Study on the Dynamic Viscoelasticity of Bamboo Kraft Black Liquor

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The dynamic viscoelasticity of bamboo kraft pulping black liquor under various temperatures (ranging from 50 to 80 °C) and solids concentrations (60 to 80 wt.%) was studied. Rotational rheometer analysis data indicated that the viscoelastic motion law with a high solids concentration in black liquor was in accordance with the Kelvin model, and black liquor with a medium concentration conformed to the Maxwell model. As a result, the temperature and solids concentration greatly influenced the dynamic viscoelasticity of bamboo kraft pulping black liquor. For instance, the modulus increased as the solids concentration increased, indicating that the viscous component of black liquor was prominent. For this reason, it was easier to soften the bamboo black liquor, providing a favorable condition for the pure viscosity of black liquor. Steady shear thinning was apparent during the frequency shear process. The dynamic viscosity, storage viscosity, and complex viscosity of the black liquor decreased as the shear frequency increased. The quantitative relationship between dynamic viscosity and angular frequency can be described using the Power Law model.

Keywords: Bamboo kraft black liquor; Rotational rheometer; Dynamic viscoelasticity

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INTRODUCTION

Because of the shortage of wood resources, non-wood fiber materials are being used for papermaking purposes in Europe and Asia. The bamboo forest area of China ranks second in the world, and bamboo is considered a favorable papermaking material (Sun and Hui 2002). Bamboo is a type of non-wood raw material that grows quickly and has been used in the production of ordinary paper, dissolving pulp, fluff pulp, microcrystalline cellulose, and other products (Lin *et al.* 2014). Therefore, taking full advantage of abundant bamboo resources for pulping and papermaking would be beneficial, considering China's national forest conditions.

Black liquor is the major byproduct in chemical pulping, as well as a fuel for pulp mills. In the kraft, sulfate, and soda processes, cellulose fibers are disassociated from lignin by chemical reactions (Das *et al.* 2013). Black pulping liquor consists of organic and inorganic materials. In recent years, studies have focused on the chemical composition and physical properties of black liquors (Cardoso *et al.* 2009; Garron *et al.* 2015). During the chemical pulping process, approximately 50 wt.% of the wood raw material was dissolved in the cooking liquor (Zhan 2009), including lignin, polysaccharides, and resinous compounds of a low molar mass. Inorganic compounds present in black liquor consist mostly of sodium salts and small amounts of potassium, calcium, magnesium, silicon, and irons salts in an aqueous medium (Zhang *et al.* 2013).

The rheological properties of black liquor are affected by temperature, solids concentration, and shear rate, as reported by a previous study (Zaman and Fricke 1995). Other important parameters, such as droplet formation, drying characteristics, and swelling characteristics in the furnace, also affect the rheological properties of black liquor (Llamas *et al.* 2007). However, the rheological properties of black liquor vary from liquor to liquor because of the cooking conditions and the wood species type. Bamboo black liquor can be concentrated and burned, and its high viscosity restricts the solids concentration to an upper limit of 50 wt.%, which makes the recovery of bamboo black liquor more difficult to complete (Alg 2004). As a result, the rheological properties of black liquor play an important role in alkali recovery and the evaporation process.

Several studies have discussed the rheological properties of black liquor, such as shear viscosity and linear viscoelasticity; however, most of the studies merely refer to softwood or broadleaf wood black liquor (Zaman and Fricke 1995; Cardoso *et al.* 2006). Additionally, fewer studies highlighted the linear viscoelastic functions of black liquor at high temperature and solids concentration (Li and Li 2000; Boladale 2010).

Some research results regarding the rheological properties of black liquor have been published (Soderhjelm 1988; Lu and Bin 2001; Andreuccetti *et al.* 2011). However, there has been relatively little research on the dynamic viscoelasticity of bamboo black liquor. In this study, the dynamic viscoelasticity of bamboo kraft cooking black liquor was examined using a rotational rheometer. Useful information on shear viscosity and linear viscoelastic functions of well-characterized bamboo black liquors can be obtained. The critical error problems resulting from viscous heating and the flow of black liquor through the nozzle can be solved with the dynamic viscosity measurement method, which is more accurate and simple. Additionally, the study is of importance to provide an overview of the physical and chemical properties of bamboo kraft black liquor. Meanwhile, novel approaches for evaporation and combustion can be developed based on the findings of the study.

