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Preparation and characterization of cellulose gels from corn cobs[☆]

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ABSTRACT

Aqueous cellulose gels were prepared by extraction of ground corn cobs with hot aqueous sodium hydroxide/sodium hypochlorite and shearing. Initial shearing in a blender broke up cob tissue structure into individual cells and resulted in a gel. Subsequent shearing in a high pressure homogenizer increased viscosity by 50–100×. Rheological studies showed all samples were gel-like from 0.5 to 2.0% and that G' increased following a power law with exponents of 3.7 and 3.2 for blended and homogenized samples, respectively. G' and G'' were maximal after two passes through the homogenizer and were about ten times larger than typical literature values for microfibrillar cellulose suspensions. SEM and AFM of two-pass sample showed networks of microfibrils and larger expanded fibrillar aggregates while bundles of more separate microfibrils were observed after eight passes. These results should improve understanding of the relationships between processing, morphology and properties of cellulose from corn stover and lead to new applications.

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1. Introduction

Cellulose gels can be produced in a number of ways such as solvent exchanging a cellulose solution with water (Chang & Zhang, 2011), extraction/concentration of bacterial cellulose (Czaja, Young, Kawecki, & Malcom, 2007) and high shear processes (Yano, 2005). Herrick, Casebier, Hamilton, and Sandberg (1983) and Turbak, Snyder, and Sandberg (1983) first described the shearing of refined wood pulp with a high pressure homogenizer to prepare gels and termed this microfibrillar cellulose (MFC). MFC has been the subject of a number of recent reviews (Kamel, 2007; van Siro & Plackett, 2010; Yano, 2005) and consists of lateral aggregates of cellulose microfibrils with widths typically 20–40 nm and lengths of several μm. MFC is usually prepared by chemical or enzymatic refining of wood or other lignocellulosic feedstock to at least partially remove lignin and hemicellulose followed by mechanical disruption. MFC has some extraordinary properties such as theoretical strength as high as 5 GPa and modulus of 114–130 GPa (Hepworth & Bruce, 2000; Hsieh, Yano, Nogi, & Eichhorn, 2008). Other properties include high surface area and water absorption (Spence, Venditti, Rojas, Habibi, & Pawlak, 2010), optical transparency of films (Fukuzumi, Saito, Wata, Kumanmoto, & Isogai, 2009), and ability to form gels (Turbak et al., 1983). Applications can include polymer reinforcement (Bruce, Hobson, Farrent, & Hepworth, 2005; Malainine, Mahrouz, & Dufresne, 2005; van Siro & Plackett, 2010), transparent "paper", suspending or thickening agents (Ougiya, Watanabe, Morinaga, & Yoshinaga, 1997; Turbak et al., 1983), insoluble dietary fiber (Lundberg et al., 2006), filtration (Ruan, Lun, Addis, & Chen, 1996), etc.

Rheological properties of aqueous MFC suspensions isolated from softwood (Iotti, Gregersen, Moe, & Lenes, 2010; Paakko et al., 2007), sugar beet pulp (Agoda-Tandjawa et al., 2010; Lowys, Desbrieres, & Rinaudo, 2001) and cotton (Tatsumi, Ishioka, & Matsumoto, 2002) have been studied. Results indicated that MFC suspensions are gel-like over a wide concentration range (>0.25%) with G' scaling with concentration to power of 2.25–3.0 (Agoda-Tandjawa et al., 2010; Paakko et al., 2007; Tatsumi et al., 2002). Gels are formed as a result of hydrogen bonded-networks of shear-induced microfibrils as visualized using TEM and AFM (Paakko et al., 2007). MFC gels are shear thinning but show hysteresis at low shear (0–1000s^{-1}) and dilatancy at very high shear (180,000–330,000 s^{-1}) (Iotti et al., 2010). There have been no studies showing how intensity of shear during MFC preparation influences the resulting rheological properties.

Corn stover (cob, stalks) and corn fiber or bran (outer covering of corn kernel) represent a large underutilized source of cellulose. Reddy and Yang (2005) have reported on preparation and

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[☆] Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and use of the name by USDA implies no approval of the product to the exclusion of other that may also be suitable.

