LWT - Food Science and Technology 66 (2016) 93–100

Contents lists available at ScienceDirect

LWT - Food Science and Technology

journal homepage: www.elsevier.com/locate/lwt

Structure preservation of Aloe vera (*barbadensis Miller*) mucilage in a spray drying process

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ARTICLE INFO

Article history:
Received 9 April 2015
Received in revised form
5 October 2015
Accepted 6 October 2015
Available online 19 October 2015

Keywords:
Rheology
Molecular-weight
Viscoelastic properties
Viscosity
Polysaccharides

ABSTRACT

Aloe vera (*barbadensis Miller*) mucilage in powder form was obtained by spray-drying following by suspension in aqueous solution, to enable microstructure recovery. The rheological behavior of the reconstituted mucilage was evaluated as a function of mucilage concentration, temperature, pH and ionic-strength. Mucilage solutions exhibited shear-thinning non-Newtonian behavior. The viscosity was found dependent on ionic-strength. This dependence is more evident when divalent cations are used, although a strong rise in viscosity upon increasing pH is observed. Linear viscoelastic data show a predominant viscous behavior, but with a crossover point (storage module $G' =$ loss module G'') suggesting a change in molecular conformation to a random-coil arrangement of the mucilage microstructure. The spray-dried powders were compared with fresh mucilage, with regard to chemical composition and mechanical flow behavior. Results reveal a small structure modification during the spray-drying process, evidencing preservation of the mucilage microstructure when optimum spray-drying conditions are used, i.e., 1.5 L/h inlet flow, temperature of 150 °C and atomization rate of 27,500 rpm.

1. Introduction

Polysaccharides are used in the food industry for their ability to modify the functional properties of food systems (Medina-Torres, Brito-de La Fuente, Torrestiana-Sánchez, & Katthain, 2000). Since polysaccharides impart a functional property to a specific product, the economics and availability of polysaccharides are important in the final formulation (Whistler, 1993). A very popular plant in the Cactaceae family is Aloe vera (AV) (*barbadensis Miller*) which has been widely studied due to its healing properties. AV is a heteropolysaccharide (it is formed by several polysaccharides) of high molecular weight.

Spray-drying (SD) is a process widely used to produce powders due to several advantages such as capacity to produce powders of a specific particle size and moisture content, continuous operation, short production times, cost effectiveness, and flexibility (Keshani, Daud, Nourozi, Namvar, & Ghasemi, 2015 and references therein). Examples of recent studies of SD food products are: Blackberry (Ferrari, Germer, & de Aguirre, 2012), coffee oil (Frascareli, Silva, Tonon, & Hubinger, 2012), Yoghurt (Sakin-Yilmazer, Koç, Balkir, & Kaymak-Ertekin, 2014), among others. However, the relative high temperatures used in the SD process can negatively affect the properties of the powders causing degradation and oxidation of the product. Thus, finding the best process conditions is of paramount importance to obtain powders with optimum properties. For example, it was found that the increase in inlet air-temperature

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http://dx.doi.org/10.1016/j.lwt.2015.10.023
0023-6438/

leads to a decrease of efficiency and oil retention in the encapsulation process of coffee oil by SD (Frascareli et al., 2012). Ferrari et al., (2012) reported that a high inlet air-temperature (180 °C) leads to particles with smoother surface, lower moisture contents and higher hygroscopicity for the case of SD blackberry powders. Whereas, in the case of *Opuntia* fruits (Gandia-Herrero, Jimenez-Atenzar, Cabanes, Garcia-Carmona, & Escribano, 2010), low inlet air-temperature (120 °C) was associated with a large degree of particle shrinkage and deformation. With regard to shear-viscosity, Sakin-Yilmazer et al., (2014) reported that an increase in inlet air-temperature caused a decrease in apparent viscosity of reconstituted powders of SD yoghurt, which was related to the denaturalization of proteins and destruction of the protein network. With respect to studies on how SD process conditions affect the product structure, Paudel, Loyson, and Van de Mooter (2013) studied spray dried naproxen–polyvinylpyrrolidone (PVP) K25 amorphous solid dispersions. They found that a high inlet temperature or feed-flow lead to the formation of phase-separated dispersions with strong hydrogen-bonded fractions and higher amorphous drug fractions (resulted from fast evaporation conditions) leading to superior physical stability, while lower inlet temperature generated more homogeneous systems. Moreover, in the case of the AV mucilage, Cervantes-Martínez et al (2014) reported that the increase of inlet temperature and atomization speed led to a decrease in shear-viscosity of reconstituted AV-powder, which was attributed to sample degradation. A combination of high atomization speed and low inlet temperature were reported as key factors in reducing sample degradation which was inferred from rheological measurements (viscoelasticity and first normal-stress difference). In this regard, there are few studies about the rheological properties of reconstituted mucilage after a (SD) process.

The purpose of this study is to characterize the flow-thickening properties of the reconstituted AV-mucilage powders obtained by SD to obtain the optimum conditions to avoid sample degradation, maintaining the molecular weight of the AV powders.

2. Materials and methods

2.1. Raw materials

AV leaves were collected from a dry area of northern Mexico (Durango, Dgo.), from a cultivated area of 2500 m^2, with a production of 2.5 tons per year under controlled irrigation and constant organic fertilizer every two months. These plants have a thick and short herbaceous stem with a diameter of 10 cm and height of 20–25 cm on average, prior to the stage of flourishing. The leaves have *S* shape towards the tip (center are erect or slightly curved and thinner) with 70–90 cm on average height and 8 cm thick. Only the bright green leaves without brown spots with 24–30 months-old on average that grew in the outer part of the plant were cut.

