Dynamic Viscoelasticity of Kraft Black Liquor at a High Dry Solid Content with the Addition of Sodium Aluminate

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Black liquor is not only a by-product of the papermaking industry but also an energy source that is often burned at a high solids content in a recovery furnace because of its high combustion efficiency and stability. However, the silicon content of bamboo kraft black liquor (BKBL) is much higher than that of softwood kraft black liquor, and the presence of silicon causes serious problems in the recovery cycle. Sodium aluminate, when used as a desilicating agent during combustion, has an excellent effect on the removal of silicon from BKBL. In this work, the dynamic viscoelasticity of BKBL with the addition of sodium aluminate was studied using a rotational rheometer. The results indicated that the BKBL was a pseudo-plastic fluid. A power-law model and the Cross model accurately described the relationship between the dynamic viscosity and angular frequency. The zero shear rate viscosity of BKBL was relatively high, even at a high temperature. The addition of sodium aluminate increased the viscosity of BKBL when the loading was 1.5 wt.%, but it had the opposite effect when its loading was 0.5 wt.%. With an increase in the angular frequency, the effect of sodium aluminate on the viscosity became less apparent.

Keywords: Dynamic viscoelasticity; Black liquor; Complex viscosity; Dynamic viscosity

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INTRODUCTION

Black liquor is an environmentally harmful waste liquor resulting from the kraft pulping process that consists of complex organic and inorganic compounds (Trung *et al.* 2015). The main organic compounds in black liquor are lignin, polysaccharides, and resinous compounds, which are extracted from papermaking materials. An expensive mixture of cooking chemicals is used to separate cellulose fibers from raw material (Garcia *et al.* 2009). Hence, the inorganic compounds in black liquor primarily include large amounts of sodium salts and small amounts of calcium, potassium, magnesium, silicon, and iron salts (Liu *et al.* 2013). To maintain the cost-effectiveness of the pulping process and protect the environment, black liquor is burned in a specially designed furnace to recover the energy and chemicals in an alkali recovery system. Usually, black liquor is concentrated to a solid content above 60 wt.% by multiple effect evaporators before being burned in the recovery furnace. To improve the combustion efficiency and stability, the black liquor can be burned at a higher solids content (Sandquist 1983; Llamas *et al.* 2007). At Hainan Jinhai Pulp and Paper Co., Ltd., the solids content of black liquor is above 80 wt.%, obtained through passivation and crystallization evaporation technology. Other benefits, such as economic and environmental outcomes, including lowering the discharge amount of sulfur dioxide, can be achieved when the black liquor is burned at a high solids content.

Bamboo, which is widely grown in China, is considered a favorable non-wood fiber material for papermaking because of its excellent pulping properties (Sun and Hui 2002). However, the silicon content of bamboo kraft black liquor (BKBL) is much higher than that of softwood pulp black liquor (Cardoso *et al.* 2009). This characteristic leads to a series of silicon-related problems in the recovery system. More serious silicon scaling occurs in the pipe and evaporation system because the silicon in black liquor reacts with sodium hydroxide (NaOH) to produce sodium silicate (Na_2SiO_3) during the cooking process (Xu *et al.* 2015c). The viscosity of black liquor increases due to the higher silicon content, and more energy is needed to pump and atomize the black liquor (Ramamurthy *et al.* 1993; Karlsson *et al.* 2013). In addition, the alkali recovery rate decreases with increasing silicon content due to the formation of calcium silicate ($CaSiO_3$) in the lime mud. Recently, a new method to remove silicon from black liquor was proposed (Xu *et al.* 2015a). Sodium aluminate ($NaAlO_2$), which has typically been used as a desilicating agent, was added to the black liquor before combustion. The Na_2SiO_3 in the black liquor can react with $NaAlO_2$ to produce $Na_2O{\cdot}Al_2O_3{\cdot}4SiO_2$ during combustion. Then, the combustion product is dissolved in water to form green liquor. The $Na_2O{\cdot}Al_2O_3{\cdot}4SiO_2$ forms a precipitate, which can be filtered from the green liquor. The decrease in silicon content in green liquor is beneficial to the causticizing process (Xu *et al.* 2015b).