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properties of native cellulose fibers from corn husks. Few studies have, however, reported on preparation and properties of cellulose gels from these sources. Ruan et al. (1996) extracted corn cobs and husks with hot aqueous NaOH, bleaching with hydrogen peroxide followed by 10 passes through a homogenizer (Gaulin) at 35–40 MPa (5000–6000 psi). SEM's suggested partial fibrillation with some larger particles still present. The only property measured was water holding capacity of the cellulose gels. Subsequent work (Lundberg et al., 2006) included characterization of surface area. Inglett (1998) and Inglett and Carriere (2001) treated corn bran with aqueous sodium hydroxide in a blender, extruder or other device followed by bleaching with hydrogen peroxide to give cellulose gels. Morphology was that of 25–50 μm sized swollen spheres so there was no fibrillation detected. Rheological properties were characterized and utility in various foods as a thickener was demonstrated. Agblevor, Ibrahim, and El-Zawawy (2007) prepared microcrystalline cellulose by heating corn cobs with 1 M sulfuric acid at 90 °C. Thus, there have been few detailed studies of cellulose gels from corn stover and there is little understanding of the relationship between morphology and rheological properties of corn stover cellulose gels.

The purpose of this study was to determine the effects of shear history on the morphology and rheological properties of cellulose gels from corn cobs. Cellulose was isolated and purified from corn cobs by successive hot aqueous NaOH extractions followed by NaOCl bleaching. Gels were formed by a moderate shear process (blender) and high shear homogenizer (1–8 passes). Morphology was assessed by SEM and AFM. Rheological properties were measured by a parallel plate rheometer.

2. Materials and methods

2.1. Materials

Corn (*Zea mays*) was obtained from a local field, kernels were removed manually, cobs were air dried then ground in a Thomas mill with a 2 mm screen. Moisture content was 7%. Chemicals (sodium hydroxide, 25% aqueous sodium hypochlorite) were reagent grade from Sigma–Aldrich.

2.2. Preparation of cellulose gels

The cellulose purification procedure was similar to that of Siqueira, Bras, and Dufresne (2009). Ground cobs (220 g) and 2 l of 1 M NaOH were added to a resin flask and heated at 80 °C with slow stirring for 2 h. After cooling, suspension was filtered with Whatman 541 paper (hardened, ashless cellulose with 22 μm pore size) then washed exhaustively with water. The NaOH extraction was then repeated two times followed by two extractions with 0.6% NaOCl for 2 h at 80 °C. The white, water-swollen cellulose gel (11% solids) was stored wet in a refrigerator.

Initial reduction in particle size of the cellulose was performed by shearing a 2% suspension in water in a Waring blender on high for 1 min. This gave a gel-like material. Further reduction in particle size was conducted using a Panda 2K high pressure homogenizer (Gea Niro Soavi, Hudson, WI) at approximately 1000 bar. In these experiments, the blended cellulose was diluted to 0.5% to reduce viscosity. Even at this low concentration, the cellulose suspension formed a gel after initial passage through the homogenizer so a pressurized feed tank was necessary for subsequent passes. Total number of passes through the homogenizer was 1–8. Temperatures of the gels were maintained at 50–60 °C by cooling in an ice bath between passes. Concentration of cellulose in suspensions/gels was measured by drying in an oven for 30 min at 110 °C, 1 h at 110 °C in vacuo then weighing.

2.3. Compositional analyses

Carbohydrate composition of cellulose was determined after sulfuric acid hydrolysis by HPLC analysis (Biorad HPX-87P and HPX-87H, Bio-Rad Labs, Hercules, CA) following an NREL LAP (Sluiter et al., 2008).

2.4. Polarized light microscopy

Aqueous dispersion of samples (~0.5%) on glass slides were observed at 100–400× between crossed polarizers using an Olympus CX31-P microscope (Olympus America, Inc., Center Valley, PA).

2.5. Scanning electron microscopy and sample preparation

Cellulose samples were diluted to 0.05% with water then a drop was placed on a piece of glass cover slip and air dried. This was then affixed to an aluminum stub using carbon filled tape and the assembly was coated with Au. Specimens were examined with a JEOL 6400V scanning electron microscope (JEOL USA, Inc., Peabody, MA).

