly by potentiometric measurement at 25 °C (32.010, AOAC, 1984).

2.5. Rheological measurements

All the rheological measurements were performed in a controlled stress rheometer (AR-2000 TA Instrument, U.K.) using a concentric cylinder geometry (diameter of internal cylinder = 20.38 mm; diameter of external cylinder = 21.96 mm; height = 59.50 mm). A constant temperature of 25 ± 0.1 °C was maintained during the measurement using a circulatory water bath (Haake-F3T, Germany).

2.5.1. Steady-shear viscosity measurements

Shear viscosity measurements were studied as a function of increasing shear rate $\eta(\dot{\gamma})$ over the range 0.3–300 s^{-1}.

The experimental data of reconstituted mucilage solutions were analyzed using the models of Ostwald-de Waele and Cross.

The Ostwald-de Waele model is expressed by:

$$\eta = k\dot{\gamma}^{n-1} \quad (1)$$

where η is the shear viscosity (Pa s), $\dot{\gamma}$ is the shear rate (s^{-1}), k is the consistency index (Pa s^n), and n is the fluid behavior index (dimensionless).

The Cross model is expressed by:

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{1 + (K\dot{\gamma})^m} \quad \text{Equivalently as : } (K\dot{\gamma})^m = \frac{\eta_0 - \eta_\infty}{\eta - \eta_\infty} \quad (2)$$

where η is the shear viscosity (Pa s), $\dot{\gamma}$ is the shear rate (s^{-1}), K is the Cross constant (s), m is the flow index (dimensionless), and η_∞ and η_0 are the asymptotic viscosities at high and low shear rates in Pa s, respectively (Kirkwood & Ward, 2008).

2.5.2. Viscoelastic measurement

The viscoelastic properties, storage modulus (G') and loss modulus (G'') were determined though small amplitude oscillatory shear flows at frequencies ranging from 1 to 600 rad/s. Prior to any dynamic experiments, a strain sweep test at a constant frequency of 10 rad/s was performed fixing the upper limit of the linear viscoelastic zone at a strain value of 20%. Thus, this strain level was used in all dynamic tests.

All rheological measurements were carried out in duplicate. The experimental rheological data were obtained directly from the TA Rheology Advantage Data Analysis software V.5.5.0 (TA Instrument Ltd., Crwaley, U.K.).

2.6. Powder size distribution of mucilage powders

Particle size distributions (PSD) of the reconstituted mucilage solutions (6%, w/v) were quantified using a Mastersizer-2000 laser diffraction particle analyzer (Malvern Instrument Ltd., U.K.). Mucilage powder samples (R.I. = 1.334) were dispersed in deionized water (R.I. = 1.33 and absorption value = 0.1) using mechanic stirring at 500 rpm for 1 h at 25 °C. Subsequently, the samples were hydrated for a minimum of 24 h before being submitted to analysis.

3. Results and discussions

3.1. Flow behavior

Typical flow curves of reconstituted mucilage solutions of different concentrations are shown in Fig. 1. For all figures, model fits are presented as continuous lines.

In this figure, the rheological behavior of solutions reconstituted from spray dried mucilage (SDM-9) obtained at drying conditions of the central point (treatment 9) are exhibited and compared with solutions reconstituted from freeze dried mucilage (FDM). It is evident that the shear viscosity of SDM-9 is lower than that of FDM.

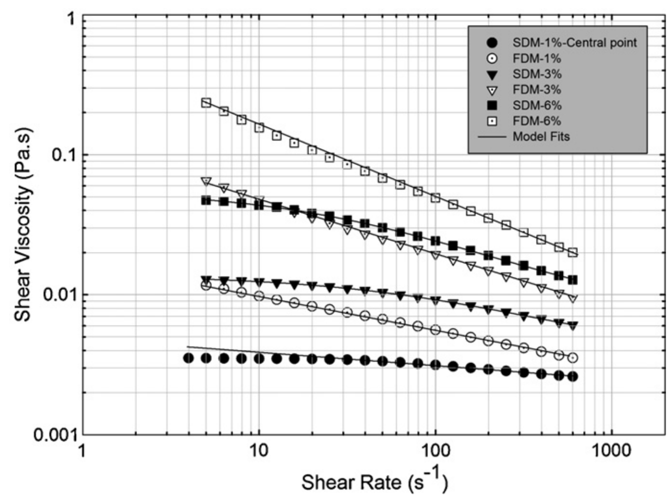

Fig. 1. Experimental flow curves at 25 °C for SDM and FDM at concentrations of 1%, 3%, and 6% (w/v). SDM-9 corresponds to the spray drying conditions of the central point (treatment 9) and FDM is lyophilized mucilage.

