CELLULOSE CHEMISTRY AND TECHNOLOGY

VISCOELASTIC PROPERTIES OF MICROFIBRILLATED CELLULOSE (MFC) PRODUCED FROM CORN STOVER

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Received October 18, 2017

The rheological properties of microfibrillated cellulose (MFC) produced from agricultural residue corn stover were investigated. The corn stover MFC gels exhibited concentration-dependent viscoelastic solid properties. Higher corn stover MFC concentrations resulted in stronger viscoelastic properties. The analysis for moduli of different concentrations and stress relaxation measurements indicated that the corn stover MFC gels were physical gels, meaning the cross-linkers between the molecules exhibited physical interactions. The non-linear steady shearing rheological properties studies implied that the corn stover MFC gels exhibited shear thinning behavior, which can be well fitted with the Power-Law Constitutive Equation. The function and behavior of the corn stover MFC gels suggest that this kind of starch-based biomaterial could be a potential candidate for applications in cosmetic gels and wound skin care materials.

Keywords: corn stover, microfibrillated cellulose (MFC), nanocellulose, rheology, viscoelastic properties

INTRODUCTION

Cellulose, the most abundant biopolymer existing in nature, can play a major role in advanced materials due to its reinforcement properties. On the other hand, agriculture-based residues provide an abundant, inexpensive and widely distributed source of biomass for cellulose. Many agricultural residues, such as corn stover and wheat straw, have little economic value other than for mulching back into the soil or for burning as fuel. These residues can be used as abundant low-cost feedstocks for production of fuel ethanol, cellulose and lignin.[1] Limited research has been conducted into developing these fractions for higher value polymer materials and applications.[2,3]

The nano-sized cellulose research area has attracted the attention of more and more researchers since Favier published on nanocellulose in 1995.[4] The properties and functions of the micro- and nano-sized cellulose depend closely on the cellulose source and the preparation process.[3] The phrase “nano-sized particles of cellulose” generally refers to cellulose particles provided with one dimension in the nanometer range. Cellulose nanocrystal (CNC or CN) or nanocrystalline cellulose (NCC), also known as cellulose nanowhiskers or just cellulose whiskers (CW),[5] nanorods[6] and rod-like cellulose crystals,[7] are normally purified from cellulose fibers through pretreatment of the source material and acid hydrolysis.[3] The CNC or NCC has a diameter of 2-20 nm and a length ranging from 100 nm to several micrometers.[8] The CNC or NCC particles are 100% pure cellulose and highly crystalline with 54-88% crystallinity.[9] Nanofibrillar cellulose (NFC),[10] which is also known as cellulose nanofiber,[11] cellulose nanofibril[12] and microfibrillated cellulose (MFC),[3,13] contains a bundle of stretched cellulose molecules with long flexible and entangled cellulose nanofibers with 1-100 nm diameters and lengths up to several tens of μm.[14]

Recently, we prepared MFC from agricultural wastes, such as corn stover. We found that the MFC can be suspended in water and formed a gel-like material. To identify potential applications of the MFC from corn stover, we explored the concentration-dependent viscoelastic properties of this MFC suspension gel. Both linear and non-linear viscoelastic properties of this biopolymer are reported.

EXPERIMENTAL

Raw material and purification

The corn stover (hybrid corn: Golden Harvest H-8211GT) was first passed through a chipper shredder to reduce the size, and then passed through a Thomas mill (Thomas Scientific, Swedesboro, NJ, USA) to be ground into a fine brown powder. The dry powdered corn stover was washed with water and then treated with alkali extraction using 4 wt% sodium hydroxide at 80 °C for 2 hours with shaking to remove the soluble polysaccharides.[15] Afterwards, the sample was washed thoroughly with water and this sodium hydroxide treatment was repeated. After the alkali treatment, the sample was then washed with water and bleached with sodium chlorite and acetic acid.[16] The bleaching process removes most of the lignin or polyphenols and proteins. After bleaching, the product was washed with water and dried. The final product contained about 93.1% cellulose, 2.5% hemicellulose and 3.4% lignin, as determined by the NREL method (http://www.nrel.gov/biomass/analytical_procedures.html). The ash content was less than 1%.

