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Research paper

The influence of polymer adsorption, and fiber composition, on the rheology of aqueous suspensions of aspen, cotton, and corn stover pulps

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ABSTRACT

The mechanisms governing the ability of water-soluble polymers (WSP) to alter the rheological properties of lignocellulosic biomass to achieve processing advantages are investigated. Lignocellulosic fiber surface chemistry is found to be an important factor in the efficacy of WSPs as rheological modifiers, and a strong correlation between the amount of adsorbed polymer at fiber surfaces and the yield stress of the fiber suspension indicate that adsorption of polymer is important for rheological modification. Three fiber suspensions of varying physical chemistry were produced from Aspen wood chips, and a number of additional fiber suspensions with chemically functionalized surfaces were generated from cellulose pulp. Polymer adsorption and suspension rheology are found to correlate in every case examined, but the amount of adsorbed polymer alone cannot be used to predict the efficacy of a WSP as a rheological modifier, suggesting that there are contributions from additional variables such as adsorbed-polymer conformation.

1. Introduction

Conversion of lignocellulosic biomass to fuels and other chemicals can be accomplished with many different processes, but generally at some point in each of these processes there is a need to mix, pump, or pour, suspensions of biomass at various solids mass fractions [1–3]. Regardless of the process used, handling and processing biomass suspensions at high solids concentrations has advantages, including lower utility costs and lower capital costs [4,5]. However, designing a process for highly concentrated biomass is challenging because of heat and mass transfer limitations [6,7]. Mixing to overcome these limitations is difficult because concentrated biomass suspensions possess large yield stresses that prohibit homogeneous flow in conventional equipment. Additives that modify the rheological properties of concentrated biomass have been shown to decrease apparent viscosity and lower yield stress, making mixing, pumping, and conveying easier [8–10]. A particular class of rheological modifiers, water-soluble polymers (WSPs), are capable of reducing yield stress in biomass by 50–80%, even at mass fractions as low as 0.01, with mass fraction defined as the polymer mass divided by the total solid mass, both soluble and insoluble, of the biomass [11]. Mass of the suspending fluid is not included. Such reduction in yield stress facilitates extrusion at high solids concentrations [12,13], a technique that can be used for continuous processing of biomass at multiple stages of processing including pretreatment [14]. Using carboxymethyl cellulose (CMC), Zauscher et al. [8] were able to extrude newsprint at 45 wt percent (wt.%) solids, and Scott et al. [15] used CMC to extrude corn stover at 29 wt.% solids, with wt.% solids defined as the combined soluble and insoluble mass divided by the total mass of both solids and fluid, expressed as a percentage.

It is worthwhile to consider the relative importance of yield stress compared to other significant factors such as mat

Abbreviations: WSP, water-soluble polymer; CPM, colloidal probe microscopy; CMC, carboxymethyl cellulose; PAM, polyacrylamide; TMP, thermo-mechanical pulping; HPLC, high-performance liquid chromatography; SEM, scanning electron microscopy; RO, reverse osmosis; CTAC, (2-chloroethyl)trimethylammonium chloride; LR, lignin-rich; HR, hemicellulose-rich; CR, cellulose-rich.

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formation when discussing the potential processing benefits that can come from using WSPs as rheological modifiers. A major concern in processing biomass, and other concentrated fibers suspensions with a low viscosity continuous phase, is that bulk deformation often causes the low-viscosity phase to be 'filtered' out of the suspending solid phase such that mats of fibers are formed [16,17]. This mat formation leads to an inhomogeneous material that is prone to clogging process equipment. Both mat formation and yield stress are significant concerns in processing these materials, as equipment still must be designed to overcome such stresses with or without mat formation. An important characteristic of WSPs is that they dramatically reduce the propensity for mat formation, resulting in a more homogeneous suspension under flow. This characteristic of WSPs has been exploited to develop a method to facilitate fiber alignment in flow through high shear nozzles [18]. For concentrated suspensions, the rheology of the more homogeneous suspension is then dominated by a yield stress that is often in the tens or hundreds of kilopascals [19]. As a result, the addition of WSPs tends to reduce mat formation concerns, resulting in a heightened importance of the yield stress.

How WSPs act to reduce yield stress in biomass is not completely understood. Zauscher and Klingenberg [20] used colloidal probe microscopy (CPM) to show that adsorbed CMC reduced the coefficient of sliding friction between a cellulose bead and a cellulose film. Particle-level simulations of fiber suspensions have shown that reducing sliding friction between fibers decreases the network stress in the suspension [21]. Samaniuk et al. [11] showed that the properties of WSPs, such as molecular weight and polymer type, significantly influenced the extent to which the polymers altered the rheological properties of corn stover by introducing measures of torque reduction and torque drop rate to further characterize the efficacy of WSP. The CPM results from Zauscher and Klingenberg [20] suggest that WSP adsorption on fiber surfaces is important for WSPs to act as rheological modifiers. However, there has been no comprehensive investigation of the relationship between the physical chemistry of the polymer-fiber interactions in suspension, i.e., the tendency of these polymers to simultaneously hydrate and adsorb onto biomass fibers, and related changes in suspension rheological properties. Zauscher [22] quantified the adsorption of polyacrylamide (PAM) and CMC on cellulose beads and cellulose films using a depletion technique. Adsorption values agreed with similar measurements made by Tanaka et al. [23] who used polyelectrolyte titration, and by Hoffmann et al. [24] who used fluorescence spectroscopy. Adsorption isotherms of PAM and CMC were generated, but no attempt to correlate adsorption and rheological properties was made.

