

The Effect of Water-Soluble Polymers on Rheology of Microfibrillar Cellulose Suspension and Dynamic Mechanical Properties of Paper Sheet

Arja-Helena Vesterinen,¹ Petri Myllytie,² Janne Laine,² Jukka Seppälä¹

¹Polymer Technology Research Group, Faculty of Chemistry and Materials Sciences, Helsinki University of Technology, P.O. Box 6100, FIN - 02015 HUT, Helsinki, Finland

²Forest Products Surface Chemistry Research Group, Faculty of Chemistry and Materials Sciences, Helsinki University of Technology, P.O. Box 6400, FIN - 02015 HUT, Helsinki, Finland

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ABSTRACT: Rheological properties of fiber/polymer suspensions and dynamic mechanical analysis (DMA) of paper sheets containing the same polymers were measured. Correlations between viscoelastic properties of suspensions and strength of paper sheet are presented. Rheological properties of suspensions of microfibrillar cellulose (MFC) and a set of water soluble polymers were measured. Rheological properties of these complex fluids vary considerably depending on the added polymer. A suspension of fiber and carboxymethyl cellulose (CMC) exhibits a viscosity higher than the sum of the viscosity of the individual components in the suspension. In contrast,

when cationic starch (CS) is used together with the fiber, the yielding behavior rather than the viscosity is characteristic of the suspension. Dynamic mechanical properties of paper sheets containing CMC or CS as additives were studied at different humidity levels. Different yielding behavior observed in oscillatory rheology can be correlated with straining behavior in dynamic mechanical properties. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 2990–2997, 2010

Key words: rheology; mechanical properties; strain; stress; structure-property relationship

INTRODUCTION

Wet strength is one of the most important properties of paper with respect to the papermaking process. The wet strength affects, for example, process runnability. The strength of paper is normally improved with various high molecular weight polyelectrolytes. For the most part, the polymers used are cationic get better retention,¹ since the surface of wood fiber is anionic. Paper sheet consists of fiber, polymer, and water or moisture. That means that paper consists of two mechanically different phases: water, which is a newtonian fluid with no strength properties, and mechanically strong fiber. Mechanical properties of the material depend on compatibility of the components, and the weakest part of the paper is the interface with the fiber. The surface of wood fiber consists of microfibrillar material. The lateral dimension of MFC (microfibrillar cellulose)² is in the range of 5 to 20 nm depending on its flocculation, although bigger particles can also be present. Comparable dimensions for normal wood fiber are in the millimeter range.

Rheology is commonly used in research on pulp and paper processes, with simple rheological measurements being done both for polymer and fiber suspensions.³ Measuring rheological properties of macroscopic fibres⁴ with conventional rheometers with narrow gap sizes often gives inaccurate results. Particle size of MFC is small enough to be suitable for commercial rotational rheometers with narrow gap sizes.⁵ MFC is suitable as a model substance as its shear thinning⁶ characteristic is close to macroscopic fiber. There are several studies where rheological properties of fiber suspensions in water have been measured.^{6,7} Only a few studies have considered rheological properties from the point of view of paper strength.^{8,9} Most studies have concentrated primarily on charge density of the polymer, polymer concentration, salt concentration,¹⁰ and dry substance content,⁶ whereas rheological studies have mostly concentrated on flocculation behavior.¹¹ The stress behavior of modified MFC with increasing shear rate has been reported.¹²

While being processed, paper is under nonconstant stress. With oscillating DMA (dynamic mechanical analysis), where stress is gradually increased until the break occurs, it is possible to study strength properties of paper. Using DMA, it is easy to study what happens to the paper properties when the paper is under stress. The same thing can be studied

Correspondence to: J. Seppälä (jukka.seppala@tkk.fi).

manually by keeping paper under forced stress while drying. DMA at varying humidities has been done for paper^{13,14,15} and wood¹⁶ applications. The focus has been on mechanosorptive effects and creep.¹⁷ For some of the papers, oscillatory measurements were also made, and the focus was on changes in tan delta with different humidity levels.¹⁸ Moduli changes of cellulose nanocomposites have also been measured with increasing humidity¹⁹ and it was found that elasticity is decreased with increasing humidity. Oscillating stress sweeps of paper in humidity chamber has been presented earlier by our group.²⁰ Some evaluation of the effect of water can be done when humidity of the surrounding environment is varied.

