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ORIGINAL CONTRIBUTION

Effects of process variables on the yield stress of rheologically modified biomass

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Abstract Additives that alter the rheology of lignocellulosic biomass suspensions were tested under conditions of variable pH, temperature, and solid concentration. The effects of certain ions, biomass type, and time after the addition of rheological modifier were also examined. Torque and vane rheometry were used to measure the yield stress of samples. It was found that the effectiveness of rheological modifiers depends on pH over a range of 1.5 to 6, biomass type, concentration of certain ions, and time after addition. The time-dependent properties of rheologically modified biomass are sensitive to the type of rheological modifier, and also to mixtures of these additives, which can result in unexpected behavior. We show that time-dependent rheology is not correlated with time-dependent changes of the water-soluble polymer (WSP) in the aqueous environment, such as slow polymer hydration, suggesting that time-dependent changes in the polymer-fiber interaction may play a more significant role.

Keywords Lignocellulosic biomass · Rheology · Rheological modifier · Mixing · Yield stress · Corn stover

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Introduction

Lignocellulosic biomass is a renewable biological material that can be converted to useful chemicals, including liquid fuel, that have the potential to lessen global demand for petroleum-derived chemicals. The National Renewable Energy Laboratory (NREL) has described a process for converting lignocellulosic biomass to ethanol (Aden et al. 2002; Davis et al. 2013; Humbird et al. 2011). There are also other chemical routes for the catalytic conversion of biomass to transportation fuels (Bond et al. 2010; Huber et al. 2005), but these processes must compete economically with less expensive grain-derived ethanol and relatively low-cost petroleum-derived fuels.

A large fraction of the utility cost of processing biomass is associated with heating and cooling water (Aden et al. 2002; Humbird et al. 2011). Reducing water content lowers utility costs as well as operating costs in separation operations because of increased product concentrations. Removing water also reduces capital costs by allowing for smaller processing equipment (Wyman 2007).

Reducing water content in biomass slurries results in significant changes in rheological properties that make other aspects of biomass processing challenging. For example, yield stress increases rapidly with solid concentration, making mixing and pumping above roughly 5 wt.% solids very difficult. At higher concentrations, the formation of flocks can lead to local gradients in solid concentration, and above 15 to 20 wt.% insoluble solids, inefficient heat and mass transfer make both the dilute-acid hydrolysis and enzymatic hydrolysis operations challenging (Carrasco and Roy 1992; Hodge et al. 2008; Viamajala et al. 2010).

Pulping and refining lignocellulosic biomass often results in a complex fiber suspension with a yield stress and a plastic viscosity. Like other natural and synthetic fiber suspensions,

the yield stress increases with solid mass concentration according to

$$\tau_o = aC_m{}^b \quad (1)$$

where τ_o is the yield stress, C_m is the solid mass fraction, or mass consistency, and a and b are the empirical parameters (Bennington et al. 1990; Dalpke and Kerekes 2005; Kerekes 1985; Stickel et al. 2009). The empirical parameters in Eq. 1 depend on such properties as particle size distribution, particle aspect ratio, and fiber flexibility (Bennington et al. 1990; Dalpke and Kerekes 2005). Values for b range from 2.3 to 6.0 and depend on the type of lignocellulosic biomass (Bennington et al. 1990; Derakhshandeh et al. 2010; Ehrhardt et al. 2010; Knutsen and Liberatore 2009, 2010).

In pulp fiber suspensions, yield stress is an important rheological property (Bennington et al. 1991). Mixing, pumping, and conveying equipment must be designed to overcome this stress, as the relatively small plastic viscosities of lignocellulosic materials (Ehrhardt et al. 2010; Longdill and Duffy 1988) are less significant when designing processing equipment. Thus, efforts to understand the rheology of biomass have focused primarily on yield stress and the factors that affect it.

Recent research efforts on characterizing the rheology of biomass have focused on acid-hydrolyzed corn stover with the goal of improving process economics of the relatively expensive dilute-acid prehydrolysis and enzymatic-hydrolysis unit operations (Ehrhardt et al. 2010; Stickel et al. 2009). However, there are many other ways to convert biomass to fuels and chemicals that do not involve dilute-acid prehydrolysis (Bond et al. 2010; Kilpelainen et al. 2007; Mohan et al. 2006). Thus, it is desirable to understand and control rheological properties of biomass in many different processing schemes under different treatment conditions.

The rheological properties of biomass can be modified with additives. Water soluble polymers (WSPs) such as carboxymethyl cellulose (CMC), polyacrylamide (PAM), guar gum, and xanthan gum decrease yield stresses in concentrated biomass at polymer concentrations below 1 wt.% (based on mass of dry biomass) (Ehrhardt 2008; Samaniuk et al. 2012; Singh 1985). Surfactants have also been shown to alter biomass rheology but at higher additive concentrations (Knutsen and Liberatore 2010). Using polymers to alter certain rheological properties is also common in both the food and paper product industries (Batdorf and Rossman 1973; Zauscher and Klingenberg 2001). Zauscher and Klingenberg (2001) used colloidal probe microscopy to investigate the mechanism by which polymers alter network forces in a pulp suspension, and the results suggested that WSPs act by decreasing friction between the fibers of a suspension.