2.2. Extraction of the AV mucilage

The tip, base, thorns and bark on both sides of the leaves were separated after cutting, washing and cooling. Semi-frozen pulp was placed in a commercial juice extractor Hamilton Beach® HealthSmart; then the juice was clarified in a tabletop centrifuge brand Heraeus Labofuge model 400/400 R to remove suspended solids; the juice was stored in sterilized jars at low temperatures (−4 °C). pH (AOAC, 1990), degrees Brix, refractometer (model RF-10-CAT), moisture (OHAUS, thermo-balance MB2000), and total solids (NMX-F-510-1998) were measured in the mucilage samples.

2.3. Chemicals

The monosaccharide standards: L-Rhamnose, L-Fucose, L-Arabinose, D-Xylose, D-Mannose, D-Galactose, D-Glucose grade reactive and 2-Deoxy-Glucose (>99%) were used as internal standards, and sodium nitrate was purchased from Sigma–Aldrich. Reagent-grade Sulfuric acid and dicloromethane were supplied by Scharlab S. L. (Spain).

2.4. Physicochemical characterization of fresh AV mucilage

2.4.1. Moisture content fresh samples

The moisture content of raw samples was determined with an automatic thermo-balance (model Sartorius® MA35), with a 0.01% error, automatic selection of time (0.1–99 min), with a temperature range of 1–150 °C and infrared heating-system. The thermo-balance was programmed at 90 °C for 40 min during the initial processing of the samples (non-destructive). Subsequently, in the development of this process, second and third treatments were applied, reaching 30 min at 110 °C. Results are expressed in g/kg of wet sample.

2.5. Spray Drying (SD)

A Mobile Minor parallel-flow spray-dryer (model Niro, Copenhagen, Denmark) equipped with a rotary atomizer (Minor TS M02/A) was used to dry the AV-mucilage solution. SD conditions (see Table 1) were used according to previous reports (Cervantes-Martínez et al., 2014) to obtain the optimum mechanical and functional properties of the SD process (inlet: 150 °C, 1.5 L/h and 27,500 rpm).

2.5.1. Moisture content of the SD powders

The moisture content of the SD powder was determined with an infrared thermo-balance AD-4714[a], at a temperature of 110 °C for a period of 60 min and a weight of 5 g per sample for each test, performed in duplicate. Results were expressed in percentage of dry matter.

2.6. Analytical determinations

2.6.1. Total Phenolic Content (TFC)

The TFC was determined by the Folin-Ciocalteu method modified by Heimler, Vignolini, Dini and Romani (2005). To prepare the reference sample, dry powders of mucilage (1 mg) were dissolved in de-ionized water (1 mL), homogenized in a Vortex analog mixer (Fisher Scientific) for 10 min, until a homogeneous mixture was obtained. In the presence of dim light, 125 μL of the standard sample, 500 μL of distilled water and 125 μL of Folin-Ciocalteu reagent were mixed in test tubes. The mixture reacted for 6 min. Then 1250 μL of sodium carbonate (7 g/L) and 1 mL of distilled water were added to the reaction mixture. This mixture was incubated for 90 min at room temperature and in total absence of light; finally, absorbance was measured at 760 nm with water as blank. The TPC was expressed as mg of gallic acid equivalent (GAE, GAE/g of spray dried powder) through the calibration curve of gallic acid.

2.6.2. Antioxidant capacity measured by trapping free radicals (DPPH method, 2,2-diphenyl-1-picrylhydrazyl)

Antioxidant capacity was measured in terms of the radical scavenging capacity (RSC) using the DPPH method * (2, 2-diphenyl-1-picrylhidrazyl) (Brand-Williams, Cuvelier, & Berset, 1995). In this study 0.025 mg/mL of DPPH were used as a standard reagent and dried samples were dissolved in methanol/water (1:1 in volume), which were also used as target. Samples were prepared in duplicate

Table 1
Spray drying conditions, yield (Y) and Humidity (Hum) content for all treatments including fresh mucilage sample. Ti=Inlet temperature, To = Outlet temperature, Tw = wall temperature, Ff = Inlet flow, Y = yield, M = Moisture.

Treatment	Ti (°C)	To (°C)	Tw (°C)	Ff (L/h)	As (rpm)	Y (g/kg)	M (g/kg)
T1	170	98	55.12	1.5	23,000	0.090	0.08
T2	170	98	46.3	1.5	27,500	0.120	0.10
T3	170	98	55.12	1.7	23,000	0.080	0.080
T4	170	95	46.3	1.7	27,500	0.130	0.110
T5	150	67	48.63	1.5	23,000	0.060	0.080
T6	**150**	**98**	**40.85**	**1.5**	**27,500**	**0.110**	**0.120**
T7	150	75	48.63	1.7	23,000	0.160	0.080
T8	150	78	40.85	1.7	27,500	0.160	0.110
T9, Freeze drying	–**40**	**25**	–	–	–	**0.180**	**0.100**
T10, Fresh mucilage	–	–	–	–	–	–	90

Bold letters indicate the best spray drying conditions and the commercial freeze dryed sample for comparison.
*($P < 0.05$).

considering five concentrations within a range of 100–2500 mg/mL. In presence of dim light, 0.5 mL of each sample was added to test tubes and then 3.5 mL of the DPPH solution were added, previously adjusted to an absorbance of 0.78 at a wavelength of 515 nm. The absorbance of the mixtures was measured 7 times every 5 min, up to a reaction time of 30 min. The free-radical scavenging capacity is expressed as a percentage according to the following Equation (1):

$$\%(RSC) = \left\{1 - \left(\frac{Abs_{515\ sample}}{Abs_{515\ DPPH\ solution*}}\right)\right\} \times 100 \quad (1)$$