The importance of biomass-fiber surface chemistry is explored in this study in two parts. In the first part, an Aspen wood sample is sequentially processed to generate three fiber pulps of different surface chemistries and physical properties. We show that the rheological properties of WSP-modified biomass differs significantly among these three pulps. In the second part, the pulps are exposed to WSP at various mass fractions to determine the relationship between WSP adsorption and rheological behavior. The results show that in each polymer-fiber system examined the yield stress of the suspension decreases with increasing quantity of adsorbed WSP on fiber surfaces. However, when comparing across polymer-fiber systems of different types, there is no clear trend between the maximum amount of adsorbed WSP and the maximum decrease in yield stress. This suggests that factors other than quantity of adsorbed polymer, such as the adsorbed WSP structure, play a significant role.

2. Materials and methods

2.1. Aspen wood pulp

Aspen (Populos tremuloides) was selected as a fiber source due to its consistent fiber quality, e.g., uniform length and aspect ratio and relatively smooth surface character. Aspen wood sourced from the northern mid-west was obtained as chips from a paper mill in northern Minnesota, USA. The chips were screened to eliminate those smaller than 6 mm, and those larger than 38 mm. The thickness of the final batch of chips ranged from 1 mm to 5 mm. All chips were stored at 16 C, and were used within 12 months of initial storage. Ultimately chips were sequentially processed to obtain three pulps with different surface chemistries. Prior to processing, the chips were saturated to approximately 30% water by mass, and then refined at 600 kPa gauge (165 C) in a pressure refiner (Sprout-Waldron 12-1CP) with high-intensity refining plates of pattern D2B-505, to generate a lignin-rich pulp. At this temperature, approximately the T_g of lignin under these conditions [25], it is expected that the lignin will soften in the middle lamella, the interstitial regions between fibers, such that the chip will disintegrate into individual fibers without significant damage to the fibers, resulting in fibers coated with lignin [26]. This process is known as thermo-mechanical pulping (TMP). Next, approximately half of this lignin-rich (LR) pulp was exposed to a chloro-acetate bleaching process to remove a large fraction of the lignin [27] thereby exposing a hemicellulose-rich surface. This second pulp, with the lignin removed, is composed mostly of cellulose and hemicellulose, and is referred to as “hemicellulose-rich” (HR) pulp. In the final pulping sequence, about half of the HR pulp was treated with xylanase enzymes [28] to remove a large fraction of the hemicellulose, primarily xylans. Xylanase enzymes (Novozymes HTec2), which may have some FPU activity despite being an endoxylanase [29], were added to the HR pulp at a pH of 4.8 and a temperature of 50 C for 24 h under continuous mixing in a batch mixer. This third pulp, with most of the hemicellulose removed, is referred to as the “cellulose-rich” (CR) pulp.

The chemical composition of the Aspen pulps was determined using high-performance liquid chromatography (HPLC) at the USDA Forest Products Laboratory in Madison, WI. Fiber length distributions were measured using a Kajaani FS-100 fiber length analyzer. Particle physical properties of the Aspen pulps were also examined using scanning electron microscopy (SEM). SEM samples were prepared by depositing 0.2 mL of diluted sample (1.5 wt.% solids) onto a 10 mm diameter SEM sample disk. The samples were allowed to air-dry for 48 h before being gold plated.

2.2. Whatman pulp

A relatively pure cellulosic pulp was generated from Whatman 1 filter paper (cotton linters, 1001-185, Fischer Scientific). Approximately 25–30 g of filter paper was slowly added to 3 L of reverse osmosis (RO) water in a 5 L container with a pneumatic mixer having a 3-bladed, 4 cm diameter impeller spinning at approximately 8.33 Hz. The pulp was allowed to mix for 10 min after all filter paper was added. The pulp was then dewatered with vacuum filtration.