High-temperature, high-pressure homogenization

The sample was suspended with water at five different concentrations (0.25 wt%, 0.5 wt%, 1 wt%, 1.5 wt% and 2 wt%) and then blended with a Polytron homogenizer (PT10-35 GT KINEMATICA AG, Switzerland) at 12,000 rpm for 5 min. The sample was then subjected to high pressure homogenization with 30 passes through a GEH NiroSoavi Panda 2K (43100 Parma, Italy), at 500 bars of pressure and a temperature of 90-95 °C, as described by Dufresne *et al.*[17]

Transmission electron microscopy (TEM)

The MFC samples were applied to carbon stabilized 300 mesh formvar coated nickel grids and were negatively stained with 1% uranyl acetate, and then viewed in a JEOL 100C Transmission Electron Microscope (JEOL Solutions for Innovation, Peabody, MA) at 80 kV.

Rheology measurements

A strain-controlled Rheometric ARES rheometer (TA Instruments, New Castle, DE, USA) was used to perform the rheology studies.[18] The 50-mm diameter plate-plate geometry was adopted. The temperature was controlled at 25 ± 0.1 °C by a water circulation system. For linear viscoelastic measurements, to ensure that all the measurements for the materials were made within the linear range for the linear viscoelastic properties studies, the strain-sweep experiments were conducted initially. An applied shear strain valued in the linear range was adopted for the other linear viscoelastic property measurements for the same material; fresh samples were used for each experiment. The linear viscoelasticity indicates that the measured parameters are independent of the applied shear strain. Small-amplitude oscillatory shear experiments were conducted over a frequency (ω) range of 0.1-500 rad/s, yielding the shear storage or elastic (G’) and loss or viscous (G”) moduli. The storage or elastic modulus (G’) represents the non-dissipative component of the mechanical properties. Elastic or “rubber-like” behavior is suggested if the G’ spectrum is independent of frequency and greater than the loss modulus over a certain range of frequency. The loss or viscous modulus (G”) represents the dissipative component of the mechanical properties and is characteristic of viscous flow. The phase shift or phase angle (δ) is defined by $\delta = \tan^{-1}$ (G”/G’), and indicates whether a material is solid with perfect elasticity (δ = 0), or liquid with pure viscosity (δ = 90°), or something in between ($0 < \delta < 90°$). Stress relaxation experiments measured the stress relaxation with the time after the material is subject to a step-increase in linear range shear strain. The non-linear steady shearing experiments were performed with a shear rate range of 0.1 s^{-1} to 500 s^{-1}.

RESULTS AND DISCUSSION

Before high pressure homogenization, the cellulose sample did not stay in suspension, but rather would fall out and settle to the bottom. After high pressure homogenization, the sample resembled a thick white gel-like material and remained in that state. The sample was observed with transmission electron microscopy (TEM) shown in Figure 1. From Figure 1, we can clearly see the cellulose microfibrils’ diameters are in the range of 20-40 nm, indicating that the corn stover cellulose fiber becomes microfibrillated cellulose (MFC) after the high-temperature high-pressure homogenized shearing.

The viscoelastic properties for five concentrations of corn stover MFC from 0.25 wt% to 2 wt% were investigated at 25 °C. The corn stover MFC exhibited viscoelastic solid behavior at all the measured concentrations, and the storage or elastic moduli (G’) were all greater than loss or viscous moduli (G”) within the measured frequencies (Figs. 2 and 3). The magnitude of complex dynamic modulus $|G^*| = (G'^2 + G''^2)^{1/2}$, which also represents the viscoelastic property of the material. Therefore, the viscoelasticity of the corn stover MFC strengthened with the increasing concentration: the higher the concentration, the stronger the viscoelasticity (Figs. 2 and 3). At a lower concentration, of 0.25 wt%, the moduli for the corn stover MFC were slightly dependent on the frequency, especially the loss (viscous) moduli (Fig. 2). The storage modulus (G’) at 1 rad/s for the 0.25 wt% MFC was 4.8 Pa (Fig. 2), and the phase shifts were in the range from 5.3° to 28.3°. Meanwhile, at 0.5 wt%, the moduli for the corn stover MFC became more frequency-independent (Fig. 2). The storage modulus (G’) at 1 rad/s for the 0.5 wt% MFC dramatically increased to 205.9 Pa, showing much stronger elasticity than the 0.25 wt% MFC (Fig. 2); and the phase shifts decreased to the range from 5.3° to 13.6°, exhibiting more solid-like behavior than the 0.25 wt% MFC. From 0.25 wt% to 0.5 wt%, the concentration only increased one time; however the storage modulus increased nearly 42 times, which was extremely conspicuous. At higher concentrations, of 1 wt%, 1.5 wt% and 2 wt% corn stover MFC, the curves of both storage (G’) and loss moduli (G”) for the all the measured materials were nearly frequency-independent (Fig. 3). The elastic moduli (G’) at 1 rad/s for the 1%, 1.5% and 2% corn stover MFCs were of 672.9 Pa, 1898.6 Pa and 5229.0 Pa, respectively (Figs. 3 and 4). The phase shift ranges for these three concentrations of MFCs were all in the range from 4.8° to 12.4°. These results indicated that all the measured corn stover MFCs exhibited rubber-like gel or viscoelastic solid behaviors,[19] and their rheological behavior could be manipulated by the concentration or water content. For reference, the G’ for the synthetic rubbers can be 10^4 to 10^7 Pa, depending on cross-linking, while their phase shifts can be around 11°. The trend of value of log (G’) *versus* log (C) for these five concentrations of corn stover MFCs followed the power law model described for physical gels.[20] The modulus of MFCs gel varied as $C^{3.07}$ (Fig. 4). The power law index is dependent on the kinetics that the gel formed.[20]

