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Viscoelastic Properties of Pulp Suspensions of Bleached Sugarcane Bagasse: Effects of Consistency and Temperature

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The viscoelasticity of pulp suspensions of bleached sugarcane bagasse was studied in a stress/shear rate-controlled rheometer using concentric cylinders geometry. Results for the elastic (G') and viscous (G'') modulus, as well as complex viscosity (η^*), are presented as a function of the suspension consistency (1.0 wt% ≤ C_m ≤ 6.0 wt%) and temperature (20, 40, and 60 °C). The results show an effect of the concentration and temperature on the viscoelastic moduli and cross-over point. A power law model was fitted to the experimental results for elastic modulus, $G' = aC_m^b$. It was found that the complex viscosity exhibited shear-thinning behavior for all the suspensions. Only the pulp concentration had an influence on this material function.

Keywords: Elastic modulus; Viscous modulus; Complex viscosity; Pulp suspension; Sugarcane bagasse.

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INTRODUCTION

The manufacture of pulp, paper, and paper products has reached values that situate the industry among one of the largest in the world because of their wide applicability in daily life in packaging, hygiene, and communications (Derakhshandeh *et al.* 2011). In the most recent years, there has been an increasing trend towards utilization of agro-industrial residues, as sugarcane bagasse, which can be used as raw material for paper production (Chandel *et al.* 2012) and transformed in fermentable sugars for conversion to biofuels and other value-added products of commercial significance (Pandey *et al.* 2000; Chandel *et al.* 2012; Lou *et al.* 2014). Many of these processes deal with handling of pulp suspensions at different consistencies and temperatures. Pulp suspensions consist of wood or other lignocellulosic fibers, broken down by physical or chemical processes, and dispersed in water (Biermann 1996). The potential of fiber suspensions to form networks that help transmit stresses, in addition to the flocculation phenomena, among other factors, results in a non-Newtonian behavior (Kerekes 2006; Bousfield 2008; Derakhshandeh *et al.* 2011), exhibiting viscoelastic properties. This has practical implications in many stages of the papermaking and bioconversion processes, *e.g.*, during the transport of fiber suspensions, the forming of paper (Tatsumi *et al.* 2002), and mixing of biomass slurries (Nutsen and Liberatore 2009). Therefore, is then of crucial interest to know the rheology of bagasse suspensions to ensure optimal process implementation and the right selection of equipment.

Viscoelastic properties of pulp suspensions have been studied by several researchers. Thus, Swerin *et al.* (1992) measured the viscoelastic behavior of bleached kraft pulps at consistencies ranging between 3% and 8%. The suspension showed linear

viscoelasticity below a critical strain level independent of consistency, whereas above the critical level, a strong non-linear viscoelastic behavior was observed. Damani *et al.* (1993) found that the elastic modulus G', for a thermomechanical pulp, is insensitive to frequency over the range 10^{-2} to 5 s^{-1}, but a significant effect of applied strain reduces the modulus by half. Similar results were obtained by Tatsumi *et al.* (2008) for softwood bleached kraft pulp. Additionally, the elastic modulus was correlated to volume concentration through a power law $G' = kc_v^{\alpha}$. Furthermore, Swerin (1998) determined that, for cellulosic fiber suspensions flocculated by cationic polyacrylamides, G' increases as a function of frequency and the viscous modulus G'' remains almost constant in the interval 0.001 to 5 Hz. The effect of the chemical flocculant on the shear moduli was large; both the elastic and the viscous modulus increased. On the other hand, Stickel *et al.* (2009) performed rheological measurements of a lignocellulosic biomass slurry at concentrations up to 30%. The elastic modulus was found to be almost an order of magnitude larger than the viscous modulus and weakly dependent on frequency. Finally, it has been found that the rheological behavior of synthetic fiber suspensions shows "shear-thinning", and a complex viscosity tending toward a Newtonian plateau at high frequencies (Petrich *et al.* 2000; Keshtkar *et al.* 2009).

Despite the research studies mentioned above, viscoelastic properties of pulp suspensions of sugarcane bagasse have not been widely discussed. Hence, in this paper we present experimental results concerning the rheology of pulp suspensions of bleached sugarcane bagasse at various fiber mass concentrations and temperatures. We study the effect of consistency and temperature on the viscoelastic properties of the suspension using a stress/shear rate-controlled rheometer, implementing a vane rotor in a large cup geometry. Additionally, a mathematical model is proposed to correlate the elastic modulus with consistency.