The effect of variables such as pH, temperature, biomass type, and biomass solid concentration on the efficacy of rheological modifiers is unknown. Rheological changes observed with the addition of CMC in our previous work differ with those reported by Knutsen and Liberatore (2010). They observed an increase in yield stress with the addition of CMC to low pH, acid-hydrolyzed corn stover, while our results show a decrease in yield stress in neutral, untreated corn stover. The different results in these studies imply that the effect of rheological modifiers depends on variables such as biomass type and pH. In this report, we investigate the influence of variables relevant to biomass processing on the efficacy of rheological modifiers.

Materials and methods

Biomass preparation

Corn stover was obtained from the Arlington Research Station at the University of Wisconsin-Madison, hammermilled, washed by mixing approximately 1 kg dry biomass in 100 L of water, and then bladder-pressed to a total solid concentration of 30–35 wt.%. Soluble solid concentration was estimated by measuring the difference in dry solid mass before and after washing 200 g samples of bladder-pressed corn stover in a Buchner filter with 20 L of reverse osmosis (RO) water. Three such measurements resulted in a fraction of soluble solids of 0 wt.% within the uncertainty of the solid mass measurements. From visual inspection, hammermilled corn stover contained particles that ranged in size from fractions of a millimeter to several centimeters. Hammermilled corn stover is shown in Fig. 1a.

The hammermilled and washed corn stover described above is referred to herein as "untreated" corn stover. "Treated" corn stover was prepared by dilute-acid hydrolysis of the untreated corn stover following the NREL Laboratory Analytical Procedure 007 (Hsu 1995). Switchgrass was obtained from the Arlington Research Station at the University of Wisconsin-Madison at a total solid concentration of 45 wt.% and was used as received (Fig. 1d). Recycled newsprint, a spruce groundwood (mechanical) pulp (Fig. 1c), was rinsed by re-pulping at 10 wt.% total solids in a 50 L Voith hydropulper and dewatered in a bladder press to 25–30 wt.% total solids. A cellulose pulp was rinsed by repulping Whatman 1 filter paper (1001–185, Fischer Scientific) at approximately 5 wt.% solids and dewatering with vacuum filtration. For all biomass samples, the desired solid concentration was obtained by adding the appropriate amount of RO water to the concentrated pulp.

The chemical composition of the Whatman 1 filter paper pulp is approximately 99 % cellulose, but in the other pulps studied, the relative amount of cellulose, hemicellulose, and lignin is varied. The composition is partly characteristic of the species the pulp is derived from but can vary regionally, seasonally, and during the course of a single growth cycle. Typical values for corn stover and switchgrass are 32–25 % cellulose, 25–36 % hemicellulose, and 16–27 % lignin, while softwoods like those used in the newsprint pulp studied here

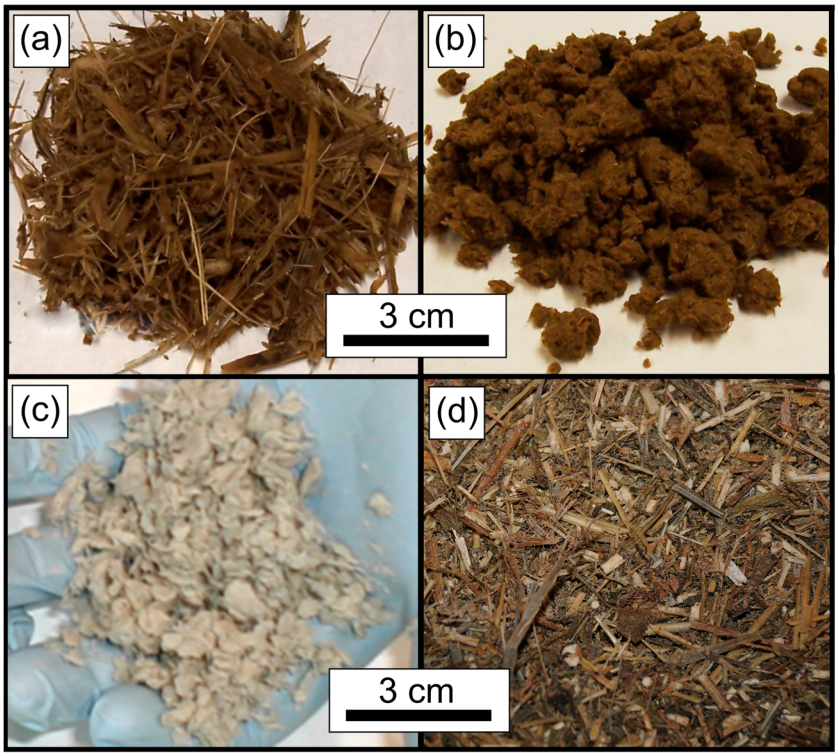

Fig. 1 **a** A photograph of hammermilled corn stover prior to mixing in a torque rheometer, **b** a photograph of corn stover after undergoing the torque rheometry procedure described in the following section, **c** a photograph of pulp produced from recycled newsprint, and **d** a photograph of switchgrass prior to undergoing the torque rheometry procedure described in the following section. All materials are at 25 wt.% solids