EXPERIMENTAL

Materials

The bamboo black liquor used in this investigation was kindly supplied by Chitianhua Pulp and Papermaking Co., Ltd., Guizhou, China. The properties of the black liquor were as follows: solids content, 72.26 wt.%; SiO_2 content, 1.03 wt.%; total alkali content, 29.60 wt.%; total sulfur content, 4.43 wt.%; and fuel value, 11.18 MJ/Kg.

Three kinds of black liquor with different solids content (72.26 wt.%, 77.38 wt.%, and 63.10 wt.%) were selected for analysis. The black liquor with a solids concentration of 72.26 wt.% was used as the control specimen. The thick black liquor was oven dried at 105 °C until the solids concentration reached 77.38 wt.%. The sample with a solids concentration of 63.10 wt.% was obtained through dilution using distilled water.

Rheometer Measurement

The rheological behavior of the kraft black liquor was determined using an AR2000ex rotational rheometer (TA Instruments, USA) equipped with a coaxial cylinder. The cylinder system was cleaned with ether, dried, and then assembled. The main parameters were as follows: the rheometer jig was a stainless steel parallel plate with a diameter of 60 mm; the measuring space was 1000 μm; Samples were run at 50, 60, and

80 °C on cone plate geometry. The rheological investigation was carried out varying the shear rate from 0.1 to 100 rad/s, and the strain was 1%. The rheometer was connected to a computer for acquisition and analysis of the data, so the equipment directly displayed the shear stress, shear rate, apparent viscosity, speed, and torque.

RESULTS AND DISCUSSION

Effects of Solids Content and Temperature on the Dynamic Modulus of Bamboo Kraft Black Liquor

The viscoelastic characteristics of the three experimental bamboo kraft black liquors, with solids concentrations ranging from 63.10 wt.% to 77.38 wt.%, were investigated at temperatures ranging from 50 to 80 °C. Figures 1 to 5 show the typical results for the storage modulus (*G*'), loss modulus (*G*''), and tan δ as a function of frequency at various solids concentrations and temperatures.

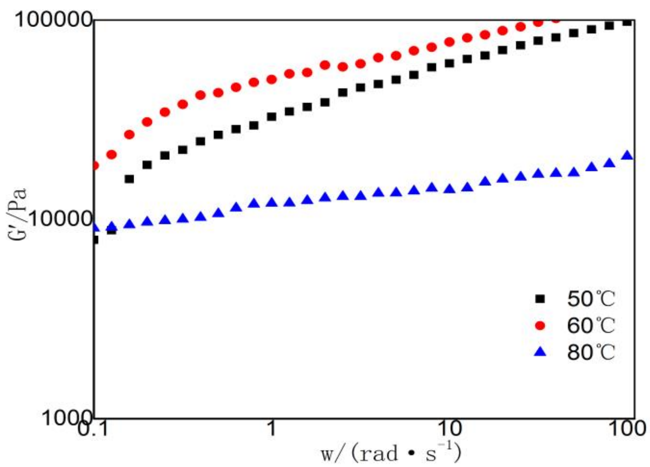

Fig. 1. *G' vs.* frequency for 63.10 wt.% solids concentration black liquor at 50, 60, and 80 °C