2.6.3. Analysis of carbohydrate composition

Carbohydrate analysis was performed as described by Simões, Nunes, Domingues, Coimbra, and Domingues (2012) for neutral sugars. Sugars were released from residues by acid hydrolysis. Approximately 5 mg of fresh and dried AV-mucilage were dispersed in 12 mol/L H_2SO_4 solution for 3 h followed by dilution to 1 mol/L and hydrolyzed at 100 °C for 2.5 h (Saeman, Moore, Mitchell, & Millett, 1954). A second sample was hydrolyzed only with 1 mol/L H_2SO_4 (100 °C for 2.5 h). The cellulose content was estimated by the difference in glucose obtained by Saeman hydrolysis and the second (mild) hydrolysis method. The neutral sugars as alditol acetate derivatives were separated with dichloromethane and analyzed by gas chromatography with a flame ionization detector equipped with a 30 m column DB-225 (J&W Scientific, Folsom, CA, USA) with internal diameter and film thickness of 0.25 mm and 0.15 μm, respectively. The oven temperature program included an initial temperature of 200 °C, a rise in temperature at a rate of 40 °C/min up to 220 °C, keeping this temperature for 7 min, followed by a rate of 20 °C/min up to 230 °C and maintaining this temperature for 1 min. The injector and detector temperatures were 220 and 230 °C, respectively. The flow rate of the carrier gas (He) was set at 1.7 mL/min. Uronic acids were determined by colorimetry, as total uronic acid (Blumenkrantz & Asboe-Hansen. 1973) using a hydrolyzed sample (3 h at 20 °C in 12 mol/L H_2SO_4, followed by heating at 100 °C for 1 h in 1 mol/L H_2SO_4).

2.6.4. Molecular weight

The molecular weight of mucilage was measured using HPLC (Perkin–Elmer Model 250) equipped with a G 2000 SW column (TSK-GEL), a IR refractive index detector (Perkin–Elmer series 1000) and an integrator (Spectra-Physics, SP4270 model). Sodium nitrate (50 m mol/L) was eluted at 50 °C with a flow rate of 0.7 mL/min. Dextrans (commercial grade, Sigma EE.UU, *Leuconostoc mesenteroides*: B-152 strain and dextran T70 produced by Pharmacia Biotechnology, Sweden) with molecular weights from 5000 to 87,000 were used as standards.

2.7. Morphology by scanning electron microscopy (SEM)

The sample was placed in copper seats, fixed with conductive tape and coated with gold at 1 kPa during 90s (model Desk II, Denton Vacuum, NJ, USA). Samples were observed in a scanning electron microscope (JEOL Mod. JSM6300 Jeol, Japan) with voltage of 20 kV and 1000× magnification.

2.8. Rheological properties

2.8.1. Mucilage reconstituted solutions

SD powder mucilage samples were re-suspended in de-ionized water using a magnetic stirrer (Thermo Scientific, Telesystem 15) at 500 rpm at 24 ± 1 °C for 90 min. Samples with 0.06 g/mL were prepared to study the effects of changes in pH, temperature and ionic strength on the rheological behavior of mucilage. All rheological measurements were performed in a stress controlled rheometer (AR-G2, TA Instruments) using a cone and plate geometry (d = 60 mm, 1° angle) with a Peltier plate system attached to a circulating water bath (Haake, Germany, Mod. F3T). Samples were characterized under simple shear flow. The viscoelastic properties, storage (G′) and loss modulus (G″) were measured under small-amplitude oscillatory with frequency range from 0.1 to 200 rad/s.

Finally, the first normal stress difference under steady-shear (*N1*) was measured to determine the elastic properties under shear flow.

2.9. Experimental design

The experimental design is shown in Table 1. Experiments were performed according to a 2^3 factorial design: two different inlet air-temperatures (Ti = 150 and 170 °C), two inlet flows (Ff = 1.5 and 1.7 L/h) and two atomization speeds (As = 23,000 and 27,500 rpm). Outlet (To) and wall temperatures (Tw) were measured but not controlled in the SD process. A freeze-dried sample (T9) and fresh mucilage (T10) are used for comparison (see Table 1). Three replications were performed for each test for a total of 24 SD runs. Data were analyzed by ANOVA with statistical significance of $P < 0.05$.

3. Results and discussion

3.1. Analytical determinations

3.1.1. Physical characteristics of powders obtained by SD

The process conditions, yield and moisture content of SD powders (T1–T8), freeze-dried powder (T9, used for comparison

purposes) and fresh mucilage (T10), the latter with 3 °Brix, pH of 4.6 and total solids content of 0.12 g/kg, are shown in Table 1. According to the operation conditions of SD, the time that the particles remain inside the dryer (residence time) related to the inlet flow (F_f) and spraying speed (rotary atomizer velocity) has ample influence on the moisture content (Hum) and degree of particle agglomeration (stickiness) (Chiou & Langrish, 2007). For example, sample T5 reveals the lowest-attainable yield, which is related to the low inlet-flow (1.5 L/h) which represents a long residence time combined with a high temperature gradient $\Delta T = Ti - To$ (150 − 67 °C). Sample T6 in comparison, reveals a higher yield, attributable to the lower temperature gradient and larger atomization speed (As = 27,500 rpm), as compared to sample T5 (23,000 rpm).