To be able to predict how a polymer additive affects paper strength, it can be beneficial to start study from how the polymer behaves in dilute suspensions. Complex fluids consisting of fiber and polymer can be considered to be structured fluids²¹ and rheological behavior of fiber-polymer system has been explained using several theoretical models.²² Viscoelastic behavior of structured fluids with high deformations is nonlinear, and the linear viscoelastic (LVE) region of many fluids is very small. Structured fluids are multicomponent systems where no linear correlation between, for example, polymer and fiber concentration exists.²³ Strength does not necessarily increase with increasing concentration. Typically, when under high strain, the storage modulus of structured fluids changes dramatically. Therefore, it can be fruitful to focus on changes in fluids under applied stress rather than properties inside the LVE area.

The purpose of this study was to examine paper strength by methods commonly used in polymer science. The study consists of two parts. The main part is a rheological study of suspensions of MFC and polymers, where MFC suspension is considered as a structured fluid. The other part is dynamic mechanical analysis of paper sheets with the same polymers used as wet strength agents. Viscoelastic properties of the microfibrillar cellulose in water suspension and the dynamic mechanical properties of the paper sheets are compared to evaluate if strength properties of paper sheets can be estimated from the viscoelastic behavior of dilute suspensions. It is also speculated as to whether there is a correlation between strength of the paper and the strength of the continuous phase of the fiber suspension.

EXPERIMENTAL

Materials and methods

The polymers used in the experiments were carboxymethylcellulose (CMC, Aldrich), cationic polyacryl-

amide (CPAM, Kemira), cationic starch (CS, Ciba) and poly(ethyleneoxide) (PEO, Dow). The polymers tested were all commercially available and detailed information is listed in Table I. Polymers were dissolved in distilled water and the salt used was NaHCO₃ (J.T. Baker).

Preparation of microfibrillar cellulose

Microfibrillar cellulose (MFC) was prepared from chemical birch pulp samples with a special pulp refining apparatus, i.e., a super mass colloidier. Fibres were refined in several stages using very narrow gaps between the stones and hence were reduced to fibrils and microfibrils. The differently treated pulps were then refined in a Masuko refiner several times. The first pass was done to homogenize the pulp, with a gap of 200 μm . The two subsequent passes were done with a 120 μm gap, and the last two passes with an 80 μm gap. After refining, the MFC's were stored in a cold storage room.

Preparation of suspensions

1% polymer solutions were prepared in salt solutions prepared with distilled water. The salt used was NaHCO₃ and the salt levels were 0.5 and 10 mmol. Solutions were warmed up if needed to dissolve all sediments. 1% MFC suspensions were prepared to the right concentration by diluting 2% MFC gel in salt solution. Suspensions were homogenized with a magnetic stirring bar. Concentrations of the solutions and suspensions were double the target concentrations. MFC-polymer suspensions were prepared by mixing these two fluids in 1 : 1 proportions. This procedure was done instead of direct dilution in order to obtain homogeneous suspensions.

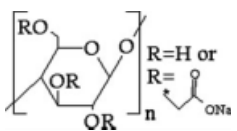
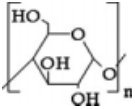
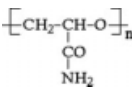
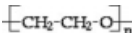
Preparation of paper sheets

Laboratory sheets of 60 g/m² were prepared from fines-free bleached pine pulp fibers. The targeted amount of polymer was 1 g/m² paper sheet. Fiber was filtrated after 90 min adsorption and fiber consistency during adsorption was 5 g/L. Paper sheets were prepared according to standard ISO 5269-1:1998.

