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DISPERSION OF PULP SLURRIES USING CARBOXYMETHYLCELLULOSE

Manish Giri, John Simonsen, Willie E. Rochefort

ABSTRACT

Extrusion has recently emerged as a promising technology for processing high-consistency pulp slurries with high inorganic filler content. A critical factor in successful pulp extrusion is the use of dispersants. This study investigated the relationship between dispersibility of pulp slurries and the molecular weight of a carboxymethylcellulose (CMC) dispersant. Both macro- and micro-rheological experiments revealed a predictable dependence on CMC molecular weight. Furthermore, the macro and micro experiment results were correlated. Pulp dispersion is more closely related to amount of CMC adsorbed than to amount in solution. Changing ionic strength had little effect on the dispersive effect of the CMC.

APPLICATION

Utilizing waste from the paper industry to make useful materials through the process of high-consistency pulp extrusion.

KEYWORDS

extrusion, carboxymethylcellulose, CMC, rheology, adsorption, ionic strength, pulp, sludge, dispersant, slurry

EXECUTIVE SUMMARY

The pulp and paper industry produces about 4 million tons per year of waste sludges that contain wood fibers and inorganic fillers. Recently, extruders similar to food extruders have been used to process high-consistency (~ 30% fiber) pulp slurries into panels and profiles that can be dried into useful products. To date, extruded products with strengths and stiffnesses comparable to medium-density fiberboard (MDF) and high-density hardboard have been achieved. Successful pulp extrusion requires the use of dispersants. In the absence of dispersants, the pulp fibers flocculate, separate from the water, and subsequently surge out of the extruder; the final product possesses low integrity and typically cracks upon drying.

This project investigated the effect of carboxymethylcellulose (CMC) molecular weight on the extrusion behavior of pulp. We measured torque reduction of pulp slurry due to CMC addition in a simulated extruder environment (macro-rheological measurement), and crossover point and critical shear stress in a Bohlin rheometer (micro-rheological measurements). Torque reduction upon CMC addition correlated with both CMC concentration and molecular weight; the molecular weight dependence was modeled with empirical equations. Adsorption of CMC on

pulp fibers appeared to reduce the frictional forces at the fiber contact points, thereby reducing the viscosity of the pulp network. Ionic strength appeared to have little or no effect on pulp slurry rheology. These experiments support the hypothesis that extrusion of high-consistency pulp slurries is a viable and promising method of utilizing the solid waste generated by the pulp and paper industry.

INTRODUCTION

Paper mills produce 4.1 million tons of sludges per year, containing up to 30% pulp fibers (*1*). Currently, 69% of these sludges are landfilled and 29% are incinerated (*2*). One emerging technology for processing pulp slurries with high inorganic filler content is extrusion. Extruders similar to food extruders have been used successfully to process slurries with consistencies (solid contents) of about 30% (*3*); to date, extruded products from recycled paper, with strengths of 15–30 MPa and moduli of 3–6 Gpa, have been produced. These strength properties compare well with those of medium-density fiberboard (MDF) and high-density hardboard (*3*).

A key factor in the successful extrusion of pulp slurries is the use of dispersants (*4–6*). In the absence of dispersants, the pulp fibers flocculate, separate from the water, and surge out of the extruder. The extrudate possesses low integrity and typically cracks upon drying. Dispersants improve the uniformity and flow of the pulp fiber slurry during the extrusion process as well as improve the strength properties of the final extrudate. Zauscher and coworkers (*3*) report that the best known dispersant for pulp slurry extrusion is CMC.

While the use of dispersants is clearly critical for successful pulp extrusion, the mechanism of the dispersive action is not well understood. In this project we sought to shed light on this mechanism by examining the effect of CMC molecular weight on the rheology of the pulp slurry under simulated extrusion conditions. To eliminate the large number of variables involved in using actual sludges, we used a slurry composed of bleached kraft fiber in purified water.

EXPERIMENTAL

Materials

Pulp. Ultranier J, a southern pine bleached Kraft softwood pulp provided by ITT Rayonier, Jessup, Georgia, with a Kajani weighted average fiber length of 2.4 mm, an ISO brightness of 84.0, and a Frazier porosity (unbeaten) of 65 ml/sec cm^2.

Carboxymethylcellulose (CMC). We used four CMC products in our study. All had the same degree of substitution (0.9) but different average molecular weights (M_w): 90,000, 250,000, 700,000, and 800,000. All but the 800,000 M_w product were purchased from Aldrich Chemical Co., Milwaukee, WI. The 800,000 M_w CMC was contributed by Hercules Inc., Wilmington, DE, as Aqualon 7H4F.

Macro-rheological experiment: Dependence of torque drop on CMC M_w

Torque is a measure of pulp slurry viscosity, which in turn is a function of fiber network strength. The purpose of this experiment was to determine the relationship between torque drop of slurry solutions and CMC molecular weight. Extrusion conditions were simulated in a Brabender Plasticorder J with cam blades and bowl mixer attached, operating at ambient temperature and 30 rpm. The cam blades rotated at a differential angular speed of 3:2. The Brabender's torque rheometer was connected to a computer data acquisition system, which recorded the torque in the bowl mixer in real time.