3.1.2. Total Phenolic Content (TPC)

Table 2 shows the TPC expressed in mg of gallic-acid equivalent for the 10 samples (sample identification, same as Table 1). According to Wang et al. (2013) a major decrease in TPC is found in the low-temperature dehydrated product probably due to long residence times required to reach the pre-set final moisture. This is confirmed with sample T2, where a combination of high inlet-temperature (170 °C) and low inlet-flow (1.5 L/h, see Table 1) leads to long residence times with high temperature, and hence the lowest phenol content (Table 2). A higher temperature in conjunction with high feed-flow reduces the particle residence-time and improves the retention of functional groups, as the particles stay shorter periods at high temperatures. This is the case of samples T3 and T4 (see Table 1).

3.1.3. Antioxidant capacity measured by trapping free radicals (DPPH method, 2,2-diphenyl-1-picrylhydrazyl)

In general, the high phenolic content implies a high antioxidant capacity, which is strongly linked to the molecular structure. The use of the DPPH technique was made according to Brand-Williams et al. (1995) providing a straightforward way to evaluate the antioxidant activity of trapping radicals; however, some care must be taken when interpreting the data. In Table 2, the percentage of trapping free radicals for all samples is presented. A widely-used parameter to estimate the antioxidant capacity is the median effective concentration (EC_{50}) (Cuvelier, Richard, & Berset, 1992; Sánchez-Moreno, Larrauri, and Saura-Calixto, 1998). EC_{50} is the concentration than inhibits 50% of the DPPH* radicals in solution; the lower the EC_{50}, a higher antioxidant activity is found.

Treatments T1 and T3 show the lowest % RSA (<0.06 g/mL) with concentrations higher than 5000 mg/mL. This may be due to the degradation of the molecule caused by high drying temperatures; while in treatments T7 and T8, low antioxidant levels are caused by high feed-flow and low atomizing pressure, accompanied with high residence times within the drying chamber, leading to degradation of the biopolymer (through chain scission). Sample T9 also shows a low percentage of trapped free-radicals due to the drying process (freeze-drying). According to these results, interaction with DPPH depends on the presence and preservation of the conformational structure of mucilage.

Table 2
Total phenolic content expressed by mg of gallic acid equivalents and antioxidant activity (free radical method) for all treatments including fresh mucilage sample (Data at 25 °C, pH = 4).

Treatment	Gallic acid equivalents (mg)	%, Radical scavenging activity
T1	137 ± 10	7 ± 3
T2	15 ± 1	52 ± 5
T3	85 ± 5	7.5 ± 0.3
T4	91 ± 3	47 ± 5
T5	88 ± 4	51 ± 6
T6	87 ± 3	52 ± 5
T7	98 ± 6	12 ± 2
T8	60 ± 5	6 ± 2
T9	88 ± 5	6 ± 3
T10	356 ± 15	55 ± 7

*(P < 0.05).

3.1.4. Analysis of the carbohydrate composition

Experimental results for the samples with the highest monosaccharide contents (T6 and T10) are summarized in Table 3. Sample T6 shows the highest monosaccharide content in comparison to fresh mucilage (T10), evidencing the optimum drying conditions according to total phenolic content and antioxidant activity (Table 2). Rodríguez-González et al., (2011) reported that the high mannose and glucose contents suggest the occurrence of the acemannan polymer, the main bioactive ingredient of AV. Femenia, García-Pascual, Simal, and Rosselló (2003) evaluated the effect of dehydration at different air-drying temperatures on the bioactive polysaccharides of AV.

In general, carbohydrate analysis revealed that the AV-mucilage mainly contains mannose and significant amounts of uronic acids, arabinose, and xylose. Acemannan, the main active component of AV originates from mannose, which has been reported to occur in large quantities in AV (McAnalley, 1993).

3.1.5. Molecular weight

From elution profiles using HPLC, the molecular weight of the SD-mucilage was determined; a value of 4.18×10^4 for sample T6 was found, while for fresh mucilage amounts to 5.96×10^4. The reduction in Mw is expected due to the thermal treatment and high shear-forces present in the SD chamber. However, the difference is less than 10% of the reference Mw, which evidences the structure preservation achieved using the optimum drying conditions while preserving the antioxidant activity. Also, the reduction in monosaccharide content (see Table 3) of sample T6 as compared with the fresh mucilage (T10) is a remarkable result of the mild degradation caused by the SD process, since the reductions for all monosaccharide samples range in the order of 10% or less.

3.2. Scanning Electron Microscopy (SEM)

Fig. 1 shows micrographs of powders obtained by the SD process (A) and the lyophilized sample (B), where the morphology of the SD micro-particles consists of semi-spherical shapes (sample T6 see Table 1 for SD process conditions). Furthermore, freeze-dried micro-particles (sample T9) have rough surfaces with cavities and, sometimes, structural cracks. These morphological irregularities are possibly due to the removing water process during drying. Ball-struck type particles were observed in SD samples (T6) similar to those reported by Alamilla-Beltrán, Chanona-Pérez, Jiménez-

Table 3
Sugar composition of the mucilage of the Aloe vera (*barbadensis Miller*).

Composition, % mol	Fresh, (T10)	SD, (T6)
Mannose	47 ± 2	43 ± 2
Glucose	41 ± 2	37 ± 3
Uronic acids	6.1 ± 0.5	4.8 ± 0.5
Galactose	4.5 ± 0.4	2.1 ± 0.2
Xylose	7.0 ± 1.1	0.70 ± 0.05
Arabinose	1.9 ± 0.1	1.6 ± 0.1
Rhamnose	0.90 ± 0.03	0.7 ± 0.1
Fucose	0.80 ± 0.02	N.D

*(P < 0.05).