This behavior agrees according to that reported for other spray dried products, i.e. flaxseed gum, and reconstituted tomato solutions (Abu-Jdayil et al., 2004; Morris, Cutler, Ross-Murphy, & Rees, 1981; Wang et al., 2009). Freeze drying as drying method most likely causes less damage in biopolymer structure than spray drying, resulting in a higher water retaining capacity (Sanz, Salvador, Jiménez, & Fiszman, 2008).

The parameters of the rheological models are shown in Tables 2 and 3, for Ostwald-de Waele and Cross, respectively.

In all the SDM, rheological behaviors conformed to essentially the same profile (non-Newtonian), and differed only in the values of the parameters of the rheological model used. In general, all reconstituted mucilage solutions at different levels of concentration exhibited non-Newtonian "shear-thinning" behavior. Shear-thinning behavior is attributed to the presence of high molecular weight materials (Barnes, 2000; Morris et al., 1981). This is the result of an orientation effect. As shear rate is increased, the long chain of polymer molecules and randomly positioned chains become increasingly aligned in the direction of flow resulting in less interaction between adjacent polymer chains (Koocheki, Mortazavi, Shahidi, Razavi, & Taherian, 2009). It is characteristic in biopolymer as such pectins, gums, cellulose, carrageenan, and

Table 2
Ostwald-de Waele model parameters for reconstituted mucilage solutions at 25 °C.

Treatment	Concentration % (w/v)	Model parameters: n	k (Pa s^n)	R^2	SE	pH
1	1	0.9006	0.00495	0.912	2.285	5.38
2	1	0.8981	0.00464	0.872	2.581	5.24
3	1	0.9000	0.00489	0.861	3.055	5.33
4	1	0.9278	0.00327	0.911	0.808	5.44
5[a]	1	–	–	–	–	–
6	1	0.8962	0.00519	0.899	2.575	5.43
7	1	0.8900	0.00529	0.895	2.844	5.13
8	1	0.8940	0.00461	0.869	3.428	5.25
9	1	0.9048	0.00489	0.881	3.752	5.30
10	1	0.8980	0.00499	0.895	2.400	5.25
11	1	0.8959	0.00503	0.885	2.659	5.28
FDM	1	0.7436	0.01818	0.999	1.249	5.38
FDM	3	0.6108	0.11630	0.997	3.634	5.15
FDM	6	0.5031	0.48510	0.997	4.813	5.10

–: FDM refers to freeze dried mucilage.
[a] No data available.

Table 3
Cross model parameters for reconstituted mucilage solutions at 25 °C and at concentrations of 3% and 6% (w/v).

Treatment	Model parameters						
	m	η_0	η_∞	K	R^2	SE	pH
3% (w/v)							
1	0.7143	0.0117	0.0031	0.0048	0.999	2.664	5.21
2	0.4592	0.0168	0.0013	0.0107	0.999	3.160	5.19
3	0.7541	0.0125	0.0032	0.0047	0.999	8.644	5.20
4	0.5734	0.0103	0.0012	0.0029	0.999	5.320	5.23
5[a]	–	–	–	–	–	–	–
6	0.7802	0.0135	0.0038	0.0070	0.999	4.004	5.33
7	0.4392	0.0175	0.0000	0.0062	0.991	15.04	5.06
8	0.8275	0.0114	0.0033	0.0044	0.994	4.275	5.20
9	0.7048	0.0132	0.0033	0.0070	0.999	1.436	5.11
10	0.7122	0.0132	0.0033	0.0066	0.999	1.938	5.15
11	0.7997	0.0126	0.0036	0.0070	0.999	3.302	5.22
6% (w/v)							
1	0.6368	0.0538	0.0044	0.0183	0.999	1.052	5.02
2	0.5613	0.0761	0.0026	0.0416	0.999	2.823	5.11
3	0.6608	0.0537	0.0047	0.0197	0.999	1.255	5.10
4	0.4172	0.0625	0.0000	0.0589	0.999	3.824	5.20
5[a]	–	–	–	–	–	–	–
6	0.6876	0.0631	0.0053	0.0241	0.999	4.309	5.29
7	0.6297	0.0422	0.0033	0.0128	0.998	19.33	4.87
8	0.7099	0.0566	0.0054	0.0178	0.999	3.077	5.02
9	0.6791	0.0576	0.0053	0.0230	0.999	3.370	5.19
10	0.6938	0.0559	0.0047	0.0193	0.999	2.095	5.06
11	0.6302	0.0619	0.0040	0.0255	0.999	1.277	5.13

[a] No data available.

starch (Abu-Jdayil et al., 2004; Barnes, 2000; Koocheki et al., 2009; Wang et al., 2008, 2009, 2010).