generally have higher levels of cellulose (40–45 %) and lignin (25–30 %) (Kadla and Dai 2006).

The particle sizes and shapes of the pulps vary, such that different types of particle size analysis are appropriate for different samples. In the case of recycled newsprint and repulped Whatman 1 filter paper, narrow fiber length distributions around a weight-averaged fiber length of 1.08 and 0.60 mm, respectively, were measured with a Kajani FS-100 fiber length analyzer. In the case of untreated corn stover, a broad distribution of particle sizes and shapes makes it more challenging to characterize. However, after size reduction in a torque rheometer, a Bauer-McNett screen classifier can be used. A dilute suspension of biomass cascades through several increasingly finer screens to separate the sample into different size fractions. Figure 2 contains data from the Bauer-McNett classification of the corn stover sample shown in Fig. 1b. Initially, 10 g of insoluble solids is added to the screen classifier, and the value of mass collected represents the insoluble solids recovered for each size fraction. The finest screen (200 mesh) retained particles larger than 90 μm. The mass lost (4.7 g) was fine enough to pass through the 200 mesh screen. For acid-hydrolyzed corn stover, a Pulmac Masterscreen was used to separate fibers from fiber bundles and other non-disintegrated anatomical components in the suspension. The retained mass represented 31 wt.% of the total solid mass of the original sample, and the liberated fibers were found to have a weight-averaged fiber length of 0.68 mm using the Kajani FS-100 fiber length analyzer.

Rheological modifiers

The rheological modifiers used are listed in Table 1. All chemicals were used as received from the manufacturer. In cases where cationic additives were mixed with anionic ones, the cationic additives were added first. All references to CMC are for high molecular weight (700 kDa) unless otherwise specified.

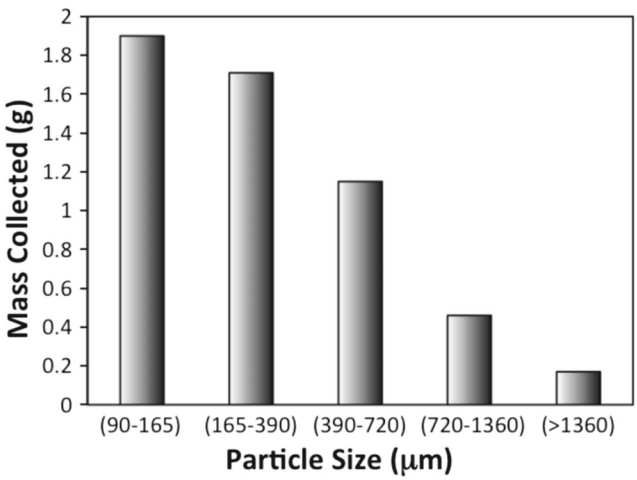

Fig. 2 Particle size distribution obtained from a Bauer-McNett screen classifier for corn stover at 25 wt.% solids after undergoing the torque rheometry procedure described in the following section. Mass collected is a measure of total solids mass, and the starting mass of the sample was 10 g of total solids

Table 1 Additive name, molecular weight, and supplier information

Compound	Commercial name	Abbreviation	MW (kDa)	Supplier
Carboxymethyl cellulose (anionic)	Aqualon (7H4F) Aqualon (7MF)	CMC	700 250	Ashland, Inc.
Polyethylene oxide (nonionic)	Polyox	PEO	2000 7000	DOW Chemical
Guar gum (nonionic)	–	Guar	200	Aldrich Chemical Company
Xanthan gum (anionic)	–	Xanthan	15,000	–
Hydroxypropyl methyl cellulose (nonionic)	Methocel 240	HPMC	180	DOW Chemical
Polyacrylamide (nonionic)	–	PAM	6000	Polysciences, Inc.
Cetyl trimethylammonium bromide (cationic)	–	CTAB	0.365	Fisher Scientific

