

Rheological properties and surface tension of *Acacia tortuosa* gum exudate aqueous dispersions

José Muñoz^a, Fernando Rincón^{b,*}, M. Carmen Alfaro^a, Isabel Zapata^a,
Julia de la Fuente^a, Olga Beltrán^b, Gladys León de Pinto^b

^a Departamento de Ingeniería Química, Facultad de Química, Universidad de Sevilla, c/P. García González, 1, E41012 Sevilla, Spain

^b Centro de Investigaciones en Química de los Productos Naturales, Facultad de Humanidades y Educación, La Universidad del Zulia, Apartado 526, Maracaibo, Venezuela

Received 30 July 2006; received in revised form 14 March 2007; accepted 27 March 2007

Available online 31 March 2007

Abstract

Steady shear flow properties of *Acacia tortuosa* gum aqueous dispersions at different concentrations (15–40% w/v) were studied at 20 °C using a controlled shear rate Couette rheometer and Mooney–Ewart sensor systems. Flow curves showed shear thinning non-Newtonian behaviour with a tendency to a Newtonian plateau at high-shear rate. The results obtained fitted the Sisko model very well. The influence of temperature (5–40 °C) on the flow curves was studied at given gum concentration (40% w/v). The infinite-shear rate Newtonian viscosity derived from the Sisko model fitted an Arrhenius-type equation. A controlled stress rheometer was used to conduct small amplitude oscillatory shear tests with the double cone geometry on *A. tortuosa* gum dispersion (40% w/v). It was clearly observed that the gum dispersion exhibited viscoelastic properties in a given temperature range (5–25 °C). The elastic component was always higher than the viscous one. The frequency dependence of the dynamic moduli and the failure of the Cox–Merz rule supported the existence of a soft gel-like structure which weakened with temperature. The surface tension of *A. tortuosa* aqueous solutions was measured in a concentration range (0.01–1.5% w/v). The equilibrium value reached at (0.5% w/v) was (42.6 mN/m), which is significantly lower than the corresponding to *A. senegal* gum (46.9 mN/m). The rheological behaviour and surface tension of *A. tortuosa* gum suggest that it may compete with arabic gum in some industrial applications.

© 2007 Elsevier Ltd. All rights reserved.

Keywords: Rheological properties; Surface tension; Gum exudate; *Acacia tortuosa*

1. Introduction

Acacia tortuosa (Mimosaceae), a Gummiferae species, located in Venezuela, South America, produces a clear brown gum very soluble in water. The gum has a negative specific rotation. This unusual feature for *Acacia* Gummiferae Series has also been reported for *A. ehrenbergiana* and *A. macracantha* gums (Anderson, Bridgeman, & León de Pinto, 1984; Martínez, León de Pinto, & Rivas, 1992). The intrinsic viscosity number of *A. tortuosa* gum

(0.084 dl g⁻¹) (León de Pinto, Martínez, Ortega, Villavicencio, & Rojas, 1993a), is in the range reported for others Gummiferae gums, i.e. *A. ehrenbergiana* (Anderson et al., 1984), *A. nubica* and *A. nilotica* (Anderson & Karamalla, 1966). Although, the value is lower than the range values reported for *A. senegal* gum (0.15–0.60 dl g⁻¹) (Anderson & Weiping, 1991; Duvallet et al., 1993; Mothé & Rao, 1999; Sánchez et al., 2002). The nitrogen content (4.98%) is relatively high (Martínez et al., 1992) in comparison with other Gummiferae Series (Beltrán, León de Pinto, Martínez, & Rincón, 2005a). The amino acidic composition showed high proportion of hydroxyproline, serine, lysine and glycine. Threonine, glutamine, proline, alanine, valine, isoleucine, tyrosine, phenylalanine and histidine are also

* Corresponding author.

E-mail addresses: jmunoz@us.es (J. Muñoz), frinconciqpn@gmail.com (F. Rincón).

found as minor constituents (Beltrán et al., 2005a). These amino acids have been reported for others Gummiferae and Vulgares *Acacia* gums (Islam, Phillips, Sliivo, Snowden, & Williams, 1997; Siddig, Osman, Al-Assaf, Phillips, & Williams, 2005).

The polysaccharide, isolated from the *A. tortuosa* gum, is mainly constituted by galactose, arabinose and uronic acids, represented by glucuronic acid and its 4-*O*-methyl derivative. Xylose is also present as traces (León de Pinto et al., 1993a). This sugar, very unusual in *Acacia* gum exudates, has been reported in *Grevillea* spp. (Anderson & León de Pinto, 1982), *Cercidium praecox* (León de Pinto, Rodríguez, Martínez, & Rivas, 1993b) and *Anacardium occidentale* gums (Anderson, Bell, & Millar, 1974; León de Pinto, Martínez, Mendoza, Ocando, & Rivas, 1995). A combination of chemical methods and ^{13}C NMR spectroscopy showed that the core of the gum structure is a branched $\beta(1\rightarrow3)$ galactan. Arabinose and uronic acid residues could not be removed from the core. Arabinose (as furanose and pyranose residues) exists as terminal and 3-*O*-linked, while xylose is present as terminal residues (León de Pinto, Martínez, Bolaño de, & Rivas, 1998).

Size exclusion chromatography with multiangle laser light scattering data demonstrated that *A. tortuosa* gum is a highly polydisperse system, (polydispersity index 2.4) (Beltrán et al., 2005b). The weight average molar mass ($M_w = 410,000 \text{ g mol}^{-1}$) and number average molar mass ($M_n = 170,000 \text{ g mol}^{-1}$) are within the typical values reported for many *Acacia* gums (Al-Assaf, Phillips, & Williams, 2005). The fractionation and characterization of *A. tortuosa* gum suggest the presence of arabinogalactan and a complex arabinogalactan–protein, as has been reported for *A. senegal* gum (Picton, Bataille, & Muller, 2000). These structural features may be related to some interfacial activity and emulsifying properties like those found for gum arabic (Fauconnier et al., 2000).