EXPERIMENTAL

Pulp fiber suspensions for experiments were prepared from bleached cellulose of sugarcane bagasse kindly supplied by a local company located in Cali-Colombia. The bleached cellulose was characterized through the determination of alpha-cellulose content by the TAPPI test method T-203 (2006), intrinsic viscosity by the standard method ASTM D1795-13 (2013), and morphological parameters, such as mean length and diameter, fiber distribution, and coarseness, using a morfi compact ISO/FDIS 16065-2 analyzer (Techpap SAS, Grenoble, FR). The bleached cellulose properties are summarized in Table 1.

Rheological measurements were carried out in a DHR-2 rotational viscometer (TA Instruments, New Castle, DE, USA), using a four-bladed vane rotor, 42 mm in height and 28 mm in diameter, placed in a cylindrical container. The container consisted of a jacketed glass cylinder having an internal height of 10 cm and an internal diameter of 6 cm, to guarantee a gap between rotor and housing larger than five times the characteristic size of the suspended particles (Dalpke and Kerekes 2005). Through the container jacket, water from a thermostatic bath circulated to control the temperature of the suspension (25, 40, and 60 °C). Suspensions of 1.0, 2.0, 3.0, 4.0, 5.0, and 6.0 wt% were prepared by disintegration of bleached cellulose for 30 min at 3000 rpm in a JSR Pulp Disintegrator (Fibretec Instruments, Roorkee, IN). To obtain consistent rheological data for pulp suspensions and to eliminate thixotropic effects after loading the sample into the measuring

device, all suspensions were pre-sheared with a shear rate of 100 s^{-1} over 20 s to rupture any fiber structure, followed by a relaxation time to recover their structure to a certain level.

Table 1. Properties and Morphological Parameters of Bleached Cellulose

Characteristic	Value	Units
α-Cellulose	78.5	%
Intrinsic viscosity	642	cm^3/g
Mean length	0.956	mm
Mean diameter	27	µm
Coarseness	0.160	mg/m
Mean curl	8.8	%

The viscoelastic properties of pulp suspensions were determined by the "small amplitude oscillatory shear" (SAOS) method (Morrison 2001). In this technique, a small sinusoidal strain is applied to the suspension and the stress response is measured. The elastic modulus, viscous modulus, and complex viscosity were measured as functions of frequency, within the linear viscoelastic regime of the sample, for each consistency and temperature.

RESULTS AND DISCUSSION

The strain dependence measurements of the elastic modulus of the suspensions were carried out to determine the range in which the system exhibited linear viscoelasticity. A representative result is plotted in Fig. 1 for a 3.0 wt% pulp suspension at 25 °C.
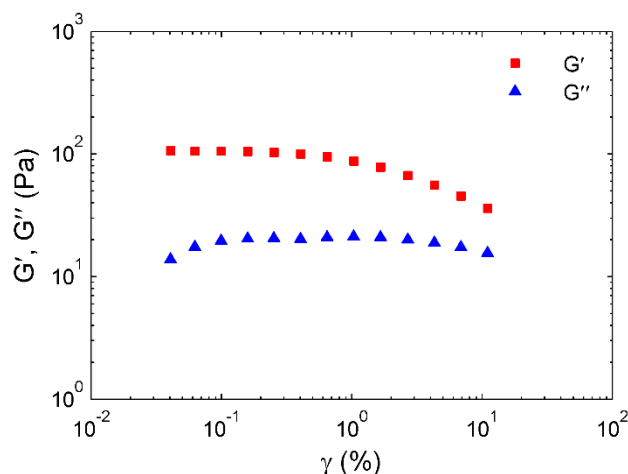
Fig. 1. Elastic and viscous modulus as functions of strain for a 3.0 wt% suspension at 25 °C

As can be seen, for strain amplitudes less than 1.0%, the suspension showed linear viscoelasticity, *i.e.*, the modulus was almost constant. The value of this plateau is regarded as a pseudo-equilibrium modulus, which shows the rigidity of the fiber network (Tatsumi *et al.* 2008). The strength of the network arises from mechanical interaction between fibers, such as adhesive forces, friction forces, and fibers bending and flexibility (Farnood *et al.* 1994; Andersson *et al.* 1999; Keshtkar *et al.* 2009). Above this critical strain, a structural breakage in the suspension took place (Swerin 1998) and *G′* decreased. The elastic