Torque rheometry

Torque rheometry was used to measure apparent rheological properties and to prepare fiber-WSP blends for aging tests in the vane geometry. Details about the device geometry and the calibration procedure used here can be found elsewhere (Monz 2007; Samaniuk et al. 2012). Because torque rheometry with biomass can alter particle size (Samaniuk et al. 2012), the procedure employed to measure the rheological properties of biomass under different conditions must be followed precisely to control for expected mechanical damage and particle size changes during measurements. Once the rheometer is full, the rotation rate is set to 110 rpm for 600 s, which concludes the loading phase of the experiment. To make a single yield stress measurement, the rotation rate is held for 100 s at each of 55, 110, 220, 110, and then 55 rpm. Three such cycles are performed, and the last cycle is used to calculate rheological parameters. Average torque and rotation rates are used to calculate apparent shear stress and apparent shear rate, respectively, and yield stress is estimated by extrapolation of the apparent shear stress to zero apparent shear rate. This procedure, employed in neutral conditions and 35 °C, is described in greater detail by Samaniuk et al. (2012), and the qualitative difference between corn stover before and after this procedure is apparent in a comparison between Fig. 1a (corn stover before the procedure) and Fig. 1b (corn stover after the procedure).

Measuring rheological properties at various pH and temperature requires additional steps in the measurement procedure described previously in Samaniuk et al. (2012). All biomass underwent the same loading procedure as experiments at neutral pH and 35 °C, but in the case of variable pH, H_2SO_4 was added after the 600 s interval at 110 rpm. For measurements in which temperature was varied, all experiments began at 35 °C and the usual measurement procedure was used. Immediately after obtaining torque-rotation rate data at 35 °C, the temperature was raised to 50 °C and torque-rotation rate data were recorded. The temperature was then lowered to 21 °C, and torque-rotation rate data were again recorded.

Vane rheometry and time-dependent rheology

Yield stress measurements for the time-dependent rheology of modified biomass were made with a vane rheometer (Nguyen and Boger 1992). The vane geometry consisted of a four-bladed vane and a baffled cup. Yield stress was obtained by measuring stress at a constant shear rate and equating the maximum stress to the yield stress. An apparent shear rate of 0.0085 s^{-1} was chosen because the maximum stress was not a function of shear rate below this value. Additional details concerning the device geometry and calibration can be found elsewhere (Monz 2007).

Addition of rheological modifier to biomass samples for time-after-addition experiments was accomplished using the torque rheometer as a mixer. Eighty grams of untreated, hammermilled corn stover at 25 wt.% solid concentration was added to the rheometer over a 60 s period while operating at 55 rpm. Once added, corn stover was subjected to an additional 100 s of mixing at 55 rpm. Rheological modifier was added at the end of the 100 s mixing period, and the modified corn stover underwent an additional 100 s of mixing at 55 rpm before being removed and transported to the vane rheometer. Time 0 s in these experiments began at the moment rheological modifier was added to the biomass. Once a measurement was made with the vane rheometer, the sample was removed from the cup and stored in an air-tight container at room temperature. The sample was reloaded for each additional measurement. In all cases, except experiments involving xanthan gum, measurements were made with the vane rheometer until the yield stress of the sample exceeded the maximum value measureable by the rheometer, 22.5 kPa. In the case where xanthan gum was the rheological modifier, measurements were made over a 10 day time period.

Yield stress data presented in Figs. 3 through 8 were measured using the torque rheometer, while the data presented in Figs. 9 through 11 were measured using the vane rheometer. Data from the two instruments obtained from a variety of biomass types at various solid concentrations show that yield stress measurements from the two devices agree within a

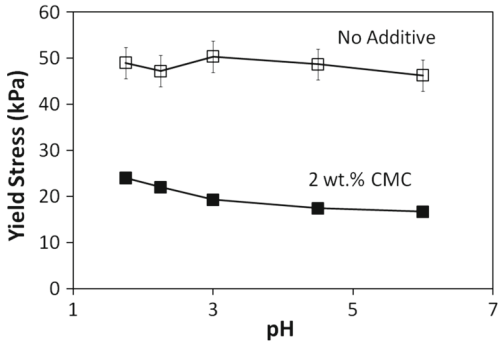

Fig. 3 Yield stress measured with the torque rheometer of unmodified corn stover at 25 wt.% solids as a function of pH. *Open symbols* indicate corn stover without any additive, while *filled symbols* indicate that the corn stover contains 2 wt.% CMC (700 kDa)

factor of 2. This is good agreement considering that other studies on the rheology of biomass show that yield stress values can vary by a factor of 10 in measurements made on different devices (Knutsen and Liberatore 2009).

Results and discussion

Effect of pH

Yield stress is plotted as a function of pH in Fig. 3 for 25 wt.% untreated, hammermilled corn stover, both with and without 2 wt.% CMC (700 kDa). For all pH values, the addition of CMC reduces the yield stress. The yield stress is reduced by 60 % at pH=6 and by 51 % at pH=1.75. For samples without added CMC, the yield stress appears to be independent of pH. The yield stress of samples containing CMC increases slightly as the pH is decreased.