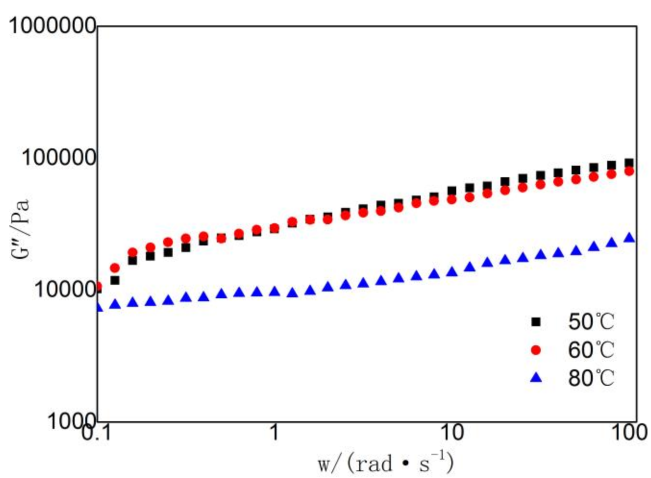

Fig. 2. *G*'' *vs.* frequency for 63.10 wt.% solids concentration black liquor at 50, 60, and 80 °C

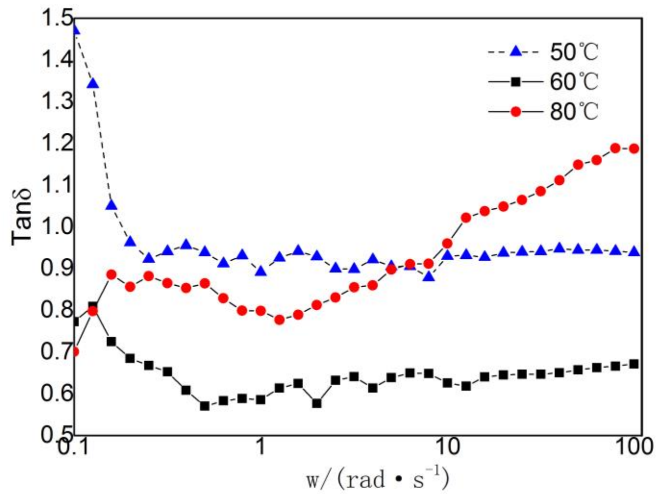

Fig. 3. Tan δ *vs.* frequency for 63.10 wt.% solids concentration black liquor at 50, 60, and 80 °C

At 50 °C, the storage modulus (*G*') was similar to the loss modulus (*G*''), as both increased with increasing frequency. The phase angle was approximately 45°, meaning that the viscous component was equal to the elastic ingredient. These results indicate that the network structure formed between the lower strength lignin polymers in bamboo kraft black liquor was relatively weak (Feldman *et al.* 1986).

At 60 °C, the storage modulus and loss modulus of bamboo kraft black liquor also increased with increasing frequency, ranging from 0.1 to 100 Hz. Given the constraints, *G*' was always greater than *G*'', and the phase angle was less than 45°. Therefore, the strength of the crosslinked network structure between organic polymers in black liquor was relatively strong. Moreover, the properties of elastic solids in black liquor held a dominant position. For this reason, the Kelvin model can be used to simulate the viscoelastic body motion of bamboo kraft black liquor (Yang *et al.* 2002).

When the temperature reached 80 °C and the shear frequency was less than 12.59 rad/s, *G*' was greater than *G*'' in black liquor. In this situation, the black liquor exhibited the property of an elastic solid. However, when the frequency exceeded 12.59 rad/s, *G*' was less than *G*''. The phase angle was greater than 45° and increased as the frequency increased under this condition. The results showed that when the elastic component of the black liquor decreased, the viscous property in black liquor became dominant. Additionally, the bonding strength between polymers drops and the free space for molecular activity increased. This indicates that the black liquor had begun to soften, which creates favorable conditions for black liquor to exhibit pure viscous flow. Because of the relatively large loss modulus (*G*''), the viscoelastic body motion for bamboo kraft black liquor in this instance can be described by the Maxwell model (Lorenz *et al.* 2012).

Figures 4 and 5 illustrate the storage modulus (*G*') and loss modulus (*G*'') as a function of frequency for black liquor with solids concentrations of 72.26 and 77.38 wt.%, respectively. Clearly, *G*' is always greater than *G*'' in the shear vibration frequency range, and the phase difference is less than 45°. Hence, the black liquor principally shows the property of an elastic solid. For this reason, the Kelvin viscoelastic mechanical model is appropriate to demonstrate the rheological behavior of the black liquor under such conditions.

