

1 **Effect of concentration on shear and extensional rheology of guar gum solutions**

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21 **Effect of concentration on shear and extensional rheology of guar gum solutions**

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23

24 **Abstract**

25 The steady shear and extensional rheology of aqueous guar gum solutions was studied for  
26 concentrations,  $C$ , ranging from 1 g/L to 20 g/L. Extensional rheometry measurements were made  
27 using the Cambridge Trimaster filament-stretching device. The steady shear tests indicated a  
28 transition between a semi-dilute regime, below 10 g/L, and an entangled regime at higher  
29 concentrations. The solutions were shear-thinning solutions and obeyed the unmodified Cox-Merz  
30 rule in the dilute regime, but deviated from Cox-Merz and exhibited strongly viscoelastic behaviour  
31 at higher concentrations. The surface tension at higher concentration also deviated from the  
32 Szyszkowski model, exhibiting behaviour consistent with entanglement. The filament-thinning data  
33 did not fit the model for polymer solution behaviour presented by Entov and Hinch (1997), but gave  
34 a good fit to a modified form where time was normalized by the time for filament break-up. This  
35 scaling was independent of concentration effects, as reported by Chesterton *et al.* (2011) for cake  
36 batters. The modified model parameters approached asymptotic values for entangled solutions. The  
37 estimated apparent extensional viscosity exhibited a peak at unit strain followed by a constant value.  
38 The former increased as  $C^n$ , where  $n > 1$ , while the latter increased linearly with  $C$ .

39

40 **Keywords** Elasticity; Extensional; Non-ionic hydrocolloids; Relaxation time; Viscosity

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## 41 Nomenclature

### Roman

$a$	fitting parameter, Szyszkowski equation, N/m
$b$	fitting parameter of Szyszkowski equation, g/L
$b'$	parameter Equation [16], -
$Bo$	Bond number, -
$C$	concentration, g/L
$c^*$	critical concentration, g/L
$D_b$	diameter at break-up ( $\mu\text{m}$ )
$D_{\text{mid}}$	diameter of the filament at midpoint ( $\mu\text{m}$ )
$D_0$	initial sample diameter ( $\mu\text{m}$ )
$D_1$	diameter of the filament when first formed ( $\mu\text{m}$ )
$F$	normal force correction, N
$F_{\text{normal}}$	normal force generated by the flow between plates, N
$k$	time constant, $\text{s}^{1-n}$
$g$	gravitational constant, $\text{m/s}^2$
$G'$	storage modulus, Pa
$G''$	loss modulus, Pa
$L$	number of relaxation times, -
$M_n$	number-average molar mass, g/mol
$M_w$	weight-average molar mass, g/mol
$M_z$	higher-average molar mass, g/mol
$n$	flow index, -
$N_1$	first normal stress difference, Pa
$N_2$	second normal stress difference, Pa
$N_{Tr}$	Trouton number, -
$p$	probability, -
$R_{pp}$	radius of parallel-plate geometry, m

$R^2$	square of the correlation coefficient, -
$t$	time, s
$t_{cap}$	capillary time, s
$t_{F0}$	time to capillary break-up (water), s
$t_F$	time to capillary break-up, s
$T$	torque, N m
$X$	filament shape factor, Equation (5), -

**Greek**

$\varepsilon$	Hencky strain, -
$\dot{\varepsilon}$	Hencky strain rate, s <sup>-1</sup>
$\dot{\gamma}$	shear rate, s <sup>-1</sup>
$\dot{\gamma}_R$	shear rate experienced at the rim of the parallel plates, s <sup>-1</sup>
$\Gamma$	surface tension between liquid phase and the air, N/m
$\Gamma_0$	surface tension between the solvent and air, N/m
$\eta_{app}$	apparent viscosity, Pa s
$\eta_e$	estimated apparent extensional viscosity, Pa s
$\eta_0$	zero-shear-rate viscosity, Pa s
$\eta_p$	polymeric contribution to the viscosity, Pa s
$\eta_s$	solvent viscosity, Pa s
$ \eta^* $	magnitude of the complex viscosity, Pa s
$\lambda$	relaxation time, s
$\rho$	density, kg/m <sup>3</sup>
$\tau$	shear stress, Pa
$\omega$	angular frequency, Hz
$\Omega$	angular velocity, rad/s

## 43 Introduction

44 Solutions of water-soluble polysaccharides such as guar gum are widely used as thickeners,  
45 stabilisers or gelling agents for food applications as well as in pharmaceutical, biomedical, chemical  
46 and cosmetic products (Rosell *et al.*, 2007). The molecular interactions between the polymer and  
47 water as well as polymer chain length determine the rheology of these solutions; polysaccharide  
48 chemical structure and size can, therefore, be exploited to develop new products, control processing  
49 quality and optimise the design of process equipment (Durand, 2007).

50

51 Guar gum is a galactomannan and one of the most cost effective natural hydrocolloids due to its  
52 ready availability and ease of manufacture by extraction from *Cyamopsis tetragonolobus* seeds  
53 (Cunha *et al.*, 2007). This long-chain polysaccharide biopolymer is highly polydisperse  
54 (Sittikijyothin *et al.*, 2005), has a semiflexible random coil conformation composed of a linear  
55 mannan backbone bearing side chains of a single galactose unit (Imeson, 2010), and contains a  
56 mannose to galactose ratio of ~1.6-1.8:1 (Cunha *et al.*, 2007). Aqueous guar gum solutions are  
57 widely used in food products (*e.g.* Miquelim and Lannes, 2009; Moreira *et al.*, 2011) at different  
58 concentrations as a thickening and stabilising agent (Duxenneuner *et al.*, 2008; Bourbon *et al.*,  
59 2010). In contrast to synthetic polymers, guar gum can form highly viscous solutions at low  
60 concentrations (< 1%) which are relatively insensitive to pH, addition of electrolytes and heating  
61 (Sittikijyothin *et al.*, 2005).

62

63 As a viscosity modifier, knowledge of the effect of concentration on solution rheology is required for  
64 both product and process design (Moreira *et al.*, 2011). The shear rheology of aqueous guar gum  
65 solutions has been investigated by many researchers who have probed structure-function-property  
66 parameters to gain insight into how, for example, molecular structure and solubility affect the  
67 resultant solution properties (*e.g.*, Launay *et al.*, 1997; Oblonsek *et al.*, 2003; Cunha *et al.*, 2005;  
68 Chenlo *et al.*, 2009, 2010). Guar gum solutions usually exhibit non-Newtonian, shear-thinning,  
69 behaviour, where the apparent viscosity decreases with increasing shear rate. The apparent viscosity  
70 depends mainly on the molar mass while synergistic interactions are determined by the  
71 mannose/galactose ratio and the fine structure of the galactomannan chain.

72

73 The majority of studies of guar gum rheology have considered shear rheology: relatively few have  
74 investigated the extensional rheology of these solutions despite its importance in many food  
75 processing operations, consumer perception studies and product quality evaluation (Padmanabhan *et*  
76 *al.*, 1995; Bourbon *et al.*, 2010). Much of the work on extensional rheology has considered well  
77 characterised, model synthetic polymer solutions, and there is little published on the behaviour of  
78 systems containing guar gum and its derivatives, besides that by Tatham *et al.* (1995), Duxenneuner  
79 *et al.* (2008) and Bourbon *et al.* (2010). Duxenneuner *et al.* (2008) presented a comprehensive study  
80 of the shear and extensional rheological properties of hydroxypropyl ether guar gum solutions at  
81 concentrations up to 5 g/L. They investigated the effect of concentration on either the characteristic  
82 relaxation times or the transient uniaxial apparent extensional viscosities of dilute and semidilute  
83 modified guar gum solutions using a capillary breakup extensional rheometer (CaBER) device.  
84 Bourbon *et al.* (2010) studied the steady shear and extensional flow of aqueous guar gum solutions  
85 with concentrations between 0.39-0.97 g/L. They reported that the break-up time, relaxation time  
86 and elastic modulus increased with increasing polymer concentration. These results were confirmed  
87 here. The use of these devices to study biopolymers is increasing, including entagled cellulose  
88 solutions (Haward *et al.*, 2012) and pitcher plant liquids (Gaume and Forterre, 2007).

89

90 This paper presents an investigation of the effects of concentration on the shear and extensional  
91 rheology of guar gum solutions, extending previous work undertaken by other researchers by  
92 examining a wider range of solution concentrations (1-20 g/L, covering the range from dilute to  
93 entangled behaviour), and linking these observations to synthetic polymer solution behaviour. The  
94 aim is to improve the understanding of the rheological behaviour of guar gum solutions in extension  
95 to allow these materials to be used more efficiently, with reduced development time.

96

97 The present work follows on from investigations of bubbly liquids with a non-Newtonian liquid  
98 phase (Torres *et al.*, 2013) and moderately high bubble volume fractions (25 %), where the presence  
99 of a significant number of bubbles gave rise to viscoelastic behaviour that could not be described  
100 adequately by the existing literature. Similar findings were reported for cake batters by Meza *et al.*

101 (2011) and Chesterton *et al.*, (2011). The results reported here allow the contribution from the guar  
102 gum solutions to the viscoelastic behaviour observed in guar gum-based bubbly liquids to be  
103 computed.

104

#### 105 *Extensional rheology*

106 Measurements of extensional rheology are needed to characterise fluid properties fully (Odell &  
107 Carrington, 2006). Experimental investigation of extensional flows is challenging, particularly for  
108 viscoelastic materials (Vadillo *et al.*, 2012a), partly due to difficulties in creating a purely  
109 extensional flow. During a shear deformation, the fluid elements within the material move in the  
110 same direction and slide over each other, whereas in extension the fluid elements either move away  
111 or towards each other as the material is stretched or compressed, respectively (Entov and Hinch,  
112 1997). Various testing methods are used (Steffe, 1996; Macosko, 1994) and this study employs the  
113 filament thinning technique. The relaxation and decay of a necked sample is controlled by a balance  
114 between inertial, viscous, elastic, gravitational and capillary forces (Anna and McKinley, 2001).

115

116 The extensional viscosity of synthetic polymer solutions is sensitive to molecular weight and extent  
117 of long chain branching (Anna and McKinley, 2001). Addition of polymer increases the shear and  
118 extensional viscosity of the fluid and promotes viscoelastic behaviour, which can strongly affect  
119 filament thinning and break-up mechanisms (McKinley, 2005; Tuladhar and Mackley, 2008; Vadillo  
120 *et al.*, 2010; Haward *et al.*, 2012). There are very relatively few investigations of the effect of  
121 concentration on the extensional properties of synthetic polymer solutions. Behaviour analogous to  
122 shear rheology is expected, where at higher concentrations the molecules entangle with each other,  
123 limiting the length to which the molecule can be extended. Another effect of concentration is the  
124 impact of the polymer chain on the flow field itself (Gupta *et al.*, 2000). A transition from the dilute  
125 to the entangled regime behaviour is therefore expected for guar gum solutions.

126

127 Many mathematical approximations for extensional rheology behaviour have been implemented and  
128 several closed form constitutive equations exist (Bird *et al.*, 1987; Larson, 1988). Most testing has  
129 been conducted with shear flows, and the reliability of these equations for strongly extensional



130 flows, where a substantial degree of stretching is anticipated, is not well understood and the  
131 available constitutive equations are not able to predict all the measured transient extensional stresses  
132 (Gupta *et al.*, 2000).