The addition of 2 wt.% CMC (700 kDa) to acid-hydrolyzed corn stover gave different results than those observed for the untreated corn stover. The yield stress of acid-hydrolyzed corn stover (25 wt.%) is plotted as a function of pH in Fig. 4 for samples with and without 2 wt.% added CMC (700 kDa).

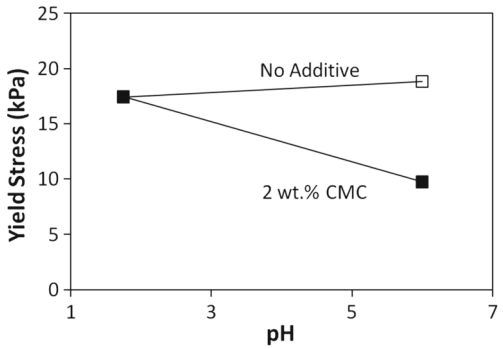

Fig. 4 Yield stress measured with the torque rheometer of acid-hydrolyzed corn stover at 25 wt.% solids as a function of pH. *Open symbols* indicate corn stover without any additive, while *filled symbols* indicate that the corn stover contains 2 wt.% CMC (700 kDa)

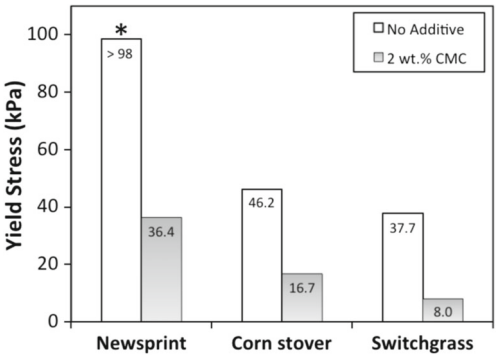

Fig. 5 Yield stress of newsprint, unmodified corn stover, and switchgrass at 25 wt.% solids. Results before and after the addition of 2 wt.% CMC (700 kDa) are shown. *Asterisk* indicates that the yield stress of newsprint with no additive was larger than 98 kPa, the maximum measureable yield stress in the torque rheometer

Like the untreated corn stover, the yield stress of the unmodified, acid-hydrolyzed biomass is independent of pH. The addition of CMC decreased yield stress by 50 % at pH 6, but at pH 1.75, a 0.5 % increase in the yield stress was observed. An increase in the yield stress of acid-hydrolyzed corn stover with the addition of CMC was also reported by Knutsen and Liberatore (2010). They observed an 800 % increase in yield stress with a 10 wt.% addition of CMC (700 kDa) to acid-hydrolyzed corn stover at a pH less than 2. The authors did not report results for CMC-modified biomass at higher pH values.

Increasing yield stress with decreasing pH is consistent with the behavior of aqueous CMC solutions. Below a pH of approximately 4, the free acid form of CMC predominates and the viscosity increases significantly (Hercules.Incorporated 1999). Below a pH of 2, CMC becomes insoluble in solution and precipitates. The different behavior observed at pH 1.75 for the untreated corn stover (Fig. 3) and the acid-hydrolyzed corn stover (Fig. 4) suggests that factors other than pH, such as particle surface chemistry, have a significant influence on the rheological properties of CMC-modified corn stover. There are a number of differences between the two pulps including particle size and shape distribution and physical chemistry. Acid hydrolysis breaks down hemicellulose and lignin components,

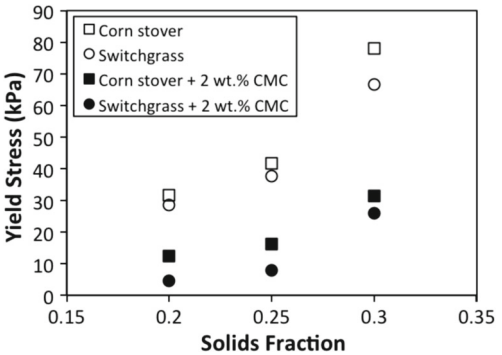

Fig. 6 Yield stress of untreated corn stover and switchgrass as a function of solid concentration, before and after the addition of 2 wt.% CMC

reducing fiber strength and decreasing suspension yield stress. One would expect the influence of inter-fiber friction on yield stress to decrease in a pulp with reduced fiber strength; a reduction in fiber strength should reduce stresses that originate primarily from fiber bending, which also depend on inter-fiber friction (Bennington et al. 1990). Thus, in a system with weaker fibers, as one expects after acid hydrolysis, one might also expect a decrease in the influence of CMC on yield stress.