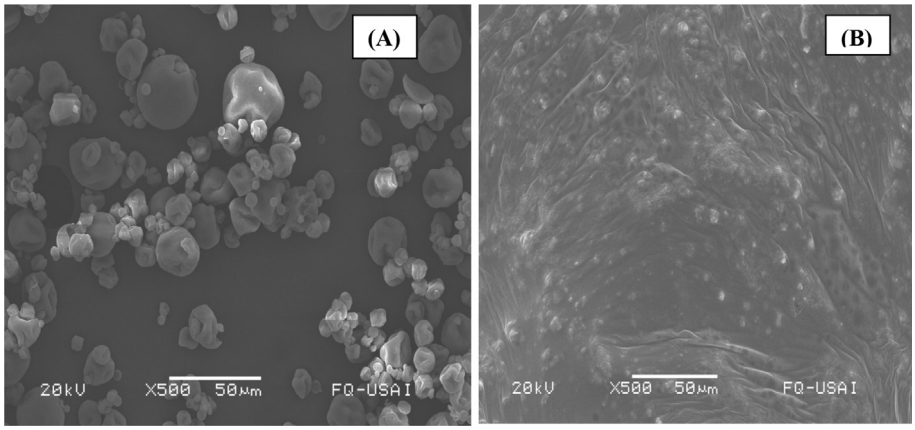

Fig. 1. Micrographs of spray dried Aloe vera powders: A) Sample T6 (Spray dried at 150 °C inlet temperature, 1.5 L/h inlet flow and 27,500 rpm atomization speed) and, B) Sample T9 (Freeze dried at −40 °C inlet temperature, used for comparison purposes).

Aparicio, and Gutiérrez-López (2005). Using air at low temperature in the SD process leads to irregular micro-particles with folds on its surface, while air at high temperature results in more rigid porous surfaces and micro-particles. In this study, using the SD process (T6) leads to semi-spherical micro-particles, with no apparent cracks without agglomerations or tack processes.

3.3. Rheological behavior. Steady-state simple-shear

3.3.1. Concentration effect

Shear viscosity as a function of mucilage concentration is shown in Fig. 2. The sample with treatment T6 is used here at two different concentrations (0.03 and 0.06 g/mL) and compared with either fresh mucilage, freeze-dried mucilage and xantham gum. In general, mucilage solutions behave as shear-thinning fluids ($n < 1$) i.e., the viscosity decreases with increasing shear-rate.

The shear-viscosity of polysaccharide solutions in a wide range of strain-rates has been modeled with a power-law model (Equation (2)):

$$\eta = K\dot{\gamma}^n \tag{2}$$

where η is the shear viscosity (Pa s) and $\dot{\gamma}$ is the shear strain rate (1/s). K is the consistency index (Pa s^n) and n is the shear-thinning index.

Morris, Cutler, Ross-Murphy, Rees, and Price (1981) empirically found a value of 0.76 for the slope of the viscosity (η) vs shear rate (γ) at high shear rates for "*random-coil*" polysaccharides in solutions with high polydispersity. Note that the flow properties of commercial biopolymers (xanthan gum) are similar to those of the AV-mucilage 0.06 g/mL (Fig. 2). Viscosity values of a solution of 0.06 g/mL mucilage are comparable to those of a xanthan solution (0.03 g/mL).

3.3.2. Temperature effect

The influence of temperature on the viscous properties of fresh, spray-dried and lyophilized mucilage is shown in Fig. 3. The curve shape is not affected by temperature, suggesting temperature stability in the analyzed range. Dependence of viscosity on temperature can be represented by the Arrhenius equation (Lewis, 1987):

$$\eta = A \exp\left[\frac{Ea}{R(1/T - 1/T_0)}\right] \tag{3}$$

where Ea is the activation energy (kcal mol^{-1}), R is the gas constant: 1.987207 cal mol^{-1} K^{-1}, A is the constant related to the

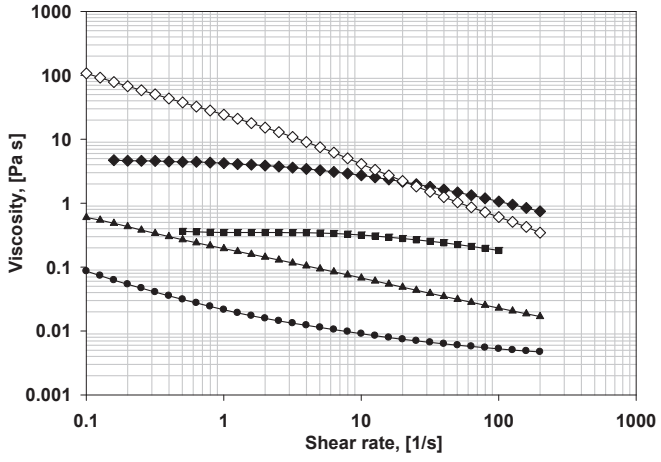

Fig. 2. Effect of mucilage concentration on steady-shear viscosity at 25 °C of fresh Aloe vera mucilage at 3 °Brix (sample T1 ●), Freeze dried at 0.03 g/mL (T9 ▲), Spray Drying sample (T6) reconstituted at two concentrations 0.03 (■) and 0.06 (◆) g/mL, and Xantham gum at 0.03 g/mL (◊) (for comparison purposes).