2.6. Atomic force microscopy

Aqueous cellulose gels were diluted to 0.05% and aliquoted onto freshly cleaved mica and allowed to dry. Micrographs were obtained using a Veeco Nanoscope IV microscope and controller (Veeco Instruments, Santa Barbara, CA) in tapping mode. Scans were taken at rates of 0.5–2 Hz.

2.7. X-ray diffraction

X-ray powder diffraction was carried out using a Philips PW1820/1830 goniometer/generator (PANalytical, Bollingbrook, IL). Powder samples were scanned from 3 to 30 degrees 2 theta in 0.05 degree steps at 8 s per step. Samples were equilibrated at 23 °C and 50% r.h. for 2 days prior to analysis.

2.8. Rheology

Blended samples of 0.5, 1.0 and 2.0% cellulose concentration (B1, B2 and B3, respectively, in Fig. 5) were prepared by dilution of the original blended 2% sample with water. One-pass homogenized samples of 0.5, 1.0 and 2.0% cellulose concentration (H1, H2 and H3 respectively in Fig. 5) were prepared by concentration of 0.5% one-pass sample by filtration. Measurements were also conducted on 0.5% samples after 1–8 passes through the homogenizer (Fig. 7).

Dynamic rheology was measured using a Rheometrics ARES Series V fluids system controlled-strain rheometer driven by Rheometrics Orchestrator version 7.2.0.2 software (TA Instruments, New Castle, DE). Stainless steel parallel plate geometry was used with two different sizes; 25 and 50 mm diameter. The 25 mm diameter plates were used for the high viscosity 1 and 2% homogenized samples and the 50 mm diameter plates were needed to increase the response of the lower viscosity (all three blended and the 0.5% homogenized) samples. The gap ranged from 1.2 to 1.9 mm. Initially each sample underwent a strain sweep from 0.1 to 10% at 25 °C and a frequency of 1 Hz to determine the linear viscoelastic range. Strains of either 0.5 or 1.0%, both of which were clearly in the linear viscoelastic range, were used for the frequency sweeps. In the frequency sweep experiments, G' and G'', the storage and loss moduli, respectively, were measured at 25 °C. Each sample was allowed to rest for 5 min before testing. Shear viscosity was also tested by increasing the shear rate from 0.01 to 100 s^{-1} at 25 °C. In that experiment the measurement time was 10 s with a 15 s delay before each data point. Temperature sweep experiments measured the storage and loss moduli from 20–80 °C at a frequency of 1 Hz and 1% strain at a ramp rate of +1 °C per minute.

3. Results and discussion

3.1. Composition and structure of corn cob cellulose

Yield of cellulose was 55 g or 27% of the total weight of the starting ground corn cob. The cellulose content of corn cobs is about 35% (Duguid et al., 2009) so this represents 77% of the theoretical yield. Compositional analysis was (by weight) 89% glucose, 9% xylose, 0.1% arabinose and 0.4% mannose. No galactose, glucuronic acid or lignin was detected. pH of the cellulose/water gels was 6.0–6.5.

X-ray powder diffraction of purified corn cob cellulose and ground corn cobs are shown in Fig. 1. For cellulose, peaks were observed at 16 and 22 degrees two theta. This pattern is characteristic of cellulose I and is typical of cellulose isolated from other fiber sources (Abe & Yano, 2010). The pattern for corn cobs is similar but broader due to the presence of non-crystalline hemicelluloses and lignin.

Polarized light micrographs of cellulose samples are shown in Fig. 2. Large aggregates of fibrous tissue were observed for cellulose after alkali/bleach treatment (Fig. 1A). After blending for 1 min (Fig. 1B), individual rod and oval shaped particles about 30–500 μm long were observed. These likely correspond to different individual cells and fragments thereof which constitute corn cob structure. After 1 pass through the high pressure homogenizer (HPH) (Fig. 1C), cellulose particles were visibly reduced in frequency and size to 5–50 μm. After 2 passes (1D) few particles could be observed by light microscopy.

Scanning electron micrographs for the cellulose after 1, 2, 3 and 8 passes through the high pressure homogenizer at 0.5% concentration are shown in Fig. 3. After high pressure homogenization, aggregates composed of fibrils approximately 0.5–1 μm wide as well as flatter structures were noted. As the number of passes increased, the size and relative abundance of structures visible in the SEM decreased. After 8 passes, no fibrils were visible suggesting that all cellulose had been converted to microfibrils or particles smaller than the resolving power of the SEM.