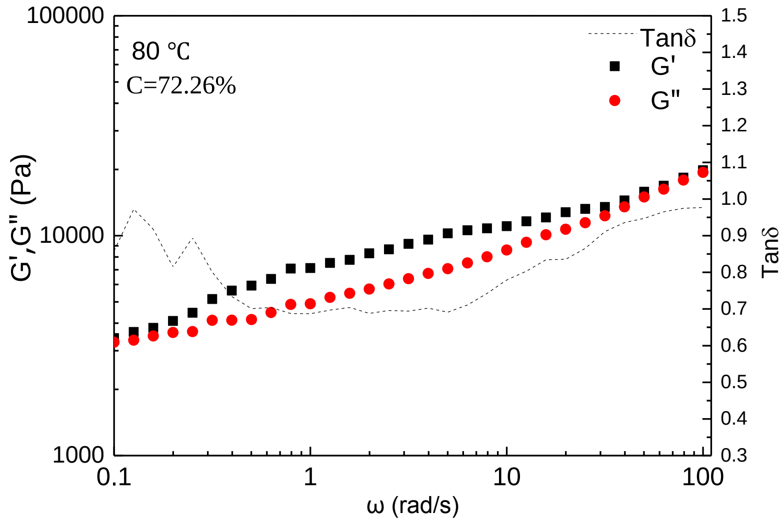

Fig. 4. Dynamic modulus *vs*. frequency for 72.26 wt.% solids concentration black liquor at 80 °C

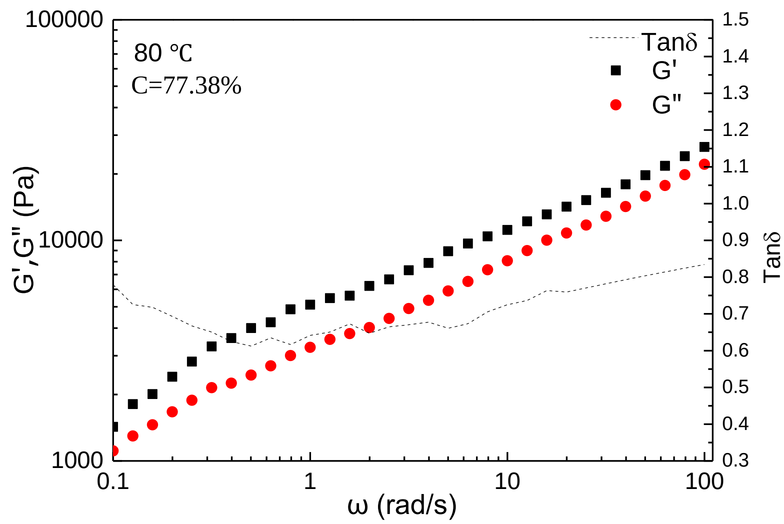

Fig. 5. Dynamic modulus *vs*. frequency for 77.38 wt.% solids concentration black liquor at 80 °C

Compared with Figures 1 to 3, one can draw the conclusion that when high solids concentrations black liquors maintain a constant temperature, they display elastic solid features. As a result, greater yield stress is required to destroy the intermolecular structure of the polymers.

Effects of Solids Concentration on the Viscosity of Bamboo Kraft Black Liquor

Figures 6 to 8 show the relationship between frequency and dynamic viscosity, storage viscosity, and complex viscosity of bamboo kraft black liquor. Clearly, the viscosities are decreasing with the increase of frequency under different solids concentrations.

Bamboo kraft black liquor with a 63.10 wt.% solids concentration initially followd Newtonian phenomenon at a low shear frequency (Xu *et al.* 2004). However, the oscillation frequency, ranging from 0.1 to 100 rad/s, lay within the region of shear thinning. As a function of this frequency, dynamic viscosity, storage viscosity, and complex viscosity decreased sharply as the frequency was increased. The relevant frequency range is also referred to as the oscillation shear-thinning zone. Meanwhile, when the oscillation frequency lies in the range of 0.1 to 10 rad/s, the dynamic viscosity will be lower than the storage viscosity.