The rheological properties of black liquor, which strongly depend on temperature, solid content, shear rate, and cooking conditions (Yang *et al.* 2007; Singh *et al.* 2016; Zhang and Chen 2016), have a significant impact on the operational factors of a furnace, such as the droplet formation, the power requirements for transport, and drying and swelling characteristics (Zaman and Fricke 1995a). According to the authors' previous research, BKBL exhibits a shear-thinning phenomenon only when the solid content is above 50 wt.% during the shear process (Xu *et al.* 2016a). Furthermore, the temperature and solid content have a marked effect on the dynamic viscoelasticity of BKBL (Xu *et al.* 2016b). However, most studies have focused only on the rheological properties of black liquor at a low or middle solid content. The knowledge of BKBL rheological properties at a high solid content is essential for improving the design and operation of the recovery system.

Considering the conditions, *i.e.*, the temperature of the BKBL from the evaporators is approximately 120 °C and is gradually reduced along the flow direction, this paper focuses on the dynamic viscoelasticity of 70.2 wt.% BKBL and 79.9wt.% BKBL with various sodium aluminate loadings at greater than 70 °C. The storage modulus (G'), loss modulus (G''), dynamic viscosity (η'), and complex viscosity (η^*) were studied with a rotational rheometer to explore the viscoelasticity behavior of thick black liquor and the effect of sodium aluminate on the droplet formation of black liquor.

EXPERIMENTAL

Materials

The BKBL was kindly supplied by Chitianhua Pulp and Papermaking Co., Ltd., Guizhou, China. The solids content was 70.2 wt.%. The total alkali content was 25.0 wt.%.

The effective alkali was 23.9 g/L. The total sulfur content was 4.43 wt.%. The fuel value was 11.2 MJ/kg. The silicon content was 1.03 wt.%.

Sodium aluminate ($NaAlO_2$) was supplied by Sinopharm Chemical Reagent Co., Ltd., Beijing, China.

Specimen preparation

The thick black liquor was dried at 80 °C in a vacuum drying oven until the solid concentration reached 79.9 wt.%. Sodium aluminate (0.5 wt.% and 1.5 wt.%, based on the solid weight in black liquor) was added to the BKBL at two different solid contents (70.2 wt.% and 79.9 wt.%). The mixtures were stirred at 260 rpm for 10 min at 40 °C.

Rheology measurement

The dynamic modulus of BKBL was measured with an AR2000ex rotational rheometer (TA Instruments, New Castle, DE, USA) at 70 °C and 98 °C. The displacement resolution of the rheometer is 0.04 μrad. The jig of the rheometer was a stainless steel parallel plate with a diameter of 25 mm. The measuring space was 700 μm. The angular frequency ranged from 0 to 100 rad/s. Silicone oil, which did not mix with the black liquor and had a negligible effect on torque generation because of its lower density and viscosity, was used to cover the specimens to prevent water evaporation during measurements.

Methods

Measuring the shear viscosity of black liquor is difficult, especially at high shear rates, because of viscous heating, whereas the complex viscosity is easier to measure (Zaman and Fricke 1995b). The complex viscosity (η^*) is defined as

$$\eta^* = \eta' - \mathrm{i}\,\eta'' = \frac{G''}{\omega} - \mathrm{i}\,\frac{G'}{\omega} \tag{1}$$

where η' is the dynamic viscosity (Pa·s), η'' is the storage viscosity (Pa·s), G' is the storage modulus (Pa), G'' is the loss modulus (Pa), and ω is the angular frequency (rad/s).