Atomic force micrographs in height mode for cellulose after 2 and 8 passes through the homogenizer are shown in Fig. 4. A large scale (25 μm × 25 μm) scan of the 2 pass sample (Fig. 4A) shows the presence of fibril networks and aggregates. A smaller scale scan (1 μm × 1 μm) of the 2 pass sample (Fig. 4B) shows a web-like network of microfibrils about 5 nm wide and larger fibrils 20–100 nm wide. MFC is typically visualized in the AFM or TEM as networks of microfibrils and microfibril aggregates having widths of 5–40 nm (Paakko et al., 2007). It was difficult to estimate lengths of individual microfibrils or fibrils since they form frequent junctions (Fig. 4A and B). After 8 passes, a large scale scan (Fig. 4C) showed the presence of fibril aggregates as in Fig. 4A but some separate fibrils up to

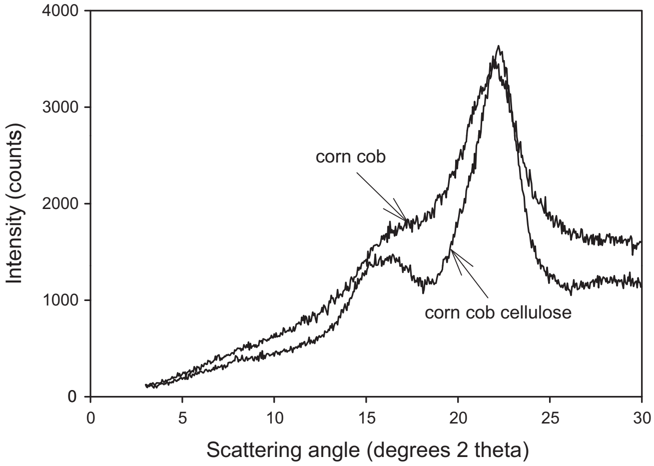

Fig. 1. X-ray powder diffraction of ground corn cobs and purified corn cob cellulose.

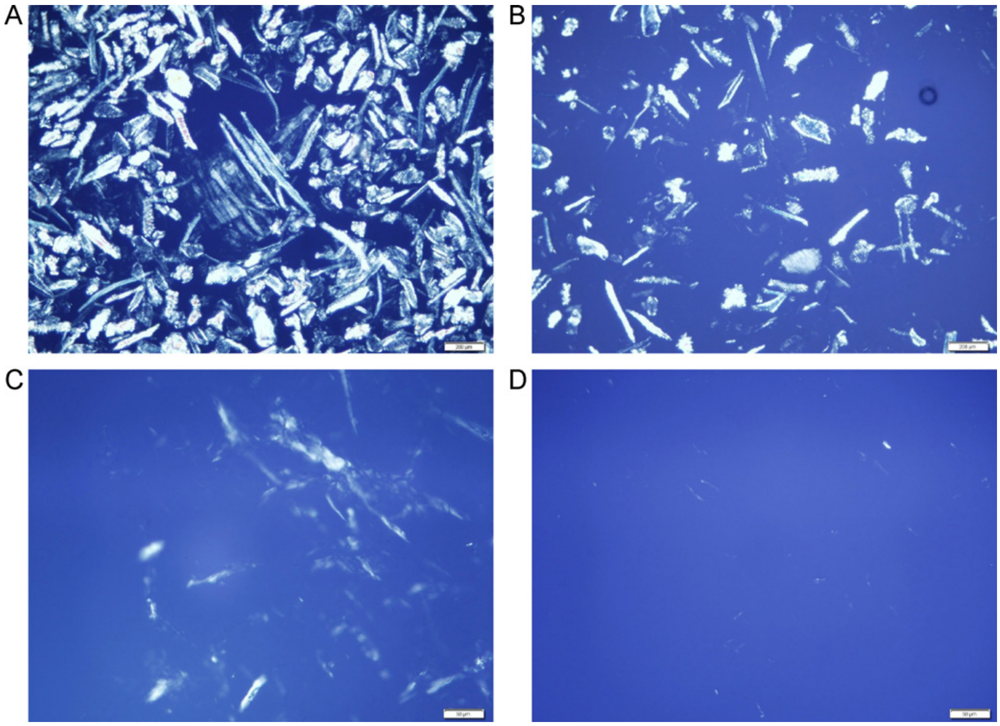

Fig. 2. Polarized light microscopy of corn cob cellulose after aqueous NaOH/NaOCl extraction (A), 1 min blending (B), HPH 1 pass (C) and HPH 2 passes (D). Magnifications are 100× (A and B) and 400× (B and C); scale bar is 200 μm in A and B and 50 μm in C and D.