Rheological measurements

Viscoelastic properties of suspensions of MFC and polymer were measured with stress-controlled rotational rheometry (Rheometric Scientific). Bob-and-cup measuring geometry was used. Two runs were performed: one for steady and one for dynamic shear stresses. Steady shear stress sweeps were run

TABLE I
Commercial Polymers Used in the study

Polymer	Commercial name	Molecular weight	Repeating unit	Other information
CMC, Sigma-Aldrich	419338	700,000		Anionic, DS = 0.9, Mp = 270°C
CS, Ciba	Raisamyl 50,021	Not known		Cationic, R4N ⁺ C1 ⁻ , DC = 0.035
CPAM, Kemria	Fennopol K3400R	6,000,000		Cationic, R4N ⁺ C1 ⁻
PEO, Dow	Ucarfloc 309	8,000,000		Non-ionic

from 0.02 Pa up to 50 Pa. Stress was increased stepwise with the rate of 5 points per decade. The data was collected when equilibrium reached. Dynamic runs were done at 1 Hz from 0.02 Pa up to 10 Pa. The focus for data analysis was on viscosity, moduli and stress-strain correlation. Tan delta was calculated as a ratio between loss modulus and storage modulus, G''/G' .

Dynamic mechanical analysis

DMA measurements were done with TA Instruments DMA Q800 equipment. The maximum force was 18 N and maximum frequency 200 Hz. The measurements were carried out at ambient pressure using a Film/Tension measuring head. Stress sweeps of the samples were done between 0 and 30 MPa. Amplitude increased from zero until the samples broke down. The frequency used was 1 Hz. Dimensions of the samples were $w \times t \times l = 3 \text{ mm} \times (0.12 - 0.17) \text{ mm} \times (11.8 - 17.6) \text{ mm}$. The length was measured automatically by the equipment, whereas other dimensions were measured manually before each run. The data was collected when equilibrium reached, and each data point was collected for 2 seconds.

The humidity of the measuring chamber was stabilized with an external humidity element connected to the measuring chamber (Kep Technologies Wetsys Setaram Instrumentation). The samples were stabilized for 30 min. Stabilization time was adjusted to allow sufficient time for the humidity content in the sample to stabilize. Targeted humidity levels were 10, 40, and 70% relative humidity. Measurements were done at three different temperatures, 30, 50, and 70°C, except for the highest humidity and temperature combination, where a stable atmosphere

could not be obtained and moisture had a tendency to condense on the walls of the chamber.

RESULTS AND DISCUSSION

Rotational rheometry

The focus of the experiment was to investigate how a set of polymers listed in Table I would respond to rheological tests in a salt solution environment and also with the addition of MFC. The salt environment and addition of MFC are included to simulate the conditions that the polymer would be subjected to when used in the paper-making process.

Flow Curves

Figure 1 presents flow curves of four different polymer samples at 0.5 and 10 mmol salt levels. The viscoelastic behavior of all of the materials is non-newtonian. The effect of salt can clearly be seen in these curves. The viscosities of all of the polymers, except PEO, decrease dramatically with increasing salt content and the material becomes less shear thinning. CPAM has the highest viscosity value but it is strongly shear thinning. Therefore, CMC has a higher viscosity at higher shear stresses. CMC also tolerates more salt, and the viscosity is affected very little by increasing the amount of salt. The cationic wet strength agent CPAM is strongly affected by salt and it loses most of its viscosity in an ionic environment. Viscosity loss can be explained by a decrease in intramolecular repulsion. Repulsive forces typically enlarge the hydrodynamic size of the molecule, which increases viscosity. At high salt content this repulsion does not exist anymore because there are enough ions in solution to interact with ionic groups of the polymer molecules, and interaction within the polymer disappears. Viscosity loss was also seen at