modulus, G', was almost ten times larger than the viscous modulus, G''. Although such behavior was similar at all consistencies and temperatures, there were differences in the strain at which the onset of nonlinearity was observed. Thus, in the subsequent frequency dependence measurements, the strain value was fixed in the linear region for each consistency and temperature.
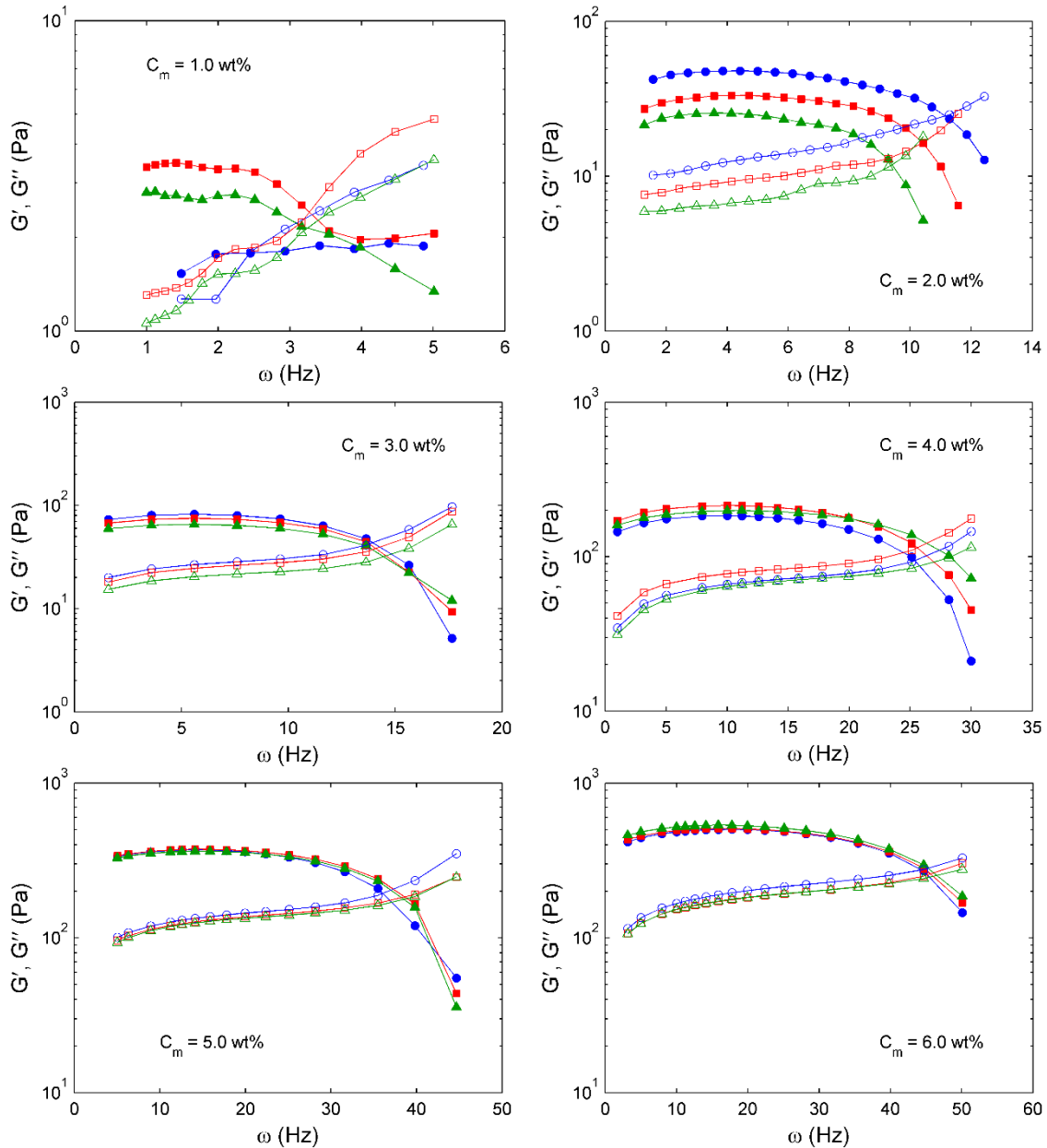

Fig. 2. Elastic (G', closed symbols) and viscous (G'', open symbols) modulus as functions of frequency for pulp suspensions ranging from 1.0 to 6.0 wt%. (●, ○) 25 °C, (■, □) 40 °C, (▲, △) 60 °C

Figure 2 shows the variation of elastic and viscous modulus with frequency for all suspensions considered in this study. At low and moderate frequencies, the elastic component exceeded the viscous component and a plateau was observed, indicating a "spring behavior", which may be due to the entanglement and hooking of fibers in the