Hydrocolloids or gums have many industrial applications (Whistler & Bemiller, 1993). They have mainly been used in food systems. The applications of gum solutions are based on their functional properties, which have been related to their water-holding capacity and their ability to enhance the stability of emulsions and foams. The main contribution of the gums has been related to their rheological properties in the continuous phase. The possible surfactant activity of several food gums has been studied in order to evaluate their potential emulsifying properties (Dickinson, 2003; Garti & Reichman, 1994; Garti, Slavin, & Aserin, 1999; Williams, Phillips, & Randall, 1990).

Gums used as stabilisers embrace a high viscosity at low shear, shear thinning properties at higher shear rates and eventually a high-shear rate Newtonian region. A fast time-dependent recovery of viscosity after cessation of shear and linear viscoelastic properties, characterized by a predominance of the elastic component on the viscous one, are also suitable rheological properties. The rheological behaviour of some aqueous dispersion of gum exudates have been published (De Paula, Santana, & Rodríguez,

2001; Mothé & Rao, 1999; Oliveira, Silva, De Paula, Feitosa, & Paula, 2001; Williams et al., 1990; Zakaria & Rahman, 1996). However, the information on the viscoelastic properties of such systems is rather scarce (Goycoolea, Morris, Richardson, & Bell, 1995; Sánchez et al., 2002).

The main objective of this research deals with the potential application of *A. tortuosa* gum exudate by the determination of the shear flow properties, linear viscoelastic properties and surface tension of aqueous dispersions of the gum.

2. Materials and methods

2.1. Origin and purification

The gum from *A. tortuosa* Wild, commonly known as uveda, was collected by the authors during February–April, 2002 (no raining season), from trees growing in the location of Los Puertos de Altigracia, East of Maracaibo lake, Zulia state, Venezuela, South America. The gum was collected 2 weeks after incision were made at the trunk. Taxonomic identification of the specimens was done by Dr. Lourdes Cardenas, Botanical taxonomist of the Universidad Central of Venezuela. The gum exudate was purified by dissolution, dialysis and freeze-dried.

2.2. Rheological measurements

Acacia tortuosa gum dispersions were prepared at different concentrations (15%, 20%, 25%, 30%, 40% w/v), in distilled water at $20 \pm 0.1^\circ\text{C}$. Sodium azide (0.02% w/v) was added as preservative. The dispersions were stirred at 800 rpm for 24 h, at 20°C . Rheological measurements were determined 24 h, after the dispersion preparation, the pH was around 6.2.

The influence of the gum concentration on the shear rate dependence of viscosity was studied using a Couette-type controlled-rate (CR) rheometer RV-20/CV100 (Haake) at $20 \pm 0.1^\circ\text{C}$. A step-wise procedure was applied to run the flow curves with a critical slope change for steady state (~ 0.01) and maximum shearing time per point of 90 s. The Mooney–Ewart sensor ME-45 ($R_e/R_i = 1.078$) was used for the lowest concentration (15% w/v) and the ME-31 ($R_e/R_i = 1.037$) for the remaining concentrations. The radius ratio was lower than 1.1, therefore, no shear rate correction was applied (Prentice, 1983). Small amplitude oscillatory shear (SAOS) tests were carried out in the present study to determine the linear dynamic viscoelastic properties of the highest concentration gum dispersion studied (40% w/v) at different temperatures (5, 10, 20, 25, 30 and 40°C) with a controlled-stress RS-150 rheometer (Thermo-Haake). A double-cone sensor system (1° , $R_i = 32 \text{ mm}$; $R_e = 32.35 \text{ mm}$) was used in order to obtain sensitive readings. The equilibration time after filling the sensor systems was 600 s. The results provided, the average of two independent runs, are accurate better than $\pm 5\%$ and $\pm 12\%$ in the flow curve and SAOS results, respectively.

2.3. Surface tension measurements

The influence of hydrocolloid concentration (0.01–1.5% w/v) of the gum on the surface tension was measured with a Sigma 701 tensiometer (KSV), with a jacket linked to a water circulating system (25 ± 0.1 °C). The Wilhelmy plate method was used with a roughened platinum plate (length: 19.6 mm, thickness: 0.1 mm). Surface tension data were taken 24 h, after placing the plate on the dispersion surface, to ensure the steady-state response had reached. The results ($\pm 2\%$) are the average of three measurements.

3. Results and discussion

3.1. Flow properties of *Acacia tortuosa* gum aqueous dispersions

Acacia tortuosa gum aqueous dispersions (15–40% w/v) at 20 ± 0.1 °C, Fig. 1, exhibited a non-Newtonian behaviour. They showed flow curves nearly parallel to each other and the shear thinning response dampened down above roughly 3 s^{-1} ; therefore, a limiting Newtonian high-shear viscosity could be estimated by fitting the experimental results to the Sisko model (Sisko, 1958). This model predicts the occurrence of a power-law behaviour at low-shear rate and a Newtonian response at high-shear rate.

$$\eta = K_S \dot{\gamma}_s^{n-1} + \eta_\infty$$

where η is the apparent viscosity (Pa s), K_S (Pa s^n) and n_s are the consistency index and the flow index of the Sisko model, respectively; $\dot{\gamma}$ is the shear rate (s^{-1}) and η_∞ (Pa s) stands for the so-called infinite-shear rate viscosity.