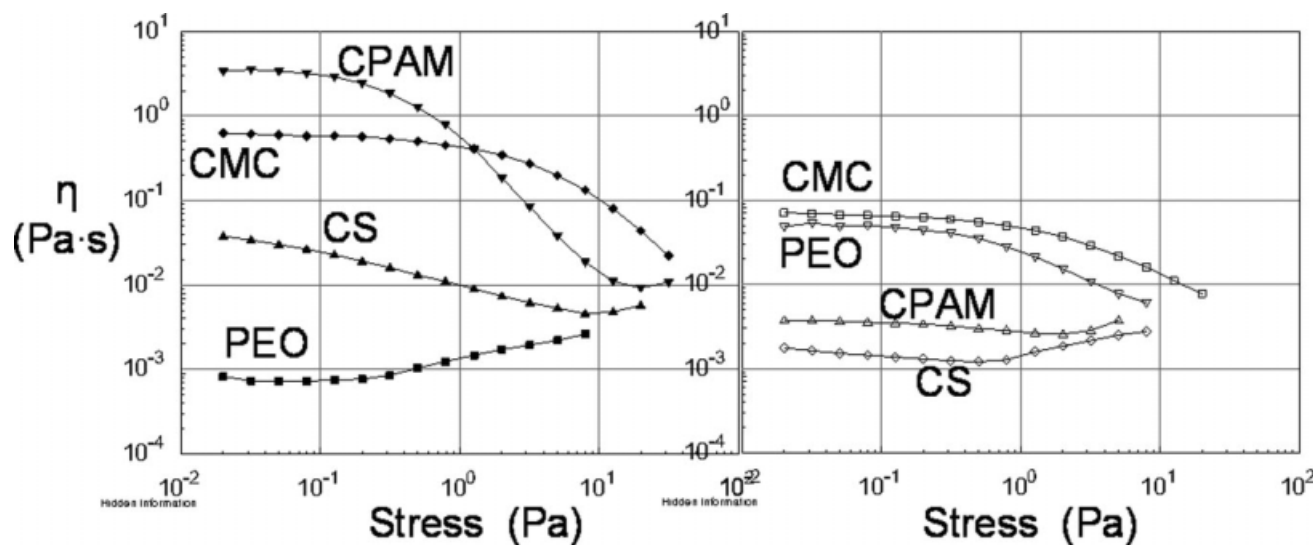


Figure 1 Viscosity curves of 1% polymer solutions at 0.5 mM (left) and 10 mM (right) salt levels.

5 mM salt, but 10 mM salt was used in further studies to be sure that repulsive effects of the polymers were eliminated.

Comparison of suspension and polymer solution

Relative viscosity of the suspension is determined by the ratio between viscosities of the matrix solution and the fiber suspension in the matrix.²⁴ It has typically been used to describe the interaction between fibers,²⁵ usually in some polymeric matrix.²⁶ In this study it is used as a tool to study how different polymeric matrices affect the viscosity of MFC suspension. In this study, relative viscosity is determined by

$$\eta_{rel} = \frac{\eta_{susp}}{\eta_{sol}}$$

where *susp* consists of 0.5% polymer + 0.5% MFC and *sol* is 0.5% polymer solution.

Figure 2 presents relative viscosity values for four different polymers. It can clearly be seen that viscosity of the MFC/CMC suspension follows the viscosity of the CMC solution, and the strongly shear thinning behavior of MFC disappears. CS seems to maintain strongly shear thinning behavior of the MFC suspension and the relative viscosity at low stresses remains quite high. Also, it is remarkable that for CPAM the relative viscosity is about 1 at high shear stresses. This is in spite of the total content of high viscosity material in the water increasing from 0.5% to 1% when MFC is also added. This means that when fiber is added, the whole system collapses somehow and the viscosity of the suspen-

sion is same as the viscosity of the polymer solution. CMC suspension seems to be the only material in which there is an increase in relative viscosity even at higher shear stresses. It has also been reported in the literature that the viscosity of a pure polymer solution is higher than that of a colloidal dispersion formed in solution.²⁷

Apparent yield stress can also be seen in Figure 2. CMC and PEO suspensions are not yielding, whereas MFC causes yielding for both CS and CPAM suspensions. It is notable that the yielding behavior typical for MFC totally disappears when the suspension is stabilized with PEO or CMC. It has been reported in the literature that at low shear rates the adhesive forces are dominant, whereas at high shear rates the distance between fibers play a key role.²⁵ CMC seems to have a certain dispersing effect in the system, and it probably decreases the amount of free water in the suspension.