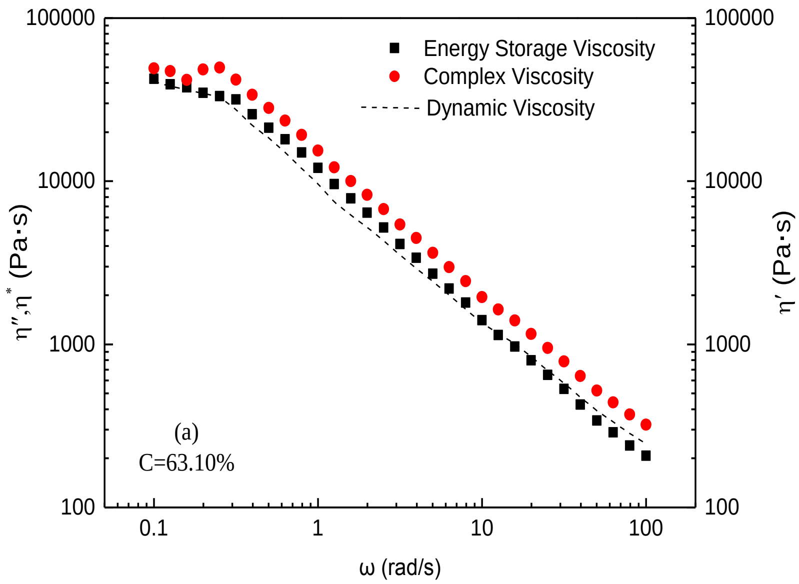

Fig. 6. Storage viscosity, complex viscosity, and dynamic viscosity as a function of frequency for 63.10 wt.% solids concentration black liquor at 80 °C

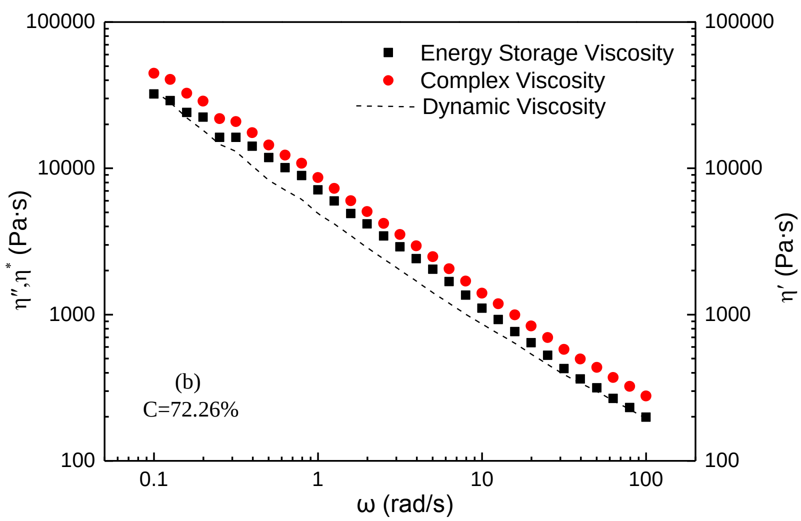

Fig. 7. Storage viscosity, complex viscosity, and dynamic viscosity as a function of frequency for 72.26 wt.% solids concentration black liquor at 80 °C