A cationic cellulose was generated by reacting the Whatman pulp with (2-chloroethyl) trimethylammonium chloride (CTAC) (CAS RN 999-81-5, Acros Organics) under similar reaction conditions as those reported in Ref. [30]. The reaction was prepared by placing 5 g of dry Whatman paper in a 250 mL sealable glass container with 190 mL RO water, 10 mL of isopropanol and 10 mL of 30 wt.% aqueous NaOH. The mixture was stirred using a magnetic stir-bar for 1 h at 25 C. At the end of the hour, 5 g of CTAC was

added and the temperature was raised to 70 C for 3 h. The reaction was stopped by diluting the contents, vacuum filtering and washing the solid reaction product with approximately 10 L of RO water. Five CTAC reactions were carried out at the same time to generate enough cationic cellulose for both adsorption measurements and rheological measurements. All five reaction products were mixed together to form a large batch prior to testing. The degree of substitution of the cationic cellulose was 0.16, determined using conductimetric titration [31]. The CTAC reaction did not alter the fiber length distribution of the original Whatman pulp, which was estimated to be 0.6 ± 0.02 mm using the Kajaani FS-100 fiber length analyzer, as discussed above.

2.3. Corn stover

Corn stover from dent corn (Zea mays var. indentata) was obtained from the Arlington Research Station at the University of Wisconsin-Madison (43 18′07″N, 89 20′42″W). Stover was obtained directly from fields after the grain harvest, and consisted of various plant components including stalk, husk, and cob, and was stored as received at 16 C until used. All stover was used within 12 months of initial cold storage. The corn stover was hammer-milled, washed to remove sediments by mixing approximately 1 kg dry biomass in 100 L of tap water, and then bladder-pressed to a total solids content of 30 wt.%. Weight percent solids (wt.%) is defined here and throughout the rest of this work as the total solids mass, both soluble and insoluble, divided by the total mass of the combined solids and fluid, expressed as a percentage. To reduce particle size further, 80 g of corn stover was intensively mixed in a torque rheometer [32] for 10 min at 1.66 Hz. To eliminate soluble solids, the 80 g of refined material was washed in a Buchner filter with approximately 25 L of RO water, at which point the filtrate was clear.

Suspensions of biomass inevitably vary in both chemical and physical composition depending on a wide variety of factors including geological origin, climactic conditions, species type, and even sub-species type. Though it is reasonable to assume that the nature of the pulp may influence results, we believe the conclusions arrived at in this work are generalizable to the rheological behavior of fibrous biomass pulps containing similar mass fractions of water, and that repeated experiments utilizing biomass pulps obtained and prepared in similar ways as those described above will lead to the same conclusions that have been arrived at here.

2.4. Polymer solutions

The CMC (CAS 9004-32-4, Aqualon 7H4F, Ashland Inc., Ashland, KY) has a molecular weight of 700 kDa and a degree of substitution of 0.7. The PAM (CAS 9003-05-8, Polysciences Inc., Warrington, PA) has a molecular weight of 6000 kDa. In rheological measurements with biomass, polymer mass fraction is the mass of polymer divided by the mass of dry biomass solids, including any soluble or insoluble components.

To prepare polymer solutions, water was added to polymer and the solution was shaken lightly in a temperature-controlled water bath at 30 C for 24 h. The solution was then kept at approximately 3 C for a minimum of 7 days before being used. All solutions were prepared with RO water.

2.5. Adsorption measurements

Adsorption measurements were made by calculating the change in polymer concentration in the supernatant after adding, and then removing via centrifugation, biomass fibers. Polymer concentrations were calculated from viscosity measurements made with Ubbelohde dilution viscometers (531-3, 531-10 and 531-20, Schott-Gerate, Germany). A calibration curve of viscosity as a function of polymer concentration was generated from polymer solutions of known concentration. Adsorption measurements were made by preparing 40 g of solution at a known polymer concentration, and then adding 1 g of dry biomass. The polymer solution and the biomass were gently mixed in a wrist-action shaker for 30 min, and then immediately centrifuged at 5000*g* for 5 min. The supernatant was decanted and the viscosity measured. A control sample of polymer solution without added fiber showed no significant settling of polymer when centrifuging at 5000*g* for 5 min. The concentration of the polymer after adsorption was calculated from the viscosity and the previously generated calibration curve. Adsorption quantities are reported in milligram polymer per gram of dry fiber.

2.6. Rheological measurements

Yield stress measurements were made with a vane rheometer [33]. All yield stress measurements were made with fiber suspensions at 8.5 wt.% solids based on the dry mass of fibers. 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 [34].

3. Results and discussion

3.1. Fiber chemistry

The HPLC results from the three pulps produced from Aspen wood chips are included in Table 1. The lignin-rich TMP pulp produced from pressure refining contained about 22% lignin by mass. The HR pulp obtained after the lignin was removed by chloro-acetate bleaching contained about 18% xylan by mass. The CR pulp obtained after treatment with xylanase enzymes contained about 72% glucan by mass.