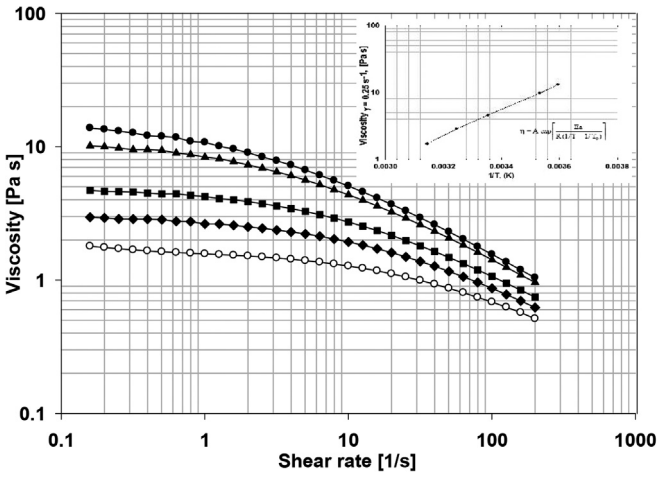

Fig. 3. Effect of the temperature on the steady shear viscosity of reconstituted spray dried Aloe vera mucilage powders 5 °C (●), 10 °C (▲), 25 °C (■), 35 °C (◆), 45 °C (○).

molecular collision frequency between T and T_0 (K). The reference temperature T_0 is 273.15 K for data shown in Fig. 3.

Values obtained from the linear regression are: Ea = 124.35 J/mol for the fresh mucilage, 790.5 J/mol for the reconstituted freeze-dried mucilage, and with the SD process 1831.3 J/mol with 0.03 g/mL and 3.824 kcal/mol with 0.06 g/mL (correlation of $R^2 = 0.9998$). It is interesting to note that several biopolymers such as xanthan gum have revealed fairly stable viscous properties with respect to temperature (Rajinder, 1995) similarly to the value obtained with low AV concentrations (0.03 g/mL).

3.3.3. Effect of ionic strength

Experimental results regarding the effect of ionic strength on the viscous properties of mucilage (concentration of 0.06 g/mL) are shown in Fig. 4. Viscosity values are taken from the flow curve at a shear rate of 0.25 s^{-1}. The effect of the ionic concentration on the viscosity is important to determine the dependence of rheological properties on the presence of functional ions. Charged molecules show a strong viscosity dependence of ionic strength. Medina-Torres et al., (2000) represented this functionality by using the following Equation (4):

$$\eta = \eta_\infty + SI^{-1/2} \tag{4}$$

where, η_∞ is the extrapolation of η to infinite ionic-strength. S is the slope of the function of η versus $I^{-1/2}$ related to the rigidity of the polymer chain.

Predictions of Equation (4) are also shown in Fig. 4 (dotted line). It is clear that for increasing ion concentration η decreases, as expected for polyelectrolyte solutions composed of several polysaccharides such as the AV-mucilage. Typical values of the slope (S) for xanthan samples are in the range of 0.55 and 0.66 (Lillford & Norton, 1991). S-values of the AV-mucilage range from 0.335 to 0.360, revealing that S depends on the ionic strength. According to data shown in Fig. 4, the viscosity reduction depends more on the Na^+ ions concentration than that of Ca^{++} ions.

Ionic strength (or a negative charge) produces a strong intermolecular repulsion, which explains the high mucilage viscosity in de-ionized water. Otherwise, the addition of positive ions causes a reduction in the repulsion forces. These results are similar to those previously reported by Trachtenberg and Mayer (1982).

3.3.4. pH effect

The effect of pH on viscosity in simple-shear flow is shown in Fig. 5, where viscosity values are taken from the flow curve at a shear rate of 0.25 s^{-1}. Upon increasing pH causes an increase in the viscosity. In the alkaline region, the viscosity tends to a plateau (saturation effect). Moreover, a sharp increase is observed between pH 4 and 6. The ionization of the carboxyl groups of the mucilage molecule above pH 4.0 may explain this sharp increase in viscosity.

A similar argument was reported by Trachtenberg and Mayer (1982) to explain the increase in the intrinsic viscosity of mucilage with pH (to almost zero-shear conditions). Consequently, it is clear that both pH and ionic strength influence the hydrodynamic volume of the AV-molecule. Conformational changes in the molecule should be considered to determine the functional properties of the AV-mucilage.

3.4. Elastic properties of simple shear flow

The first normal stress difference under simple-shear flow (N_1) is a material function that allows the evaluation of the elastic properties of the material under flow. Fig. 6 shows N_1 as a function of shear stress τ_{12}, revealing that aqueous solutions of mucilage are elastic under flow.

In comparison, a standard solution of polyisobutylene is shown in Fig. 6 (with the slope of 2 at low shear-rates). These results are represented by the following equation suggested by Broadbent and Lodge (1971):

$$N_1 = m'[\tau_{12}]^{n'} \tag{5}$$

where: m′ is the characteristic consistency index, τ_{12} is the shear stress (Pa) and n′ is the flow behavior index (which can vary between 0 and 2). For the mucilage concentration studied in this work, N_1 is reasonably predicted by Equation (5), where m′ and n′ are given in the caption of Fig. 6. Values of N_1 are higher in the case of SD-mucilage as compared to fresh mucilage but the slope remains the same. This is expected since the total solid content between the samples is different. Similar trends were observed in the literature for a wide range of synthetic biopolymers (Ait-Kadi, Choplin, & Carreau, 1989).