Non-Newtonian behavior in mucilage gum solutions has been observed by other research groups (Cárdenas et al., 1997; Medina-Torres et al., 2000; Trachtenberg & Mayer, 1982). They found an increase in pseudoplasticity corresponding to an increase in the mucilage concentration, as well a marked dependence of viscosity on the ionic strength and pH. This is due to the fact that mucilage is a polyelectrolyte molecule.

The drying method affected the value of rheological parameters of the models used. The FDM at 1% (w/v) had significantly greater values of consistency index (k = 0.018 Pa s^n) for the Ostwald-de Waele parameters than did SDM ($k \sim 0.005$ Pa s^n). The fluid behavior index for FDM samples (n = 0.74) was less than for SDM samples ($n \sim 0.89$), indicating that FDM has a more pronounced shear-thinning behavior than SDM. The consistency index values (k > 0.025 Pa s^n) reported by Orozco et al. (2007) for spray dried mucilage were higher than those obtained in this study, while values of n were <0.6 for mucilage solutions at 1% concentration. These results indicate that the rheological properties of mucilage depend on the dryer type (laboratory or pilot scale), as well on the drying conditions. The principal factors that may affect the molecular structure of mucilage are the sprayer (pneumatic nozzle atomizer and rotary atomizer) and the residence times; these factors were not homogenous for two.

The low values for the viscous properties of the SDM may be attributed to thermal degradation of the polysaccharides present in *Ofi* mucilage. Both the high drying temperature and the acidic pH (<6) of fresh mucilage in the feed could cause partial hydrolysis of the biopolymer, thus generating smaller molecules of the original polymer. Similar results have been reported in reconstituted mucilage of tomato and flaxseed gum (Abu-Jdayil et al., 2004; Wang et al., 2009).

The fits of Ostwald-de Waele model for diluted concentrations at 1% (w/v) were better than for higher concentrations in SDM. At higher mucilage concentrations, the Cross model gave the best fit, due to the presence of the Newtonian plateau (see Fig. 1).

The values of η_0 for reconstituted mucilage solutions are higher at 6% than at 3% concentration (see Table 3). Similarly, the K values indicative of the time needed for chains to disentangle increase as concentration rise.

With an increased concentration in the solution, a transient entanglement network arises where polysaccharide molecules entangle and disentangle after a period time (Barnes, 2000). This network is stabilized by the intermolecular associations of hydrogen bonding and non-covalent interactions (Van der Waals forces, electrostatic forces). At high mucilage concentrations and low shear rates, the entanglements make flow more difficult; hence the higher η_0 values (Fig. 1). At very high shear rates, the entanglements disappear as the flow 'combs' them out; dependence on molecular weight disappears, and viscosity is only dependent on concentration (Barnes, 2000).

The increase in mucilage concentration had an important effect on the Cross model constant "m". This exponent is related to