133

## 134 **Materials and Methods**

### 135 **Sample preparation**

136 Commercial guar gum was supplied by Sigma-Aldrich (batch no. 041M0058V, India) with a  
137 reported molecular weight of  $2.9 \times 10^6$  g/mol. The weight-average molar mass ( $M_w$ ) was determined  
138 by gel permeation chromatography (GPC) with a Dawn Heleos-II instrument (Wyatt Technologies)  
139 at room temperature, around  $21^\circ\text{C}$ , using a PL-aquagel-OH Mixed-H column ( $7.5 \text{ mm} \times 300 \text{ mm}$ ,  
140 Agilent Technologies), flow rate of 0.5 mL/min, polysaccharide concentration of 0.1% (w/v) with  
141 water as the solvent. A differential refractometer was used as the detector. Pullulan samples (Shodex  
142 Denko) of  $M_w$   $5.9 \times 10^3$ ,  $1.18 \times 10^4$ ,  $4.73 \times 10^4$ ,  $2.12 \times 10^5$  and  $7.88 \times 10^5$  g/mol were used as standards.  
143 This yielded a  $M_w$  value of  $3.0 \times 10^6$  g/mol and a small degree of polydispersity, characterised by  $M_w/$   
144  $M_n = 1.13$  and  $M_z/M_n = 5.15$ , where  $M_n$  and  $M_z$  are the number average molecular weight and higher  
145 average molecular weight, respectively.

146

147 Aqueous solutions of guar gum at concentrations of 1, 2, 5, 10, 15 and 20 g/L were prepared  
148 following the procedure reported by Chenlo *et al.* (2010). The polymer was dispersed in tap water by  
149 stirring at 1400 rpm on a magnetic hotplate stirrer (VMS-C4 Advanced, VWR, UK) at room  
150 temperature, between  $19^\circ\text{C}$  and  $21^\circ\text{C}$ , overnight to ensure complete hydration of the guar gum.  
151 Some air was incorporated into the solution during stirring and deaerated samples of the continuous  
152 phase were obtained by centrifugation at 2250 rpm (500 g) for 5 min. All samples were, at  
153 minimum, duplicated.

154

### 155 **Shear rheology**

156 Shear rheological measurements (under steady and oscillatory shear) were performed on a Bohlin  
157 CVO120HR controlled-stress rheometer (Malvern Instruments, Malvern, UK) using sand-blasted  
158 parallel plates (25 mm diameter and 1 mm gap) to prevent wall slippage. Preliminary tests with

159 different gap sizes (0.25, 0.5, 0.75 and 1.0 mm) showed good agreement, indicating the absence of  
 160 significant slip effects. Samples were loaded carefully to ensure minimal structural damage, and held  
 161 at rest for 5 min before testing to allow stress relaxation and temperature equilibration. A thin film of  
 162 a Newtonian silicone oil (viscosity 1 Pa s) was applied to the exposed sample edges to prevent  
 163 evaporation. All measurements were made under isothermal conditions (20 °C) and, at minimum,  
 164 duplicated. Error bars corresponding to experiment variation of repeated tests are plotted where the  
 165 measurement uncertainty was greater than the symbol size.

166

### 167 *Steady shear measurements*

168 Viscous behaviour was investigated using steady shear measurements. The apparent viscosity,  $\eta_{app}$ ,  
 169 was determined as function of shear rate,  $\dot{\gamma}$ , over the range of 0.1 to 1000 s<sup>-1</sup>. Samples were sheared  
 170 for 5 s at each shear rate in order to obtain steady-state. Since the shear rate varies with radial  
 171 position in the parallel plate geometry, the apparent viscosity data were calculated using (Steffe,  
 172 1996):

$$173 \quad \eta_{app}(\dot{\gamma}_R) = \frac{T}{2\pi R_{pp}^3 \dot{\gamma}_R} \left( 3 + \frac{d \ln T}{d \ln \dot{\gamma}_R} \right) \quad (1)$$

174 where  $\dot{\gamma}_R$  is the shear rate evaluated at the rim considering angular velocity and geometry,  $R_{pp}$  is the  
 175 radius of the parallel plates and  $T$  is the torque. Using linear regression, a relationship between the  
 176 torque and shear rate data can be obtained in this study, being the slope term defined as  $\frac{d \ln T}{d \ln \dot{\gamma}_R}$ .

177

178 The shear-thinning behaviour of guar gum solutions was fitted to the Cross-Williamson model  
 179 (Cross, 1965):

$$180 \quad \frac{\eta_{app}}{\eta_0} = \frac{1}{1 + k \dot{\gamma}^{(1-n)}} \quad (2)$$

181 where  $\eta_0$  is the zero-shear rate viscosity,  $k$  is the time constant and  $n$  is the flow index.

182

183 The normal force,  $F_{normal}$ , generated by the flow between plates was measured in steady shear tests  
184 on the Bohlin rheometer. Measurements of axial thrust were used to estimate the normal stress  
185 difference,  $N_1 - N_2$  via (Steffe, 1996):

$$186 \quad N_1 - N_2 = \frac{2F_{normal}}{\pi R_{pp}^2} \left( 1 + \frac{1}{2} \frac{d \ln F_{normal}}{d \ln \dot{\gamma}_R} \right) \quad (3)$$

187 The normal stress difference data were compared to the computed shear stress and apparent viscosity  
188 results to give an indication of when elastic forces became significant. The normal force correction  
189 due to inertial effects was estimated using (Kulicke *et al.*, 1977):

$$190 \quad F = -0.075 \pi \rho \Omega^2 R_{pp}^4 \quad (4)$$

191 where  $\Omega$  is the angular velocity and  $\rho$  the liquid density. This force correction was negligible for all  
192 tests conducted here.

193

#### 194 *Oscillatory shear measurements*

195 Viscoelastic behaviour was studied using small amplitude oscillatory shear testing. A strain sweep  
196 was performed from 0.01 to 10% at frequencies of 0.01 and 10 Hz prior to each frequency sweep to  
197 ensure that tests were performed in the linear viscoelastic (LVE) region for each solution. Frequency  
198 sweeps were carried out over the range 0.01 to 10 Hz at a strain amplitude of 1% (well below the  
199 LVE limit) and the storage modulus,  $G'$ , loss modulus,  $G''$ , and magnitude of the complex dynamic  
200 viscosity,  $|\eta^*|$ , were determined using the rheometer software.

201

#### 202 *Extensional rheology*

203 Extensional rheology was investigated using the Cambridge Trimaster, a high-speed filament stretch  
204 and break-up device described by Vadillo *et al.* (2010). The apparatus consists of two cylindrical 1.2  
205 mm diameter stainless steel stubs which are moved vertically apart at high speed with high spatial  
206 precision. Measurements reported here featured an initial gap spacing of 0.6 mm, final gap spacing  
207 of 1.5 mm and piston separation speed of 75 mm s<sup>-1</sup>. All experiments were performed at least in  
208 duplicate in an air-conditioned room at 20 °C.

209

210 The filament stretching and thinning profiles were monitored using a high speed camera (Photron  
211 Fastcam 1024 PCI) which allows the diameter of the filament midpoint,  $D_{mid}(t)$ , to be measured to  
212  $\pm 0.1 \mu\text{m}$  at a rate of 6000 frames per second. The device did not feature a force transducer so  
213 separating forces were not recorded. Estimates of the apparent extensional viscosity,  $\eta_e$ , can be  
214 obtained from the filament regime using (Vadillo *et al.*, 2010):

$$215 \quad \eta_e = (2X - 1) \frac{-\Gamma}{dD_{mid}(t)/dt} \quad (5)$$

216 where  $X$  is a coefficient which accounts for the deviation of the filament shape from a uniform  
217 cylinder due to inertia and gravity,  $\Gamma$  is the surface tension between the liquid phase and the air, and  $t$   
218 is the elapsed time. Several authors report  $X$  values of  $\sim 0.7$  for polymer solutions at approximately  
219 zero Reynolds number (McKinley and Tripathi, 2000; Vadillo *et al.*, 2010) whereas  $X$  values  
220 equalling 0.5912 have been derived by Eggers, 1997 (and further reported by McKinley and  
221 Tripathi, 2000) from the universal similarity solution describing the breakup of a Newtonian fluid at  
222 non-zero Reynolds numbers. Although the non-zero Reynolds number condition can be shown to be  
223 met for the solution containing 1 g/L of guar gum, it introduces an unphysical discontinuity in the  
224 trends of extensional viscosity as a function of concentration, presented later, hence  $X$  values  
225 equalling  $\sim 0.7$  were used in Equation (5).

226

227 The equilibrium surface tension between the guar gum solutions and air at 21 °C was determined  
228 experimentally using the sessile drop method with a Kruss Drop Shape Analyser 100 device. Values  
229 reported are the mean from at least ten measurements.

230

231 Filament measurements were obtained using automatic image treatment in the Cambridge Trimaster  
232 software. Three characteristic diameters were recorded:  $D_0$ , the initial sample diameter, being that of  
233 the plates;  $D_1$ , the diameter of the filament when first formed, and  $D_b$ , the diameter at break-up. The  
234 symmetry of the sample during thinning was checked by comparing the filament diameter at  
235 positions 100  $\mu\text{m}$  above and below the mid-plane, and asymmetric results discarded. The influence  
236 of gravity is characterised by the Bond number:

237 
$$Bo = \frac{\rho g D_0^2}{4\Gamma} \quad (6)$$

238 where  $g$  is the gravitational constant. The sample density was estimated by weighing a 150 mL  
 239 plastic cup filled with guar gum solution. The surface was levelled off using a spatula, the cup  
 240 weighed and the density determined as the ratio of the mass of sample to cup volume. The material  
 241 parameters lie in the range  $\rho \sim 1086 \text{ kg m}^{-3}$ ,  $g = 9.81 \text{ m s}^{-2}$ ,  $D_0 = 1.2 \text{ mm}$  and  
 242  $\Gamma \sim 0.067 \text{ N m}^{-1}$ , giving  $Bo$  values around 0.04. Gravitational effects are therefore expected to be  
 243 negligible. Transient profiles recorded on the Trimaster for guar gum concentrations of 1 g/L, 10 g/L  
 244 and 20 g/L can be found in the Supplementary Data.

245

246 The Hencky strain,  $\varepsilon$ , experienced by the sample at the axial midplane at time  $t$  is defined using the  
 247 midfilament diameter:

248 
$$\varepsilon = 2 \ln \left( \frac{D_1}{D_{mid}(t)} \right) \quad (7)$$

249 The apparent extensional viscosity is compared with the apparent viscosity *via* the Trouton number,  
 250  $N_{Tr}$ . This is the ratio of apparent extensional to shear viscosity at equivalent shear rates, which, for  
 251 non-Newtonian fluids is given by (Steffe, 1996):

252 
$$N_{Tr} = \frac{\eta_e \left( \dot{\varepsilon} \right)}{\eta_{app} \left( \sqrt{3} \dot{\varepsilon} \right)} \quad (8)$$

253 where  $\dot{\varepsilon}$  is the Hencky strain rate. For Newtonian fluids at small strains,  $N_{Tr} = 3$ . Departure from this  
 254 result is due to viscoelastic material behaviour (Steffe, 1996).