The dynamic viscosity data were fitted according to a power-law model (Eq. 2) and the Cross model (Eq. 3), which are often used to describe the relationship between the dynamic viscosity (η') of black liquor and the angular frequency (ω) (Zaman and Fricke 1995b). The equations are as follows,

$$\eta' = \mathrm{m}\omega^{\mathrm{n}-1} \tag{2}$$

where m is a measure of the consistency of the fluid, known as the consistency index (Pa·s^n), n is a measure of the degree of non-Newtonian behavior, known as the power law index, and ω is the angular frequency (rad/s); and,

$$\eta' = \eta_\infty + \frac{\eta_0 - \eta_\infty}{1 + (\lambda\omega)^\alpha} \tag{3}$$

where η_0 is the zero shear rate viscosity (Pa·s), η_∞ is the viscosity of black liquor when ω approaches infinity, λ is a constant parameter (s^{-1}), and α is a dimensionless constant.

RESULTS AND DISCUSSION

Effect of Sodium Aluminate on the Dynamic Modulus of BKBL

Figures 1 and 2 show typical results for the storage modulus (*G′*) and loss modulus (*G″*) of BKBL as a function of angular frequency (ω) at different solid contents and temperatures with the addition of sodium aluminate. The storage modulus (*G′*), which represents the amount of energy that can be stored in a fluid structure during a cycle of oscillation, increased with increasing angular frequency.

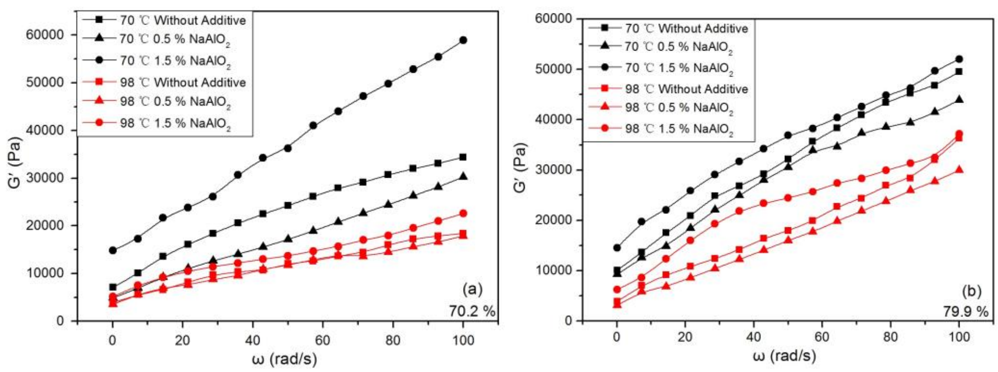

Fig. 1. Storage modulus of BKBL with the addition of sodium aluminate at various loadings: (a) 70.2 wt.%; and (b) 79.9 wt.%

At 70 °C, the *G′* values of thick BKBL with two different solid contents were both greater than those of BKBL when the temperature was 98 °C, indicating that the network structure of BKBL was destroyed because of the higher temperature. At the same temperature, the *G′* values of BKBL with 1.5 wt.% additive were greater than those of the BKBL without additive. However, the *G′* values of BKBL with 0.5 wt.% additive were lower than those of the BKBL without additive. This phenomenon can be explained by consideration of two aspects. On the one hand, the extra sodium ions from sodium aluminate could destroy the network structure of black liquor by breaking the aggregation of lignin molecules (Zaman and Fricke 1996), resulting in a reduction of the energy that can be stored in the structure of BKBL. On the other hand, an increase in the composition of inorganic compounds, providing by the addition of sodium aluminate, could increase the amount of energy stored in the network structure during a cycle of oscillation. Hence, the weakening effect of sodium ions on the structure was judged to be the main cause of the reduction of *G′* values when the sodium aluminate loading was 0.5 wt.%. When the loading was 1.5 wt.%, the increase in the composition of inorganic compounds may have played a major role in the increase in *G′* values because of the greater amount of sodium aluminate.