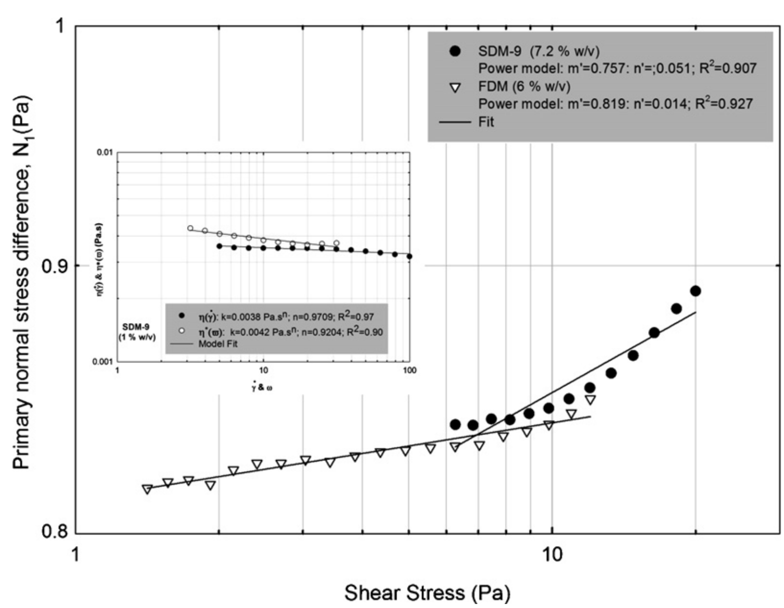

Fig. 2. Primary normal stress difference as a function of shear stress for reconstituted solutions of SDM-9 (7.2%, w/v) and FDM (6%, w/v). The inset graph shows the comparison between complex and apparent viscosities for SDM-9 at 1% (w/v). All data were obtained at 25 °C.

shear-thinning behavior; more Newtonian liquids have values of m tending to zero, while most shear-thinning liquids have m values tending to unity (Barnes, 2000). In general, m decreased with an increase in the concentration of mucilage powder in the solution (0.82–0.41). This parameter's response could explain the partial destruction of the microstructure of the mucilage polymer as a result of the spray drying process, and the presence of the Newtonian plateau.

Elastic flow properties are important due to the multiples industrial applications of mucilage (Medina-Torres et al., 2000). In order to evaluate the elastic properties of mucilage in steady flow, the primary normal stress difference (N_1) as a function of shear stress was compared for SDM-9 and FDM at different concentrations (Fig. 2). The normal stress difference is zero for liquids that are isotropic; however, $N_1 > 0$ for polymeric liquids, due to anisotropy in the orientation of the constituent polymers in flow (Barnes, 2000). As can be seen in Fig. 2, SDM-9 at concentrations greater than 7% (w/v) displays important elastic flow properties. It can be observed in this figure that N_1 increases as shear stress (σ_{12}) increases. The results for elasticity in steady flow were fit to the Power Law model (Medina-Torres et al., 2000) and the calculated parameters are presented in the same figure. A non-linear dependence of N_1 as a function of shear stress ($n' > 0$) was observed in both sample types. For SDM-9, R^2 was less than for FDM. This may be due to the fact that SDM displays two behaviors: one which is pseudo-lineal at lower σ_{12}, where N_1 does not change with shear stress (<10 Pa), and one which is non-linear at higher σ_{12}; where N_1 changes potentially with shear stress (<10 Pa).

The inset graph in Fig. 2 shows the data analyzed using the Cox–Merz "rule" for SDM obtained under treatment 1 at a concentration of 1% (w/v). The Cox–Merz rule Eq. (3) is an empirical relationship that has been found to be of great use in rheology (Miranda, Partal, Cordobes, & Guerreo, 2002; Resch, Daubert, & Foegeding, 2004). The principle use is to predict shear viscosity from oscillatory measurements and vice versa. The frequency dependence of complex viscosity $\eta^*(\omega)$ was fitted with the Power Law parameters, $k-n$, as described in Eq. (4) (Resch et al., 2004). The results of the fits are presented in the same figure.

$$|\eta^*(\omega)|_{\omega\to 0} = |\eta(\dot{\gamma})|_{\dot{\gamma}\to 0} \quad (3)$$

$$\eta^* = k\omega^{n-1} \quad (4)$$

As can be seen in the inset graph in Fig. 2, the magnitudes of $\eta^*(\omega)$ were higher than those of $\eta(\dot{\gamma})$, and both curves were nearly parallel to each other. The values for k and n were almost an order of magnitude less in the fit for $\eta(\dot{\gamma})$. This demonstrates a failure of these materials to adhere to the Cox–Merz rule. In general, $\eta^*(\omega)$ is higher than $\eta(\dot{\gamma})$ due to the fact that oscillatory measurements offer a nearly non-destructive measuring method (Miranda et al., 2002; Resch et al., 2004; Wang et al., 2008). Therefore the Cox–Merz rule did not hold for this material. The failure in the superposition procedure for both steady flow and linear viscoelasticity data could be attributed to microstructural change in the biopolymer due to applied strain.

The drying conditions marked as treatment 5 gave the lowest yield (data not shown). Under these drying conditions, mucilage adhered to the wall of the dryer. Rheological measurements were not possible for this treatment due to limited powder production (León-Martínez et al., 2010).