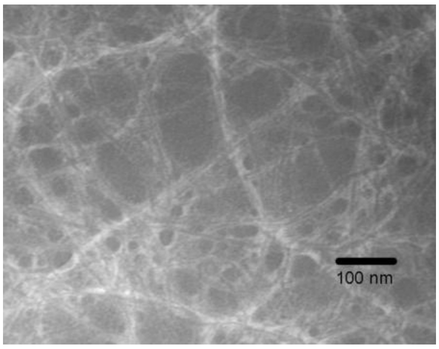

Figure 1: TEM micrograph of corn stover MFC

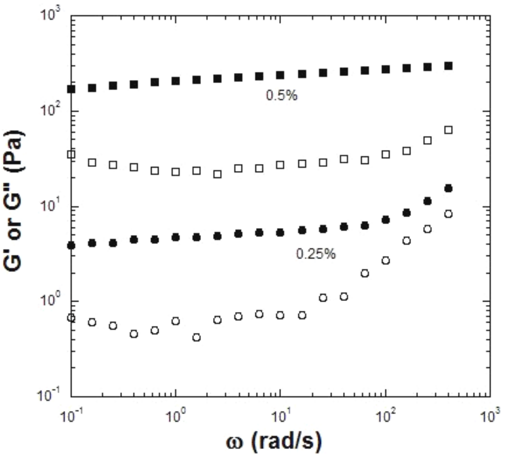

Figure 2: Linear viscoelastic properties of frequency sweep experiment for 0.25 wt% and 0.5 wt% corn stover MFC gels. Storage modulus (G’) or loss modulus (G”) as a function of frequency at 25 °C with 0.5% strain. Filled symbols: G’, opened symbols: G”. (●, ○): 0.25 wt% corn stover MFC gel, (■, □): 0.5 wt% corn stover MFC gel

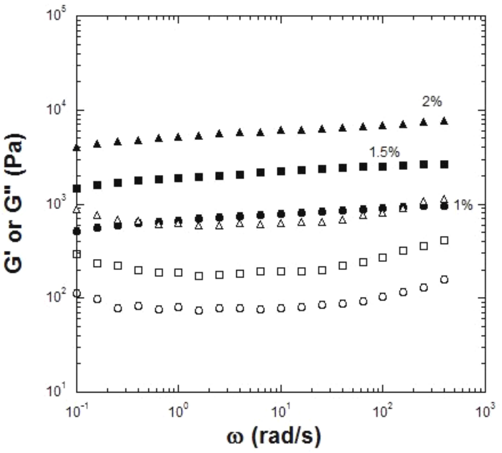

Figure 3: Linear viscoelastic properties of frequency sweep experiment for 1 wt%, 1.5 wt% and 2 wt% corn stover MFC gels. Storage modulus (G’) or loss modulus (G”) as a function of frequency at 25 °C with 0.5% strain. Filled symbols: G’, opened symbols: G”; (●, ○): 1 wt% corn stover MFC gel, (■, □): 1.5 wt% corn stover MFC gel, (▲, △): 2 wt% corn stover MFC gel