255

256 Several studies (Bazilevsky *et al.*, 1990; Renardy, 1994, 1995; Brenner *et al.*, 1996; Bazilevsky *et al.*,  
 257 1997; Entov and Hinch, 1997) have presented theoretical treatments predicting the evolution of the  
 258 midfilament diameter for both Newtonian and viscoelastic fluids. Entov and Hinch modelled the  
 259 fluid as a FENE material and reported that the midfilament diameter decreased exponentially with  
 260 time:

261 
$$D_{mid}(t) = \left( \frac{\eta_p D_1^4}{2\lambda\Gamma} \right)^{1/3} \exp\left(\frac{-t}{3\lambda}\right) \quad (9)$$

262 where  $\eta_p = \eta_0 - \eta_s$  is the polymeric contribution to the viscosity ( $\eta_s$  is the solvent viscosity), and  $\lambda$  is  
 263 the characteristic relaxation time of the polymer.

264

265 The analysis above applies to elastic fluids described by a single time constant. However, in reality,  
 266 polymer solutions can have a spectrum of time constants. Entov and Hinch (1997) showed that for  
 267 ‘intermediate elastic times’, *i.e.*, after viscous effects have become negligible relative to elastic  
 268 effects and before finite extensibility of the dumbbells becomes important, Equation [9] can be  
 269 generalized to:

270 
$$\frac{D_{mid}(t)}{D_1} = \left( \sum_{i=1}^L \left( \frac{\eta_p D_1}{2\lambda_i \Gamma} \right) \exp\left(\frac{-t}{\lambda_i}\right) \right)^{1/3} \quad (10)$$

271 The second type of characteristic time scale of importance in elasto-capillary thinning studies is the  
 272 capillary time,  $t_{cap}$ , which is the timescale for characterising capillary break-up in viscous Newtonian  
 273 fluids (Anna and McKinley, 2001). The capillary time quantifies the relative effects of capillary and  
 274 viscous forces: *viz.*

275 
$$t_{cap} = \frac{\eta_0 D_1}{2\Gamma} \quad (11)$$

276 where  $D_1$  is used instead of  $D_0$  in this study since the initial filament diameter ( $D_1$ ) varied widely  
 277 between notionally identical samples. Similar assumptions were previously made for cake batters  
 278 with good results (Chesterton *et al.*, 2011). Further details of the apparatus and method are given in  
 279 papers that describe other studies with this instrument (Vadillo *et al.*, 2010).

280

### 281 Statistical analysis

282 Linear and nonlinear regressions were used to extract rheological parameters. The parameters of the  
 283 models considered were determined from the experimental data with a one-factor analysis of  
 284 variance (ANOVA) using PASW Statistics (v.18, IBM SPSS Statistics, New York, USA). When the  
 285 analysis of variance indicated differences among means, a Scheffé test was performed to  
 286 differentiate means with 95% confidence ( $p < 0.05$ ).

287

## 288 **Results and Discussion**

### 289 Surface tension

290 The results obtained for aqueous guar gum solutions in Figure 1 shows that the guar gum reduces the  
291 surface tension of water, by up to 6 mN m<sup>-1</sup>. The data exhibit the trend expected for surfactant  
292 solutions, albeit with a modest effect. The influence of guar gum concentration was satisfactorily  
293 fitted to the Szyszkowski equation (Szyszkowski, 1908):

$$294 \quad \frac{\Gamma}{\Gamma_0} = 1 - a \ln \left( 1 + \frac{C}{b} \right) \quad (12)$$

295 where  $\Gamma_0$  is the surface tension of the solvent,  $C$  the concentration of the surfactant and  $a$  and  $b$  are  
296 fitting parameters. The data in Figure 1 suggest that the solutions exhibit behaviour associated with  
297 the onset of entanglement near 5 g/L, which is in reasonable agreement with the value of 7 g/L  
298 reported for other guar gum solutions at 25 °C by Marangoni and Narine (2002). These surface  
299 tension values were consistent with those reported for aqueous guar gum dispersions by Moreira *et*  
300 *al.* (2012).

301

### 302 *Steady shear measurements*

303 Flow curves for aqueous guar gum solutions at several concentrations are shown in the form of shear  
304 rate sweeps in Figure 2. The apparent viscosity at each shear rate increases noticeably with polymer  
305 concentration. In all cases, the solutions exhibit shear-thinning behaviour, where the apparent  
306 viscosity decreases with shear rate, and the extent of shear-thinning increases with concentration.  
307 Guar gum solutions at concentrations above 5 g/L exhibited strong shear-thinning behaviour, as  
308 reported by Chenlo *et al.* (2010); these authors found that the shear rate at which the zero-shear rate  
309 viscosity plateau ended depended on polymer concentration, which is also evident in this Figure.

310

311 The data gave satisfactory fits ( $R^2 > 0.996$ , standard error  $< 0.032$  Pa s) to the Cross-Williamson  
312 model, Eqn. [2], and the parameters  $\eta_0$ ,  $k$  and  $n$  obtained are summarised in Table 1. The  $\eta_0$  and  $k$   
313 values increased significantly with increasing polymer concentration, while the variation in  $n$  was  
314 modest, the values 0.23-0.31 being similar to those reported for synthetic polymer solutions. The

315 increase of  $\eta_0$  with polymer concentration indicates the establishment of a greater number of links  
316 between the biopolymer molecules and depends on the molar mass and on interchain interactions. A  
317 higher value of  $k$  is attributed to an increase in chains entanglement density. Bourbon *et al.* (2010)  
318 postulated that the freedom of movement of individual chains is progressively restricted and  
319 consequently increases the time needed to form new entanglements to replace those destroyed by the  
320 external deformation. Hence, the shear rates values at which the behaviour becomes shear-thinning  
321 decrease as the concentration increases, as evident in Figure 2. These results were consistent with  
322 those previously found for other guar gum solutions (Chenlo *et al.*, 2010; Duxenneuer *et al.*, 2008).

323

324 The normal stress difference data,  $N_1-N_2$ , presented in Figure 3(a) indicate that aqueous guar gum  
325 solutions generate appreciable elastic responses at high shear rates. The normal stress difference,  $N_1-$   
326  $N_2$ , for guar gum solutions at 1 g/L was practically negligible, whereas for  $C = 20$  g/L  $N_1-N_2$   
327 increased rapidly at shear rates above  $1 \text{ s}^{-1}$ . This value at which  $N_1-N_2$  increased noticeably was  
328 shifted to higher shear rates at lower concentrations. The shear rate at which  $N_1-N_2$  increased  
329 corresponds to the onset of noticeable shear-thinning in Figure 2.

330

331 The data in Figure 3(a) are plotted in dimensionless form in Figure 3(b). The normal stress  
332 difference is plotted as the approximate Weissenberg number,  $Wi$  ( $Wi = N_1/\tau \approx N_1-N_2 / \tau$ ) while the  
333 shear rate is presented as the dimensionless shear rate suggested by the Cross-Williamson model (the  
334 product,  $k\dot{\gamma}^n$ , which may be interpreted as the rate of link breakage). The data sets follow a  
335 common trend, with  $Wi$  increasing with breakage rate, which merits further investigation. The  
336 results confirm that viscoelastic responses can be generated in guar gum solutions under steady  
337 shear.

338

### 339 *Oscillatory shear measurements*

340 Selected mechanical spectra ( $G'$  and  $G''$  vs. angular frequency) of aqueous guar gum solutions  
341 prepared at several concentrations are presented in Figure 4. The elastic modulus,  $G'$ , related to the  
342 elastic response of the system, and the viscous modulus,  $G''$ , related to the viscous response of the  
343 system, increased at low frequency by roughly five orders of magnitude with increasing polymer



344 concentration. The mechanical behaviour of the guar gum solutions was dependent on frequency and  
345 followed the shape reported elsewhere for similar guar gum solutions (Steffe, 1996; Chenlo *et al.*  
346 2010). In all cases, both moduli increased with frequency by roughly three orders of magnitude  
347 between 0.01 and 10 Hz. For low polymer concentrations below 5 g/L,  $G'' > G'$  over the entire  
348 frequency range investigated, indicating predominantly viscous behaviour (Figure 4a), whereas there  
349 is a crossover in the moduli at higher concentration (above 10 g/L) and the elastic response prevails  
350 at higher frequencies (Figure 4b). These results are similar to those reported for random coil  
351 polymers. The crossover frequency (where  $G' \sim G''$ ) decreased from 4 Hz to 1 Hz as the  
352 concentration increased from 10 g/L to 20 g/L, as a consequence of longer relaxation times. Bourbon  
353 *et al.* (2010) reported similar behaviour for several other random-coil polysaccharide solutions in  
354 this concentration range. The viscoelastic behaviour of the guar gums solutions was predominantly  
355 viscous over the range of angular frequencies for other concentrations, indicating that the entangled  
356 regime is encountered between 5 and 10 g/L.

357

### 358 *Complex viscosity*

359 Figure 5 shows that the solutions obeyed the Cox–Merz rule,  $|\eta^*(\omega)| \approx \eta(\dot{\gamma})$  where  $\omega = \dot{\gamma}$ , (Cox  
360 and Merz, 1958), relating the apparent viscosity (steady shear flow) and the magnitude of the  
361 complex viscosity (oscillatory shear flow) at a given frequency and shear rate at concentrations  
362 below 10 g/L. There is a divergence in behaviour at high rates for the more concentrated solutions,  
363 which are thought to lie in the entangled regime. The deviation is related to the elastic gel-like  
364 structure, which is not affected during oscillatory measurements, but is broken during steady shear  
365 tests such that the measured magnitude of the complex viscosity is larger than the apparent viscosity  
366 (Steffe, 1996). Similar behaviour has been reported for synthetic polymers such as polyisobutylene  
367 by Liang and Mackey (1994), who also found that the largest deviations occurred at higher angular  
368 frequencies and shear rates.

369

### 370 *Extensional measurements*

371 Figure 6 shows the evolution of mid-filament diameter,  $D_{mid}$ , for different concentrations. The  
372 diameter is determined by the balance of surface tension and viscous/elastic forces: viscous forces

373 tend to stabilize the filament, while surface tension acts to destabilize it, causing the increasingly  
 374 rapid decrease in the diameter until the filament breaks apart. The decrease in  $D_{mid}$  with time is not  
 375 linear: there is a sharp step followed by an exponential decay, after which the rate of decay increases  
 376 towards break-up at time  $t_F$ . Similar trends were reported for other aqueous guar gum systems at  
 377 different concentrations (Duxenneuner *et al.*, 2008; Bourbon *et al.*, 2010), and confirm non-  
 378 Newtonian behaviour.