3.2. Effects of the drying conditions on the shear viscosity

Both inlet temperature and atomizer speed showed an inverse effect on shear viscosity (Fig. 3). An increase in these variables slightly reduced the viscous response. The SDM at higher inlet temperature and higher atomizer speed had minor viscosity and shear-thinning behavior. It is worth mentioning that high inlet air temperature can affect the biopolymer state (glassy or rubbery state), as well induce a thermal degradation of the molecular structure (Wang et al., 2009, 2010).

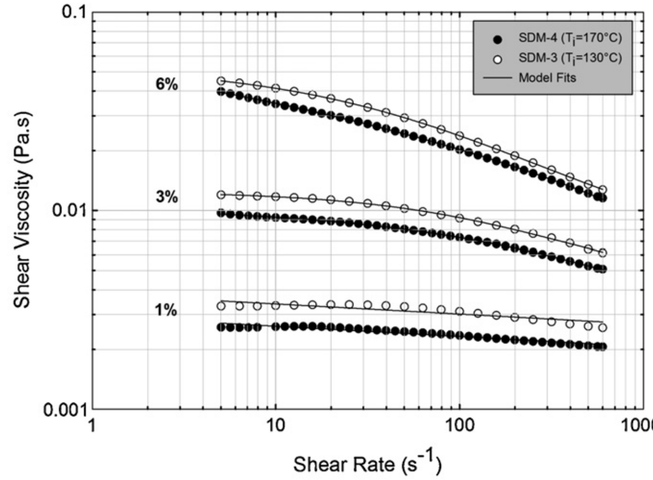

Fig. 3. Effect of inlet temperature on $\eta(\dot{\gamma})$ for mucilage solutions at different concentrations. Measurements were taken at 25 °C.

With regards to feed flow rate, an increase (data not shown) produced powder with higher viscosity than that of spray dried samples at dried at lower feed flow rates. This behavior can be attributed to the drop size generated in atomization. This drop size directly affects the process of mass and heat transfer. Drop size is directly affected by feed flow rates and inversely affected by the atomizer speed (Masters, 1991). Uniformity of drop size is important for even drying and for producing a powder with uniform PSD. Larger particles have a larger water film, and evaporation is consequently slower, resulting in a lesser degree of thermal shock.

3.3. Viscoelastic properties

Typical oscillatory flow curves as shown in Fig. 4 as a function of mucilage concentrations dissolved in deionized water at 25 °C. As can be observed, both the dynamic storage modulus G', and the loss modulus G'' show a dependency on frequency, which proportionally increases as mucilage concentration increases. The spectrum observed is typical of "random-coil" polysaccharide solu-

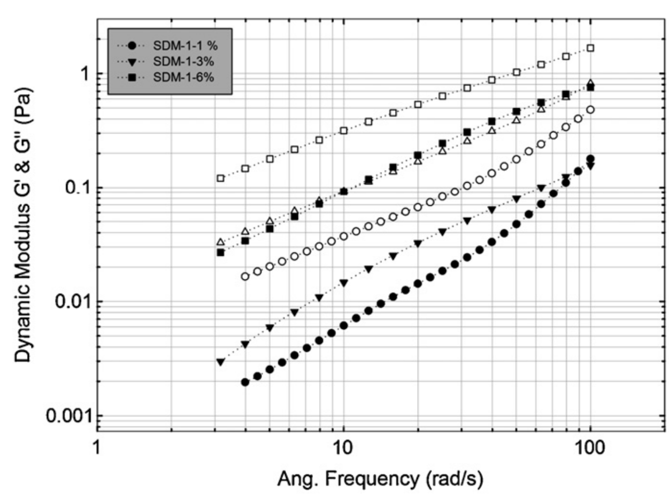

Fig. 4. Frequency dependence of elastic G' (solid black symbols) and viscous G'' (outlined symbols) modulus for different concentrations of mucilage solutions reconstituted in deionized water (SDM-1). Measurements were taken at 25 °C.