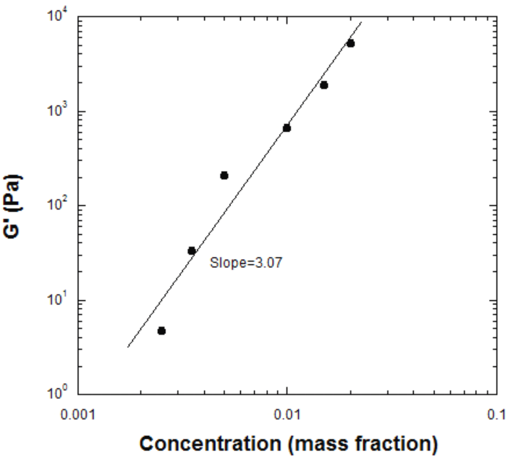

Figure 4: Storage modulus (G') values measured at 1 rad/s as a function of concentration for the corn stover MFC gels at 25 °C. The line is the fitting with the power law model

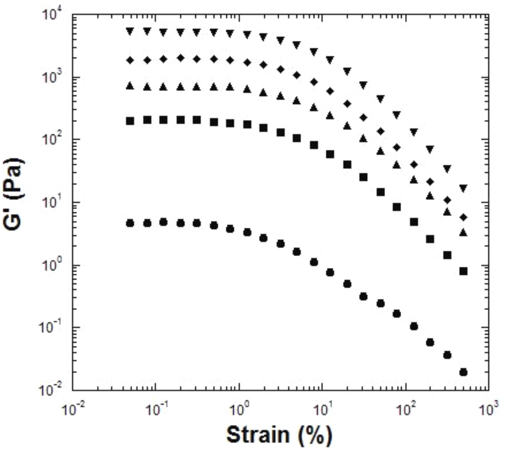

Figure 5: Strain sweep experiment for corn stover MFC gels with 1 rad/s frequency at 25 °C. (●): 0.25 wt% corn stover MFC gel, (■): 0.5 wt% corn stover MFC gel, (▲): 1 wt% corn stover MFC gel, (♦): 1.5 wt% corn stover MFC gel, (▼): 2 wt% corn stover MFC gel

The strain sweep measurements for the five concentrations of corn stover MFC gels are presented in Figure 5. The linear range of all the measured concentrations of the samples was small, around 1% or less of the shear strain, which indicated that the corn stover MFC gels were networks, so-called "weak" gels.[20] A "weak" gel is cross-linked together by linkages that are relatively stronger and more permanent than entanglements, while a gel formed by chain-chain entanglement is characteristic of a "strong" gel. However, a "weak" gel is extremely susceptible to disruption, while an entangled "strong" gel can have a linear range to 20% or more. Cross-linkers can be classified as covalent or physical junctions. To further support the evidence that the corn stover MFC gels are physical gels, we conducted stress relaxation measurements. The stress relaxation experiments showed that the corn stover MFC gels had long relaxation times. The 0.25% corn stover MFC gel relaxed quickly after 700 s, and was nearly fully relaxed after 1000 s. Higher concentrations of corn stover MFCs relaxed even less than a decade after 1000 s (Fig. 6). This result indicated that the corn stover MFC gels are physically cross-linked gels, not chemically cross-linked ones, even though they have long relaxation times. If a network is tightly cross-linked chemically, one should rarely see any relaxation and relaxation time should be infinite. The results are also consistent with the above conclusion that the corn stover MFC gels are physical gels that conform to the power law model. The behavior of the MFC gels could be manipulated and controlled by adjusting the concentration. The linear rheological properties that we investigated above for the corn stover MFC gels are similar to those for some of the cosmetic gels[21,22] and wound healing materials.[23-25] To better understand the processing behavior, the non-linear steady shear viscoelastic properties for the five concentrations of corn stover MFC gels were studied. All of the studied corn stover MFC gels exhibited shear-thinning behavior over the entire measured shear rates (Fig. 7). Shear-thinning rheological behavior can be characterized by the Ostwald-de Waele Power-Law Constitutive Equation.[26] The Power-Law Constitutive Equation may be written as follows:

$$\eta = K\dot{\gamma}^{\,n-1} \qquad (1)$$

where η is the shear viscosity, K is the flow consistency index or front factor, $\dot{\gamma}$ is the shear rate and n is the flow behavior index or Power-Law exponent. The flow behavior index n represents the extent of shear-thinning. The value of n = 1.0 is for the Newtonian fluid without shear-thinning behavior; the value of n < 1 is for the non-Newtonian polymers exhibiting shear-thinning behavior.

We used Equation (1) to fit the viscosity for all the measured samples. The experimental data were very well fitted by the Power-Law Constitutive Equation (Fig. 7). The results of the fits are summarized in Table 1. For the 0.25% corn stover MFC gel, the Power-Law exponent was equal to 0.10 (Table 1).