379

380 The time to break-up,  $t_F$ , increased with polymer concentration and Figure 7 shows that an  
 381 asymptote is reached around 10 g/L. The effect of concentration,  $C$ , on  $t_F$  fitted the empirical  
 382 expression:

$$383 \quad t_F - t_{F0} = 1 - \exp\left(\frac{C}{20}\right) \quad (13)$$

384 where  $t_{F0}$  is the break-up time observed with water. The square of the correlation coefficient,  $R^2$ , was  
 385 0.995. This behaviour is consistent with the results obtained for the shear rheology, suggesting that  
 386 above 10 g/L guar gum solutions lie in the entangled region. The  $t_F$  values also increased with  $D_1$   
 387 (see the inset on Figure 7), following an exponential dependency given by:

$$388 \quad t_F = 15.2 \exp(0.0042D_1) \quad (14)$$

389 with the square of the correlation coefficient,  $R^2$ , being 0.998. A similar dependency between  $t_F$  and  
 390  $D_1$  was reported for cake batters by Chesterton *et al.* (2011).

391

392 The individual data sets in Figure 6 collapsed to a common form when the capillary diameter,  
 393 normalised against  $D_1$ , as in Equation (16), was plotted against the timescale was normalised against  
 394  $t_F$  (see Figure 8):

$$395 \quad \frac{D_{mid}(t)}{D_1} \propto \exp\left(\frac{-t}{t_F}\right) \quad (15)$$

396

397 The data sets were also analysed in the form employed by Anna and McKinley (2001) to present  
 398 data obtained for Boger fluids, namely plots of  $[D_{mid}(t)/D_1]$  vs.  $[t/t_{cap}]$ . These plots showed an  
 399 initially linear region, characteristic of viscoelastic behaviour, followed by a sharp descent towards

400 filament break-up at  $t_F$  (data not presented). The time scaling showed that the decay timescale and  
 401 the approach to break-up are not determined by the characteristic capillary time. Deviations from the  
 402 simple form expected for a dilute polymer solution as discussed by Anna and McKinley (2001),  
 403 were reported for another complex entangled biopolymeric system, cellulose in ionic liquid  
 404 solutions, using a CaBER device by *Haward et al.* (2012). These authors showed very similar trends  
 405 for the shear viscosity, linear viscoelastic and extensional data as the present work.

406

407 Anna and McKinley (2001) successfully fitted their data for synthetic polymer solutions to Equation  
 408 (9), relating the observed behaviour to polymer relaxation times and the finite extensibility of  
 409 polymer molecules. In the current study, however, poor agreement was obtained when experimental  
 410 data were fitted to Equation (9), with one relaxation time, or to Equation (10) using up to eight  
 411 relaxation times, as illustrated by the example in Figure 9. An alternative physical mechanism is  
 412 operating, which is consistent with those observations made by Tembely et al. (2012) and Vadillo et  
 413 al. (2012), where computational fluid dynamic simulations for predicting the fast filament stretching,  
 414 relaxation and break up of low viscosity weakly elastic fluids were presented. The authors of this  
 415 work have also tried mono and multi mode approach to fit the filament thinning of such fluids, rather  
 416 unsuccessfully, using Oldroyd-B and FENE-CR constitutive equations.

417

418 Equation (9) was modified by the addition of an empirical constant,  $b'$ , which yielded a significantly  
 419 better fit to the experimental data (see Figure 9):

$$420 \quad \frac{D_{mid}(t)}{D_1} = \left( \left( \frac{\eta_p D_1}{2\lambda_1 \Gamma} \right) \exp\left(\frac{-t}{\lambda_1}\right) \right)^{1/3} - b' \quad (16)$$

421

422 Chesterton *et al.* (2011) reported that their cake batter data fitted this empirical relationship for  
 423 several different flours.

424

425 All the data sets fitted the expression shown in Equation (16) satisfactorily ( $R^2 > 0.990$ ). The  
 426 empirical model proposed in Equation (16) exhibits the form expected for a Giesekus fluid (as  
 427 reported by Yesilata *et al.*, 2006); further exploration of this relationship is currently ongoing. The

428 relaxation times and  $b'$  values obtained are presented in Figure 10. The relaxation times increase  
429 with increasing polymer concentration, approaching an asymptotic value of 17 ms around 10 g/L,  
430 whereas the  $b'$  values decrease with concentration, approaching an asymptotic value of unity at 10  
431 g/L. Bourbon *et al.* (2010) reported the existence of two relaxation times for aqueous guar gum  
432 solutions with values ranging from  $\lambda_1 \sim 15$  ms and  $\lambda_2 \sim 1$  ms for 1.9 g/L, to  $\lambda_1 \sim 58$  ms and  $\lambda_2 \sim 4200$   
433 ms for 9.7 g/L. These data can be contrasted against those from this study where the relaxation time,  
434  $\lambda_1$ , ranges between  $\lambda_1 \sim 8$  ms for 2.0 g/L and  $\lambda_1 \sim 17$  ms for 10 g/L. Bourbon *et al.* (2010) proposed  
435 that the two relaxation times arise from the structure of the studied polysaccharides, one related to  
436 the expansion of the polymeric chains, the other relating to interactions between the chains delaying  
437 the relaxation phase.

438

439 Duxenneuner *et al.* (2008) studied modified guar gum solutions and reported that the relaxation time  
440 followed a power-law scaling dependency in the semi-dilute concentration regime, from  $3c^*$  up to  
441  $9c^*$ . These authors defined  $c^*$  as the critical micelle concentration, which can be identified as the  
442 concentration where the surface tension data as a function of concentration deviate from the  
443 Szyszkowski equation (Szyszkowski, 1908) that was given in Equation (12); they found that  
444  $c^* \sim 0.58$  g/L. These authors stated that this behaviour was a manifestation of increasing interactions  
445 between hydroxypropyl ether guar gum molecules in solution with increasing concentration. The  
446 relative weak dependency suggests that the interactions between chains were overall quite weak and  
447 may be purely hydrodynamic in nature. We note that Haward *et al.* (2012) recently reported a strong  
448 dependency of relaxation times with concentration of cellulose in an ionic liquid. They found that  
449 the relaxation times obtained from CABER measurements initially increase slowly with  
450 concentration and then climb more rapidly in the semi-dilute and entangled regimes.

451

452 Figure 11 shows that  $t_F$  exhibits a linear dependency on the relaxation time parameter,  $\lambda$ . No further  
453 explanation is offered at this time as the physical basis of Equation (16) is not established.

454

455 The apparent extensional viscosity was estimated using Equation (5) and the results are presented in  
456 Figure 12. This analysis assumes that the equilibrium surface tension values in Figure 1 can be used

457 to estimate the forces involved in extension; direct measurement of the force in the filament is  
458 required to confirm these values. Figure 12(a) plots the apparent extensional viscosity as a function  
459 of the Hencky strain. Since the apparent extensional viscosity profiles are a function of the  
460 midfilament diameter,  $D_{mid}$ , which itself changes as a function of time, the values are governed by  
461 the self-thinning of the filament, and are not a response to an imposed shear rate as in shear  
462 rheometry. The apparent extensional viscosities increase sharply at low Hencky strains, exhibiting a  
463 peak (at  $\varepsilon \sim 1.2$ ) for concentrations above 10 g/L, where entanglement is believed to be important.  
464 At higher strains,  $\eta_e$  approaches an asymptote, the value of which increases with concentration.

465

466 The effect of concentration on the peak and plateau values of the apparent extensional viscosity is  
467 presented in Figure 12(b). Both parameters increase with concentration, with the plateau value  
468 following a linear dependency but the peak value exhibiting an exponential dependency.  
469 Duxenneuner *et al.* (2010) reported two steady-state extensional trends for hydroxypropyl ether guar  
470 gum solutions: a linear dependence of the plateau values up to  $\sim 3$  times the critical polymer  
471 concentration ( $c^* \sim 0.58$  g/L), followed by a power-law dependence up to their highest-studied  
472 concentration (around 1 g/L) of  $\sim 9$  times the critical polymer concentration.

473

474 The apparent extensional viscosities are now compared with the apparent viscosities via the Trouton  
475 number (*i.e.*,  $\eta_e/\eta_{app}$ ) evaluated at  $0.1\text{ s}^{-1}$ . Figure 13(a) shows the Trouton number values calculated  
476 for aqueous guar gum solutions against the Hencky strain. An exponential increase in the Trouton  
477 number with Hencky strain was observed in all cases. Moreover, the Trouton number decreased  
478 noticeably with an increase of polymer concentration (Figure 13(b)). This trend is consistent with  
479 those reported for derived guar gum solutions by Duxenneuner *et al.* (2010), who found that the  
480 Trouton number values started as high as 440 for 0.1 g/L and decreased to 16 for 5 g/L over a shear  
481 rate range between  $0.1\text{ s}^{-1}$  and  $1000\text{ s}^{-1}$ . They stated that the high values of Trouton number recorded  
482 at the lowest polymer concentration indicate that most of the extensional response is due to the  
483 alignment and extension of individual chains, with increasing effects of chain-chain interactions at  
484 higher polymer contents.

485

## 486 **Conclusions**

487 The shear and extensional rheology of aqueous solutions of guar gum with concentrations has been  
488 studied over the range 1 g/L to 20 g/L. The molecular weight of the guar gum was  $3.0 \times 10^6$  g/mol,  
489 with a polydispersity ( $M_w/M_n$ ) of 1.13. The behaviour of the guar gum solutions was predominantly  
490 viscoelastic, with the extent of the viscoelasticity being determined by polymer concentration. At  
491 concentrations below 10 g/L, the rheological behaviour was consistent with the polymer being in a  
492 non-entangled state, but at concentrations above 10 g/L the data suggested the presence of  
493 entanglement and the formation of an elastic, gel-like, structure. The measured surface tension  
494 values also exhibited behaviour reminiscent of micelle formation at concentrations in the entangled  
495 regime.

496  
497 The steady shear data fitted the Cross-Williamson model well and suggests that shear thinning arises  
498 from breakdown of interactions between polymer strands. The viscoelastic response accompanying  
499 breakdown, quantified by the first normal stress difference, coincided with the onset of noticeable  
500 shear-thinning. Plots of the estimated Weissenberg number against the normalised shear rate  
501 calculated from the Cross-Williamson model showed a common trend which merits further  
502 investigation.

503  
504 The filament stretching data did not fit the model presented by Entov and Hinch (1997) which has  
505 been successfully used by several workers to describe the extensional behaviour of synthetic  
506 polymer solutions, even when eight relaxation times were used. An empirical modification of the  
507 Entov and Hinch model, adding a time-independant constant, however, gave good fits with only one  
508 relaxation time. This empirical modification exhibits the form expected for a Giesekus fluid, as  
509 reported by Yesilata *et al.*, 2006; further exploration of this relationship is ongoing. Plots of the  
510 normalised filament diameter against normalised time showed a consistent trend which was largely  
511 independent of polymer concentration. This allows a coarse prediction of expected behaviour, and  
512 was also reported by Chesterton *et al.* (2011) for cake batters. The apparent extensional viscosity of  
513 the guar gum solutions was estimated by monitoring the evolution of solution filament diameter as a  
514 function of time using the method reported by Vadillo *et al.*, 2010. For dilute solutions, below 10

515 g/L, the apparent extensional viscosity increases monotonically as a function of Hencky strain,  
516 reaching a steady asymptotic value. The apparent extensional viscosity of the entangled solutions  
517 also reaches a steady asymptote at high Hencky strain, but passes through a maximum value prior to  
518 the asymptote. The asymptotic value of the apparent extensional viscosity is linearly proportional to  
519 polymer concentration for both dilute and entangled regimes, with a squared correlation coefficient  
520 of 0.995. The peak apparent extensional viscosity, however, increases exponentially across the two  
521 regimes as a function of polymer concentration with a squared correlation coefficient of 0.990.