The loss modulus (*G″*) is representative of the amount of energy that is lost by the viscous flow during a cycle of oscillation. As shown in Fig. 2 (a) and (b), *G″* increased with increasing angular frequency and was also affected by temperature and sodium aluminate loading. As a representation of viscous dissipation, *G″* depends on the strain time ($1/\omega$) and the relaxation time (τ) of the chain segment. At low frequencies, τ was less than $1/\omega$. There was plenty of time for the chain segment to finish the relaxation process. Hence, the G″ values increased with increasing angular frequency. Raising the temperature accelerated the relaxation process and reduced the viscous dissipation. The sodium ions, which broke the aggregation of lignin, resulting in the reduction of the chain segment length, reduced the viscous dissipation because of the shorter relaxation time. Thus, the G'' values of BKBL with 0.5 wt.% decreased compared with the G'' values of BKBL without the additive. However, the G'' values became larger when the sodium aluminate loading was 1.5 wt.%. One possible reason is that the excess sodium aluminate took up the movement space of the chain segment, which led to the increase in viscous dissipation.

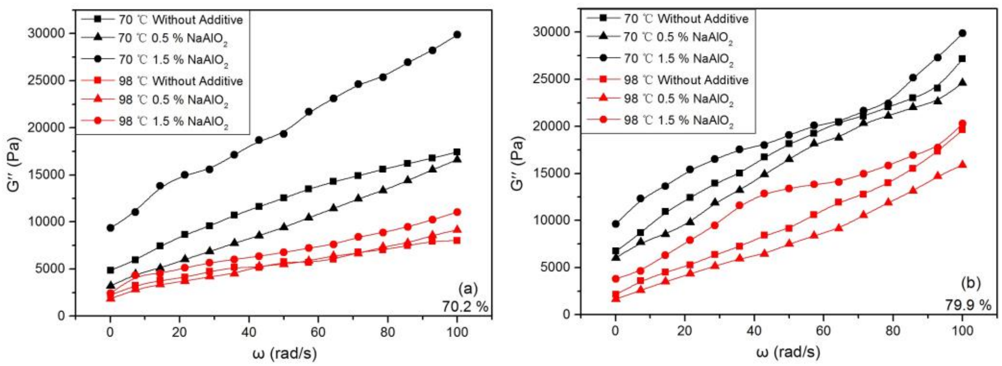

Fig. 2. Loss modulus of BKBL with the addition of sodium aluminate at various loadings: (a) 70.2 wt.%; and (b) 79.9 wt.%

Effect of Sodium Aluminate on Dynamic Viscosity and Complex Viscosity of BKBL

In the viscous flow, a part of kinetic energy is converted into heat energy due to friction. This process is called viscous heating. The measurement of dynamic viscosity is accurate and simple, which can reduce the critical error resulting from viscous heating. Plots of dynamic viscosity (η') *versus* angular frequency (ω) are shown in Fig 3. Clearly, the dynamic viscosities of BKBL with two different solid contents both decreased with increasing angular frequency. Therefore, the results indicate that BKBL, even at a very high solid content, exhibited shear thinning at high temperature. Temperature and sodium aluminate both influenced the η' of BKBL to a certain degree. Rising temperature reduced the η′ to a larger extent. The addition of sodium aluminate increased the η' values when the loading was 1.5 wt.%, but had the opposite effect when the loading was 0.5 wt.%. The sodium ions weakened the structure and decreased the η' of BKBL. However, excess sodium aluminate obstructed the motion of the chain segment, resulting in the increase in η'.