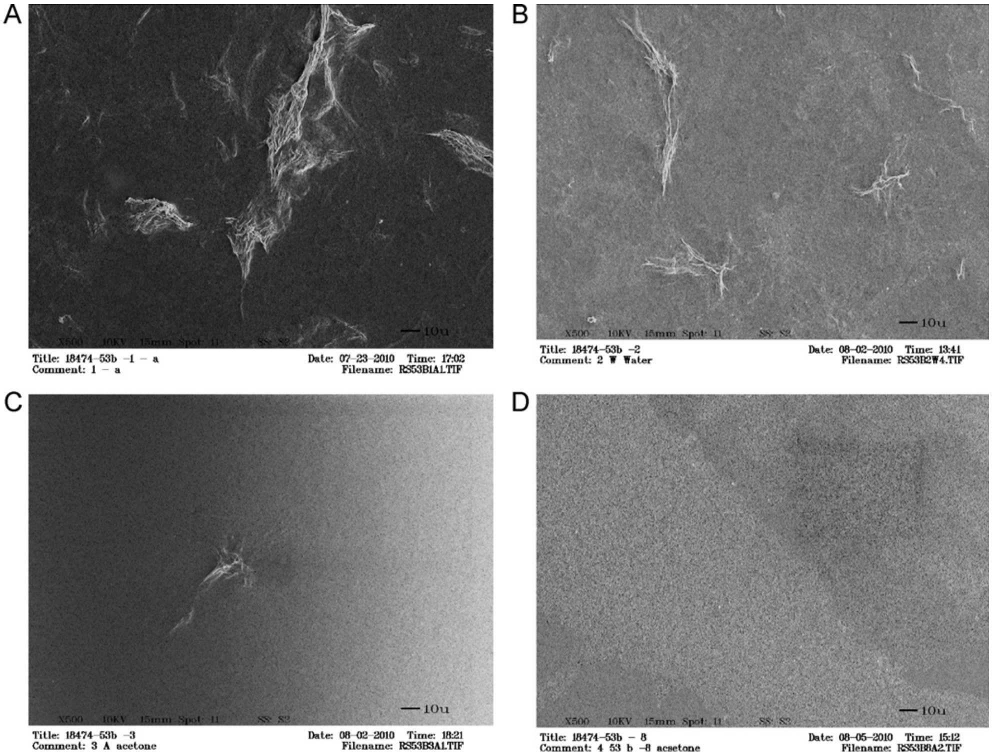

Fig. 3. SEM's of corn cob cellulose after *x* passes through high pressure homogenizer (HPH): $x = 1$ (A), $x = 2$ (B), $x = 3$ (C) and $x = 8$ (D). Magnifications were all 500× and scale bar was 10 µm.