We prepared the pulp slurry by stirring the pulp in de-ionized water at a consistency (cy), or solids content, of 30%; that is, 30 g oven-dry (od) pulp per 70 ml de-ionized H_2O. This consistency is reported as optimal for the extrusion process (*3*). We added the CMC products (in dry powder form) to the pulp slurries after 1 min of mixing. Typically, the slurry samples reached an apparent steady state torque after about 5–8 min of mixing. In multiple runs, steady state torque values showed a <5% coefficient of variability. The steady state difference between the control batch (no dispersant) and the CMC-containing slurries was termed the torque drop (T_d).

Micro-rheological studies: Dependence of network strength on M_w

To measure both the elastic (G') and viscous (G") dynamic shear moduli of pulp mats, we used a Bohlin J constant stress rheometer (model CS-50) with a parallel plate (PP) geometry using 40 mm diameter plates and operating in the dynamic oscillatory stress mode. To prevent mat slippage, we modified the PP-40 geometry by gluing sand paper to the top and bottom surfaces of the plates. Because this stress measurement was sensitive to the polymer–fiber interactions, we termed the experiment "micro-rheological"— in contrast to the bowl mixing experiments, which were more sensitive to the bulk response of the system and therefore considered "macro-rheological." We also tested the strength of the pulp mats by performing a stress sweep experiment in the PP-40 geometry. In this experiment, stress on the pulp mats was slowly increased and the resulting strain was measured. This experiment allowed us to estimate the yield stress (the point at which a small stress increase leads to a large jump in strain) of each CMC system.

Pulp samples were prepared by adding 0.096 g of the appropriate CMC to 1000 ml distilled water. We then added 6 g od basis pulp to this solution. The resulting 0.6% consistency provided adequate fiber surface exposure. The samples were left standing overnight at 25–28 °C in order to achieve system equilibrium. We then produced pulp mats of uniform thickness and 15% consistency by pouring the slurries through a sieve. (The 15% consistency would keep the rheological parameters within the sensitive measurement range of the Bohlin rheometer.) We mounted the mats in the modified Bohlin rheometer for the micro-rheological measurements.

Adsorption experiments

Adsorption was measured by determining the difference in CMC solution concentrations before and after contact with a pulp slurry. The concentrations were measured by viscometry using the Bohlin rheometer with couette geometry (C-25). A calibration curve relating viscosity to concentration was linear over the range of interest in these experiments. We assumed that the

loss in solution concentration after exposure to a pulp slurry was due solely to adsorption of the CMC on the pulp fiber.

Ionic strength experiments

Ionic strength exerts a large influence on the viscosity of CMC solutions. We measured the T_d of slurries of various ionic strengths to observe the effect of ionic strength on the dispersibility of the pulp slurries by CMC. The ionic strength was modified by adding the appropriate amount of solid NaCl in a series to form 0.00 M (control) to 0.26 M to the bowl mixer after adding the pulp, water, and CMC.

RESULTS AND DISCUSSIONS

Macro-rheological experiment: Dependence of torque drop on CMC M_w

For all molecular weights of CMC tested (**Figure 1**), torque was significantly reduced compared to that of the control.

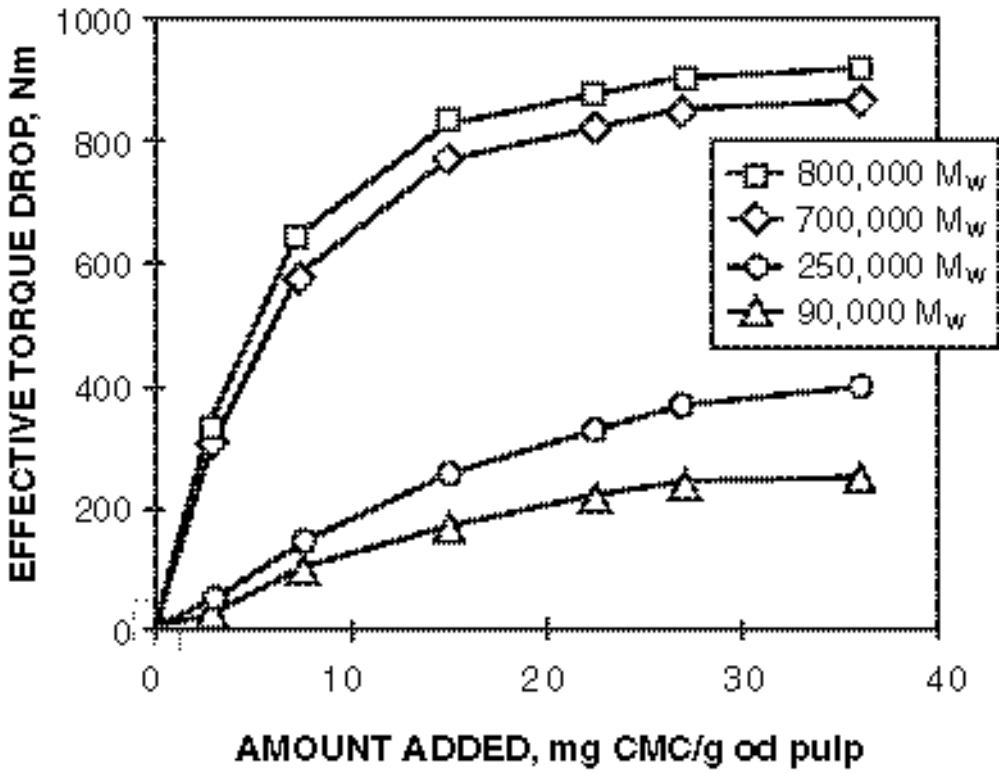

Figure 1. Dependence of slurry torque drop on CMC molecular weight and amount CMC added.