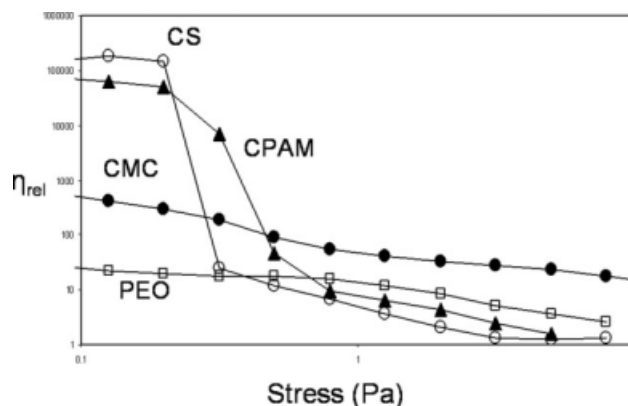


Figure 2 Relative viscosity of suspensions of polymer and MFC.

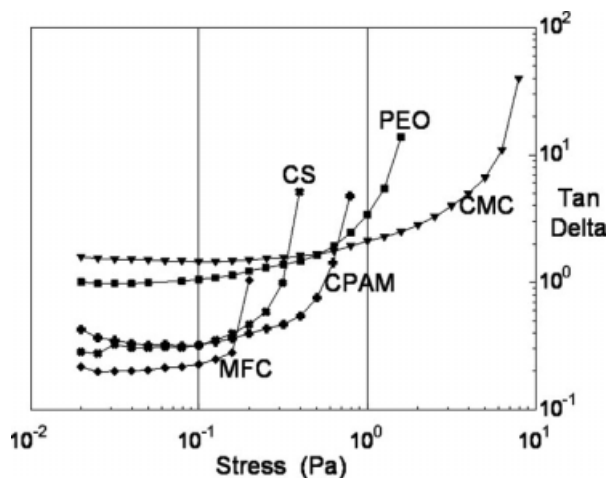


Figure 3 Tan delta of suspensions of polymer and MFC.

Dynamic stress sweep

MFC has gel-like properties over the whole range of frequencies inside the linear viscoelastic region⁶ when the concentration is sufficiently high. MFC forms a gel-like system even at very low concentrations, i.e. 0.125 mass-%. That means that tan delta is smaller than 1 over the whole LVE region. The content of MFC measured here is 0.5 mass-%. In the literature, the focus of wood fiber suspension rheology has been on elasticity. A frequency sweep within the LVE area tells about colloidal forces and interactions between particles when they are at rest. G' (elasticity module) typically stays almost constant over the whole range of frequencies.⁶ This study does not concentrate only on the linear viscoelastic region, since forces in normal papermaking processes do not remain in that region; the focus is rather on yielding behavior.

Yield stress is determined as the critical stress where the structure of the sample is strongly deformed. Deformation is most clearly seen as a decrease in G' . Tan delta is also a valuable tool to determine yielding behavior. It can be seen from the curves for tan delta in Figure 3 that MFC has a low tan delta, which is evidence of its elasticity. The behavior of the materials during dynamic stress sweeps varied a lot depending on the polymer. It can be seen that pure MFC is a strongly yielding material, but when it is mixed with a polymer, the yielding behavior of the suspension changes dramatically depending on the associating polymer. CMC and PEO seem to have a similar type of effect where they increase tan delta so that viscous properties became dominant over the whole range of stresses. This indicates that these polymers change forces and interactions in a system consisting of MFC, water and polymer. Compared with pure MFC suspension, CS and CPAM change tan delta only a little at low

shear stresses, so that the strongly yielding behavior of the suspension is maintained.