The fitting quality of the Sisko model to the experimental results obtained can be checked by comparison with the continuous line, Fig. 1, which corresponds to the fitting equation with the actual viscosity data. In addition, Table 1

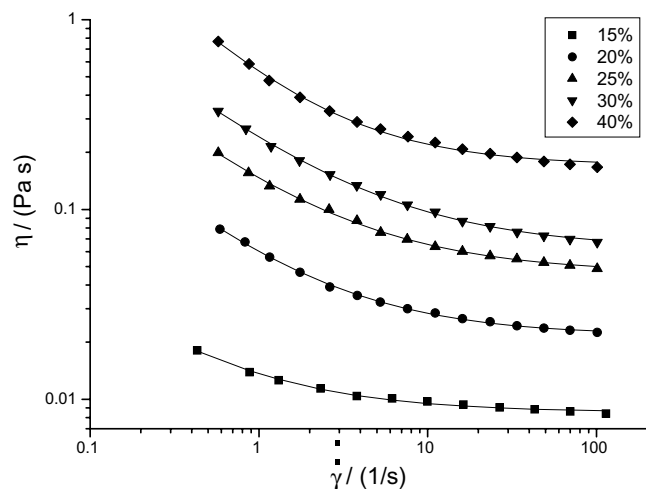


Fig. 1. Influence of *A. tortuosa* gum concentration (15–40% w/v) on the shear rate dependence of viscosity at 20 °C. Lines fits to the Sisko model. See meaning of the symbols in the inset.

shows that the addition of the squared residuals (χ^2) are quite low and the squared of the correlation index (r^2), corresponding to the linear plot of the viscosity predicted by the Sisko model versus the experimental viscosity, data are higher than 0.996. Similar qualitative flow properties have been reported for the gum exudate aqueous dispersions, above critical concentrations, from *A. senegal* (gum arabic) (Mothé & Rao, 1999; Sánchez et al., 2002; Williams et al., 1990) *A. occidentale* (cashew gum) (Mothé & Rao, 1999; Zakaria & Rahman, 1996) and *Enterolobium contortisilliquum* (Oliveira et al., 2001).

The critical shear rates above which the shear thinning behaviour dampened was found to be lower for *A. tortuosa* gum solutions (3 s^{-1}) than for *E. contortisilliquum* (from 5 s^{-1} to 10 s^{-1}), *A. senegal* and *A. occidentale* gums, (10 s^{-1}). On the other hand, *Prosopis* spp. (mesquite gum), above 20% in 0.1 M NaCl aqueous dispersions exhibit slight shear thinning behaviour along the whole shear rate range studied. No evidence of tendency towards the infinite shear-rate Newtonian viscosity up to roughly 250 s^{-1} was observed (Goycoolea et al., 1995).

The infinite-shear rate Newtonian viscosity and the consistency index of the Sisko model, which represents the difference between the viscosity at 1 s^{-1} and the infinite-shear rate viscosity, exponentially increased with *A. tortuosa* gum concentration. The average value of the Sisko flow index (0.28) was not significantly different in the studied gum dispersions (15–30% w/v). However, a further increase in the gum concentration (40% w/v) yielded a clear drop in the flow index (0.18), indicating a more marked shear thinning nature of this dispersion.

The fitting parameters obtained can be readily compared to those reported for *A. occidentale* and *A. senegal* gum dispersion (Mothé & Rao, 1999). Similar concentration range and the same rheological model were used. The flow index values obtained were lower than those reported for *A. occidentale* gum dispersions but not far from the values reported for the *A. senegal* gum at the same temperature and concentration range. However, the flow index at the highest concentration (40% w/v), reached in this study, was lower than the value reported for the corresponding *A. senegal* (gum arabic) dispersion. The values obtained for the consistency index, according to the Sisko model, were lower for *A. tortuosa* gum than those exhibited by *A. occidentale* gum and higher than those reported for gum arabic. The results obtained for the infinite-shear rate Newtonian viscosity were of the same order of magnitude.

Comparison of viscosities, at selected shear rates, revealed that *A. tortuosa* gum dispersions are less viscous than those corresponding to cashew gum dispersion, at the same concentration. The ratio of the viscosity, at 1 s^{-1} , of *A. tortuosa* gum solutions to those of cashew gum estimated from the parameters of the Sisko model, ranged from 0.19 to 0.38, depending on gum concentration. The same ratio for *A. senegal* gum, varied from 0.19 to 2.4. This fact indicates that the increase in viscosity with concentration was more important for *A. tortuosa* gum

Table 1
Influence of *A. tortuosa* gum concentration on the Sisko model parameters at 20 °C

C (% w/v)	η_{∞} (Pa s)	K_S (Pa s ⁿ)	n	χ^2	r^2
15	8.54E-3 ± 0.13E-3	5.11E-3 ± 0.20E-3	0.27 ± 0.04	3.88E-8	0.996
20	21.7E-3 ± 0.35E-3	38.4E-3 ± 0.50E-3	0.24 ± 0.02	3.23E-7	0.999
25	44.7E-3 ± 1.24E-3	100E-3 ± 1.41E-3	0.33 ± 0.02	2.21E-6	0.998
30	62.2E-3 ± 1.76E-3	179E-3 ± 2.40E-3	0.29 ± 0.02	6.85E-6	0.999
40	166E-3 ± 4.85E-3	364E-3 ± 6.40E-3	0.18 ± 0.04	6.00E-5	0.997

Confidence limits correspond to $P = .95$. χ^2 is a parameter proportional to the sum of squares of the differences between the experimental values and the calculated values for all the data points.

solutions than for the *A. senegal* gum solutions. However, differences vanish at the higher shear rates as was demonstrated by the similar values of the infinite-shear rate Newtonian viscosity.