The magnitude of the torque drop was a function of both CMC concentration and molecular weight. Up to about 3% CMC concentration (30 mg CMC/g od pulp), the torque drop increased rapidly with increasing CMC concentration. Above 3% CMC concentrations, torque drop

increased only slightly with increasing concentration. We hypothesized that this effect stemmed from saturation of adsorption sites on the pulp.

The dependence of torque drop on molecular weight can be modeled with an empirical equation:

$$T_d = a(1-e^{-bc}) \quad (1)$$

where T_d is the torque drop, c is the CMC concentration in mg CMC/g od pulp, a is the maximum torque drop possible for a particular CMC, and b is the efficacy factor.

The maximum torque drop (a) is a measure of the maximum viscosity reduction induced by a given CMC. The efficacy factor, b, relates the extent of the reduction to the CMC concentration. Both a and b gave linear correlations with respect to molecular weight (**Table I, Figure 2**). Although we were unable to measure the surface roughness of the fibers in this study, further experimentation may identify a relationship between factors a and b and CMC molecular size in proportion to fiber surface roughness. If the adsorbed molecule approximates the scale of the surface roughness, we might expect that incomplete surface coverage would provide significant friction reduction. If, however, the molecular size is significantly less than the surface roughness, the adsorbed molecule might provide little or no barrier between two approaching pulp fibers and thus less effective torque reduction.

Table I. Dependence of parameters *a* and *b* (elastic and viscous moduli) on molecular weight of carboxymethylcellulose (CMC).

Molecular weight, amu	Param. *a*	Param. *b*
90,000	300	0.49
250,000	492	0.55
700,000	864	1.47
800,000	916	1.55

Micro-rheological experiments: Dependence of network strength on M_w

In the oscillatory shear experiments, the elastic modulus (G') decreased with increasing CMC molecular weight (**Figure 3**). Futhermore, the point at which the G' vs. stress curve became nonlinear occurred at lower stresses with increasing molecular weight, with the two highest M_w samples showing no linear region at all. Since the modulus of the fiber network can be approximated as the strength of the average fiber–fiber contact point times the number of contact points in the slurry per unit volume, these results suggest that the higher M_w CMCs are more effective at reducing friction between fiber contact points.

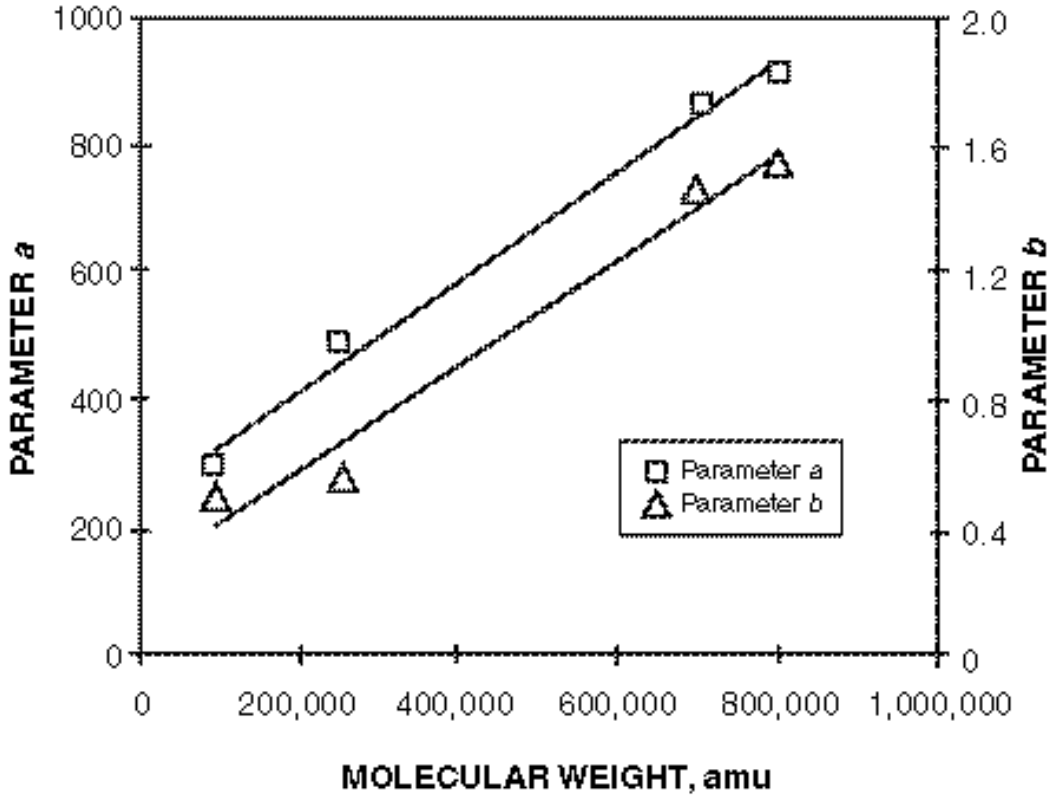

Figure 2. Molecular weight parameters *a* (maximum torque drop) and *b* (efficacy factor) for torque drop experiments.