Comparison of CS and CMC suspensions shows that even though a CS suspension is strong at lower frequencies, the mechanical properties of the suspension rapidly decrease when stress is applied. CS strengthens MFC suspensions, but the suspension still remains strongly shear thinning and maintains the gel-like behavior of MFC. It can be seen that starch has very high elasticity even though its yield stress is lower than that of CMCs. It can be seen from the tan delta curves that adding CMC completely changes the rheological nature of the system. In pure MFC, the elastic nature dominates, whereas in a CMC suspension, the fluid is more viscous, in other words, the gel-like system becomes fluidic.

The reason that the CMC-MFC suspension has practically no yield stress could be that its structure is more homogeneous. CMC could function as some kind of stabilizer in the system so that interactions between the continuous water phase and the fibers change. The structure of the suspension is not as fragile as it had been before polymer addition because the polymer changes the water-fiber interface. CMC probably binds more water than, for example, CS.

Stress-strain behavior of MFC suspension

Figure 4 presents the stress-strain behavior of CS and CMC in MFC suspension. The stress-strain curve of CMC is very linear, whereas MFC is strong at low strains but at higher strains it totally loses its strength properties. At a certain stress level the material starts to yield and strain increases without the addition of more stress. The behavior of CS is intermediate between these two extremes. It can be concluded that CS has very little capacity to compatibilize the MFC suspension. This oscillatory measurement describes the strength of the

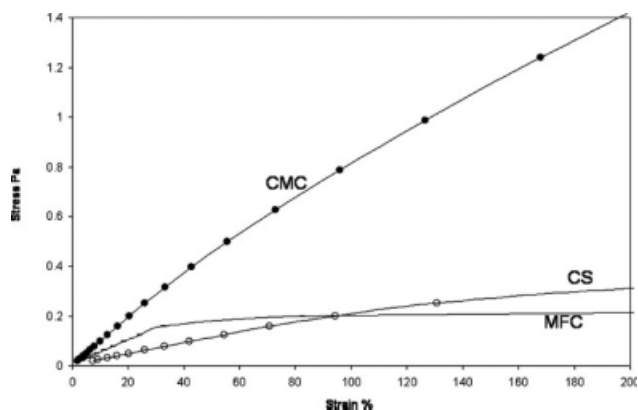


Figure 4 Stress-strain behavior of MFC suspensions from oscillatory rotational rheometry at 1 rad/s.

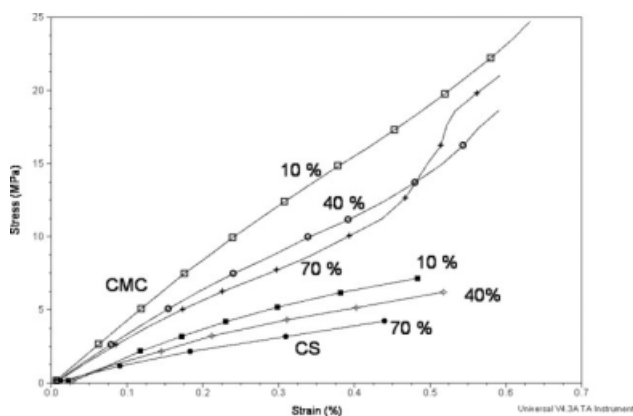


Figure 5 Stress–strain behavior of CS and CMC with different humidity levels: 10, 40, and 70% relative humidity.

suspension in simplified terms. Using this, rheological data can be compared with data from dynamic mechanical analysis.