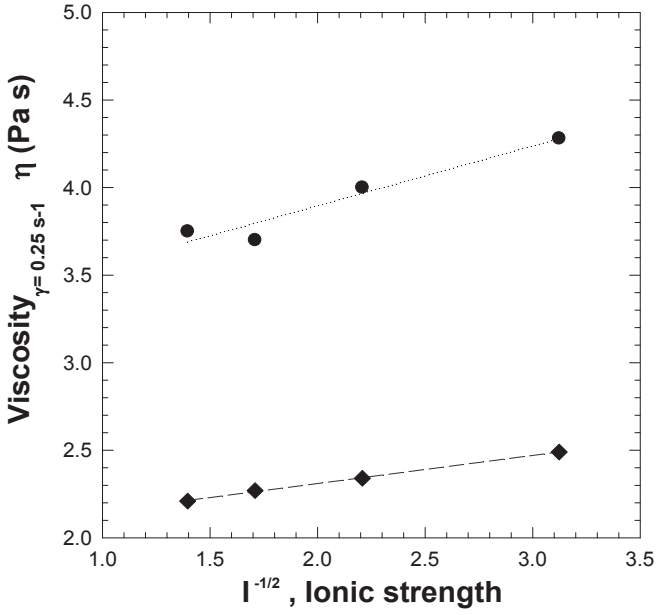

Fig. 4. Dependence of viscosity on ion strength for sample T6 at 0.06 g/mL reconstituted mucilage solution, at 25 °C. For two ions: Ca^{++} (●) and Na^+ (◆).

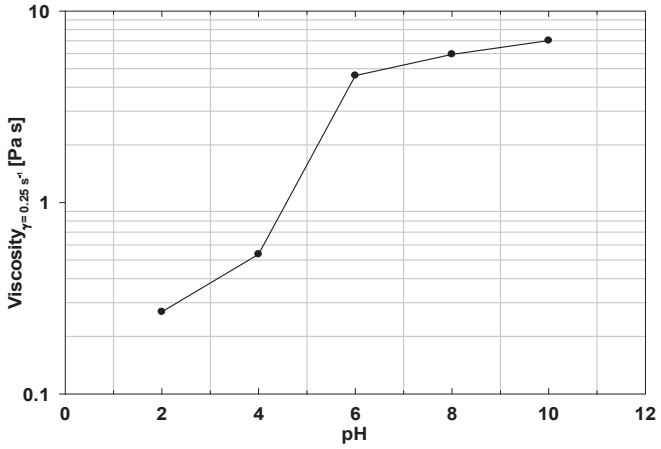

Fig. 5. pH dependence of the steady shear viscosity for mucilage 0.06 g/mL mucilage solution, and 25 °C.

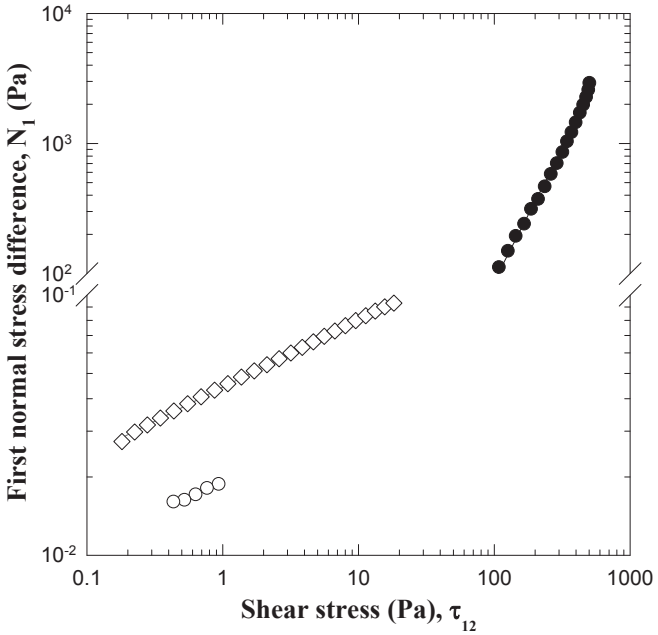

Fig. 6. First normal stress difference (N_1) as a function of shear stress τ_1 and the values of m′ and n′ are given for fresh Aloe vera (○) (n′ = 0.2181, m′ = 0.1787 $Pa^{1-n'}$), Spray dried reconstituted at 0.06 g/mL sample (T6, ◊) (n′ = 0.2613, m′ = 0.2582 $Pa^{1-n'}$), and standard solution of polyisobutylene (●) (n′ = 2.04, m′ = 0.1177 $Pa^{1-n'}$) this polymer used for comparison purposes only.

3.5. Rheological behavior of oscillatory shear flow at steady state

3.5.1. Concentration effect

Typical oscillatory flow curves of small amplitude strain as a function of concentration of mucilage in de-ionized water at 25 °C are shown in Fig. 7. The storage (G′) and viscous modulus (G″) are calculated from an oscillatory shear-flow according to the following equations:

$$G' = (\tau_0/\varepsilon_0)\cos\theta \quad (6)$$

$$G'' = (\tau_0/\varepsilon_0)\sin\theta \quad (7)$$

where τ_0 is the oscillatory stress, ε_0 is the strain and θ is the phase angle between the stress and strain oscillatory signals.

The spectrum shows a typical mechanical behavior of a random-coil configuration (Morris et al., 1981). Mucilage solutions show viscoelastic properties of a predominant viscous behavior G″ > G′ (Clark & Ross-Murphy, 1987). This behavior depends on the mucilage concentration in the dilute region (<0.06 g/mL).