The shape of the flow curves obtained for *A. tortuosa* gum concentration (40% w/v) Fig. 2, was not significantly influenced by temperature in the range studied (5–40 °C). A shear thinning drop of viscosity with lower shear rate was found which dampened above (3 s⁻¹). Therefore, the tendency to reach the infinite-shear rate Newtonian viscosity was observed. The results obtained fitted the Sisko model very well, (r^2) being always higher than 0.995. The Sisko flow index did not significantly vary in a temperature range (10–40 °C), considering the fitting error, Table 2. Nevertheless, the highest value, that corresponds to the less shear thinning system was found at 5 °C. This unusual value may indicate the presence of a possible heterogeneous microstructure (microaggregates) as has been proposed for high-methoxyl pectin dispersions (Da Silva, Gonçalves, & Rao, 1994). Similar behaviour was observed for the concentration dependence of the Sisko flow index of gum arabic aqueous dispersions (Mothé & Rao, 1999) which showed a drop in the flow index with gum concentration up to 25% w/v and the reverse effect was observed to higher concentration (from 25% w/v to 50% w/v). Small amplitude oscillatory shear experiments (SAOS) were also

carried out in the present study to confirm this interpretation.

Microgel structures also have been reported to occur in hydrophobic modified *Cyamopsis tetragonolobus* (guar) gum solutions, which exhibit wall depletion phenomena under shear and can flow above a critical shear stress like soft particles dispersed in a less viscous medium (Aubry, Bronce, & Moan, 2000).

Parameter K_S and the infinite-shear rate viscosity monotonically fell down with temperature, the latter exhibiting an Arrhenius-type dependence ($r^2 = 0.983$) as shown in Fig. 3.

$$\ln(\eta_{\infty T}/\eta_{\infty 293}) = (E/R) (1/T - 1/293 \text{ K})$$

The flow activation energy (E) for the onset of the infinite shear-rate Newtonian viscosity zone turned out to be 19.5 ± 1.8 kJ/mol ($P: .95$). This value is comparable to those from Newtonian viscosities of more diluted aqueous dispersions of gums from *Albizia lebbek* (17.2 kJ/mol for 3% w/v), *A. senegal* (15 kJ/mol for 2% w/v), *A. occidentale* (16.2 kJ/mol for 2% w/v) and *A. macrocarpa* (16.8 kJ/mol for 2% w/v) (De Paula et al., 2001).

The fact that an Arrhenius-type equation fitted the influence of temperature on the infinite-shear rate Newtonian viscosity seems to indicate that the main features of the equilibrium structure, which still remains after applying shear rates high enough to reach the high shear Newtonian plateau, were essentially the same within the range studied. It means that, the shear rates applied were high enough to eliminate the qualitative structural differences between the dispersion at 5 °C, and in the range (10–40 °C), as was later confirmed by SAOS experiments. The possible microaggregates occurring at 5 °C vanished under shear which was also supported by the fact that all the flow curves lay essentially parallel to each other above a shear rate as low as 3 s⁻¹.

3.2. Temperature influence on the dynamic viscoelastic properties of *Acacia tortuosa* gum aqueous dispersions

The high increase in the infinite-shear rate viscosity and the consistency index of the Sisko model upon increasing the *A. tortuosa* concentration from 30% w/v to 40% w/v encouraged us to undertake a study of the possible viscoelastic properties of the latter dispersion as a function of temperature. This was studied by small amplitude oscillatory shear (SAOS) using the double cone geometry.

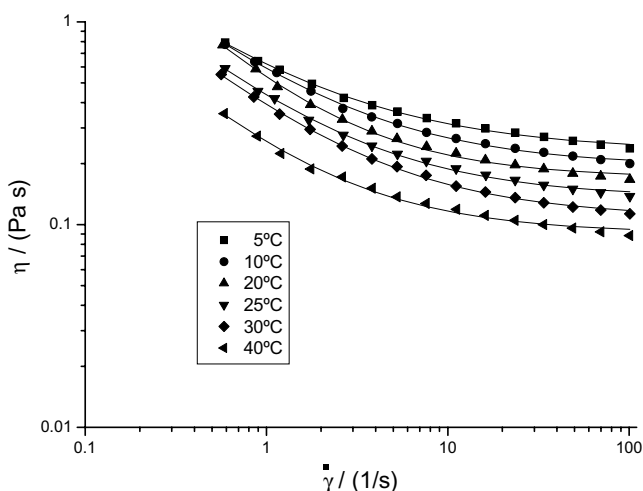


Fig. 2. Influence of temperature in a given range (5–40 °C) on the shear rate dependence of *A. tortuosa* gum aqueous dispersions (40% w/v). Lines fits to the Sisko model. See meaning of the symbols in the inset.

Table 2

Influence of temperature on the Sisko model parameters of *A. tortuosa* gum aqueous dispersion (40% w/v)

T (°C)	η_{∞} (Pa s)	K_S (Pa s ^{<i>n</i>})	n	χ^2	r^2
5	$231E-3 \pm 4.89E-3$	$388E-3 \pm 6.35E-3$	0.34 ± 0.02	$5.00E-5$	0.998
10	$194E-3 \pm 4.03E-3$	$396E-3 \pm 5.54E-3$	0.26 ± 0.02	$4.00E-5$	0.999
20	$166E-3 \pm 4.85E-3$	$364E-3 \pm 6.40E-3$	0.18 ± 0.04	$6.00E-5$	0.997
25	$136E-3 \pm 3.29E-3$	$301E-3 \pm 4.62E-3$	0.24 ± 0.02	$3.00E-5$	0.998
30	$109E-3 \pm 2.24E-3$	$282E-3 \pm 3.21E-3$	0.24 ± 0.01	$1.00E-5$	0.999
40	$90.2E-3 \pm 3.17E-3$	$166E-3 \pm 4.66E-3$	0.18 ± 0.04	$3.00E-5$	0.995

Confidence limits correspond to $P = .95$. χ^2 is a parameter proportional to the sum of squares of the differences between the experimental values and the calculated values for all the data points.