Images of the three pulps, obtained by SEM, are shown in Fig. 1. The LR pulp contained fibers composed of individual aspen fibers as well as a smaller proportion of undisintegrated cell bundles known as shives (Fig. 1a). The HR pulp was composed primarily of individual aspen fibers and had a more uniform distribution of fiber diameters (Fig. 1b). The CR pulp appears highly uniform in both fiber diameter and length (Fig. 1c). Fiber-length distributions were measured for all three pulps and the population distributions are shown in Fig. 2a. The LR and the HR pulps have very similar fiber-length distributions, indicating that the chloro-acetate bleaching process did not measurably reduce fiber length. The CR pulp had a narrower fiber-length distribution, and a smaller average fiber length. This indicates that the xylanase treatment, which removed much of the hemicellulose, also substantially reduced fiber length. Possible explanations for this reduction in fiber length are that the xylanase enzymes have some cellulase activity, or that the hemicellulose components of the fibers are interwoven with cellulose such that their hydrolysis results in a reduction in fiber length. Song et al. [29] found that the same xylanase enzyme used here, (Novozymes HTec2), has some FPU activity despite being labeled an endoxylanase, supporting the position that these enzymes have cellulase activity.

Yield stress was obtained using a vane rheometer, and results for the three pulps, each at 8.5 wt.% solids, are shown in Fig. 2b. The weight percent of polymer added is defined as the mass of polymer

Table 1
Composition of the three pulps prepared from aspen wood chips.

Pulp	Ash	Klason Lignin	ASL	Galactan	Glucan	Xylan	Mannan	Total Carbohydrate	Total Yield
LR pulp	0.0	21.3	0.7	0.20	47.52	16.44	1.95	66.11	88.0
HR pulp	0.1	1.5	0.8	0.27	60.68	18.47	2.37	81.78	84.2
CR pulp	0.5	1.8	0.5	0.11	72.39	5.30	2.73	80.53	83.3

All values indicate the mass fraction, reported in units of percent. Total yield is the mass of material that has passed through the column, divided by the mass of material introduced to the column, reported in units of percent.

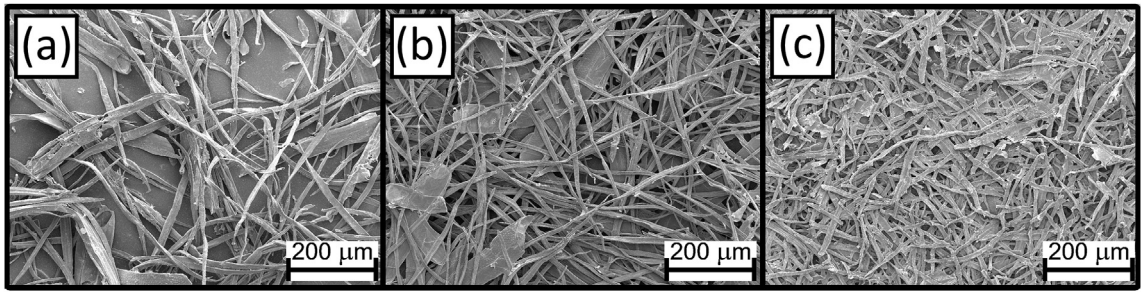

Fig. 1. Images from SEM of aspen wood pulp after: (a) pressure refining (lignin-rich: LR), (b) post chloro-acetate bleaching (hemicellulose-rich: HR) and (c) post xylanase reaction (cellulose-rich: CR). The vessel elements are apparent in (a) and (b) as large, flattened fibers. Shives are visible in the bottom left of image (a), and vessels are visible in the bottom left of image (b).

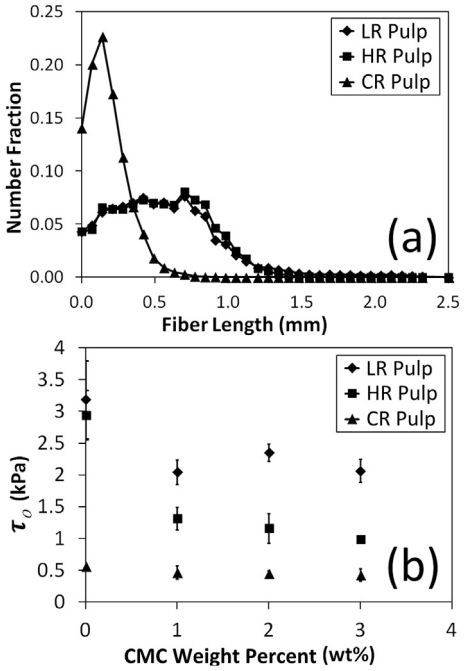

Fig. 2. (a) Fiber-length distributions of the three aspen pulps. (b) Yield stress vs CMC weight percent for the same three aspen pulps at 8.5 wt.% solids. (Amount of CMC is reported in weight percent based on mass of dry biomass solids).

divided by the mass of total biomass solids, both soluble and insoluble, expressed as a percentage. Before the addition of CMC, the LR and HR pulps had the same yield stress, indicating that despite differences in surface chemistry, there is little influence on bulk suspension rheology. However, yield stress of the CR pulp prior to CMC addition was much lower than that of the other pulps. This lower yield stress can be attributed to a much lower average fiber length, which has been shown to strongly influence suspension rheology [35].