Dynamic mechanical analysis

Two of the polymers measured in the rheological studies were chosen to be used as strength additive in paper and tested using DMA. The behavior of MFC suspension with CMC as an additive was quite different from that of most of the other polymer suspensions. CMC clearly increased viscosity in the MFC suspension. Starch had completely different rheological properties, even though starch and CMC have quite similar chemical structures. Both of them are polymers formed of glucose units, which is why these two polymers were chosen for the DMA study. To get data comparable to that from rotational rheometry, stress and strain were studied using DMA.

In Figure 5, the stress–strain behaviors of papers containing CMC and CS are compared at three different levels of humidity content. Paper containing CMC is much stronger than that containing CS at all humidity levels. However, the most remarkable phenomenon is how differently CS and CMC behave from each other when used as strengthening agents in paper sheets. It is obvious that the strength profiles of the paper sheets are different, especially with high humidity content. CMC shows clear strengthening behavior under stress, which is not seen with starch. Strain hardening behavior is quite interesting, since a similar kind of behavior can be seen when film tension measurements are done for linear polyethylene, which is a characteristically viscoelastic material.²⁸ In polyethylene, polymer chains are mobile and weakly bonded to each other. It can be speculated if CMC would also be bonded loosely to fibers rather than through crosslinked networks or ionic bonds. However, this fiber system is very com-

plex compared with homogeneous polymer film, and the reason for hardening can not be confirmed by any one case in this study.

It is obvious that the paper is stronger at low humidity content. However, paper with CS as a strengthening agent loses its strength more rapidly than paper with CMC. It can clearly be seen that CMC tolerates the highest stress and strain at break in all conditions. CS loses its strength properties, especially at 70% humidity, whereas CMC does not actually lose strength properties with humidity. The tendency to harden with applied stress results that stress at break is even higher at higher humidity levels.

Figure 6 presents the effect of temperature on stress–strain behavior for both of the paper samples. At the lowest temperature, the paper is stronger than at the highest temperature. The differences are not significant in any of the cases. The highest temperature is close to the T_g 's of the polymers, but still the decrease in strength is not substantial. It is clear that humidity is a much more important factor regarding changes in mechanical behavior than temperature. Therefore, some tests were done to estimate the amount of absorbed water in papers in different temperatures using gravimetric methods. The water content in the paper samples varied between 2 and 6%, and practically no additional water was absorbed at higher temperatures.

Comparison of rheological properties with mechanical properties of paper

When DMA results are compared with rheology results, the behavior of CMC as strength additive can be explained based on its suspension behavior in rotation rheometry. CMC has quite linear stress–strain behavior in rheometry, and the same phenomenon can also be found in DMA. In other words, CMC maintains its ability to strain and does not

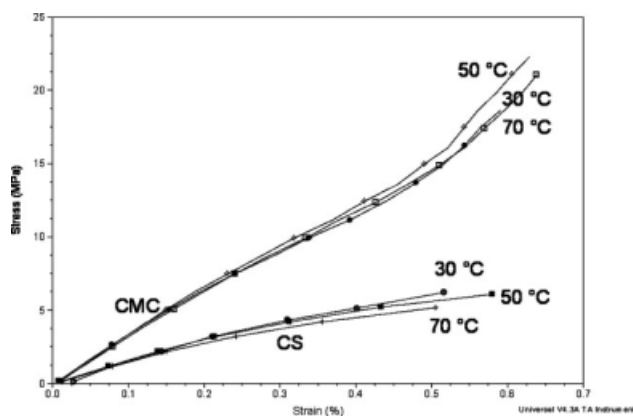


Figure 6 Effect of temperature on dynamic mechanical behavior at 40% relative humidity content.

break as easily as starch. With higher humidity content, the phenomenon is even more clearly seen. CMC even seems to favor high humidity levels, as can be seen in stress–strain curves from DMA. The fluidic nature of CMC can be seen as strain hardening of paper in DMA. Strain hardening behavior means that CMC causes internal mobility in the fiber network, so that at high stresses the paper sheet is strongest at high humidity levels.