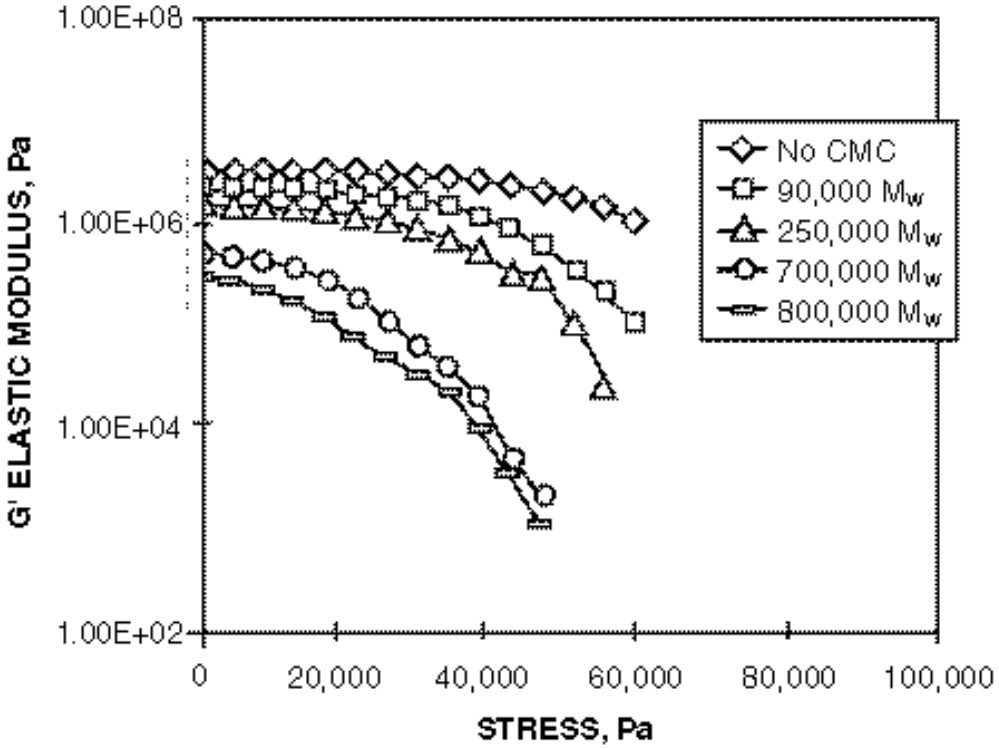

Figure 3. Dependence of pulp network strength, represented by elastic modulus (G'), on CMC molecular weight when subjected to a stress sweep at 16 mg CMC/g od pulp fiber.

Increasing CMC concentration also lowered the pulp mat G' (**Figure 4**). This effect was not as pronounced as that of increasing molecular weight, but the trend is similar for both the value of G' and the reduction in the stress at which G' becomes nonlinear. As with the macro-rheological experiments, the heightening of effects due to increasing CMC concentration diminished as the concentrations increased, with CMC concentrations >20 mg /g od pulp fiber showing little incremental effect. Taken together, these data argue that the primary effect of CMC on the dispersibility of the pulp slurry relates to reduced inter-fiber friction rather than to increased solution viscosity.

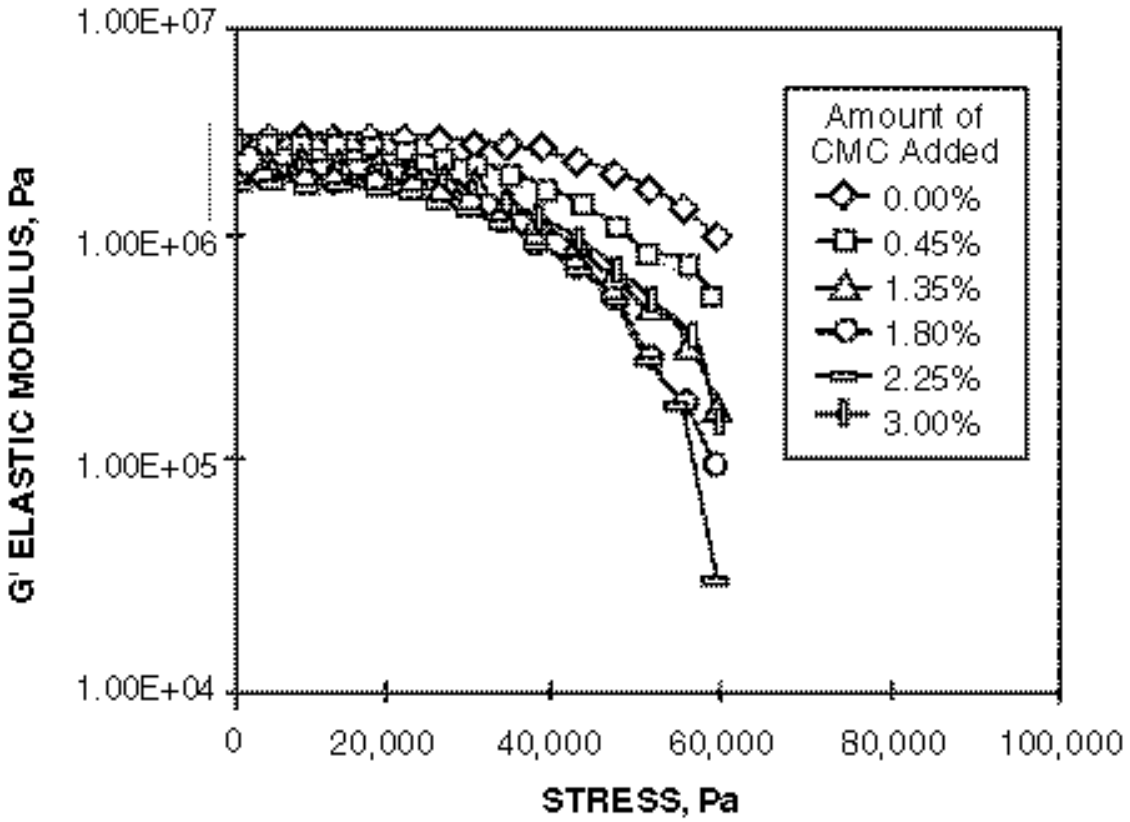

Figure 4. Dependence of pulp network strength, represented by elastic modulus (G'), on concentration of 90,000 M_w CMC.