522

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650 **Figure Captions**

651 **Figure 1** Effect of guar gum concentration on surface tension relative to water. Solid trend line  
652 shows Equation [12] fitted to the guar gum data with parameters  $a = 0.0123$  and  $b = 0.0045$   
653 g/L. Experimental data showed high reproducibility and estimated uncertainty is smaller  
654 than symbol size.

655  
656 **Figure 2** Flow curves of aqueous guar gum solutions prepared at several concentrations. Symbols:  
657 circles – 1 g/L, triangles - 2 g/L, squares – 5 g/L, diamonds - 10 g/L, dashes – 15 g/L,  
658 crosses - 20 g/L. The solid line shows the best fit to the guar gum solutions obtained with  
659 the Cross model (Equation [2]), with parameters given in Table 1. In this and subsequent  
660 plots, error bars are not plotted if the uncertainty in data values is smaller than the symbol  
661 size.

662  
663 **Figure 3** Stress parameters measured for aqueous guar gum solutions prepared at different polymer  
664 concentration: (a) normal stress differences ( $N_1-N_2$ ) and (b) estimated Weissenberg number  
665 ( $= (N_1-N_2)/\tau$ ). Symbols: circles – 1 g/L, triangles - 2 g/L, squares – 5 g/L, diamonds - 10  
666 g/L, dashes – 15 g/L, crosses - 20 g/L.

667  
668 **Figure 4** Mechanical spectra of representative aqueous guar gum solutions prepared at  
669 concentrations of (a) 1, 5, (b) 10 and 20 g/L. Symbols: closed –  $G'$ , open –  $G''$ , circles – 1  
670 g/L, squares – 5 g/L, diamonds - 10 g/L, triangles - 20 g/L. Solid and dashed lines in (b)  
671 shows  $G'$  and  $G''$  values for aqueous guar gum solution at 5g/L, respectively.

672  
673 **Figure 5** Comparison between the apparent viscosity (symbols) and the complex viscosity (dashed  
674 lines) for aqueous guar gum solutions prepared at several concentrations, Cox-Merz rule  
675 (Cox & Merz, 1958). Symbols: circles – 1 g/L, triangles - 2 g/L, squares – 5 g/L, diamonds -  
676 10 g/L, dashes – 15 g/L, crosses - 20 g/L.

677  
678 **Figure 6** Dimensionless filament diameter profiles for aqueous guar gum solutions prepared at  
679 several concentrations. Symbols: circles – 1 g/L, triangles - 2 g/L, squares – 5 g/L,  
680 diamonds - 10 g/L, dashes – 15 g/L, crosses - 20 g/L. The non-linear profiles indicate non-  
681 Newtonian behaviour.

682  
683 **Figure 7** Correlation between time break-up ( $t_F$ ) and polymer concentration ( $C$ ) or initial filament  
684 diameter ( $D_1$ ) for aqueous guar gum solutions prepared at several concentrations. Dashed  
685 lines show exponential trends:  $t_F - t_{F0} = (1 - e^{-C/20})$  and  $t_F = 15.2e^{0.0042D_1}$  ( $R^2 = 0.998$ ).  
686

687 **Figure 8** Dimensionless filament diameter profiles with dimensionless time for aqueous guar gum  
688 solutions prepared at several concentrations. Symbols: circles – 1 g/L, triangles - 2 g/L,  
689 squares – 5 g/L, diamonds - 10 g/L, dashes – 15 g/L, crosses - 20 g/L.  
690

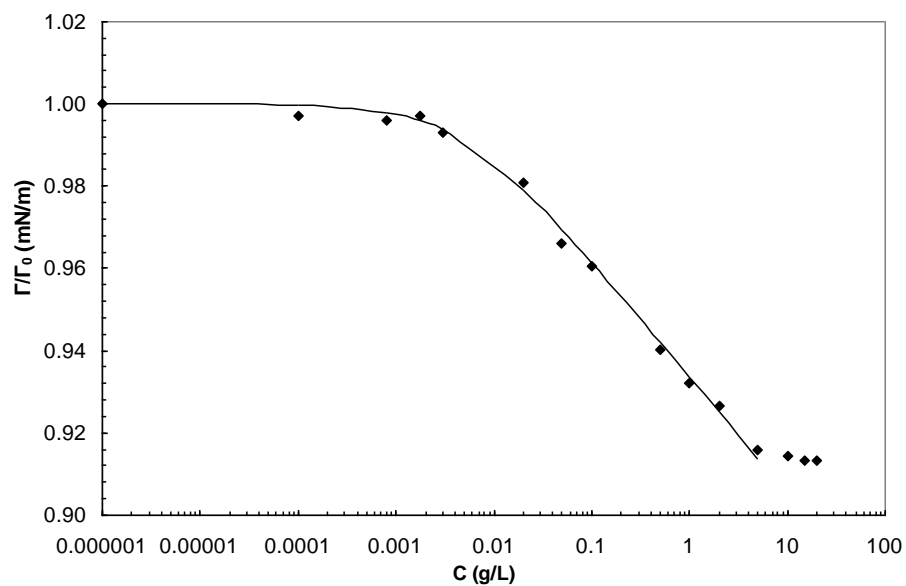
691 **Figure 9** Dimensionless filament diameter profiles with time for representative aqueous guar gum  
692 solutions prepared at 10 g/L. Dashed lines shows the fitting achieved with Equation [9] and  
693 solid lines with Equation [16].  
694

695 **Figure 10** Effect of polymer concentration on initial relaxation time ( $\lambda_1$ ) and parameter  $b'$  (Equation  
696 [16]) for aqueous guar gum solutions prepared at several concentrations. Open symbols,  
697  $\lambda_1$ ; and closed symbols,  $b'$ . Dashed line shows the power-law trend obtained for  $\lambda_1$  by  
698 Duxenneuner *et al.* (2008).  
699

700 **Figure 11** Correlation between initial relaxation time ( $\lambda_1$ ) and break-up time ( $t_F$ ) for aqueous guar  
701 gum solutions prepared at labelled concentrations. Dashed line shows linear trend, with  $t_F =$   
702  $8.06\lambda_1 - 34.3$  ( $R^2 = 0.987$ ).  
703

704 **Figure 12** Extensional viscosity versus (a) Hencky strain and (b) polymer concentration ( $C$ ) for  
705 aqueous guar gum solutions. Symbols: circles – 1 g/L, triangles - 2 g/L, squares – 5 g/L,  
706 diamonds - 10 g/L, dashes – 15 g/L, crosses - 20 g/L. Dashed line (maximum extensional  
707 viscosities) shows exponential trend, with  $\eta_e = 5.4 e^{0.035C}$  ( $R^2 = 0.990$ ). Solid line (steady  
708 extensional viscosities) shows linear trend, with  $\eta_e = 0.14C + 5.6$  ( $R^2 = 0.995$ ).  
709

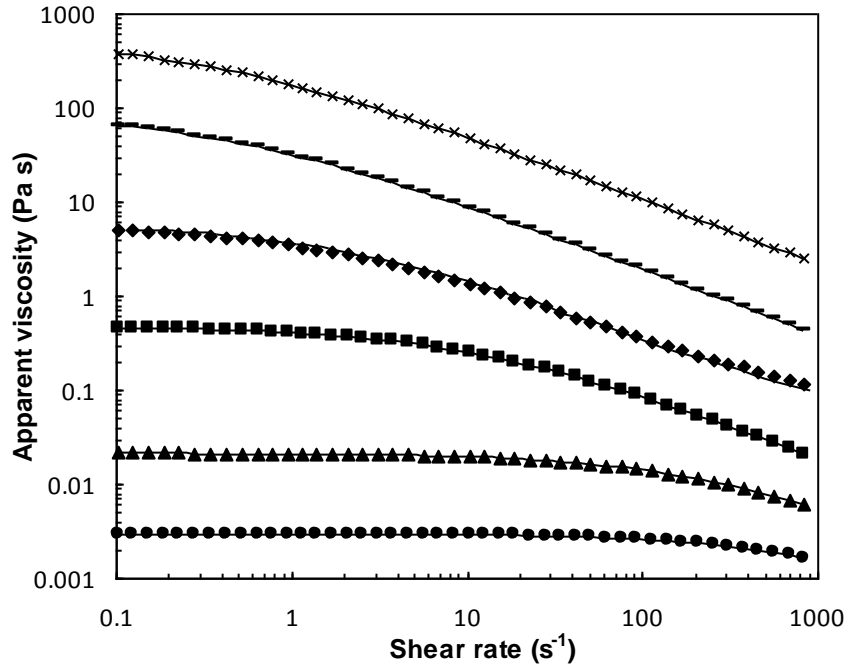
710 **Figure 13** Correlation between Trouton ratio and (a) Hencky strain and (b) polymer concentration  
711 for guar gum solutions. Symbols: circles – 1 g/L, triangles - 2 g/L, squares – 5 g/L,  
712 diamonds - 10 g/L, dashes – 15 g/L, crosses - 20 g/L. Dashed line in (b) shows the trend  
713 obtained by Duxenneuner *et al.* (2008).  $N_{TR}$  in (b) evaluated at  $0.1 \text{ s}^{-1}$ .



714

715

716 **Figure 1** Effect of guar gum concentration on surface tension relative to water. Solid trend line  
 717 shows Equation [12] fitted to the guar gum data with parameters  $a = 0.0123$  and  $b = 0.0045$   
 718 g/L. Experimental data showed high reproducibility and estimated uncertainty is smaller  
 719 than symbol size.



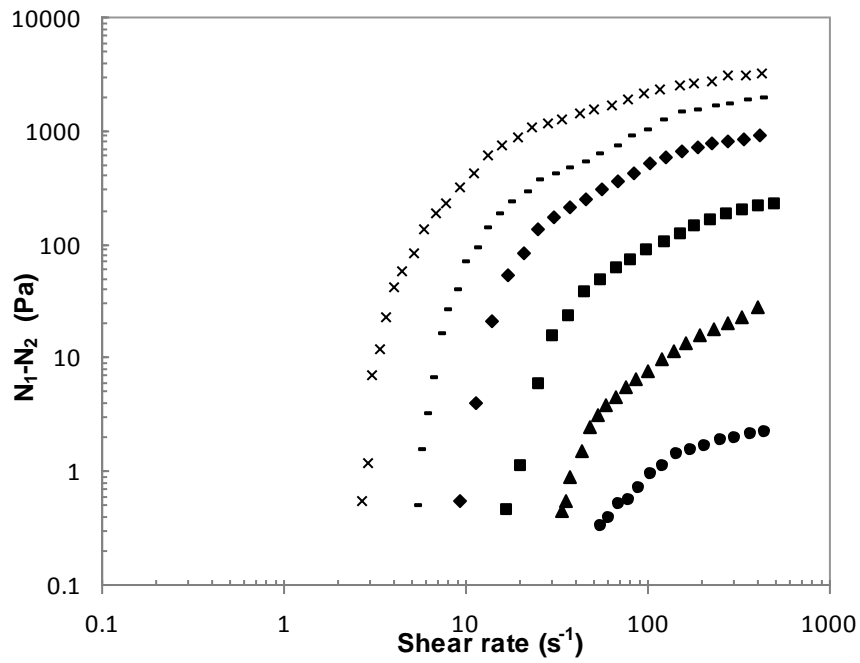
720

721

722 **Figure 2** Flow curves of aqueous guar gum solutions prepared at several concentrations. Symbols:  
 723 circles – 1 g/L, triangles - 2 g/L, squares – 5 g/L, diamonds - 10 g/L, dashes – 15 g/L,  
 724 crosses - 20 g/L. The solid line shows the best fit to the guar gum solutions obtained with  
 725 the Cross model (Equation [2]), with parameters given in Table 1. In this and subsequent  
 726 plots, error bars are not plotted if the uncertainty in data values is smaller than the symbol  
 727 size.