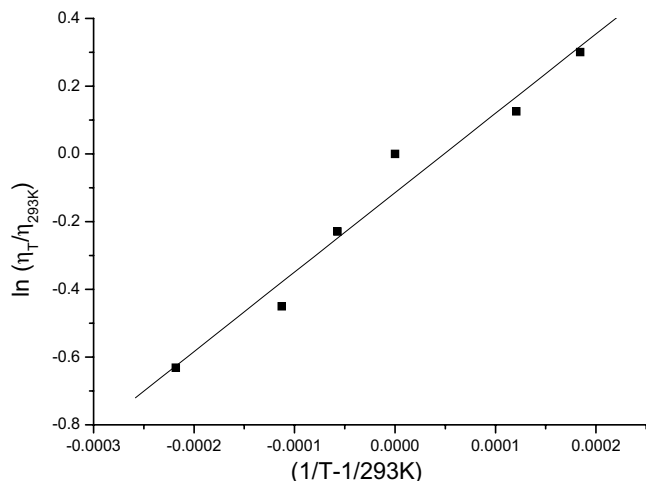


Fig. 3. Natural logarithm of the infinite-shear rate of *A. tortuosa* gum aqueous dispersion (40% w/v) vs $(1/T)$. Linear fit to an Arrhenius type equation.

The first step of the experimental protocol used was to conduct stress sweeps under oscillatory shear, at 1 Hz, to estimate the limit of the linear viscoelastic response. Accordingly, frequency sweep measurements were carried out at a strain amplitude within the linear region, which decreased from 1% to 0.1% as temperature increased from 5 °C to 25 °C. The linear response was also checked by running frequency sweeps at increasing frequencies followed by sweeps at decreasing frequencies. The fact that the storage modulus (G') as well as the loss modulus (G''), obtained by a downward frequency ramp, were the same as those calculated from the upward one. The results obtained corresponded to the linear viscoelastic region, where the microstructure of the gum dispersion is not irreversibly broken down during the test.

The mechanical spectra of *A. tortuosa* gum dispersion (40% w/v), Fig. 4, exhibited clearly viscoelastic properties (5 °C and 25 °C).

The G' values were higher than those of the G'' along the whole frequency range studied, which demonstrated that the elastic component was more important than the viscous one. In fact, the loss tangent (G''/G') values were lower than 1, on account of the existence of a phase lag between the input sinusoidal signal and the response one, lower than $\pi/4$ radians, Fig. 5. If the response oscillatory function

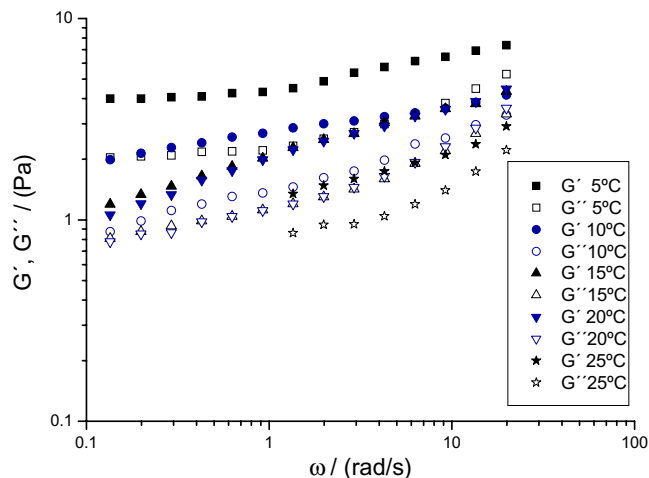


Fig. 4. Influence of temperature on the mechanical spectra of *A. tortuosa* gum aqueous dispersion (40% w/v). See meaning of the symbols in the inset.

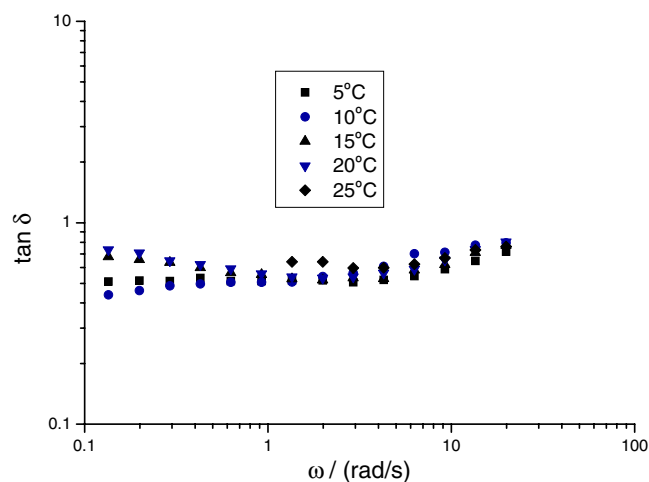


Fig. 5. Influence of temperature on the loss tangent of *A. tortuosa* gum aqueous dispersion (40% w/v). See meaning of the symbols in the inset.

of strain had been in phase with the input oscillatory function of the torque, this material would have been classified as solid. Conversely, if the response had been $\pi/2$ radians out of phase with the input signal, it would have been classified as a pure viscous (liquid-like) system (Morrison, 2001).