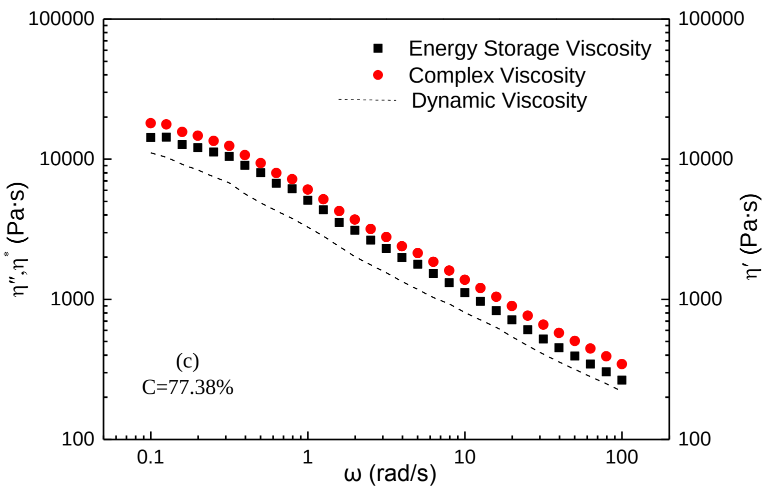

Fig. 8. Storage viscosity, complex viscosity, and dynamic viscosity as a function of frequency for 77.38 wt.% solids concentration black liquor at 80 °C

On the contrary, if the oscillation frequency continues to increase, the dynamic viscosity will exceed the storage viscosity. This phenomenon may be attributed to the elastic fluid characteristics of black liquor; however, the storage viscosity was larger than the dynamic viscosity because of the increasing frequency in the temperature of 80 °C and 63.10 wt.% solids content. The movement of the organic polymer in the black liquor accelerated with the increasing of oscillation frequency, which weakened the three-dimensional network structure of the polymers. Therefore, the black liquor showed characteristics of a viscous liquid.

Over the whole range of oscillating shear frequency, the dynamic viscosity, storage viscosity, and complex viscosity of bamboo kraft black liquor (with a solids content of 72.26 and 77.38 wt.%) decrease by two orders of magnitude. Meanwhile, different rheological behaviors were not apparent, but only the analogous steady shear-thinning zone was apparent. This demonstrates that when the temperature was consistent, the quantity of molecules in black liquor grew with increasing solids content. Consequently, the three-dimensional network structure of polymers becomes stronger and, the steric stabilization is dominant. These results suggest that the directional rearrangement of particles within the black liquor occurred in the oscillating shear field.

The linear region of the plots of log (η') as a function of log (ω) can be applied to the power law model (Zhong *et al.* 2013), which is similar to the steady shear-thinning phenomenon, expressed as,

$$\eta' = a\omega^{b-1} \quad (1)$$

where η' is the dynamic viscosity; ω is the frequency; a refers to a constant with time dimensions; and b refers to a dimensionless constant.

The fitted curve results from the relationship between dynamic viscosity and frequency, as the Power Law model, are shown in the following table.

Table 1. Fitted Curve Results for the Relationship between Dynamic Viscosity and Frequency as a Power Law Model

Solid content (%)	ω (rad/s)	a (Pa·s^n)	b	Power law constitutive equation	R^2
63.10	0.3 to 100	9779.56	0.098	$\eta'=9779.56\omega^{-0.9}$	0.99876
72.26	0.1 to 100	4790.69	0.156	$\eta'=4790.69\omega^{-0.84}$	0.99881
77.38	0.1 to 100	3286.56	0.446	$\eta'=3286.56\omega^{-0.55}$	0.99546

CONCLUSIONS

1. In general, the motion law of viscoelasticity for high solids content conformed to the Kelvin model. For the medium solids concentration, especially at high temperatures, the Maxwell model was applicable.
2. The temperature and solids concentration of the bamboo kraft black liquor had a marked effect on the dynamic viscoelasticity of the black liquor. The dynamic modulus (such as G', and G'') increased with increasing solids content, meaning that the viscoelastic property of black liquor was greater. Meanwhile, the black liquor can easily be softened because of the increase in the loss modulus G'', which increased the adhesive character of black liquor.
3. During the process of continuous shearing, the bamboo kraft black liquor exhibited steady shear thinning. The dynamic viscosity, viscosity of energy storage, and complex viscosity decreased with increasing shear rate. The Power Law model described the quantitative relationship between the dynamic viscosity and the angular frequency. For instance, the regression formula of the solids content for 72.26 wt.% bamboo kraft black liquor was as follows: $\eta'=4790.69\omega^{-0.84}$, $R^2 = 0.99881$.

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