With the addition of CMC to the pulps we observe very different dependencies of yield stress on CMC weight percent (Fig. 2b). The yield stress in the LR and HR samples decreased with increasing CMC weight percent, and the decrease was greater and more rapid in the HR sample. Considering that both samples have the same fiber-length distribution and the same yield stress prior to CMC addition, this result can be directly attributed to the different chemical compositions of the fiber surfaces. It suggests that changes in the rheological properties are controlled in part by the physical chemistry of the polymer-fiber interface. However, the yield stress in the CR sample is nearly independent of CMC weight percent. This suggests that factors other than the physical chemistry of the system may be contributing to this result. Indeed the surface morphology of the fibers may have a significant effect on the amount and structure of adsorbed polymer, and the shorter average fiber length may diminish the effect of WSP on suspension rheology as stresses other than those originating from fiber-fiber contacts, such as hydrodynamic stresses, contribute more to suspension dynamics.

The addition of a high molecular weight polymer, such as the CMC used here, to a low viscosity continuous phase would be expected to increase the viscosity of that phase, and even result in the formation of a gel with its own yield stress [36]. In light of that it may seem odd that the addition of polymer results in such a large decrease in the suspension yield stress. The explanation lies in the dominant mode of momentum transport in concentrated fiber suspensions, which is stress transmitted through mechanical contacts between individual fibers. At these high fiber concentrations, hydrodynamic interactions between fibers due to the presence of a continuous phase are insignificant in comparison, and can be omitted from simulations of suspensions at similar concentrations [37]. While WSPs influence the continuous phase, we know that they also reduce friction between fibers in contact [20]. The stress transmitted through the bulk of a concentrated fiber suspensions is connected to inter-fiber friction [21], and it is through this mechanism that these large reductions in suspension yield stress occur. A complex behavior, and challenging phenomena to study, is the alteration of the microstructure of the suspension in response to friction reduction at the fiber level. How changes in fiber-fiber friction influence microstructure within the suspension at larger

scales, ultimately leading to changes in bulk stresses, is still not clear.

3.2. Polymer adsorption

The importance of fiber surface chemistry on the effect of WSPs as rheological modifiers is consistent with the hypothesis that adsorbed CMC molecules reduce friction between cellulose surfaces [22]. However, the mechanisms of friction reduction are not well understood. The importance of a WSP as a lubricant between fibers suggests that adsorption of polymer onto the fiber surface is a prerequisite for WSPs to alter the rheological properties of fiber suspensions. One might further expect that the amount of adsorbed polymer, and the polymer-fiber affinity, should play a role in determining the magnitude of the rheological changes.

WSP adsorption and corresponding yield stress are plotted as a function of WSP polymer weight percent in Fig. 3 for the different suspensions studied. In these systems, as the concentration of polymer in the solvent increases, the amount of adsorbed polymer increases and yield stress decreases. This behavior is the same for all of the systems examined, indicating that rheology and adsorption is strongly correlated in each system. Rheological experiments and adsorption experiments were carried out at different percentages of solids, 8.5 wt.% and 2.5 wt% respectively, which suggests an underlying importance of the polymer-to-fiber mass ratio although additional work would be needed to confirm this. Rheological experiments at lower weight percent solids are challenging because yield stresses approach the sensitivity limit of the vane rheometer and adsorption experiments at higher weight percent solids are challenging as it becomes difficult to separate fibers from the polymer solution.