Both G' and G'' significantly increased as temperature dropped, the lower loss tangent values being found at 5–10 °C, support a more marked elastic response as temperature decreased. The frequency dependence of G' and G'' , in the low frequency range, where the expected response of structured systems is quite different to that of liquid-like polymer solutions (Lapasin & Priel, 1995). A progressive drop in the characteristic exponent of the power-law frequency dependence of the G' and G'' module at the lower frequencies studied was observed as temperature decreased, Table 3. The frequency dependence of G' and G'' , below 1 rad/s at 5 °C was negligible; the characteristic slopes being 0.04 for both moduli. This indicates that the response obtained corresponded to a well-developed plateau relaxation zone, which seems to be consistent with the occurrence of a small apparent equilibrium modulus, G_e , of about 4 Pa. This value is close to the range reported for very soft gels with G' values from 5 Pa to 10 Pa. These low values were attributed to the occurrence of a sort of three-dimensional network as in stronger gels (Doublier, Launay, & Cuvelier, 1992). The results obtained at 5 °C may be consistent with the formation of a reduced number of junction zones among *A. tortuosa* gum macromolecules, characterized by extremely long relaxation times. Accordingly, the life time of such junction zones is far longer than the time scale ($1/\omega$) associated to the lower frequencies reached. It is quite clear that the results obtained (5–25 °C) were far from those typical of dilute liquid-like or entangled semi-dilute polymer solutions, which exhibit the terminal relaxation zone at low frequency, characterized by $G'' \propto \omega^{-1}$ higher than $G' \propto \omega^{-2}$ and a crossover point or zone of both moduli at high frequency, which may be followed by the onset of the plateau zone. On the contrary, the results obtained seem to be consistent with the occurrence of a faint or better soft gel-like structure which becomes weaker with temperature as indicated by the progressive increase in the frequency dependence of the moduli, Table 3. In fact, above 25 °C a linear viscoelastic response could not be obtained since the lowest reliable torque applied yielded a clear drop in both the storage (G') and the loss (G'') modulus. It is interesting to note that SAOS results, which imply that the microstructure of the sample is preserved during the test, demonstrated that the structure formed at 5 °C was to some extent different to those corresponding at higher temperature (10–25 °C), while the results derived from the flow curves run at steady shear, showed only a hardly distinctive flow index at 5 °C.

Table 3
Influence of temperature on the low frequency dependence of G' and G'' of *A. tortuosa* gum aqueous dispersion (40% w/v)

T (°C)	Slope log G' vs log ω below 1 rad/s	Slope log G'' vs log ω below 1 rad/s
5	0.042	0.046
10	0.16	0.23
15	0.28	0.16
20	0.33	0.19

The rheological properties of the gum dispersions, typical of soft-gel materials, were checked by comparison of the values of the argument of the complex viscosity $|\eta^*|$ with those of the steady shear viscosity, η , at corresponding frequencies and shear rates. The power-law equation was used to interpolate the $|\eta^*|$ values at the frequencies required for comparison. Polymer solutions and polymer melts usually exhibit shear rate dependence of viscosity which coincides with the frequency dependence of the complex viscosity argument. This empirical relationship, called the Cox–Merz rule. Fig. 6, shows values of the ratio $\eta/|\eta^*|$ as a function of shear rate and frequency in the range of values obtained for both variables. The results revealed that η values were lower than $|\eta^*|$ values along the shear rate and frequency range used for comparison; the ratio $\eta/|\eta^*|$ were lower as temperature decreased. It means that *A. tortuosa* gum aqueous dispersions did not hold the Cox–Merz rule. Departures from this rule have been reported to occur in structured polymer systems such as in polymer liquid crystals or when aggregation takes place among polymer chains (Lapasin & Priel, 1995). Conversely, concentrated (50% w/v) aqueous (0.1 M NaCl) dispersions of gum arabic and mesquite gum have both been reported to follow the Cox–Merz rule and to exhibit fluid-like mechanical spectra like those typically shown by entangled solutions of linear polysaccharides (Goycoolea et al., 1995).

It must be noted that *A. tortuosa* gum aqueous dispersion exhibited the highest elastic response (solid-like) at 5 °C, the longest relaxation time on account of the formation of the most complex structure and the most marked departure from the Cox–Merz rule. This is consistent with the rupture of the weak structure formed by *A. tortuosa* gum aqueous dispersions under steady shear, which it is not irreversibly disturbed in SAOS experiments. This is a further evidence of the occurrence of a soft-gel structure,

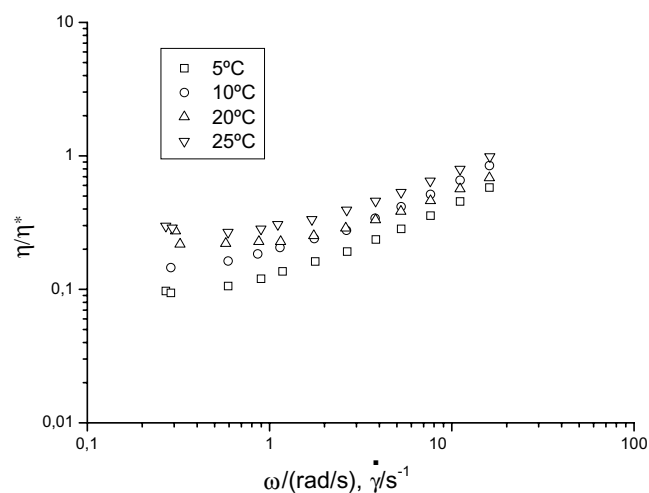


Fig. 6. Influence of temperature on the ratio $\eta/|\eta^*|$ as a function of shear rate and frequency for *A. tortuosa* gum aqueous dispersion (40% w/v). See meaning of the symbols in the inset.

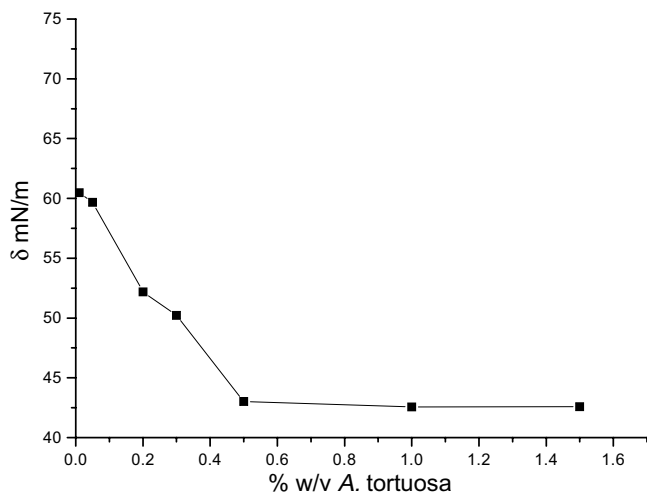


Fig. 7. Steady-state surface tension of *A. tortuosa* gum aqueous dispersions (0.01–1.5% w/v) at 25 °C.

based on non-covalent cross-links with bonds energy of a few kT units that can be easily disrupted by mechanical perturbation, as has been reported (Ross-Murphy, 1995). Electrostatic, dipole–dipole, van der Waals, hydrophobic and hydrogen bonding interactions may cooperatively contribute to the formation of such non-covalent cross-links (Kavanagh & Ross-Murphy, 1998).