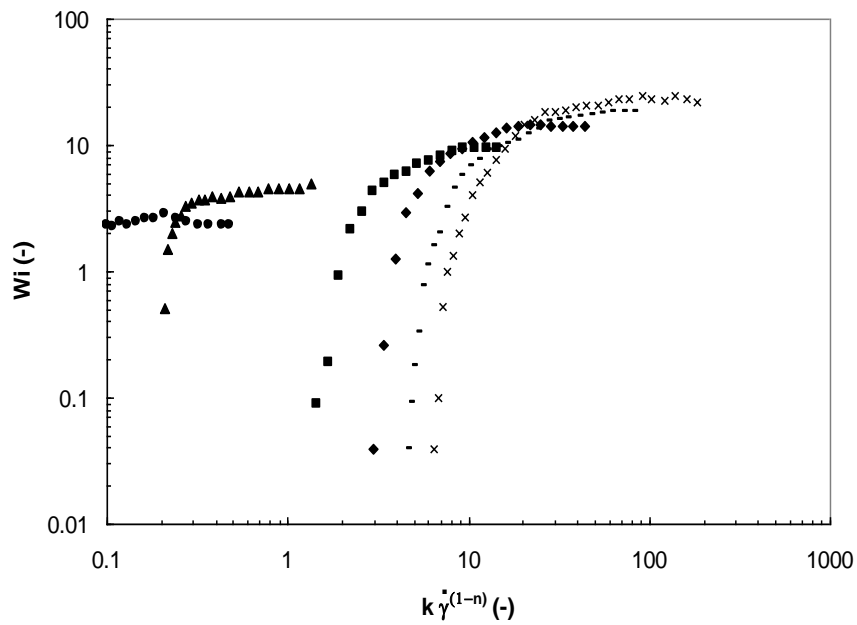
728

729 (a)



730

731 (b)

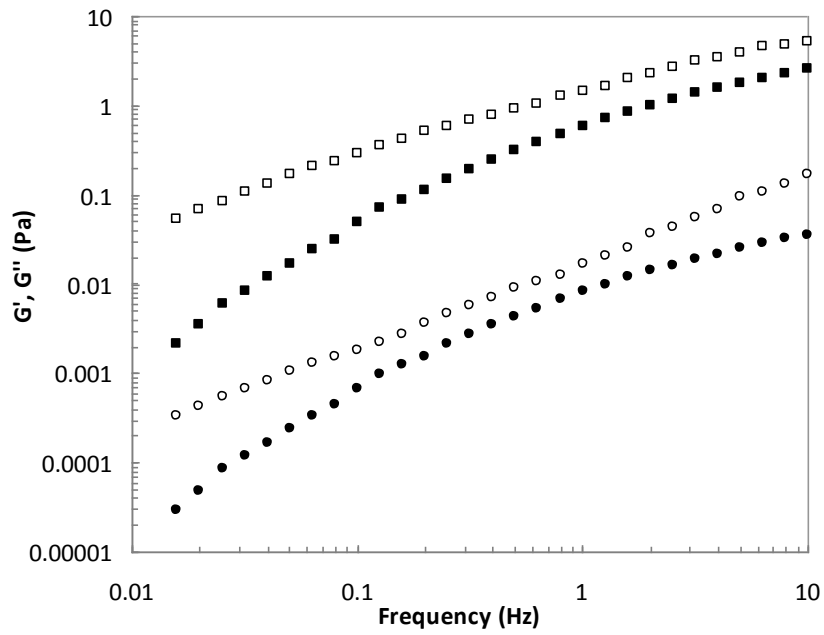


732

733 **Figure 3** Stress parameters measured for aqueous guar gum solutions prepared at different polymer  
734 concentration: (a) normal stress differences ( $N_1 - N_2$ ) and (b) estimated Weissenberg number  
735 ( $= (N_1 - N_2) / \tau$ ). Symbols: circles – 1 g/L, triangles – 2 g/L, squares – 5 g/L, diamonds – 10  
736 g/L, dashes – 15 g/L, crosses – 20 g/L.

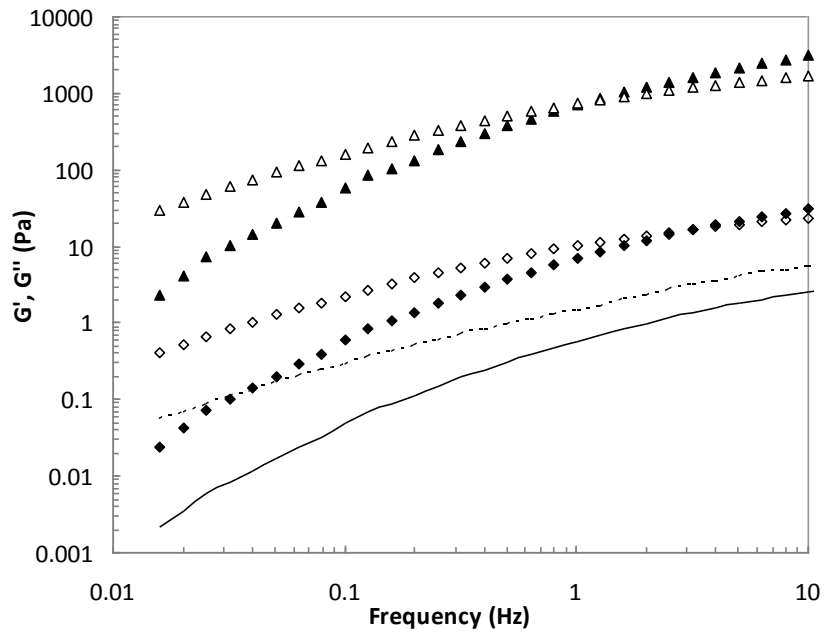


737 (a)



738

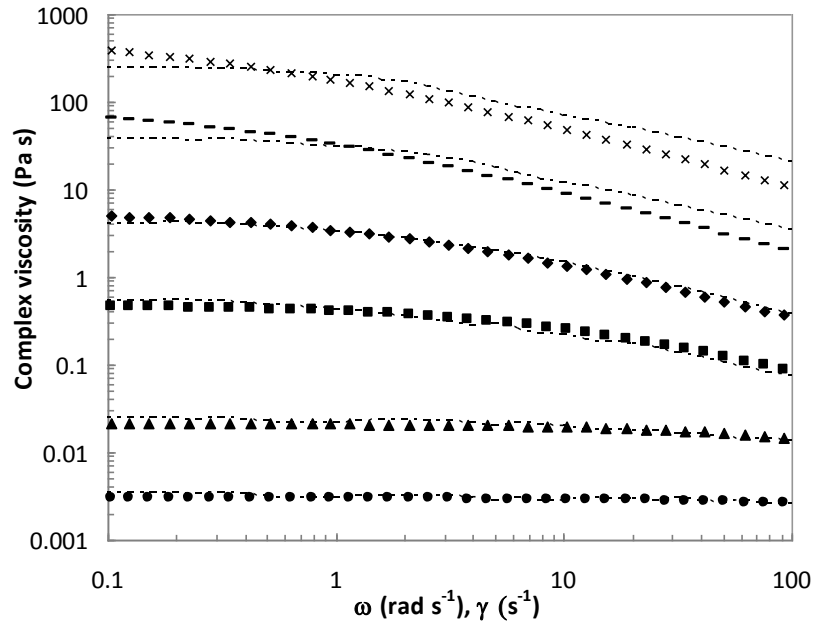
739 (b)



740

741

742 **Figure 4** Mechanical spectra of representative aqueous guar gum solutions prepared at  
743 concentrations of (a) 1, 5, (b) 10 and 20 g/L. Symbols: closed –  $G'$ , open –  $G''$ , circles – 1  
744 g/L, squares – 5 g/L, diamonds - 10 g/L, triangles - 20 g/L. Solid and dashed lines in (b)  
745 shows  $G'$  and  $G''$  values for aqueous guar gum solution at 5g/L, respectively.

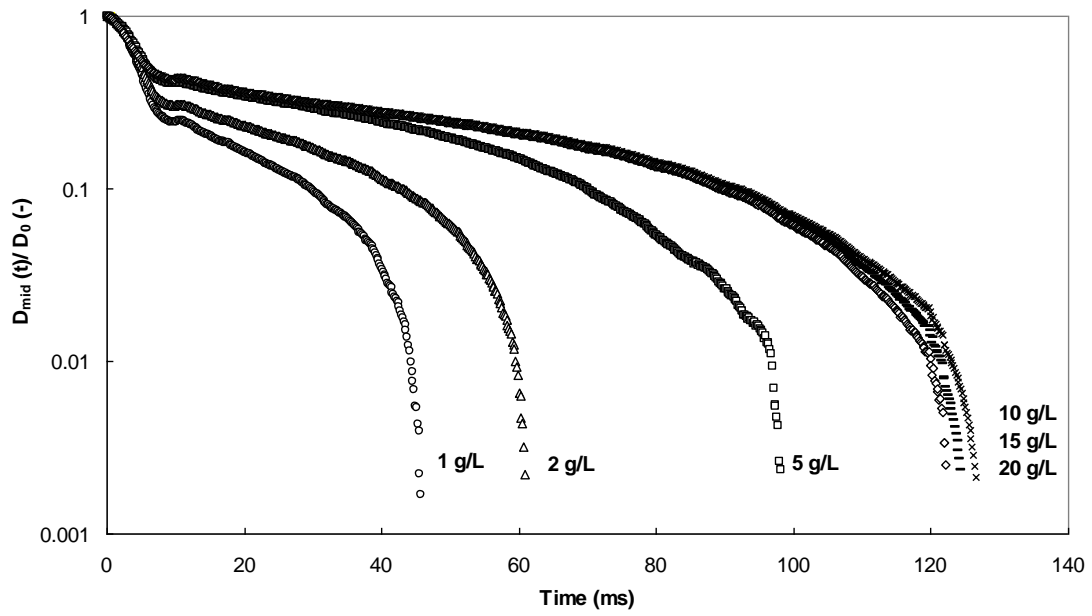


746

747

748 **Figure 5** Comparison between the apparent viscosity (symbols) and the complex viscosity (dashed  
 749 lines) for aqueous guar gum solutions prepared at several concentrations, Cox-Merz rule  
 750 (Cox & Merz, 1958). Symbols: circles – 1 g/L, triangles - 2 g/L, squares – 5 g/L, diamonds -  
 751 10 g/L, dashes – 15 g/L, crosses - 20 g/L.