Adsorption isotherms for PAM on cellulose fibers in suspension

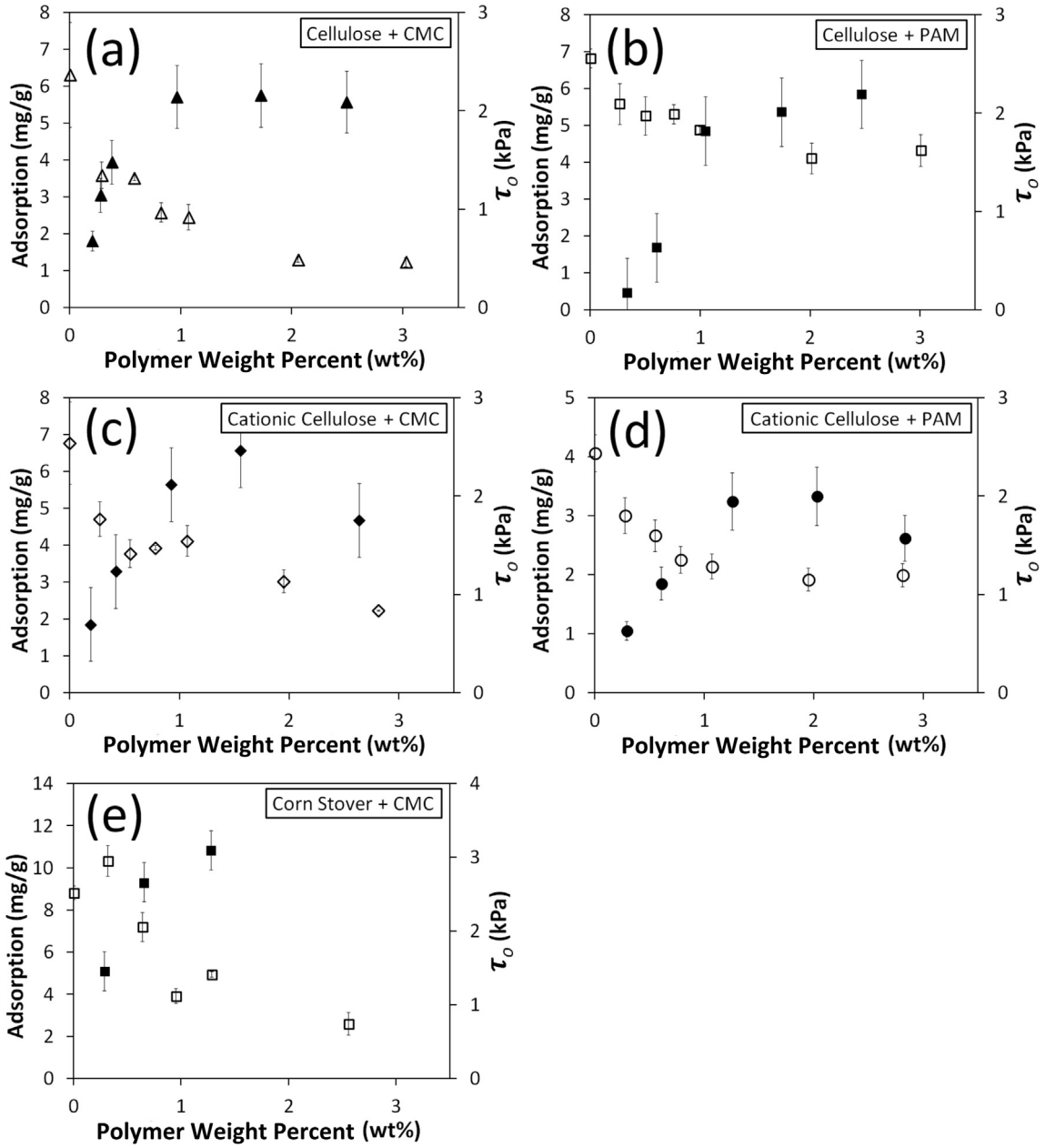

Fig. 3. Adsorption isotherms (filled symbols) and yield stress (open symbols) plotted as a function of polymer weight percent based on the mass of dry fibers for (a) cellulose fibers with CMC, (b) cellulose fibers with PAM, (c) cationic cellulose fibers with CMC, (d) cationic cellulose fibers with PAM, and (e) corn stover with CMC.

and on cationic cellulose fibers in suspension are plotted as a function of equilibrium concentration in Fig. 4a. Equilibrium concentration is reported in grams of polymer per liter, and was obtained as described in the Adsorption Measurements portion of the Materials and Methods section. The adsorption of PAM on cellulose was 50–100% more than on cationic cellulose. Less adsorption of PAM on the cationic surface can likely be attributed to electrostatic repulsion. The yield stresses of both fiber suspensions are plotted as a function of polymer weight percent in Fig. 4b. Yield stresses are lower in the cationic cellulose suspension. This direct comparison of both sets of adsorption data and both sets of yield stress data reveals that although cellulose can adsorb more PAM at equivalent weight percents, the increased adsorption does not appear to reduce yield stress as significantly as cationic cellulose with PAM.

Adsorption isotherms for CMC on cellulose and cationic cellulose fibers are plotted in Fig. 5a. The isotherms are the same within experimental error for the two fiber suspensions. This is somewhat surprising considering the results for PAM in Fig. 4a, where the adsorbed amount was greater for the case where the polymer and fiber are oppositely charged. The yield stress is plotted as a function of CMC weight percent in Fig. 5b for the same polymer-fiber system. The yield stress decreases in both fiber suspensions with the addition of CMC, but CMC is slightly more effective on the cellulose pulp. Adsorption of PAM and CMC on cellulose fibers is shown in Fig. 5c, and yield stresses for the same two systems are shown in Fig. 5d. The results are similar to those shown in Fig. 5a and b in that both adsorption curves reach the same maximum adsorbed amount, but it indicates greater CMC adsorption at low weight percents compared to PAM, and overall greater reduction in yield stress in the CMC-containing suspension. Results in Figs. 4 and 5 indicate that the adsorbed amount of polymer is not the only factor determining the efficacy of a rheological modifier. Given the strong correlation between adsorption and yield stress in all of the systems examined, it is reasonable to assume that other aspects of adsorption, such as adsorbed polymer structure, may influence suspension rheology.