3.3. Surface tension

Fig. 7 illustrates that an increase in the concentration (w/v) of *A. tortuosa* gum from 0.01% to 0.5% yielded a very high fall in surface tension as compared with the reference value of water at 25 °C (72.5 mN/m). The value surface tension (42.6 mN/m) in a given concentration (0.5% w/v) is below to the value reported for gum arabic (46.9 mN/m) at 0.5% w/w (Huang, Kakuda, & Cui, 2001) and for others food gums (65–45 mN/m) (Garti et al., 1999). The emulsifying/stabilising properties of the gum arabic (Ibanoglu, 2002; Whistler & Bemiller, 1993; Tan, 2004, chap. 12) have been related to a possible arabinogalactan–protein complex (Williams et al., 1990). This complex has also been reported for *A. tortuosa* gum (Beltrán et al., 2005b).

4. Conclusions

Acacia tortuosa gum aqueous dispersions (15–40%) displayed shear thinning non-Newtonian flow properties at 20 °C, fitting the Sisko model since, a tendency towards a high-shear limiting Newtonian viscosity was observed. At 40% w/v a substantial increase in viscosity and shear thinning properties took place, indicating the occurrence of a structured polymeric dispersion, which was progressively stronger as the temperature was decreased. The fact that the temperature dependence of the infinite shear-rate Newtonian viscosity of the 40% w/v dispersion, fitted an Arrhenius-type equation indicated that the equilibrium structure

at high-shear rate was of the same nature from 5 °C to 40 °C. The aqueous dispersion gum of *A. tortuosa* (40% w/v) exhibited clear viscoelastic properties from 5 °C to 25 °C, the elastic component turning out to be always higher than the viscous one in small amplitude oscillatory shear. The viscoelastic results indicated the occurrence of a very soft gel-like structure which became progressively weaker with temperature. The failure of the Cox–Merz rule was a further evidence that these dispersions formed a sort of three-dimensional network with a reduced number of low energy junction zones, which was more evident at 5 °C on account of both the lowest value of the $\eta/|\eta^*|$ ratio and the flat frequency dependence of both G' and G'' at low frequency.

The significant drop in surface tension with *A. tortuosa* gum concentration along with its interesting rheological properties indicate that this gum may compete with gum arabic as both emulsifier and stabiliser of some food emulsions. The results obtained open up the need to undertake comprehensive studies on the formation and characterization of emulsions formulated with *A. tortuosa* gum.

Acknowledgements

The authors kindly acknowledge the financial support provided to F. Rincon by University of Zulia (CONDES and International Relations Department), and FONACIT, Venezuela, to carry out a research work on polymers rheology in the Chemical Engineering Department of the University of Seville (Spain).

References

- Al-Assaf, S., Phillips, G., & Williams, P. (2005). Studies on *Acacia* exudate gums: Part II. Molecular weight comparison of the Vulgares and Gummiferae series of *Acacia* gums. *Food Hydrocolloids*, 19, 661–667.
- Anderson, D. M. W., & Karamalla, K. A. (1966). The composition of *Acacia* gum exudates. *Journal Chemistry Society (c)*, 762–764.
- Anderson, D. M. W., Bell, P. C., & Millar, J. P. A. (1974). Composition of gum exudates from *Anacardium occidentale*. *Phytochemistry*, 8, 167–176.
- Anderson, D. M. W., & León de Pinto, G. (1982). Gum exudates from the genus *Grevillea* (Proteaceae). *Carbohydrate Polymers*, 2, 19–24.
- Anderson, D. M. W., Bridgeman, M. M. E., & León de Pinto, G. (1984). *Acacia* gum exudates from species of the Series Gummiferae. *Phytochemistry*, 23, 575–577.
- Anderson, D. M. W., & Weiping, W. (1991). The characterization of gum arabic (*Acacia senegal*) samples from Uganda. *Food Hydrocolloids*, 5, 297–306.
- Aubry, T., Bronce, L., & Moan, M. (2000). Gap effects in a rheometrical flow of a hydrophobically associating polymer solution: Apparent slip or material instability. *Applied Rheology*, 10, 31–36.
- Beltrán, O., León de Pinto, G., Martínez, M., & Rincón, F. (2005a). Comparación de los datos analíticos de *Acacia macracantha* y *Acacia tortuosa* y otras Gummiferae. *Afinidad*, 62(517), 237–241.
- Beltrán, O., León de Pinto, G., Martínez, M., Picton, L., Cozic, C., Le Cerf, D., et al. (2005b). Fractionation and characterization of gum from *Acacia tortuosa* effect of enzymatic and alkaline treatments. *Carbohydrate Polymers*, 62, 239–244.
- Da Silva, J. A. L., Gonçalves, M. P., & Rao, M. A. (1994). Influence of temperature on dynamic and steady shear rheology of pectin dispersions. *Carbohydrate Polymers*, 23, 77–87.