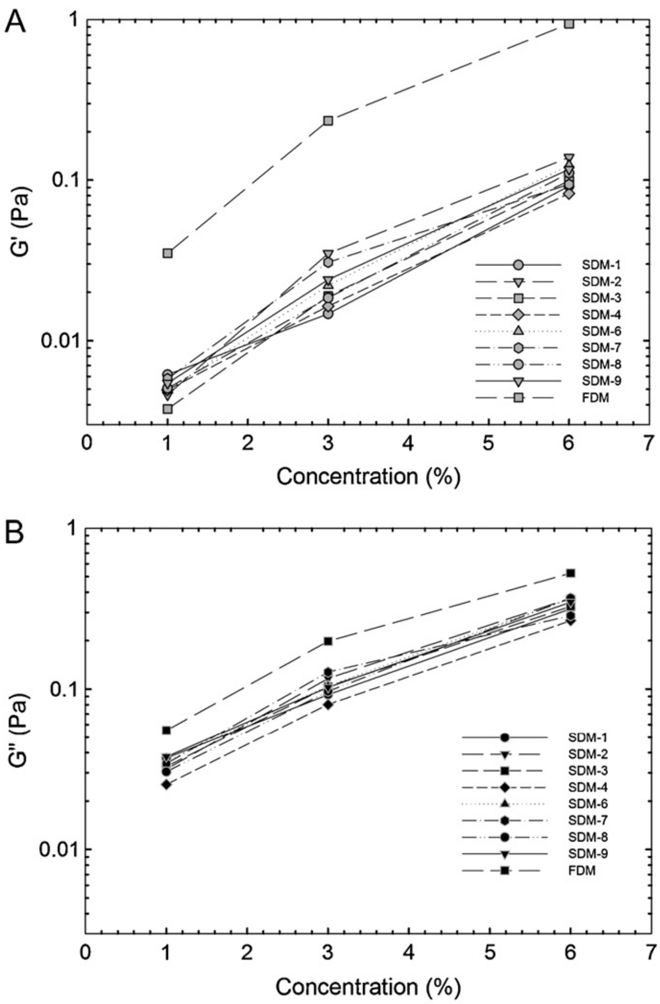

Fig. 5. Effect of mucilage concentration on viscoelastic properties (G' & G'') at 25 °C and ω = 10 rad/s. [A] is the storage modulus; [B] is the loss modulus.

tions. The frequency dependence of the viscoelastic modulus (G' and G'') was observed for mucilage gum solutions by other groups; this is characteristic in entangled networks of disordered polymer coils (Cárdenas et al., 1997; Medina-Torres et al., 2000).

For all the concentrations studied, a predominantly viscous behavior ($G'' > G'$) was observed in spray dried reconstituted mucilage solutions throughout the frequency range studied; the behavior of the samples was not that of a gel-like material, but rather that of a liquid-like material (Fig. 5).

In the freeze-dried samples, a predominantly elastic behavior ($G' > G''$) was observed for concentration > 3% (w/v) (data not shown). This result agrees with those obtained by Medina-Torres et al. (2000) for mucilage gum solutions; they reported an elastic response of mucilage aqueous solutions similar to synthetic polymers like polyisobutylene.

The Weissenberg effect for powdered mucilage obtained at the drying conditions of the central point (SDM-9) was observed at a concentration of 7.2% (w/v) in the reconstituted solution (Fig. 6). It indicates a clear tendency to form macromolecular networks with important elastic properties over long times (low frequency). The crossover frequency or characteristic relaxation time for this SDM was observed to be ~8 rad/s (λ = 0.785 s) and FDM at 3% was observed to be ~30 rad/s (λ = 0.209 s). The crossover frequency for mucilage gum in solution at 5% and 35 °C was observed to be ~10 rad/s (λ = 0.628 s) (Medina-Torres et al., 2000), in Lambda carrageenan at 5% this was 4 rad/s (1.570 s). Crossover frequency