The elastic (G') and viscous (G") moduli are plotted as a function of stress in **Figure 5**. The crossover point (stress at which G'=G") differs for each CMC system (**Table II**). This point is where fiber–fiber slippage begins to dominate the viscoelastic behavior, leading to an irreversible breakdown in the network structure.

The stress sweep experiment data are plotted in **Figure 6** which shows that measurable yield stress existed only for the control and the 90,000 and 250,000 M_w CMC pulp mats. The higher molecular weight samples (700,000 and 800,000 M_w CMC) exhibited no yielding behavior. Yield stress is an indication of network structure breakdown—a larger yield stress indicates a stronger network structure. Polymer solutions, even of very high molecular weight, typically do not exhibit yielding behavior in stress sweep experiments, while materials that tend to aggregate generally show weak yield stresses. Therefore, the absence of yield stress for the higher Mw

CMC materials indicates lower inter-fiber friction and increased fiber slippage at relatively low forces.

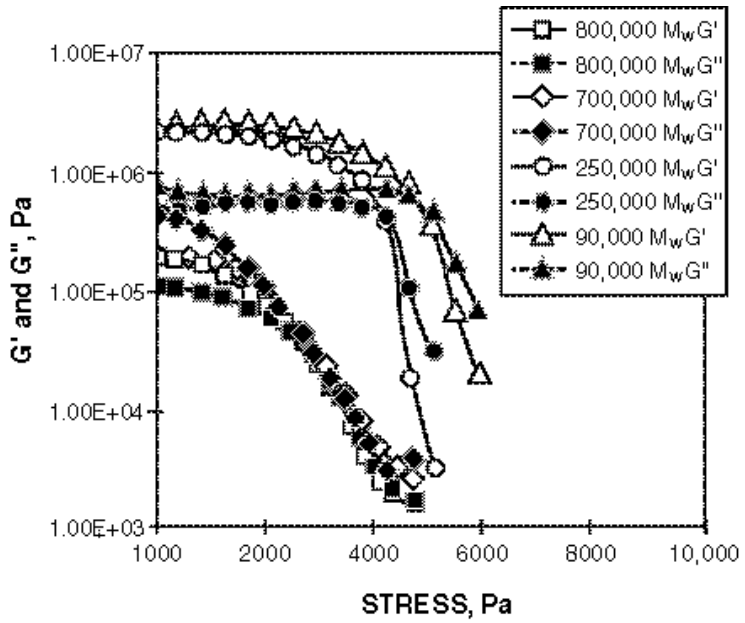

Figure 5. Elastic (G') and viscous (G") moduli of the pulp fiber mat at 15% consistency (15 g od pulp fiber /100 ml solution) for different CMC molecular weights.

Table II. Comparison of crossover shear stress and yield stress for micro-rheological experiments performed on the Bohlin constant stress rheometer (Model CS-50).

CMC molecular weight	Yield stress, Pa	Crossover shear stress, Pa
90,000	9800	9000
250,000	7700	6800
700,000	2700	5300
800,000	2100	5200

The crossover point was inversely correlated with both molecular weight (**Figure 7A**) and torque drop (**Figure 7B**). The correlation with molecular weight suggests the reduction in inter-fiber friction is largely due to CMC molecule size. Polymer theory suggests that for spherical geometries, molecular size should correlate with $M_w^{1/2}$, and for linear polymers, with M_w. However, our data are not sufficiently precise to differentiate between $M_w^{1/2}$ and M_w. Both gave good correlation coefficients. CMC is typically a fairly stiff polymer, thus we used M_w in the

figures. We also hypothesized that the friction reduction comes from adsorbed CMC molecules, as opposed to dissolved CMC molecules. This led us to adsorption measurements.

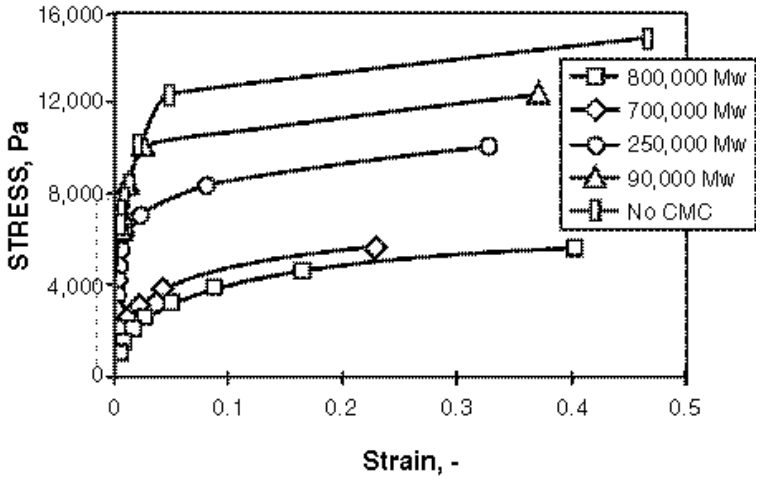

Figure 6. Shear stress behavior of pulp as a function of molecular weight at 16 mg CMC/g od pulp fiber.