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suspension (Schmid and Klingenberg 2000; Keshtkar *et al.* 2009). These forces arise from fiber curl, kinks, or highly fibrillated surfaces (as a result of pulping and bleaching processes), causing fibers to adhere to each other (Kerekes 2006). At high frequencies, both components meet (cross-over point), and finally, the viscous component becomes dominant. The effect of frequency can be explained in light of the theory of entangled polymers (Milner and McLeish 1998; Larson 1999): at low and moderate frequencies G' was greater than G'', so the Deborah number, De = $\omega\tau$, is greater than 1, implying a long relaxation time for fibers, $\tau > 1$. This behavior can be attributed to reptation motion, where fibers relax by sliding along their own contour. At high frequencies $G' < G''$ (De < 1), implying a short relaxation time of fibers, $\tau < 1$. Thus, the upturn of G'' (Fig. 2) could be caused by a faster relaxation mode, as for example Rouse motion (elastic dumbbell model).

Figure 2 also shows an increase of G' and G'' with consistency, as well as an effect of temperature at low consistencies. For the lower-consistency suspension, 1.0 wt%, the storage modulus decreased rapidly, indicating a more liquid-like behavior. At this consistency, the suspension is composed of tight flocs surrounded by a loose network of fibers (Damani *et al.* 1993), requiring a smaller rate of strain for the network to overcome its elastic limit. As the consistency rises, the flocs interact through direct contact and entanglements, establishing a continuous network that provides more rigidity to the suspension, as evidenced in Fig. 3 for the cross-over point. On the other hand, the effect of the temperature was more pronounced at low consistencies, $C_m \leq 3$ wt%, where an increase in the temperature leads to a decrease in magnitude of the viscoelastic moduli, as well as a shift to lower frequencies for the cross-over point, which may be attributed to the smaller amount of energy required to both break up the fiber networks and overcome friction between flocs (Ventura *et al.* 2007). However, at higher consistencies the effect of the temperature is not significant, showing a slight increase of the viscoelastic moduli and cross-over point, perhaps due to an increase in kinetic energy of fibers, allowing the formation of new entanglements and hookings.
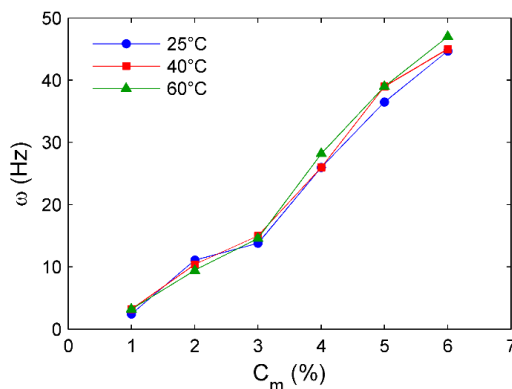
Fig. 3. Elastic and viscous modulus cross-over frequency as functions of suspension consistency at various temperatures

To obtain a relationship between the elastic modulus and the consistency of the suspension, these parameters were plotted and correlated in Fig. 4, for a frequency of 1.0 Hz. The experimental data were well-fitted by a power law of the form $G' = aC_m^b$, where a and b are constants. The value of exponent $b = 2.77$ is consistent with those reported by Damani *et al.* (1993), Swerin (1998), and Tatsumi *et al.* (2008), ranging from 2.2 to 3.3, for pulp suspensions from different sources.
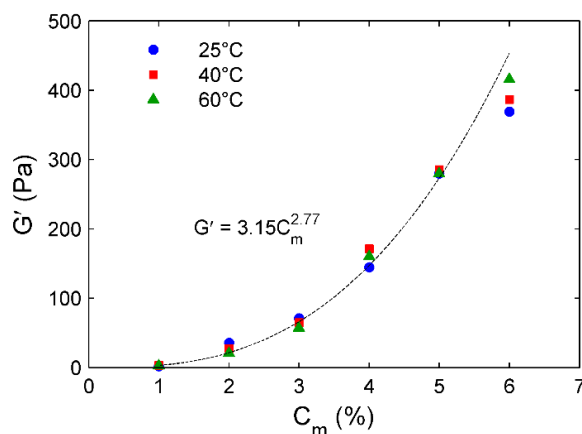
Fig. 4. Elastic modulus as a function of consistency at $\omega = 1$ Hz at various temperatures. The dashed line represents the potential fitting model.