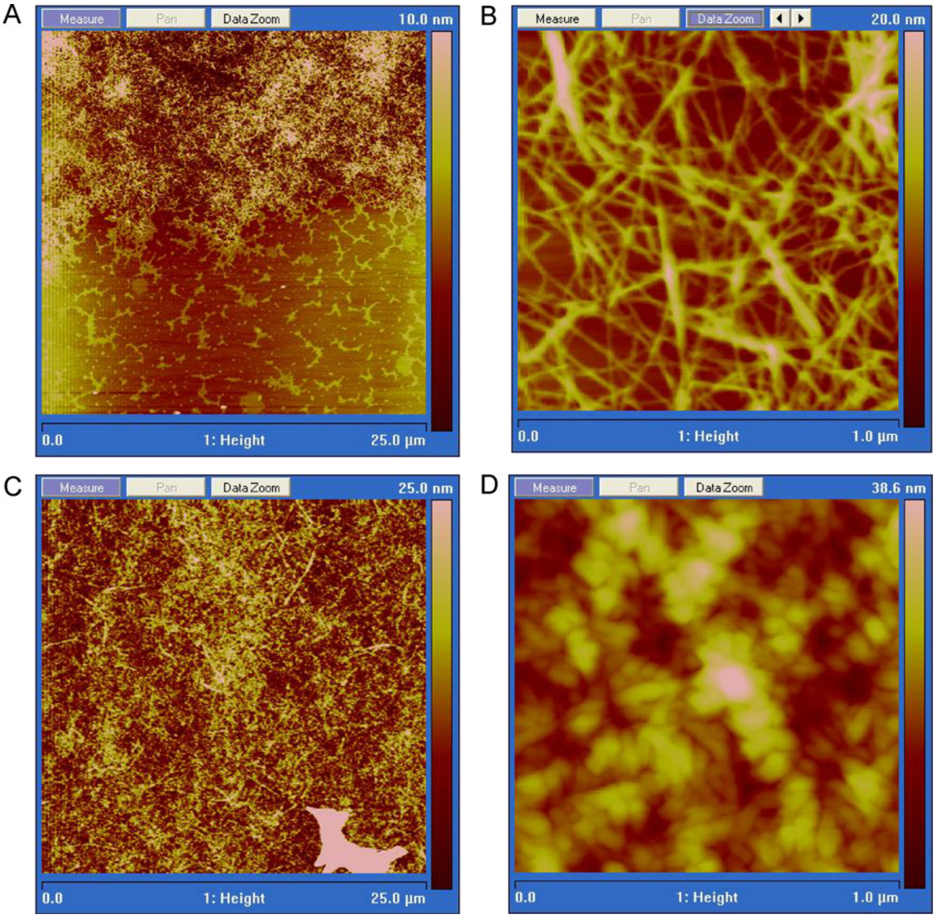

Fig. 4. AFM of cellulose after 2 (A and B) and 8 passes (C and D) through homogenizer. Scan area 25 µm × 25 µm for A and C and 1 µm × 1 µm for B and D.

about 5 μm long were also evident. For the 8 pass sample at small scale (Fig. 4D), clumps of fibrils 30–60 nm in width were observed. The fibers appeared to be curved rather than straight for the 2 pass sample and distinct junction zones were not observed as in the 2 pass sample. A possible explanation for these observations was that fibril network was disrupted into individual, shorter pieces after more homogenization and these shorter pieces then could fold and laterally aggregate into bundles like tangled rope. This hypothesis is consistent with previous findings of decrease in cellulose molecular weight (Henriksson, Henriksson, Berglund, & Lindstrom, 2007) and gradual dispersion of fibrils into microfibrils (Nakagaito & Yano, 2004) after many passes through a homogenizer.

3.2. Rheology of corn cob cellulose gels

Storage and loss moduli (G', G'') for cellulose suspensions after blending and high pressure homogenization (1 pass) are shown in Fig. 5. It was found that G' and G'' were relatively independent of angular frequency except for the most dilute (0.5%) blended sample. This behavior indicates the materials behaved as elastic gels since G' is independent of frequency for ideal gels or springs. It is also noted from Fig. 5 that $G' \gg G''$ and this is also characteristic of gel-like materials. G'/G'' were 4–7 for blended samples and 6–8 for homogenized (1 pass) samples. In contrast, for viscous liquids, G' is proportional to ω^2, G'' is proportional to ω and $G' \ll G''$. Cellulose fibrils and microfibrils are known to hydrogen bond strongly with each other and this creates the physical cross-links leading to gel formation (Agoda-Tandjawa et al., 2010; Iotti et al., 2010; Liu, Chen, Yue, Chen, & Wu, 2011; Paakko et al., 2007). At the same concentrations, G' and G'' for the high pressure homogenized samples were larger than those for the blended samples by factors of 50–100. This is due to the more expanded and fibrillated structure of the high pressure homogenized sample (see optical micrographs in Fig. 2) and to the structure formed between the single fibrils of MFC through hydrogen bonds.

