



## 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.

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## 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 (*Populus 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  $-16^{\circ}\text{C}$ , 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 ( $165^{\circ}\text{C}$ ) 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  $50^{\circ}\text{C}$  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  $25^{\circ}\text{C}$ . At the end of the hour, 5 g of CTAC was

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