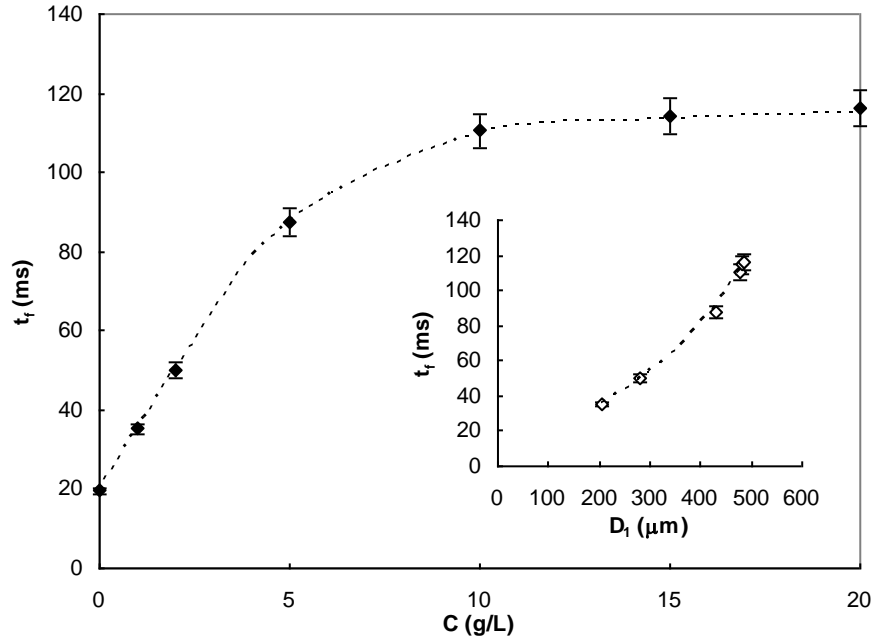
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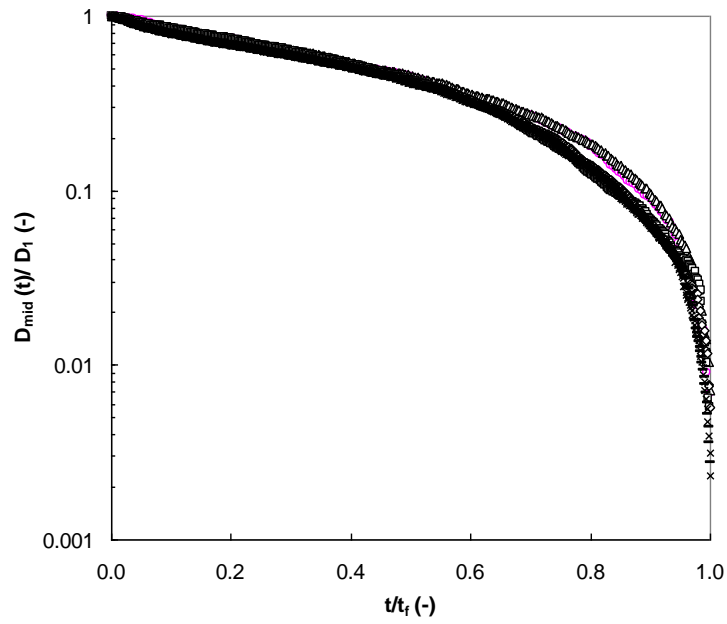
754

755 **Figure 6** Dimensionless filament diameter profiles for aqueous guar gum solutions prepared at  
 756 several concentrations. Symbols: circles – 1 g/L, triangles - 2 g/L, squares – 5 g/L,  
 757 diamonds - 10 g/L, dashes – 15 g/L, crosses - 20 g/L. The non-linear profiles indicate non-  
 758 Newtonian behaviour.



759  
760

761 **Figure 7** Correlation between time break-up ( $t_F$ ) and polymer concentration ( $C$ ) or initial filament  
 762 diameter ( $D_1$ ) for aqueous guar gum solutions prepared at several concentrations. Dashed  
 763 lines show exponential trends:  $t_F - t_{F0} = (1 - e^{C/20})$  and  $t_F = 15.2e^{0.0042D_1}$  ( $R^2 = 0.998$ ).



764

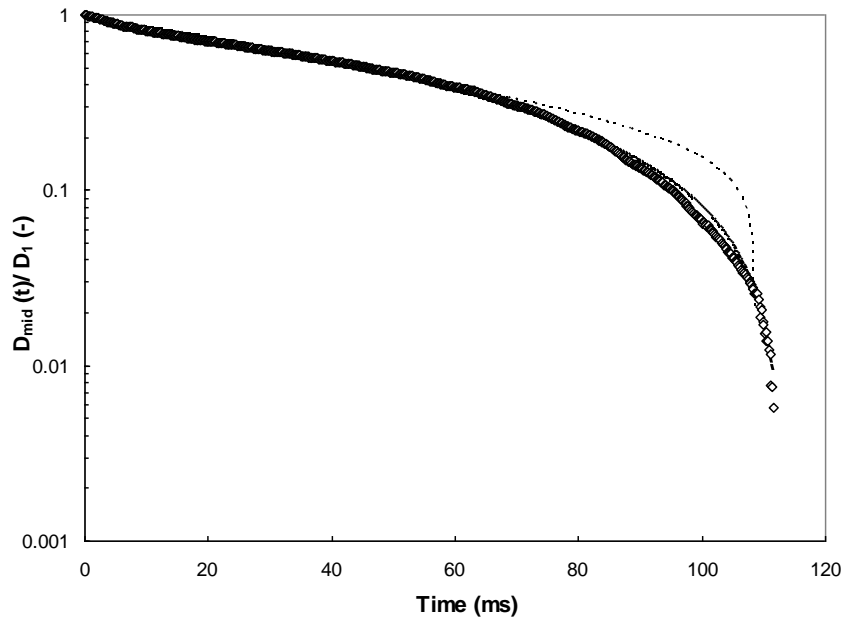
765

766 **Figure 8** Dimensionless filament diameter profiles with dimensionless time for aqueous guar gum

767 solutions prepared at several concentrations. Symbols: circles – 1 g/L, triangles - 2 g/L,

768 squares – 5 g/L, diamonds - 10 g/L, dashes – 15 g/L, crosses - 20 g/L.

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770

771

772 **Figure 9** Dimensionless filament diameter profiles with time for representative aqueous guar gum

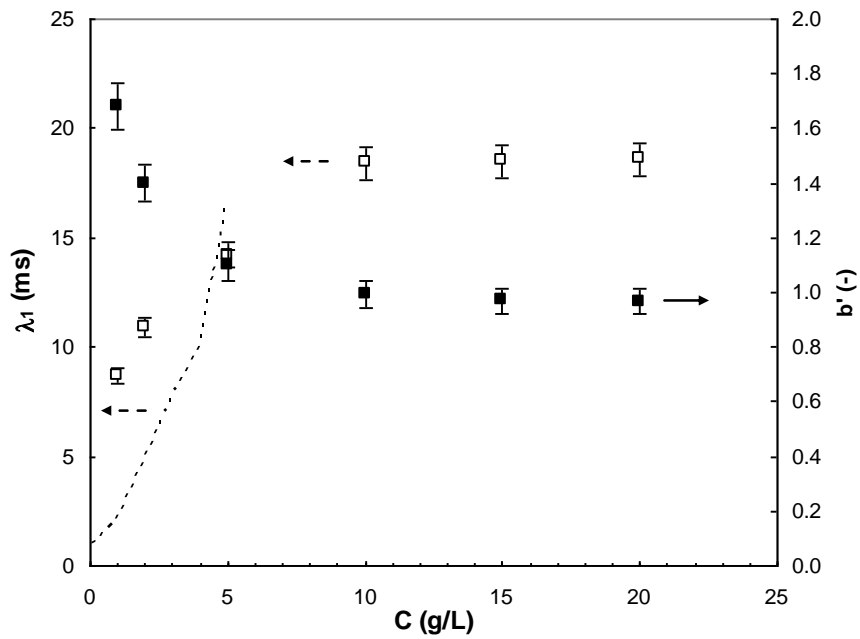
773 solutions prepared at 10 g/L. Dashed lines shows the fitting achieved with Equation [9] and

774 solid lines with Equation [16].

775

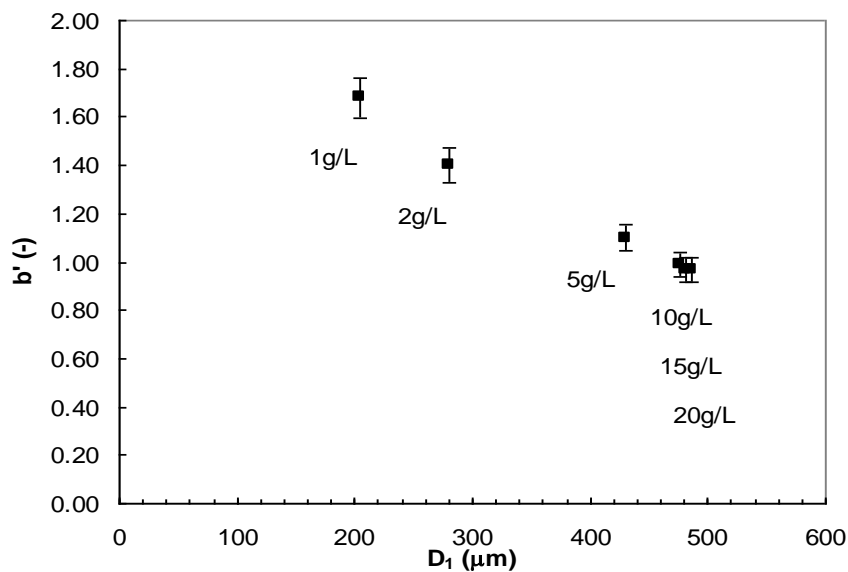
776

777 (a)



778

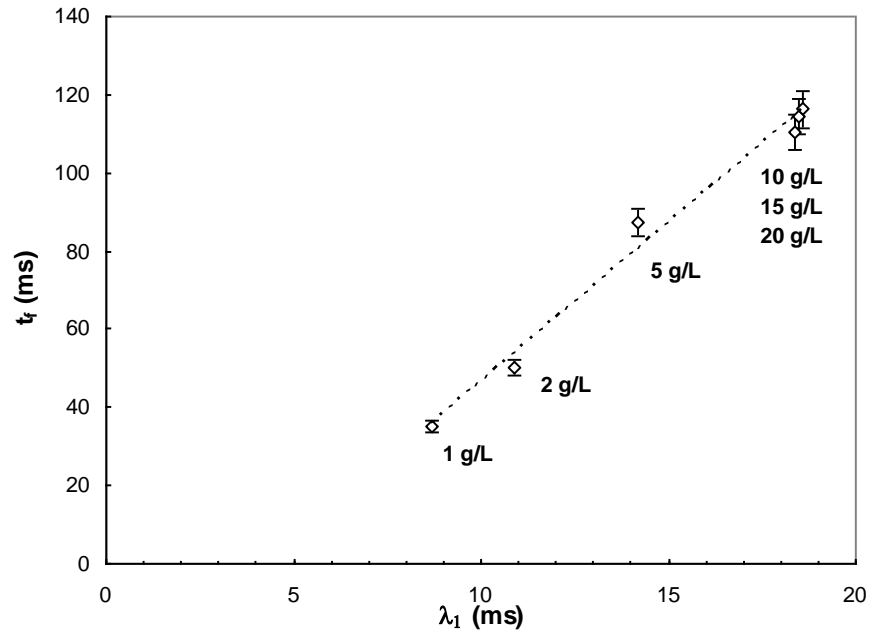
779 (b)



780

781

782 **Figure 10** (a) Effect of polymer concentration on initial relaxation time ( $\lambda_1$ ) and parameter  $b'$   
783 (Equation [16]) for aqueous guar gum solutions prepared at several concentrations. Open  
784 symbols,  $\lambda_1$ ; and closed symbols,  $b'$ . Dashed line shows the power-law trend obtained for  
785  $\lambda_1$  by Duxenneuner *et al.* (2008). (b) Relationship between parameter  $b'$  (Equation [16]) and  
786 filament formation diameter ( $D_1$ ) for aqueous guar gum solutions prepared at several  
787 concentrations.