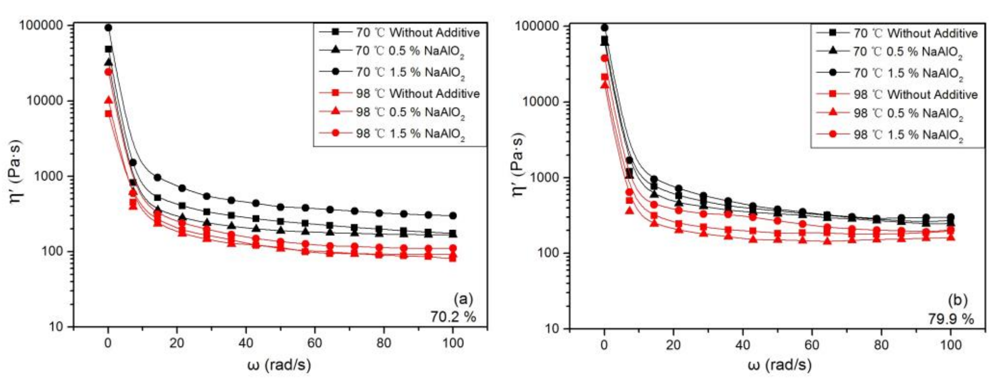

Fig. 3. Dynamic viscosity of BKBL with the addition of sodium aluminate at various loadings: (a) 70.2 wt.% and (b) 79.9 wt.%

The obtained rheological data were fitted according to a power-law model (Eq. 2) and the Cross model (Eq. 3). Power-law model is widely used due to its simple form. The Cross model is used to calculate η_0 and η_∞ of black liquor, which are often extremely difficult to measure. Therefore, η_0 and η_∞ were treated as parameters in Eq. 3. The fitted curve results are given in Tables 1 and 2, respectively. Both the power-law model and the Cross model provide an ideal fitting to the experimental data, with high determination coefficients (in which the R^2 values are greater than 0.99). All of the *n* values in Table 1 were less than one and increased with increasing temperature, indicating that thick BKBL is a pseudo-plastic fluid and the degree of shear-thinning behavior decreased with increasing temperature.

Table 1. Fitted Curve Results from the Relationship between Dynamic Viscosity and Angular Frequency Using the Power-Law Model

Temperature (°C)	Solid Contents (%)	Additive Amount (%)	*m* (Pa·s^n)	*n*	R^2
70	70.2	0	6027.330	0.0944	0.99995
70	70.2	0.5	4210.010	0.1201	0.99992
70	70.2	1.5	11155.813	0.0758	0.99997
70	79.9	0	8548.591	0.1038	0.99995
70	79.9	0.5	7525.489	0.0967	0.99994
70	79.9	1.5	11543.743	0.0799	0.99999
98	70.2	0	1513.965	0.3510	0.99995
98	70.2	0.5	1816.373	0.2566	0.99994
98	70.2	1.5	3394.129	0.1464	0.99998
98	79.9	0	3236.198	0.1813	0.99977
98	79.9	0.5	2505.457	0.1820	0.99969
98	79.9	1.5	5030.923	0.1212	0.99986

Table 2. Fitted Curve Results from the Relationship between Dynamic Viscosity and Angular Frequency Using the Cross Model

Temperature (°C)	Solid Contents (%)	Additive Amount (%)	η_0 (Pa·s)	η_∞ (Pa·s)	λ (s^{-1})	α	R^2
70	70.2	0	3.3575 E + 07	139.7648	7549.2567	0.9871	0.99996
70	70.2	0.5	5.8014 E + 04	140.9529	8.4386	1.1652	0.99998
70	70.2	1.5	4.6857 E + 07	201.8841	5399.8506	0.9878	0.99996
70	79.9	0	4.7597 E + 07	194.6611	8444.1506	0.9739	0.99997
70	79.9	0.5	2.0493 E + 05	208.0354	22.6665	1.0751	0.99992
70	79.9	1.5	5.3782 E + 06	148.1240	634.7966	0.9659	0.99994
98	70.2	0	9.4429 E + 03	43.9635	3.7812	0.9360	0.99993
98	70.2	0.5	1.6303 E + 04	64.2983	6.2956	1.0171	0.99998
98	70.2	1.5	3.9082 E + 04	77.6151	6.4751	1.1188	0.99995
98	79.9	0	2.7526 E + 04	167.4678	3.9372	1.3156	0.99990
98	79.9	0.5	2.8208 E + 04	136.2392	7.5921	1.2046	0.99991
98	79.9	1.5	1.9919 E + 04	182.4750	4.7674	1.0156	0.99987