Upon increasing the mucilage content, G′ becomes larger than G″, indicating increasing elasticity due to macromolecular network formation. This behavior has been observed for xanthan gum for concentrations above 0.03 g/mL (Rajinder, 1995). In Fig. 4, data for xanthan 0.03 g/mL are presented for comparative purposes. Results suggest that mucilage solutions with 0.06 g/mL exhibit similar viscoelastic properties than xanthan solutions with 0.03 g/mL content.

3.5.2. Temperature effect

The effect of temperature on the viscoelastic properties of SD-reconstituted mucilage is presented in Fig. 8, for a concentration of 0.06 g/mL in de-ionized water. The dependence of both dynamic moduli G′ and G″ on frequency is observed at 5 and 35 °C. A similar trend has been reported by Morris et al. (1981) for random-coil polysaccharide conformations. It is important to note that at 5 °C, the point of intersection between G′ and G″ occurs at high frequency (short times), which suggest a conformational change in the mucilage structure.

Furthermore, the elastic and viscous responses under simple-shear are also dependent on both pH and ionic strength (data not shown here), revealing that the rheological properties of mucilage are dependent on molecular conformation.

4. Conclusions

Aloe vera mucilage powders were produced by spray-drying under different process conditions; they were analyzed in relation to their moisture content, total phenolic content, antioxidant capacity, carbohydrate composition, molecular weight and morphology. Reconstituted powders were evaluated by rheological techniques.

The rheological behavior of fresh AV-mucilage, lyophilized and

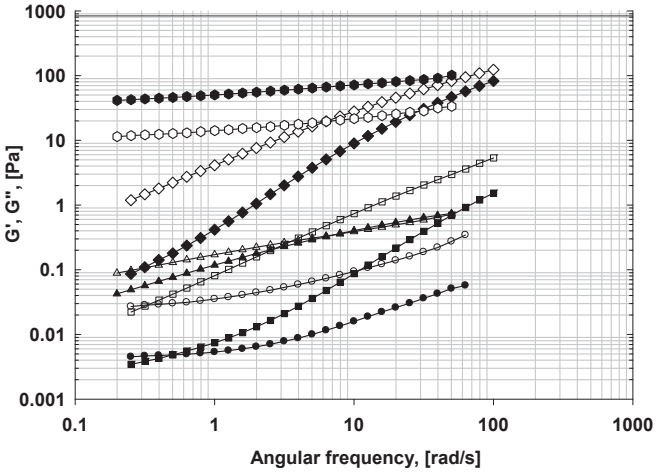

Fig. 7. Frequency dependence of the storage modulus G′ (filled symbols) and loss modulus G″ (empty symbols) for fresh Aloe vera at 3 °Brix(●, ○ small circle), freeze dried AV mucilage at 0.03 g/mL (▲, Δ), reconstituted spray dried Aloe vera mucilage at 0.03 g/mL (■, □) and 0.06 g/mL (◆, ◊) and xanthan gum solutions (●, ○ large circle) in deionized water at 25 °C.

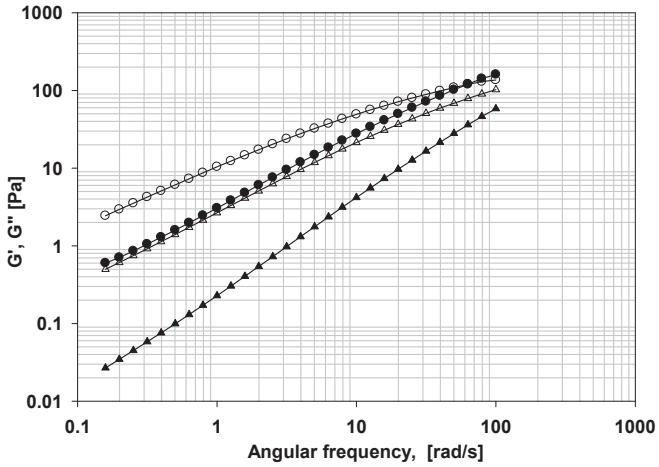

Fig. 8. Effect of temperature on the mechanical spectrum (viscoelastic moduli) of reconstituted SD AV mucilage at 0.06 g/mL. Storage G′ (filled symbols) and loss modulus G″ (empty symbols). 5 °C (●, ○) and 35 °C (▲, Δ).

re-suspended in aqueous medium after SD in powder form reveals shear thinning behavior (n < 1).

Viscous AV-mucilage solutions are found unstable to temperature changes at concentrations higher than 0.03 g/mL. Furthermore, the shear viscosity depends on the ionic strength in the same way as a common poly-electrolyte molecule; this behavior is more pronounced with divalent ions.

Viscosity depends on solution-pH and a sharp viscosity increase is found in the range 4–6 of pH.

Elastic properties under shear flow were analyzed through measurements of N_1 in SD-reconstituted mucilage samples. Similar trends as those reported in the literature were found, signaling the possibility of substitution of some commercial gums by these systems.

Results evidence the possibility to preserve the physical properties and structure of the SD-powders of Aloe vera if specific process conditions that minimize the effect of the thermal processing are employed. It is important to note that the total phenolic content and antioxidant capacity of mucilage powders show a remarkable response, scavenging free radicals in the samples processed at lower temperatures, low temperature difference ΔT (inlet and outlet) and low inlet flow. High expectations of the use of SD in natural biopolymers for possible use in the food industry are envisaged.

Acknowledgments

We acknowledge the financial support of CONACYT through Project CB-2014/235880.

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