788

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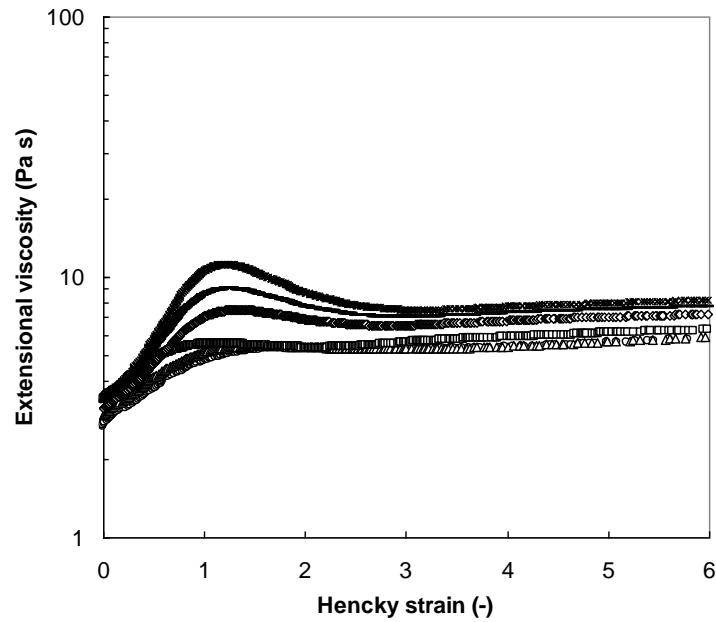
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791 gum solutions prepared at labelled concentrations. Dashed line shows linear trend, with  $t_f =$

792  $8.06\lambda_1 - 34.3$  ( $R^2 = 0.987$ ).

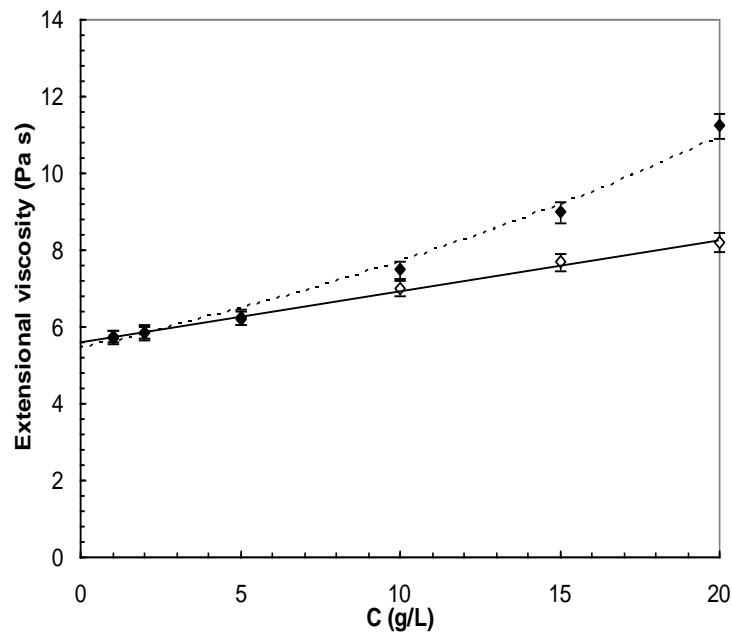


793 (a)



794

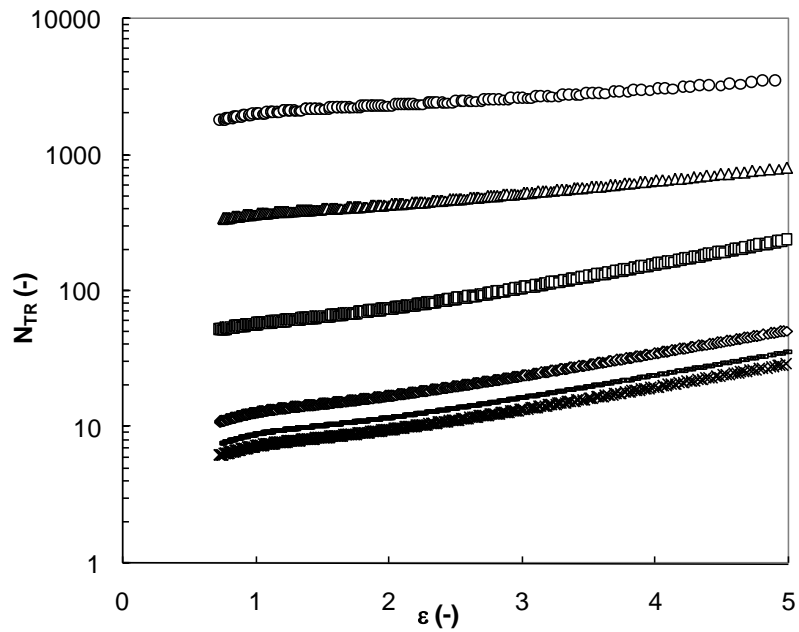
795 (b)



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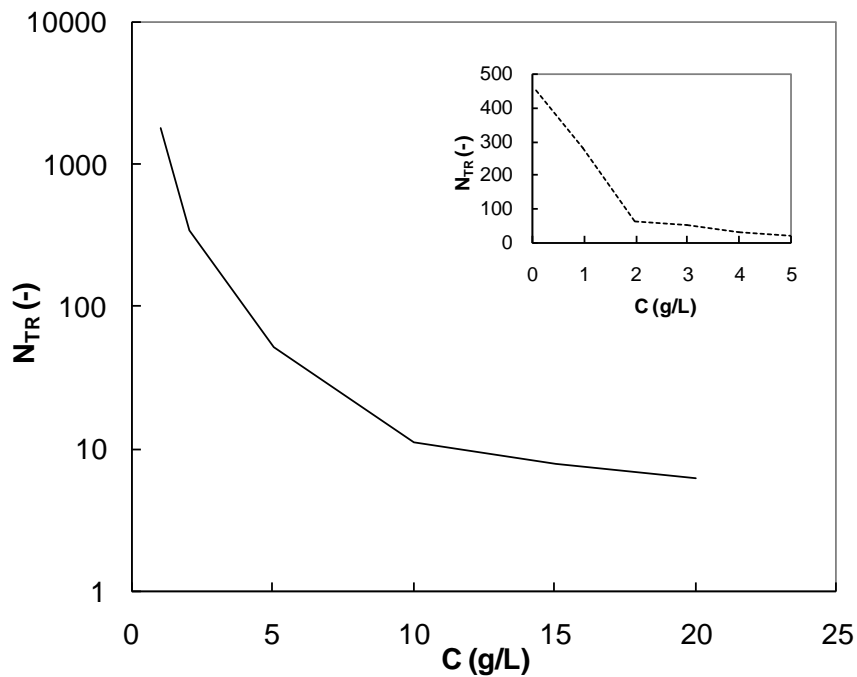
797 **Figure 12** Extensinal viscosity versus (a) Hencky strain and (b) polymer concentration (C) for  
798 aqueous guar gum solutions. Symbols: circles – 1 g/L, triangles - 2 g/L, squares – 5 g/L,  
799 diamonds - 10 g/L, dashes – 15 g/L, crosses - 20 g/L. Dashed line (maximum extensinal  
800 viscosities) shows exponential trend, with  $\eta_e = 5.4 e^{0.035C}$  ( $R^2 = 0.990$ ). Solid line (steady  
801 extensinal viscosities) shows linear trend, with  $\eta_e = 0.14C + 5.6$  ( $R^2 = 0.995$ ).

802 (a)



803

804 (b)



805

806 **Figure 13** Correlation between Trouton ratio and (a) Hencky strain and (b) polymer concentration  
807 for guar gum solutions. Symbols: circles – 1 g/L, triangles - 2 g/L, squares – 5 g/L,  
808 diamonds - 10 g/L, dashes – 15 g/L, crosses - 20 g/L. Dashed line in (b) shows the trend  
809 obtained by Duxenneuner *et al.* (2008).  $N_{TR}$  in (b) evaluated at  $0.1 \text{ s}^{-1}$ .

810 **Table Captions**

811 **Table 1** Parameter values obtained for Cross-Williamson model, Equation [2], for aqueous  
812 guar gum solutions prepared at several concentrations.

813 **Table 1** Parameter values obtained for Cross-Williamson model, Equation [2], for aqueous  
 814 guar gum solutions prepared at several concentrations. †  
 815

Concentration (g/L)	$\eta_0$ (Pa s)	$k$ (s <sup>1-n</sup> )	$n$ (-)	$R^2$	Standard deviation (Pa s)
1	0.0031±0.0002 <sup>f</sup>	0.0045±0.0002 <sup>f</sup>	0.23±0.01 <sup>c</sup>	0.999	0.025
2	0.0215±0.0001 <sup>e</sup>	0.015±0.011 <sup>e</sup>	0.25±0.01 <sup>b</sup>	0.998	0.027
5	0.48±0.02 <sup>d</sup>	0.19±0.01 <sup>d</sup>	0.28±0.01 <sup>a,b</sup>	0.999	0.026
10	5.87±0.01 <sup>c</sup>	0.61±0.01 <sup>c</sup>	0.29±0.01 <sup>a</sup>	0.997	0.030
15	89.5±2.3 <sup>b</sup>	1.81±0.01 <sup>b</sup>	0.30±0.01 <sup>a</sup>	0.996	0.032
20	550±10.4 <sup>a</sup>	2.20±0.01 <sup>a</sup>	0.31±0.01 <sup>a</sup>	0.997	0.029

816 †Data are presented as mean ± standard deviation. Data values in a column with different  
 817 superscript letters are significantly different at the  $p \leq 0.05$  level.  
 818  
 819  
 820