Effect of biomass type

Carboxymethyl cellulose was effective in modifying the rheology of different types of lignocellulosic biomass. Yield stresses of newsprint, untreated corn stover, and switchgrass before and after the addition of 2 wt.% CMC (700 kDa) are shown in Fig. 5. All biomass samples were prepared at 25 wt.% solids. The yield stress of unmodified biomass depended on biomass type. There are physical and chemical differences between these types of lignocellulosic materials which may influence the rheology, including variations in particle size distribution; relative amounts and spatial distributions of cellulose, hemicellulose, and lignin; and the varying degrees to which biomass particles absorb water and influence the availability of free water. The addition of 2 wt.% CMC decreased the yield stress in all three materials by at least 60 %, but the larger decrease in yield stress of the switchgrass (79 %) relative to the corn stover (64 %) suggests that the physical chemistry of the biomass influences the rheological properties of CMC-modified biomass. The large yield stress values in the newsprint pulp may be explained by a relatively narrow fiber length distribution around a weight-averaged fiber length of 1.08 mm, while the corn stover and switchgrass samples had broad distributions of particles sizes generally less than 1 mm. Future work that systematically focuses on the chemical and physical differences between samples such as corn stover and switchgrass will help identify the most important properties of lignocellulosic biomass that are conducive to rheological modification.

Effect of solid concentration

The dependence of yield stress on solid concentration is illustrated in Fig. 6 for corn stover and switchgrass, with and without the addition of 2 wt.% CMC. The addition of CMC decreased yield stresses in both materials, and yield stress increased with solid concentration with and without the WSP. Similar behavior was observed in PEO- and PAM-modified corn stover, both shown to be effective rheological modifiers by Samaniuk et al. (2012). Equation 1 was fit to the data in Fig. 6, and the parameters a and b are shown in Table 2. Values of b, which are expected to depend on suspension characteristics like fiber aspect ratio, elastic modulus, and polydispersity (Bennington et al. 1990), are within the range reported in other studies (Kerekes 1985; Pimenova and Hanley 2004; Stickel et al. 2009). Based on the values of the standard error, σ_b, shown in Table 2, the addition of CMC did not significantly alter the solid concentration dependence of yield stress.

Effect of aluminum salts

The presence of certain ions in biomass has an effect on rheological modifiers. In the case of rheological modification with CMC, the addition of cations which form an insoluble salt with CMC will result in the precipitation of the CMC salt (Hercules.Incorporated 1999). Trivalent and polyatomic cations such as those present in alum salts are known to form insoluble salts with CMC (Hercules.Incorporated 1999). In Fig. 7, torque and rotation rates from a torque rheometry experiment are plotted as a function of time for corn stover. At 2600 s, 2 wt.% CMC (700 kDa) was introduced to unmodified, untreated corn stover at 20 wt.% solid concentration, followed by the addition of 3.5 wt.% (based on dry biomass solids) alum salt (hydrated potassium aluminum sulfate) at 3100 s. The yield stress decreased from 32 to 12 kPa upon addition of the CMC. After the addition of alum, the yield stress increased to 28 kPa, a nearly complete reversal of viscosity. The increase in yield stress is believed to arise because the CMC precipitates upon addition of the alum. The polymer is then no longer adsorbed and swollen on the fiber surfaces and is thus no longer able to decrease the coefficient of friction between fiber surfaces. We expect that other salts that cause precipitation of the CMC would have a similar impact on the rheology of the CMC-modified biomass.

After adding CMC and alum, rapid changes in yield stress occur. Based on the definition of "drop time" proposed in Samaniuk et al. (2012), which is the amount of time required after the addition of an additive to reach 80 % of the new steady state torque value, the drop time for CMC addition is 17 s. For alum addition, the value is 6 s. The time it takes for torque values to change in the presence of additives is of great importance when processing times approach the same order of magnitude; an example is the use of rheological modifiers in the extrusion of concentrated biomass (Scott et al. 2011).

Table 2 Parameter values for fits of Eq. 1 to the data in Fig. 6

Biomass System	$\ln(a)$	$\sigma_{\ln(a)}$	b	σ_b
Corn stover	−3.2	2.1	2.2	0.6
Switchgrass	−2.9	1.7	2.1	0.5
Corn stover + 2 wt.% CMC	−4.4	2.2	2.3	0.7
Switchgrass + 2 wt.% CMC	−11.1	3.7	4.2	1.1

σ represents the standard error of the parameter estimate

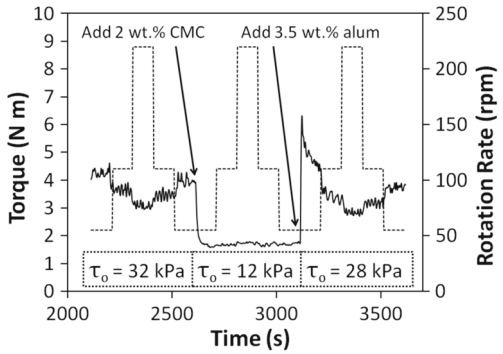

Fig. 7 Torque (*solid*) and rotation rates (*dashed*) as a function of time for corn stover at 20 wt.% solids. The following three regions are depicted: 2100–2600 s contains data for unmodified corn stover, 2600–3100 s contains data for rheologically modified corn stover (2 wt.% CMC—700 kDa), and 3100–3600 s contains data for rheologically modified corn stover after the addition of 3.5 wt.% alum salt. The yield stress for each region is shown