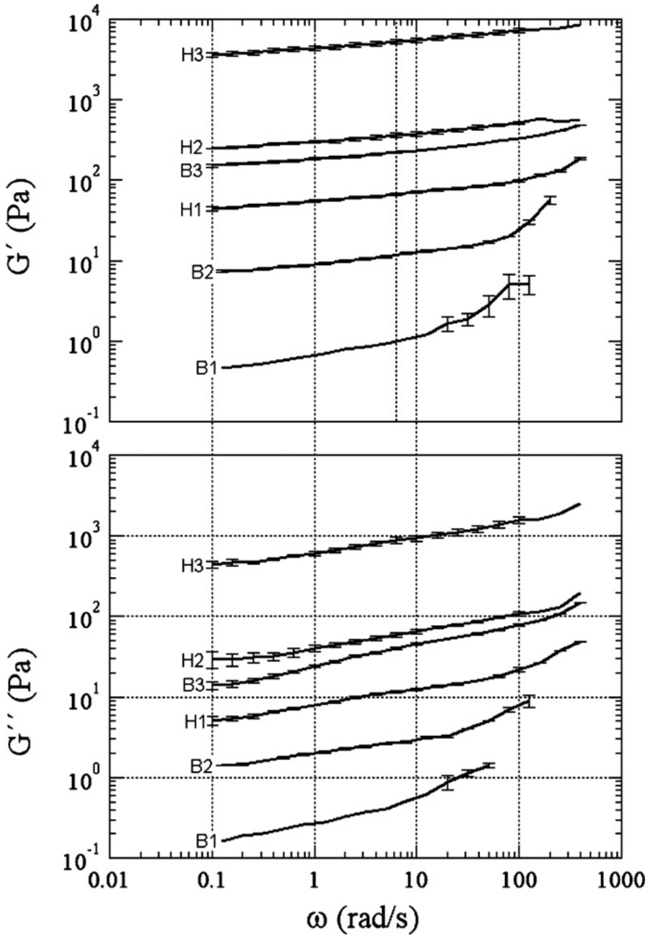

Fig. 5. Storage (G') and loss (G'') moduli for cellulose gels made by blending (B1 = 0.5%, B2 = 1.0%, B3 = 2.0%) and high pressure homogenization (H1 = 0.5%, H2 = 1.0%, H3 = 2.0%).

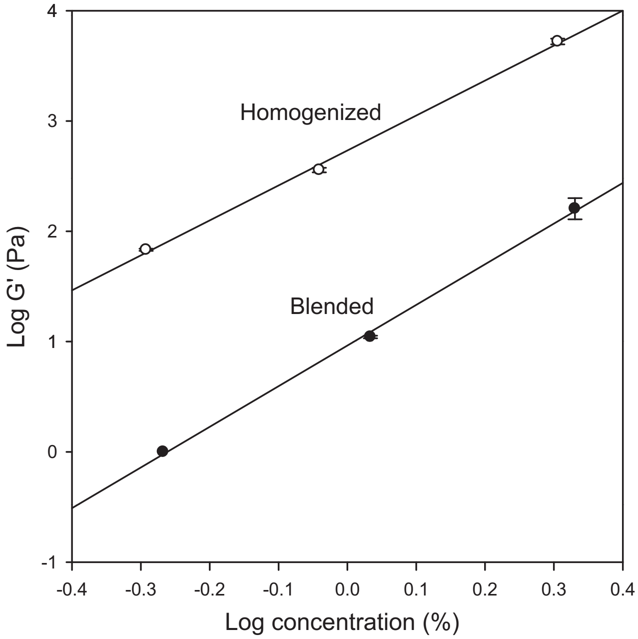

Fig. 6. Effect of concentration on G' for blended and homogenized cellulose gels.

The concentration dependence of G' is shown as double logarithmic plots in Fig. 6. Slopes of the lines were 3.2 and 3.7 for homogenized (1 pass) and blended samples, respectively. These values correspond to n in the scaling relation $G' = k\varphi^n$. For rodlike particles, n is predicted to be near 2 while the behavior of more complex branched networks can be predicted by the model of Jones and Marques, $G' = k\varphi^{(3+D_f)(3-D_f)}$ where D_f is the fractal dimension (Guenet, 2000; Paakko et al., 2007). This relation suggests fractal dimensions of approximately 1.6 and 1.8 for homogenized and blended samples, respectively. Values of $n \sim 3$ and $D_f \sim 1.5$ were found for MFC from wood (Paakko et al., 2007) while $n = 2.58$ and $D_f = 1.3$ were found for MFC from sugar beet pulp (Agoda-Tandjawa et al., 2010). The slightly higher values of D_f for corn cob cellulose suggest more branched or rounded cellulose particles than for more rodlike MFC. This may reflect the incomplete disruption of cellulose fibrillar networks into individual microfibrils for the 1 pass sample.