Results for the complex viscosity of pulp suspensions as a function of frequency, ω, are shown in Fig. 5 for various consistencies and temperatures. As can be seen, pulp suspensions of bleached sugarcane bagasse exhibit non-Newtonian "shear-thinning" behavior, which is in agreement with previous results obtained by Sánchez *et al.* (2015) for the true viscosity of this kind of suspension, and with those obtained by Keshtkar *et al.* (2009) for fiber-filled model suspensions. Additionally, the absence of a plateau at low frequencies was apparent for all the consistencies, which indicates elastic behavior resulting from the formation of network-like structures. At high frequencies, the suspensions exhibited an increase in complex viscosity, which might be a result of the sedimentation process that affects the suspension at long times of experimentation and that was evident during each of the tests performed. On the other hand, and as a consequence of the same reasons stated for viscoelastic moduli, the complex viscosity increased with the consistency of the suspension, and it was not significantly affected by temperature, as found by Sánchez *et al.* (2015) for pulp suspensions of sugarcane bagasse, and Ferreira *et al.* (2003) for kraft pulps of eucalyptus and pine.

CONCLUSIONS

1. The results show a solid-like behavior of the suspension at low frequencies and a liquid-like one at high frequencies.

2. A noticeable effect of the consistency on the elastic and viscous moduli was observed, in addition to a slight effect of the temperature, especially at consistencies less than 3.0 wt%.

3. The frequency for the cross-over point increased with the consistency and decreased with temperature.

4. A power-law equation, $G' = aC_m^b$, was fitted to the experimental data, obtaining values for fitting parameters that agree with those reported in literature.

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5. The complex viscosity showed a non-Newtonian "shear-thinning" behavior for all the suspensions, where the non-presence of a plateau at low frequencies and an increase at high frequencies were observed.

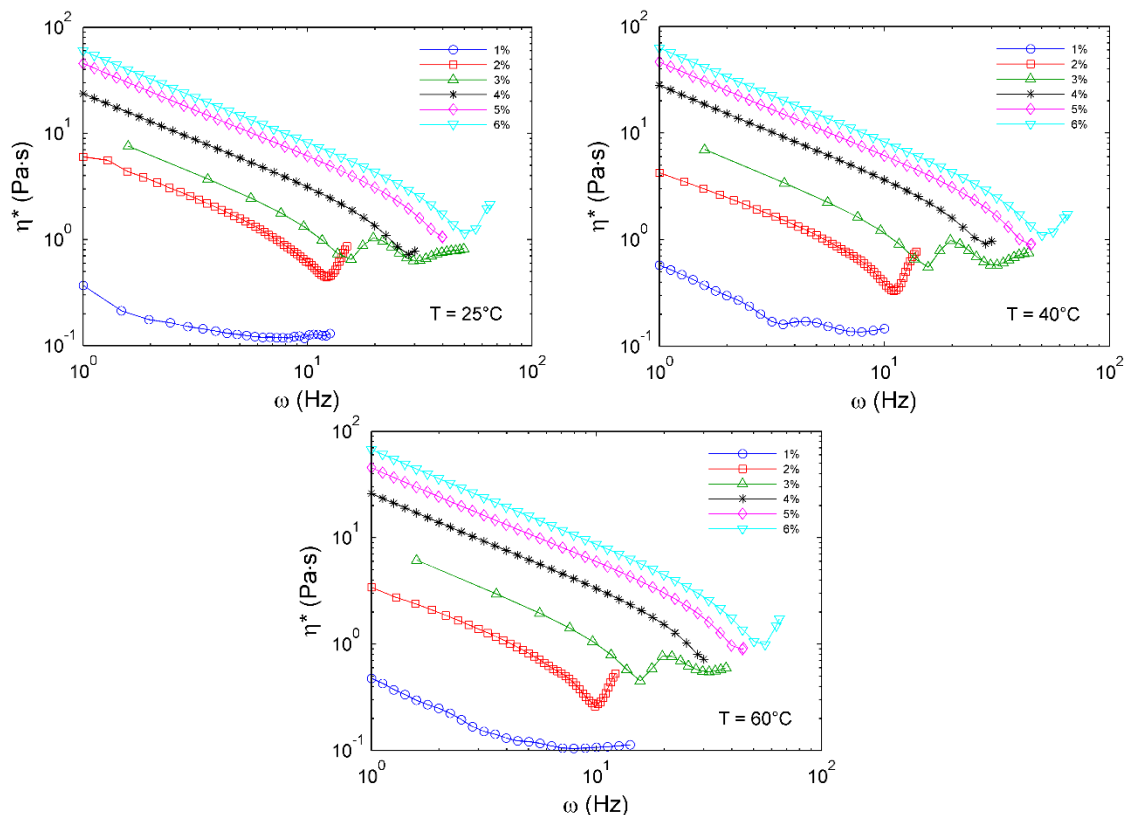6. Finally, the effect of the temperature on complex viscosity was not significant.

Fig. 5. Complex viscosity as a function of frequency at various temperatures

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