We can speculate as to the reason for the marked differences between these two materials. The rheological behavior of CMC as a matrix polymer in structuring fluid has been studied previously.²³ Its unique behavior might be the reason why it has been used frequently as a rheology modifier in many applications. Results from this study were consistent with the data reported in the literature. In our studies, CMC also showed different behavior from the other materials. Paper with CS seems to be quite fragile, as can be seen in rheological studies in which starch loses its strength properties at quite low shear stresses. The rheological properties of CMC also seem to predict its effect in paper and its dynamic mechanical behavior, even though the amount of added polymer is relatively low.

The ionic nature of these two natural polymers is different, which may explain why it appears that there is no strong bonding between fibers and CMC. CS is cationic whereas CMC is slightly anionic. The cationic nature of CS could cause a strong network to form, but the difference in rheological nature was already seen in flow curves, and it is too simplistic to claim that ionic factors are the reason for the different rheological behaviors of the two polymers. Differences in the polymer structures of starch and cellulose could be said to be negligible because both of the polymers consist of glucose units. The cellulose chain is linear and it does not form coil structures like starch does, which certainly affects the rheological properties of the material. The structure of the cellulose also seems to affect strength properties of paper in which CMC is used as a strengthening agent.

One possible reason that materials with CMC as an additive are stronger than those with CS could be that CMC has a higher $\tan \delta$. It could be said that CS is elastic whereas CMC is viscotic. The strength of CMC comes from its loss modulus rather than its storage modulus. CMC is actually strong but not elastic. According to literature of structured fluids,²⁹ if $\tan \delta$ is very low, the materials are highly associated and if it is very high, they are very unassociated. An intermediate $\tan \delta$ is desired to obtain a stable system. The CMC-MFC system seems to be stable, whereas the pure MFC or MFC-CS suspensions are not. According to the literature, strain hardening in oscillative tensile measurements in DMA demands a

certain amount of mobility from the material.¹⁹ It has also been realized that mobility and structures that are more loosely associated can result in reduced shear thinning behavior in rheological studies.²⁹ Mobility of CMC can be reason for the differences observed both in the rheological and dynamic mechanical properties measured in our study.

In many rheological studies elasticity of fiber suspension has been used as a synonym for strength.⁶ On the basis of this study it is too simplistic to determine strength based on elasticity. Normally, in industrial processes forces and shear rates are high, and typically some material deformation occurs. In such cases the deformation definitely does not occur inside the LVE region. Therefore, strongly yielding materials, which can be said to be unstable, may not be appropriate for these paper making processes even though they have high elasticity moduli. CMC, which is not strongly yielding and contributes viscosity to the system, seems to be favorable from the point of view of processability.

MFC is a gel in water solutions even at very low concentrations. Films prepared from MFC have a very high modulus. They are strong but very brittle without any softener.² The lack of toughness in DMA can be seen as a gel-like behavior in suspension. This study indicates that MFC is a suitable model substance for rheological studies. The rheological study of polymer MFC suspensions presented here can be correlated to some extent with the strength properties of the paper where these polymers have been used as additives.

CONCLUSIONS

Certain correlation could be found between the strength properties of the polymers in a paper sheet and the oscillatory rheological properties of an MFC suspension containing polymer as strength additive. Here MFC was used as a model substance to represent fibrils normally present on the surface of pulp fiber. Interactions between MFC and the polymer changed the rheological properties of the MFC suspension markedly compared with pure polymer solution. These changes in rheological properties could also be found in paper sheets, which were tested using these polymers as wet strength additives. Therefore, humidity-controlled dynamic mechanical analysis of paper sheets is a practical tool to study the effects of water on paper strength. The polymer that did not eliminate the gel-like behavior of the MFC suspension also maintained yield stress in papers as measured with DMA, whereas fluidic behavior in a suspension indicated strain hardening behavior in paper sheets. Therefore, the increased viscosity seen in MFC suspensions also indicated

changes in paper sheets when a small amount of the same polymer was used as additive.

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