- De Paula, R. C. M., Santana, S. A., & Rodrigues, J. F. (2001). Composition and rheological properties of *Albizia lebbbeck* gum exudate. *Carbohydrate Polymers*, 44, 133–139.
- Dickinson, E. (2003). Hydrocolloids at interfaces and the influence on the properties of dispersed systems. *Food Hydrocolloids*, 17, 25–39.
- Doublier, J. L., Launay, B., & Cuvelier, G. (1992). Viscoelastic properties of food gels. In M. A. Rao & J. F. Steffe (Eds.), *Viscoelastic properties of foods*. London: Elsevier Applied Science.
- Duvallet, S., Fenyo, J. C., & Vandeveld, M. C. (1993). The characterization of gum arabic from an experimental field of Ferlo (North Senegal). *Food Hydrocolloids*, 7, 319–326.
- Fauconnier, Marie-L., Blecker, C., Groyne, J., Razafindralambo, H., Vanzeveren, E., Marlier, M., et al. (2000). Characterization of two *Acacia* gums and their fractions using Langmuir film balance. *Journal Agriculture Food Chemistry*, 48, 2709–2712.
- Garti, N., & Reichman, D. (1994). Surface properties and emulsification activity of galactomannans. *Food Hydrocolloids*, 8(2), 155–173.
- Garti, N., Slavin, Y., & Aserin, A. (1999). Surface and emulsification properties of a new gum extracted from *Portulaca oleoracea*. *Food Hydrocolloids*, 13(2), 145–155.
- Goycoolea, F. M., Morris, E. R., Richardson, R. K., & Bell, A. E. (1995). Solution rheology of mesquite gum in comparison with gum arabic. *Carbohydrate Polymers*, 27, 37–45.
- Huang, X., Kakuda, Y., & Cui, W. (2001). Hydrocolloids in emulsions: Particle size distribution and interfacial activity. *Food Hydrocolloids*, 15, 533–542.
- Ibanoglu, E. (2002). Rheological behaviour of whey protein stabilized emulsions in the presence of gum arabic. *Journal of Food Engineering*, 52, 272–277.
- Islam, A., Phillips, G., Sliivo, A., Snowden, M., & Williams, P. A. (1997). A review of recent developments on the regulatory structural and functional aspects of gum arabic. *Food Hydrocolloids*, 11(4), 493–505.
- Kavanagh, G. M., & Ross-Murphy, S. B. (1998). Rheological characterisation of polymer gels. *Progress in Polymer Science*, 23, 533–562.
- Lapasin, R., & Prici, S. (1995). *Rheology of industrial polysaccharides. Theory and applications*. London: Blackie Academic & Professional, Chapman & Hall.
- León de Pinto, G., Martínez, M., Ortega, S., Villavicencio, N., & Rojas, L. (1993a). Comparison of gum specimens from *Acacia tortuosa* and other Gummiferae species. *Biochemical Systematic and Ecology*, 21, 795–797.
- León de Pinto, G., Rodríguez, O., Martínez, M., & Rivas, C. (1993b). Composition of *Cercidium praecox* gum exudates. *Biochemical Systematic and Ecology*, 21, 297–300.
- León de Pinto, G., Martínez, M., Mendoza, J., Ocando, E., & Rivas, C. (1995). Comparison of three Anacardiaceae gum exudates. *Biochemical Systematic and Ecology*, 23, 151–156.
- León de Pinto, G., Martínez, M., Bolaño de, L. M., & Rivas, C. (1998). The polysaccharide gum from *Acacia tortuosa*. *Phytochemistry*, 47(1), 53–56.
- Martínez, M., León de Pinto, G., & Rivas, C. (1992). Composition of *Acacia macracantha* gum exudates. *Phytochemistry*, 31, 535–536.
- Mothé, C. G., & Rao, M. A. (1999). Rheological behavior of aqueous dispersions of cashew gum and gum arabic: Effect of concentration and blending. *Food Hydrocolloids*, 13, 501–506.
- Morrison, F. A. (2001). *Understanding rheology*. New York: Oxford University Press.
- Oliveira, J. D., Silva, D. A., De Paula, R. C. M., Feitosa, J. P. A., & Paula, H. C. B. (2001). Composition and effect of salt on rheological and gelation properties of *Enterolobium contortisiliquum* gum exudate. *International Journal Biological Macromolecules*, 29, 35–44.
- Picton, L., Bataille, I., & Muller, G. (2000). Analysis of a complex polysaccharide (gum arabic) by multi-angle laser light scattering coupled on-line to size exclusion chromatography and flow field flow fractionation. *Carbohydrate Polymer*, 42, 23–31.
- Prentice, J. H. (1983). Precision and accuracy on viscometric measurements on foods. *Journal of Rheology*, 27, 621–635.
- Ross-Murphy, S. B. (1995). Structure-relationships in food biopolymer gels and solutions. *Journal of Rheology*, 39, 1451–1463.
- Sánchez, C., Renard, D., Robert, P., Schmitt, C., & Lefebvre, J. (2002). Structure and rheological properties of *Acacia* gum dispersions. *Food Hydrocolloids*, 16, 257–267.
- Siddig, N. E., Osman, M. E., Al-Assaf, S., Phillips, G. O., & Williams, P. A. (2005). Studies on *Acacia* exudates gums. Part IV. Distribution of molecular components in *Acacia seyal* in relation to *Acacia senegal*. *Food Hydrocolloids*, 19, 679–686.
- Sisko, A. W. (1958). Flow of lubricating greases. *Industrial Engineering and Chemistry*, 50, 1789–1792.
- Tan, C. T. (2004). Beverage emulsions. In S. Friberg, K. Larsson, & J. Sjöblom (Eds.), *Food emulsions* (4th ed.). New York: Marcel Dekker.
- Whistler, R. L., & Bemiller, J. N. (1993). *Industrial gums* (3rd ed.). San Diego: Academic Press.
- Williams, P. A., Phillips, G. O., & Randall, R. C. (1990). Structure–function relationships of gum Arabic. In G. O. Philips, D. J. Wedlock, & P. A. Williams (Eds.), *Gums and stabilisers for the food industry* (Vol. 5, pp. 25–36). Oxford: IRL Press.
- Zakaria, M. B., & Rahman, Z. Ab. (1996). Rheological properties of cashew gum. *Carbohydrate Polymers*, 29(1), 25–27.