Adsorption and yield stress as a function of CMC weight percent in corn stover and in cellulose are shown in Fig. 6. The amount of adsorbed CMC on corn stover, shown in Fig. 6a, is double the amount on cellulose fibers. Adsorption on corn stover may be larger for a number of reasons. The chemical composition and anatomy of corn stover, which also contains cellulose, hemicellulose, and lignin, is more complex than wood or cotton fibers due to a larger variety of anatomical components (e.g., rind, core, leaf, cob). In particular, corn stover contains a pithy core and cells that have cavities where polymer molecules can also adsorb. It is possible that a large percentage of the added polymer is adsorbed in the cavities of various cells, but the diffusion of charged polymer into the pores of biomass is known to be a complex problem [38]. Fig. 6b shows that the yield stress decreased approximately the same amount for both fiber suspensions with increasing CMC weight percent. The correlation between polymer adsorption and yield stress is clear, but these results show that changes in rheological behavior cannot be attributed solely to adsorbed amount of polymer.

The results reveal fiber surface chemistry to be an important variable in the efficacy of WSPs as rheological modifiers in fiber suspensions, and that the adsorbed amount correlates tightly with yield stress. However, it is evident that factors in addition to adsorbed polymer quantity, perhaps adsorbed polymer conformation, influence rheology, warranting a future investigation of the structure of the adsorbed polymer and its influence on rheology. A complete understanding of the mechanism underlying the effect of WSPs on fibrous biomass will allow for rational design of the next generation of rheological modifiers.

4. Conclusions

The mechanism through which WSPs act to reduce yield stress in concentrated suspensions of fibrous biomass is not well understood, and has been investigated here. Three pulps with similar physical properties but with different surface chemistries were prepared from an Aspen wood sample: a LR pulp, a HR pulp, and a CR pulp. The yield stress of concentrated suspensions of each pulp was measured as a function of the weight percent of added carboxymethyl cellulose, a rheological modifier. In each pulp the yield stress decreased with increasing amount of polymer, but the decrease depended strongly on the fiber surface chemistries, suggesting that fiber surface chemistry is important in the action of water soluble polymers as rheological modifiers. To further investigate the importance of polymer adsorption, various pulps derived from cotton and from corn stover were prepared. Yield stress as a function of polymer weight percent, and the adsorbed polymer per unit mass of fiber was estimated, revealing a strong correlation between adsorption and yield stress where the dynamics of both variables occurs over the same range of polymer weight percent. The implication is that adsorption is a critical component in the mechanism underlying the efficacy of WSP-based rheological modifiers.

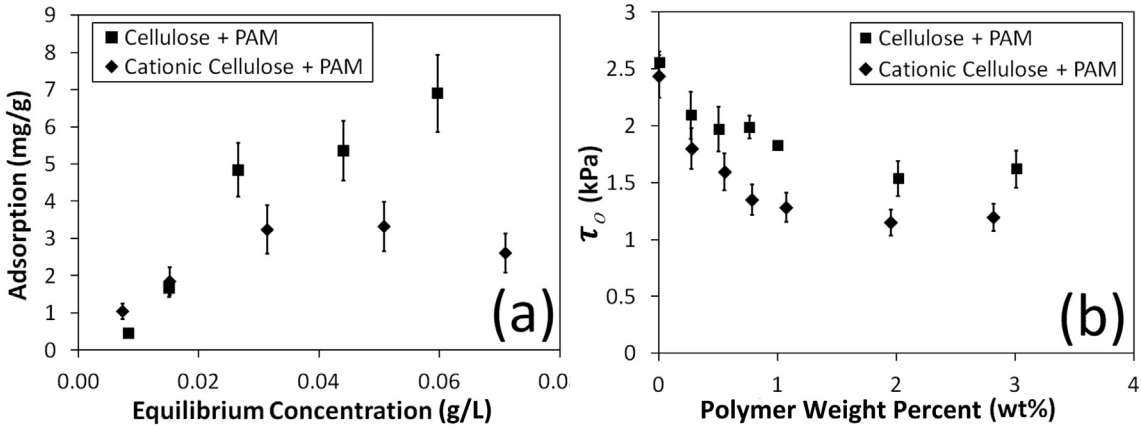

Fig. 4. (a) Adsorption isotherms for PAM on cellulose and cationic cellulose fibers. (b) Yield stress vs PAM weight percent for cellulose and cationic cellulose fiber suspensions at 8.5 wt.% solids. Amount of PAM is reported in weight percent based on mass of dry fiber solids.