According to the fitted results in Table 2, the η_0 of thick BKBL, even at a high temperature, was still relatively high. The values of η_∞ were several orders of magnitude lower than those of η_0, indicating the shear-thinning property of BKBL. Even though the viscosity decreased to a certain extent with rising temperature, the η_∞ values were all greater than 40 Pa·s. Hence, to achieve the combustion of BKBL at high solid content, problems related to its high viscosity should be solved first.

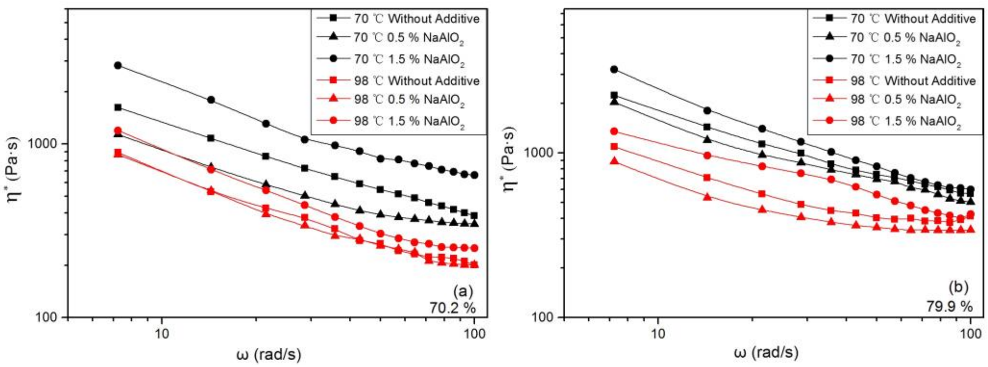

Fig. 4. Complex viscosity of BKBL with the addition of sodium aluminate at various loadings: (a) 70.2 wt.% and (b) 79.9 wt.%

To demonstrate the effect of sodium aluminate on the viscosity of BKBL more clearly, the complex viscosity (η*) was studied in the frequency range of 7 to 100 rad/s. Figure 4 (a) and (b) show typical results for η* as a function of ω.

Sodium aluminate had an obvious influence on η*, especially at low frequencies. With increasing ω, sodium aluminate's effect decreased gradually. The η* values of BKBL with the addition of sodium aluminate at various loadings were very similar to each other at high frequencies. When black liquor flows through the nozzle to form droplets, the shear rate is higher than 1000 s^{-1}. Therefore, it can be speculated that sodium aluminate, which can effectively decrease the silicon content of black liquor during combustion, will not have any additional negative effects on the droplet formation of BKBL.

CONCLUSIONS

1. Bamboo kraft black liquor (BKBL) is a pseudo-plastic fluid that exhibits shear-thinning phenomena at a solid content above 70 wt.%. The degree of shear-thinning behavior decreased with increasing temperature.
2. The power-law model and Cross model can be used to accurately describe the relationship between the dynamic viscosity and angular frequency. The macromolecules in BKBL formed a high-strength network structure resulting in a relatively high zero shear rate viscosity, even at a high temperature.
3. Sodium ions could break the aggregation of lignin molecules, resulting in a decrease in G', G'', and η' when the loading is 0.5 wt.%. However, the excess sodium aluminate increased the amount of energy that can be stored and the viscous dissipation during a cycle of oscillation, resulting in an increase in G', G'', and η' when the loading is 1.5 wt.%. With increasing angular frequency, the effect of sodium aluminate on the viscosity became less marked.

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