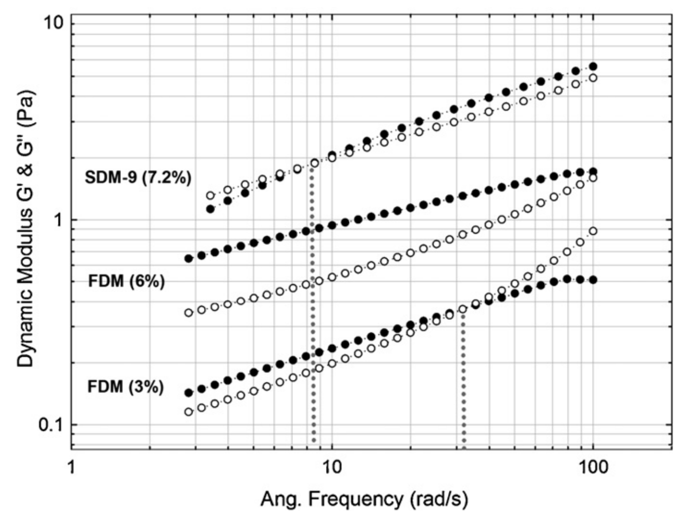

Fig. 6. Crossover point frequency ($G' = G''$) of mucilage solutions reconstituted in deionized water at 25 °C. The spray dried sample (SDM) was obtained under drying conditions of the central point (treatment 9), and FDM is the freeze dried mucilage. The solid black circles are G', and the outlined circles are G''.

($G' = G''$), can be a useful criterion for product evaluation (Steffe, 1996).

The effects of drying conditions on viscoelastic properties were similar to those found for shear viscosity (data not shown). The storage modulus G' was the response most affected by spray drying process. The high temperature induced thermal degradation of the polysaccharide (Wang et al., 2009, 2010).

3.4. Particle size distribution

Fig. 7 shows the particle size distribution for the reconstituted mucilage solutions (freeze drying and spray drying). The FDM had a mean particle diameter of 98 μm, while the SDM had a mean diameter ranging from 5 to 155 μm. In general, the spray dried powders had particle sizes smaller than that of the freeze dried sample. The PSD in the SDM showed major polydispersity, so the rheological properties, especially shear viscosity, were inversely affected. The SDM forms agglomerated forms could explain the PSD determined by particle analyzer (León-Martínez et al., 2010). The PSD in the reconstituted mucilage solutions is an important factor influencing the rheological behavior of the solutions. The

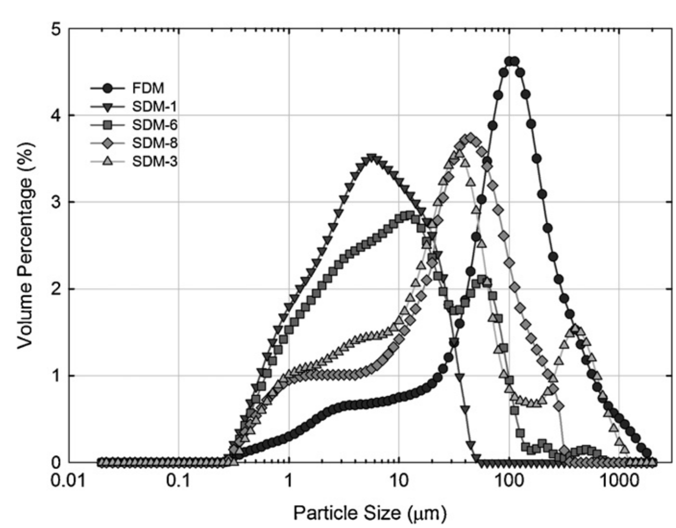

Fig. 7. Particle size distribution of mucilage reconstituted solutions at 25 °C.

decrease in rheological parameters may be associated with slip effects that are enhanced gravity systems that show a tendency to sediment (Barnes, 2000). The controlling factors for polymer rheology include concentration, molecular weight distribution, and degree of branching, as well as temperature and pressure (Barnes, 2000; Hill & Carrington, 2006).

Also, it was observed that the mean particle size tended to be lower than that corresponding to material obtained at higher temperatures (170 °C). At higher drying temperatures, particles tend to inflate, form crust and break (Walton & Mumford, 1999). These phenomena have been linked to rapid evaporation and high pressures generated in particles. The mucilage powder obtained under by drying conditions marked as 1 gave the best PSD, as well good rheological properties.

4. Conclusions

This study has shown that the use of spray drying to process *O. ficus-indica* mucilage produces a stable powdered product with rheological properties (viscous and elastic) lower than that by freeze drying. Steady-shear viscosity measurements showed a non-Newtonian shear-thinning behavior; this behavior is a function of the mucilage concentration in the solution. The viscous modulus G'' predominates over the elastic modulus G' for the spray-dried samples at concentrations $\leq 6\%$ (w/v), indicating a liquid-like material. In spray dried samples, a cross over point ($G' = G''$) at low frequency and 25 °C was observed, for a mucilage concentration of 7.2% (w/v), suggesting a random coil configuration. The rheological properties were affected inversely by the increase in inlet temperature and the atomizer speed, and directly by the increase of feed flow rate.

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