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

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ABSTRACT

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

1. Introduction

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

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

As a viscosity modifier, knowledge of the effect of concentration on solution rheology is required for both product and process design (Moreira et al., 2011). The shear rheology of aqueous guar gum solutions has been investigated by many researchers who have probed structure–function–property parameters to gain insight into how, for example, molecular structure and solubility affect the resultant solution properties (e.g., Chenlo, Moreira, & Silva, 2010; Chenlo, Moreira, Pereira, & Silva, 2009; Cunha, Castro, Rocha, Paula, & Feitosa, 2005; Launay, Cuvelier, & Salomon, 1997; Oblonsek, Sostar-Turk, & Lapasin, 2003). Guar gum solutions usually exhibit non-Newtonian, shear thinning, behaviour, where the apparent viscosity decreases with increasing shear rate. The

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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 (μm)
D_{mid}	diameter of the filament at midpoint (μm)
D_0	initial sample diameter (μm)
D_1	diameter of the filament when first formed (μm)
F	normal force correction, N
F_{normal}	normal force generated by the flow between plates, N
k	time constant, s^{1-n}
g	gravitational constant, 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
Wi	Weissenberg number
X	filament shape factor, Equation (5), –

Greek

ε	Hencky strain, –
$\dot{\varepsilon}$	Hencky strain rate, s^{-1}
$\dot{\gamma}$	shear rate, s^{-1}
$\dot{\gamma}_R$	shear rate experienced at the rim of the parallel plates, s^{-1}
Γ	surface tension between liquid phase and the air, N/m
Γ_0	surface tension between the solvent and air, N/m
η_{app}	apparent viscosity, Pa s
η_e	estimated apparent extensional viscosity, Pa s
η_0	zero-shear rate viscosity, Pa s
η_p	polymeric contribution to the viscosity, Pa s
η_s	solvent viscosity, Pa s
$\lvert\eta^*\rvert$	magnitude of the complex viscosity, Pa s
λ	relaxation time, s
λ_i	relaxation time of i^{th}mode, s
λ_1	initial relaxation time, s
λ_2	second relaxation time, as defined by Bourbon, 2010, s
ρ	density, kg/m^3
τ	shear stress, Pa
ω	angular frequency, Hz
Ω	angular velocity, rad/s

apparent viscosity depends mainly on the molar mass while synergistic interactions are determined by the mannose/galactose ratio and the fine structure of the galactomannan chain.

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

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

The present work follows on from investigations of bubbly liquids with a non-Newtonian liquid phase (Torres, Gadala-Maria, & Wilson, 2013) and moderately high bubble volume fractions (25%), where the presence of a significant number of bubbles gave rise to viscoelastic behaviour that could not be described adequately by the existing literature. Similar findings were reported for cake batters by Chesterton et al. (2011) and Meza et al. (2011). The results reported here allow the contribution from the guar gum solutions to the viscoelastic behaviour observed in guar gum-based bubbly liquids to be computed.

1.1. Extensional rheology

Measurements of extensional rheology are needed to characterise fluid properties fully (Odell & Carrington, 2006). Experimental investigation of extensional flows is challenging, particularly for viscoelastic materials (Vadillo, Mathues, & Clasen, 2012a), partly due to difficulties in creating a purely extensional flow. During a shear deformation, the fluid elements within the material move in the same direction and slide over each other, whereas in extension the fluid elements either move away or towards each other as the material is stretched or compressed, respectively (Entov & Hinch, 1997). Various testing methods are