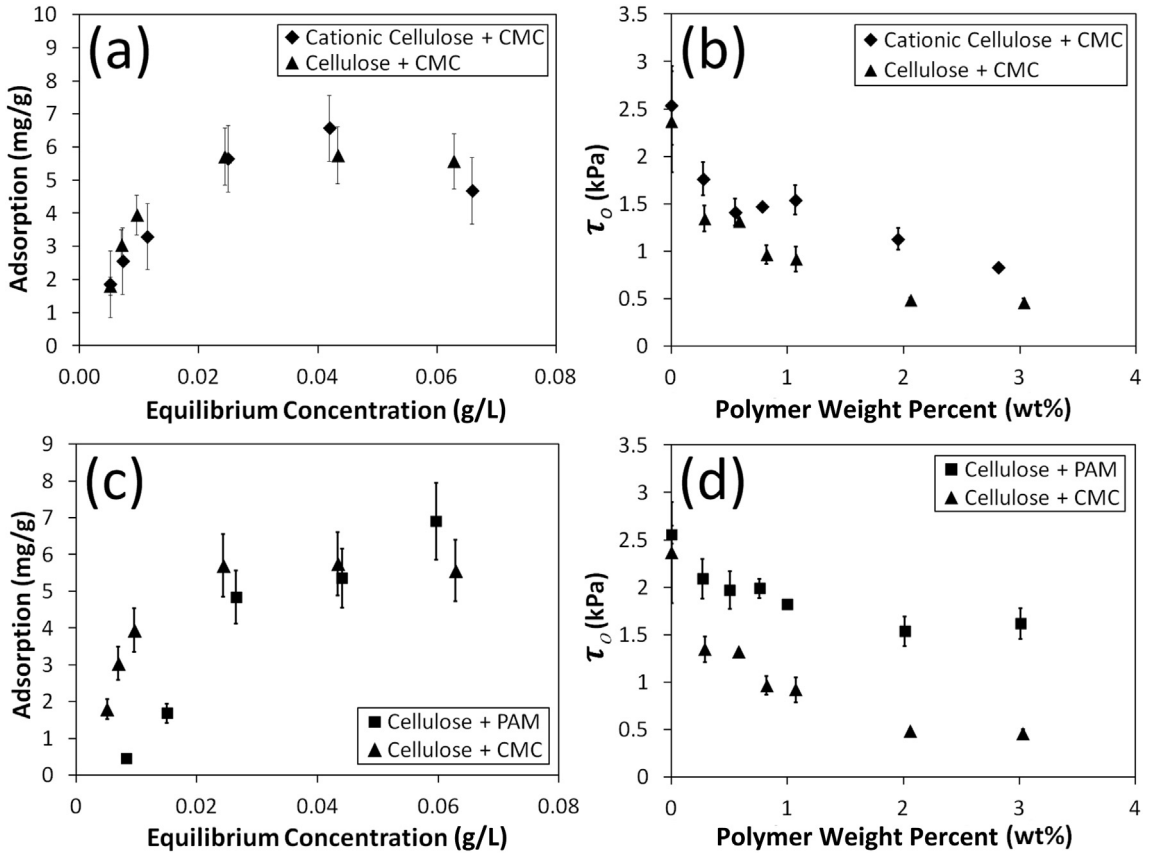

Fig. 5. (a) Adsorption isotherms for CMC on cellulose and cationic cellulose fibers and (b) yield stress vs CMC weight percent for cellulose and cationic cellulose fiber suspensions at 8.6 wt.% solids. (c) Adsorption isotherms for PAM and CMC on cellulose fibers and (d) yield stress vs polymer weight percent for PAM and CMC in a cellulose fiber suspension at 8.6 wt.% solids.

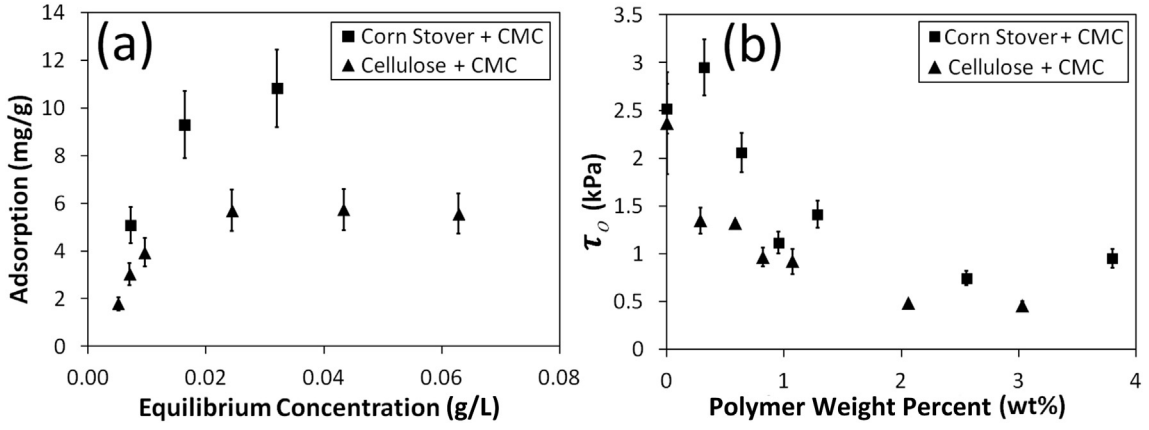

Fig. 6. (a) Adsorption isotherms for CMC on cellulose fiber and corn stover and (b) yield stress vs CMC weight percent for a cellulose fiber suspension and corn stover at 8.6 wt.% solids.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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