The high correlation coefficient between crossover point and T_d supports the accuracy of each measurement and further substantiates the dominance of fiber–fiber interactions, as opposed to solution effects, in controlling these phenomena.

Adsorption

Figure 8 shows CMC adsorption onto pulp fibers as a functions of molecular weight and solution concentration. For the different M_w samples, saturation occurred at different concentrations. This type of adsorption is similar to the adsorption of non-ionic polymers on pulp substrates (*7*). This might not be expected, since CMC is a negatively charged ionic polymer. Usually, negatively charged polymers are repelled by the negative charge on fibers. But in some cases non-ionic interactions due to close approach (i.e., hydrogen bonding and dispersive forces) are sufficiently strong to overcome the electrostatic repulsion (*7–12*). This appears to be the case in this study, also. Therefore, the adsorption, and the resulting rheological effects, would not be expected to be strongly influenced by pH; indeed, Zauscher *et al.* (*3*) observed no significant effect of pH on system rheology.

Figure 9 shows maximum adsorption of the four CMC samples on pulp fibers. For the three highest M_w CMCs, adsorption maxima are linear, which is the theoretical correlation between size and molecular weight for rigid rod polymers (*13*). This result suggests that the three highest M_w CMCs have access to similar surface areas on the pulp fiber and that the adsorption forms a monolayer of CMC on the pulp surface. The much higher maximum adsorption of the 90,000 M_w CMC suggests that at this molecular weight, CMC molecules have access to the internal pores of the pulp fiber. This access may be related to both polymer size and shape. Stone (*8*) reports that the available surface area for polymer adsorption on pulp fiber surfaces is a function of polymer size. Smaller molecules (typically <400 Å) may penetrate into the pores of the fiber and thus access a larger surface area. Although 90,000 M_w CMC has a radius of gyration of

approximately 500 Å at low ionic strengths (*14*), the 90,000 is a weight average; and so within a given batch, a considerable portion of the 90,000 M_w molecules could actually be smaller and therefore capable of penetrating the pulp fiber pores. Furthermore, CMC molecules are not spherical, but are more rod-like (much smaller diameter than length) in morphology, and the smaller the molecular weight, the more rod-like the molecule (*13*). Thus, the 90,000 M_w CMC was likely the stiffest and most rod-like of our samples and therefore the most capable of penetrating lengthwise into the fiber pores before adsorbing.