Effect of temperature

The yield stress of untreated corn stover at various solid and CMC concentrations is plotted as a function of inverse temperature in Fig. 8. Each data set is well represented by an Arrhenius-type temperature dependence,

$$\tau_o = A \exp\left(\frac{B}{T}\right) \tag{2}$$

The solid lines in Fig. 8 represent a best fit of Eq. 2 to the data, and values of the parameters A and B obtained from the least squares fits to the data are listed in Table 3. The value of B, which can be interpreted as the activation energy divided by the Boltzmann constant, is independent of solid concentration and is unchanged after the addition of 2 wt.% CMC (700 kDa). The rheological modifier has no influence on the temperature dependence of yield stress over this temperature range. The data in Fig. 8 show a consistent increase of yield stress with temperature, and the values in Table 3 are, to the authors' knowledge, the first of this kind of analysis with lignocellulosic biomass reported in the literature.

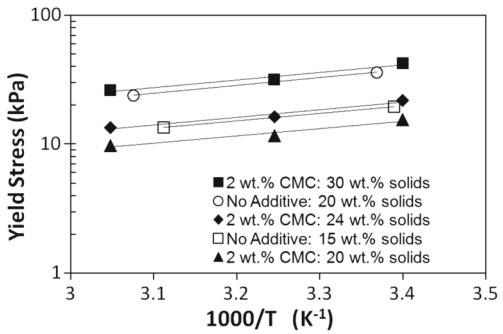

Fig. 8 Yield stress for untreated corn stover before and after rheological modification (2 wt.% CMC—700 kDa) as a function of inverse temperature. Temperature varied from 21 to 55 °C. *Solid lines* represent best fits of Eq. 2 to the data

Effect of time

The yield stress of rheologically modified biomass is plotted as a function of time after the addition of 6 wt.% rheological modifier in Fig. 9. All yield stress values shown in Fig. 9 were obtained using the vane geometry with untreated corn stover at 25 wt.% solids. The time dependence of the yield stress varies significantly with the modifier type. Rates of yield stress increase varied between 0.06 kPa/h for xanthan gum and 2.4 kPa/h for low molecular weight CMC (250 kDa). In all cases except for xanthan gum, measurements were stopped once the yield stress exceeded the maximum measuring capacity of the vane rheometer (22.5 kPa) or once the vane could no longer be inserted into the sample. Xanthan gum-modified corn stover retained its modified rheological properties the longest.

In Fig. 10, the yield stress is plotted as a function of time for 25 wt.% untreated corn stover containing mixed rheological modifiers. In each case, equal masses of modifiers were added to create a total modifier content of 6 wt.%. Yield stresses of the mixed modifier systems do not necessarily follow a linear combination of the time dependences of the pure-component rheological modifier systems. For example, a combination of 3 wt.% PAM and 3 wt.% CMC (700 kDa) resulted in lower yield stresses and a lower rate of yield stress increase than either of the single-modifier systems illustrated in Fig. 9. Similar behavior was observed when the rheological modifier consisted of a combination of 3 wt.% cetyltrimethylammonium bromide (CTAB) and 3 wt.% CMC (700 kDa). The CTAB alone had no measurable effect on the rheology of corn stover at a 6 wt.% concentration, but the combination of 3 wt.% CTAB with 3 wt.% CMC resulted in lower yield stresses and approximately half the rate of yield stress increase than that observed with 6 wt.% CMC alone. Yield stress in the sample modified with a combination of 3 wt.% guar gum and 3 wt.% xanthan gum did have a time dependence between those of the pure guar gum-modified and the pure xanthan gum-modified systems.

The cause of the time-dependent yield stress in WSP-modified biomass is not fully understood. One may suspect that it is related to time-dependent processes involving WSP in an aqueous environment, such as polymer hydration dynamics, or time-dependent processes involving the interaction

Table 3 Parameter values for the least squares fits of Eq. 2 to the data in Fig. 8

Biomass	A (kPa)	B (K)
2 wt.% CMC: 30 wt.% solids	0.41	1360
No additive: 20 wt.% solids	0.32	1400
2 wt.% CMC: 24 wt.% solids	0.27	1360
No additive: 15 wt.% solids	0.21	1340
2 wt.% CMC: 20 wt.% solids	0.18	1300