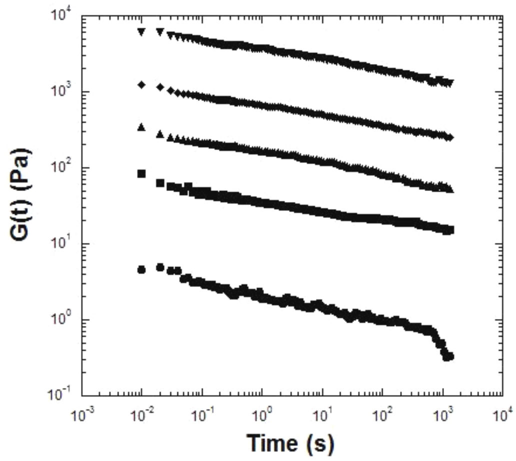

Figure 6: Stress relaxation measurements for corn stover MFC gels after being subjected to a step 0.5% strain at 25 °C; (●): 0.25 wt% corn stover MFC gel, (■): 0.5 wt% corn stover MFC gel, (▲): 1 wt% corn stover MFC gel, (♦): 1.5 wt% corn stover MFC gel, (▼): 2 wt% corn stover MFC gel

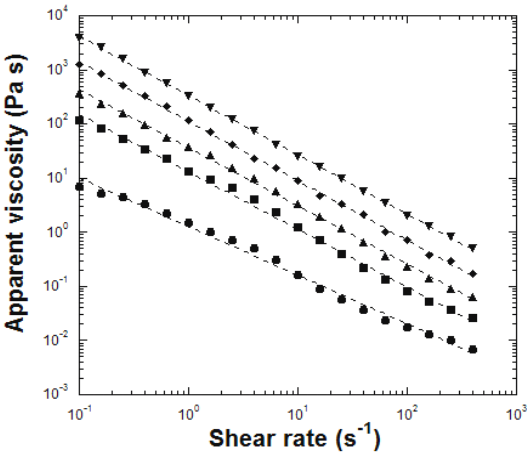

Figure 7: Non-linear viscoelastic properties of steady shear measurements for corn stover MFC gels at the temperature of 25 °C. Symbols are experimental results. Dashed lines are fitted with Power-Law model. (●): 0.25 wt% corn stover MFC gel, (■): 0.5 wt% corn stover MFC gel, (▲): 1 wt% corn stover MFC gel, (♦): 1.5 wt% corn stover MFC gel, (▼): 2 wt% corn stover MFC gel

Table 1
Power Law model parameters, flow consistency index, *K*, and flow behavior index, *n*, for the corn stover MFC gels

Concentration (wt%)	*K* (Pa s) 95% C. I.	*n* 95% C. I.	R^2
0.25	1.30 (1.28, 1.32)	0.10 (0.09, 0.11)	0.96
0.5	15.1 (15.0, 15.2)	0.06 (0.05, 0.07)	0.99
1.0	42.9 (42.7, 43.1)	0.06 (0.05, 0.07)	0.99
1.5	110.8 (110.7, 110.9)	0.06 (0.05, 0.07)	0.99
2.0	301.2 (300.9, 301.5)	0.06 (0.05, 0.07)	0.99

The shear-thinning extent became slightly stronger with increased concentration, 0.06 for all the other four concentration MFC gels (Table 1). The viscosities of the corn stover MFC gels increased with increasing concentration, and the viscosities had a tremendous increase from 0.25-0.5%, which was the same trend as the linear rheological properties dependence on concentration stated above. The non-linear rheological properties for corn stover MFC gels are also similar to those of cosmetic gels[27] and wound healing materials.[23-25] Thus, both the linear and non-linear viscoelastic behaviors studied in this work suggest that the corn stover MFC gels should be good candidates for cosmetic and wound healing applications.

CONCLUSION

The linear and non-linear rheological properties of corn stover MFC gels were investigated. The materials exhibited viscoelastic solid behaviors and their properties could be controlled by varying the concentration. The corn stover MFC gels were physical gels, which followed the physical gel Power-Law model. The stress relaxation studies also supported the hypothesis that the corn stover MFC gels were physical networks. The linear and non-linear viscoelastic behaviors for the corn stover MFC gels were similar to those of some cosmetic and wound healing gels, which suggested that this nanocellulose material can be a good candidate for developing cosmetic and skin wound healing products.

ACKNOWLEDGMENT: The authors thank Ms. Elizabeth F. Krietemeyer and Mr. Robert Caughey for their technical assistance. This work was financially supported by the United States Department of Agriculture, Agricultural Research Service.

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