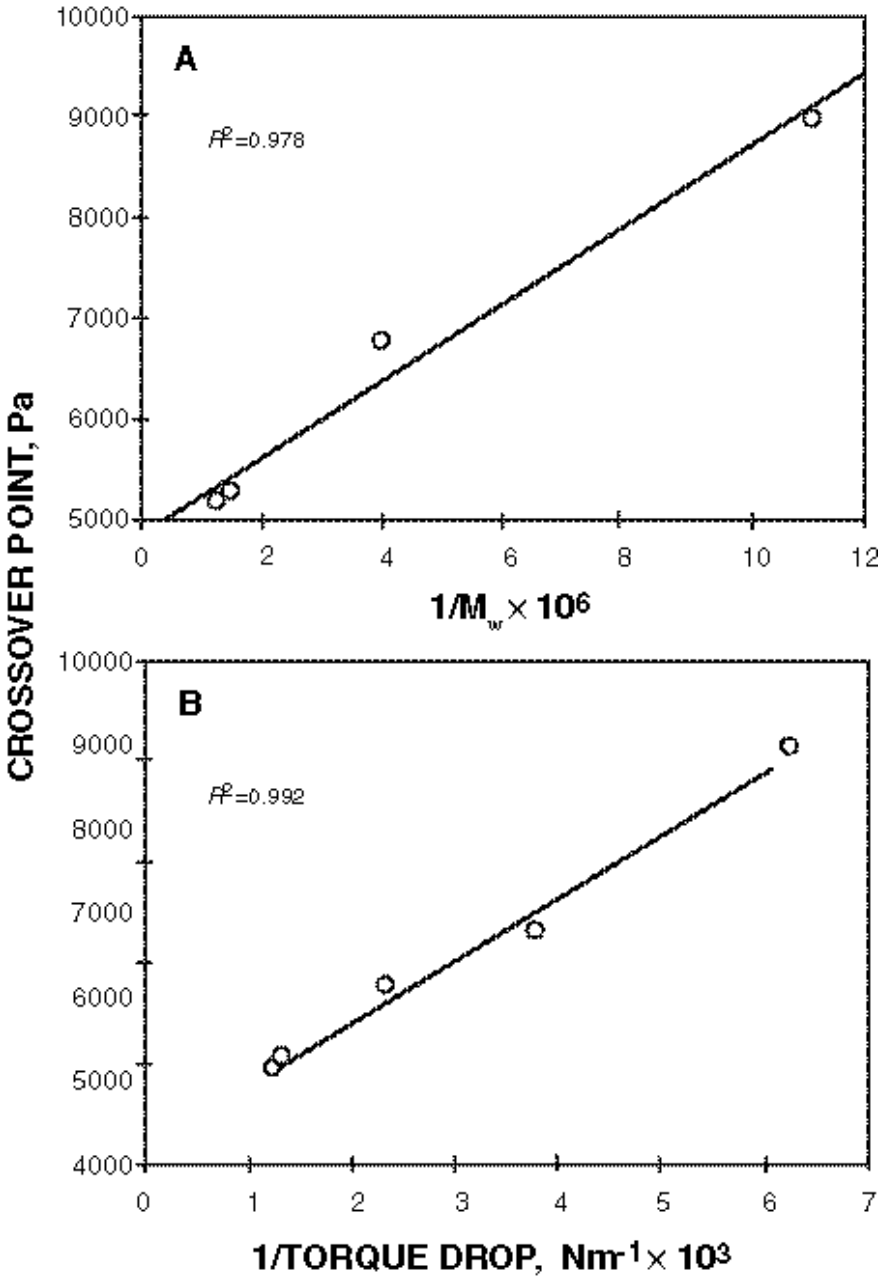

Figure 7A. Relationship between CMC molecular weight and crossover shear stress.
Figure 7B. Relationship between torque drop in mixing experiment and crossover shear stress.

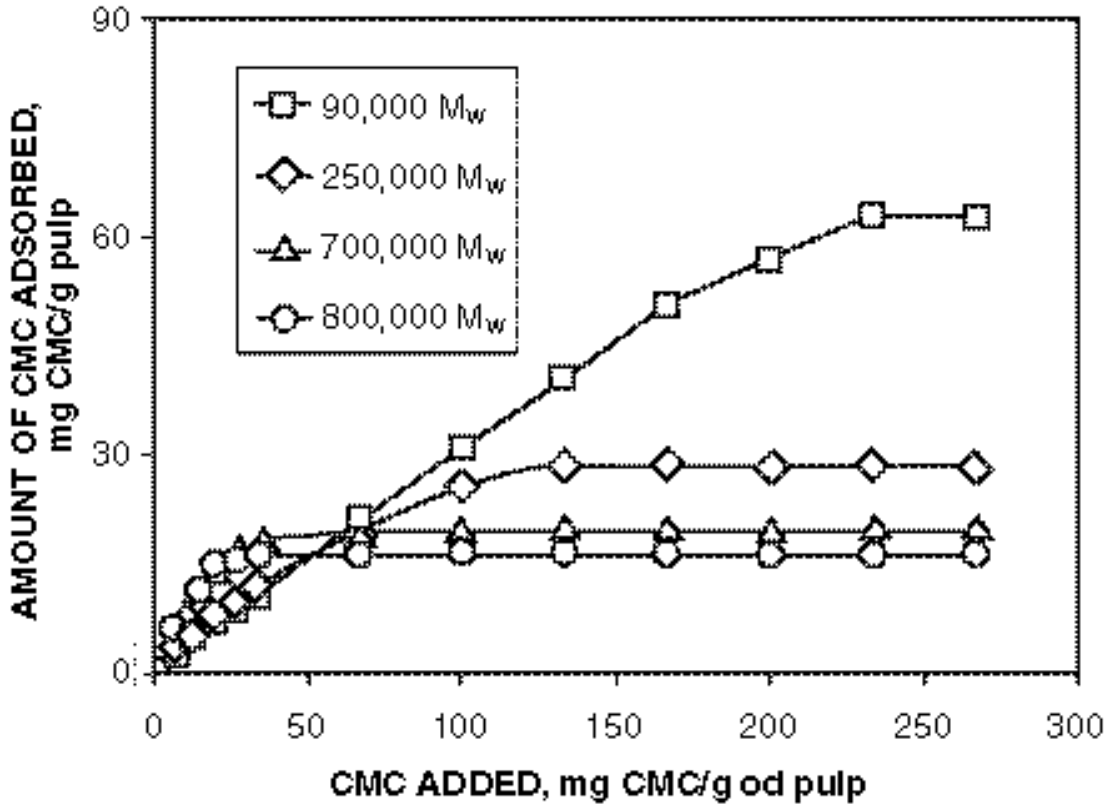

Figure 8. Adsorption of different molecular weight CMC on pulp fibers at different CMC concentrations.

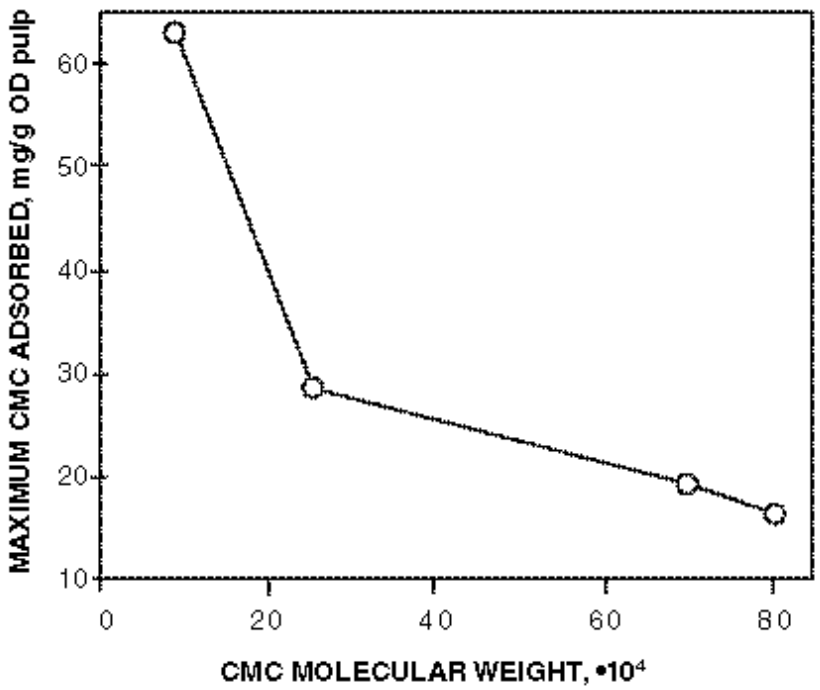

Figure 9. Maximum CMC adsorption on pulp fibers as a function of CMC molecular weight.