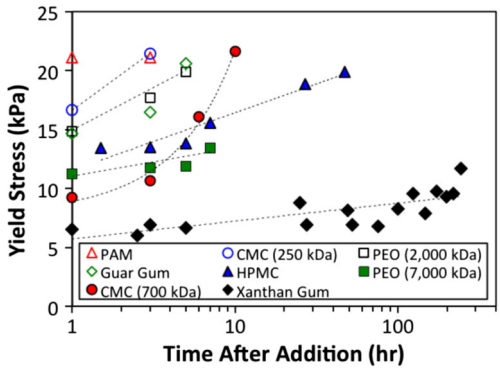

Fig. 9 Yield stress measured with the vane geometry of untreated, rheologically modified corn stover (25 wt.% solids and 6 wt.% polymer) as a function of time. The maximum measurable yield stress with this experimental setup was 22.5 kPa. Each data set consists of a single experimental run. *Dashed lines* are included to guide the eye

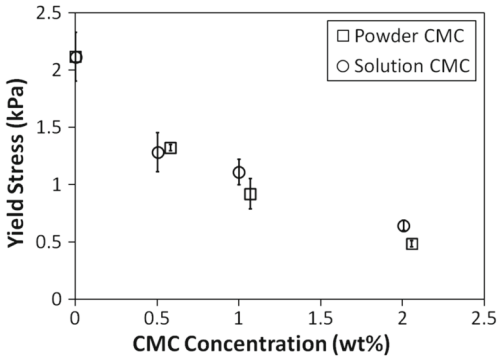

Fig. 11 Yield stress measured with the vane geometry as a function of CMC concentration in a cellulose fiber suspension. The CMC was added in the following two different ways: as a powder in one case and from an aqueous solution in the other. Suspensions were tested at 8.4 wt.% solid concentration

of WSP and fibers, such as polymer adsorption or post-adsorption changes in polymer conformation at the surface of the biomass. It is known that many hours can be required for a WSP to fully hydrate after being added to a solvent (Wang et al. 2008). Russo and Thode (1960) found that the quantity of locust bean gum adsorption on cellulose-rich pulp increased over many hours after the addition of gum. Studies on the sorption of various polymers on cellulose surfaces show similar results (Chan et al. 1970; Luce and Robertson 1961). There is also evidence that the conformation of adsorbed polymer changes with adsorbed quantity (Zauscher 2000).

The influence of polymer hydration dynamics was investigated by comparing rheological properties of cellulose fibers with WSP added as a powder and cellulose fibers with the same WSP added as an aqueous solution. The aqueous CMC solution was prepared at room temperature, stirred gently for 24 h at 30 °C, and then kept at 3 °C for 7 days before use. In all experiments, yield stress was measured in the vane rheometer immediately after the addition of CMC. Figure 11 contains yield stress as a function of CMC concentration for the two cellulose fiber pulps at 8.4 wt.% solids. There is no difference in the yield stress dependence on CMC concentration for the two samples, within the experimental error. Hydration of WSP in the aqueous environment alone does not explain the time-dependent rheology shown in Figs. 9 and 10. Future work can focus on investigating whether the time-dependent rheology of WSP-modified biomass can be attributed to time-dependent adsorption of WSP on fibers, post-adsorption changes in the conformation of WSP, or both.

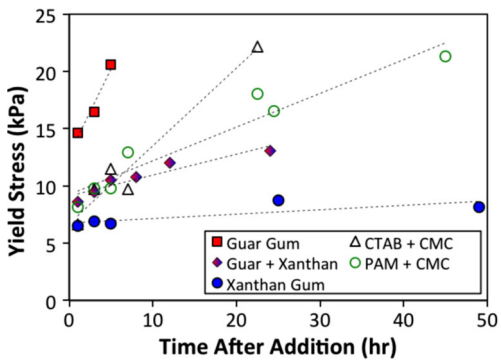

Fig. 10 Yield stress measured with the vane geometry in unmodified corn stover (25 wt.% solids and 6 wt.% additive) as a function of time for mixtures of rheological modifiers. Results for guar gum and xanthan gum are shown for comparison. CMC is high molecular weight (700 kDa). *Dashed lines* are included to guide the eye

Conclusions

The effect of rheological modifiers on the rheology of biomass can depend on pH, biomass type, the presence of certain ions, and the time after modifier is added. The sensitivity of CMC-modified biomass to pH depended on the condition of the biomass; specifically, a clear difference of the effect of CMC between untreated and acid-hydrolyzed corn stover was shown. The effect of CMC on biomass can be reversed with the application of an alum salt, a behavior expected to result from the precipitation of CMC from solution. Yield stress increased with time after the addition of rheological modifier, and the rate of increase varied from 0.06 to 2.4 kPa/h depending on the additive type. Mixtures of cationic and anionic additives tended to reduce yield stress dependence on time such that the mixture was more effective at suppressing yield stress longer than either of the two pure additives. Finally, we show that time-dependent processes of WSPs in the aqueous environment alone, e.g., polymer hydration, do not explain the time-dependent rheology of modified biomass. This result implies that time-dependent interactions between WSP and fiber, such as adsorption of the WSP to the fiber, or post-adsorption changes in the conformation of the WSP, play a significant role.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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