Torque drop by CMC molecular weight generally varied linearly with amount of CMC adsorption (**Figure 10**). This result supports a system model whereby adsorbed CMC at fiber contact points decreases the fiber–fiber contact strength. If we assume that the number of contact points doesn't change with adsorption, the network strength of a given system would be the weighted average of the strength of fiber contact points with and without adsorbed CMC. In the ideal case, where the properties of all fibers are equivalent and contact among them occurs randomly, the network strength should be linearly proportional to the surface area covered by the CMC, at least for the three higher molecular weights, for which the available surface area is the same. Thus, the torque drop, which is a measure of pulp slurry viscosity, which is in turn a function of fiber network strength, should drop linearly with the proportion of the surface area covered by the CMC, which is in turn a linear function of the amount of CMC adsorbed. This model appears to be valid for less-than-full surface coverage by CMC. As the adsorption reaches saturation, the model begins to fail and the relationship of torque drop to adsorbed CMC saturates. The non-linearity can probably be explained by a variety of causes, including solution viscosity, the effects of crowding as adsorption approaches monolayer saturation, and fiber wall penetration (especially for the lower molecular weights).

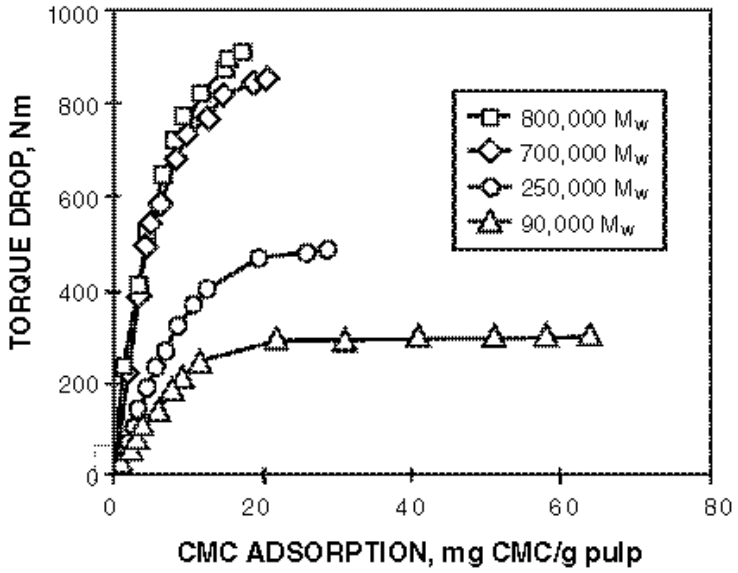

Figure 10. Torque drop in mixing experiment, as a function of CMC adsorption for different CMC molecular weights.

For the two lower molecular weight CMCs, the torque drops stabilized well below the polymer adsorption maxima. Since size was the only difference among the CMCs, a connection may exist between the size of the adsorbed polymer and the resulting fiber contact point strength. We are studying a complicated system, and there may be no single dominant factor in the dispersion mechanism. However, roughness of fiber surface in comparison to polymer size is likely an important parameter.

Behavior of CMC under different ionic strength conditions

Theory suggests that a polyelectrolyte is more expanded than the uncharged polymer molecule from which it is derived, and experimental data confirm this prediction (*13*). Increasing ionic strength reduces the radius of gyration of the CMC molecule in solution and consequently decreases solution viscosity (*13*). However, no reduction in dispersive ability, as measured by the torque drop experiments, was observed in this system as a function of ionic strength. From these data, we speculate that the change in ionic strength did not have a discernible effect on amount of polymer adsorbed or on polymer conformation on the surface. This result is also consistent with the earlier observation that adsorption is dominated by dispersive, as opposed to ionic, forces.

CONCLUSIONS

Macro- and micro-rheological measurements showed that pulp slurry dispersion improves with increasing CMC concentration up to about 3% (30 mg CMC/g od pulp) and with increasing CMC molecular weight. The molecular weight dependence is predictable using empirical equations. A linear correlation exists between results of the macro- and micro-rheological experiments.

Adsorption experiments showed that the higher the CMC molecular weight, the greater the dispersant's affinity for pulp fibers and the more effective it is as a torque reducing agent. Although ionic strength influenced the viscosity of CMC solutions, it did not influence torque drop substantially. Therefore, we conclude that the improved rheological properties were primarily due to the surface phenomenon of adsorption. The bulk polymer liquid phase had little influence on the rheological properties under the conditions of this study.

Manish Giri is currently a graduate student at the University of Maine; John Simonsen is an associate professor in the Department of Forest Products and Skip Rochefort an associate professor in the Department of Chemical Engineering at Oregon State University.

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