A plot of G' for 0.5% cellulose dispersions measured at 2.5 rad/s versus number of passes is shown in Fig. 7. G' increased to a maximum of 320 Pa after 2 passes followed by a decline. The maximum in G' is likely due to the presence of large fibrillar aggregates which have been disrupted enough to hydrogen bond strongly with each other. Further homogenization, however, disrupts these aggregates into smaller cellulose microfibrils and fragments which form weaker gels. Steady shear viscosity was also maximal for 0.5% cellulose suspensions (>1000 Pa s) after 2–3 passes through the homogenizer (data not shown).

Comparison of some values of G', G'' and η for corn cob cellulose gels with data for prior studies is shown in Table 1. G' for blended corn cob cellulose gels were lower than literature values for MFC gels while G', G'' and η for homogenized (2 pass) corn cob cellulose gels at 0.5% cellulose concentration were about 10× larger than for previous reports for MFC gels. It is likely that large microfib-

Table 1
Comparison of rheology of aqueous cellulose gels.

Source	Processing	Concentration (%)	G' (Pa)	G'' (Pa)	η (Pa s)	Authors
Corn cobs	Blender	0.5	0.7	0.3	–	This work
Corn cobs	HPH, 2 passes	0.5	300	30	150	This work
Softwood	HPH, 8 passes	0.5	20	3	10	Paakko et al. (2007)
Sugar beet pulp	HPH, 10 passes	0.5	30	3	8	Agoda-Tandjawa et al. (2010)
Softwood	HPH, 10 passes	1.0	150	30	30 (0.1 s^{-1})	Iotti et al. (2010)
Corn bran	Colloid mill	3.0	250–700	–	–	Inglett and Carriere (2001)

Note: HPH denotes high pressure homogenizer; G', G'' measured at 1 rad/s; η measured at 0.01 s^{-1}.

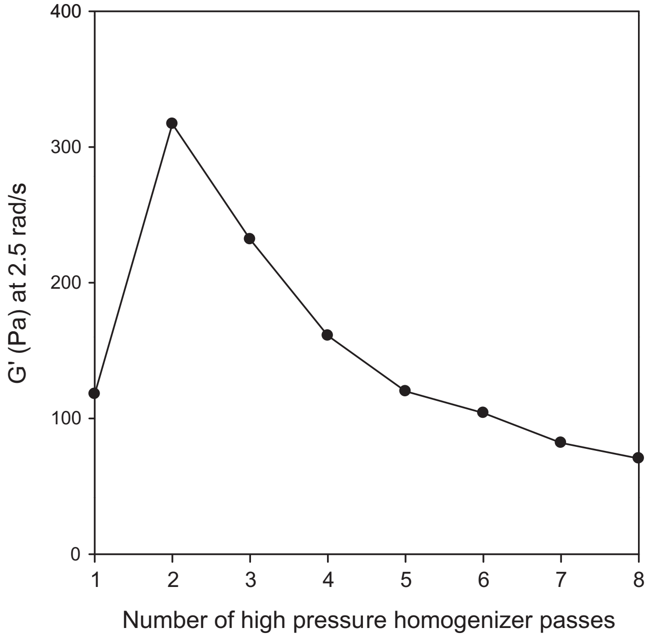

Fig. 7. Effect of number of passes through the homogenizer on G' for 0.5% cellulose gels.

rillar aggregates present in the 2 pass sample could form stronger gels than well dispersed MFC gels. There may be, however, other differences between the structure of cellulose from corn cobs and wood used in previous studies. For instance, processing of wood by the kraft process for example occurs at higher temperatures than used here so there might have been more fiber degradation. Also, since cellulose microfibrils are less tightly wound in parenchyma cell walls in corn cobs compared to long fibrous woody cell walls (Dinand, Chanzy, & Vignon, 1996; van Siro & Plackett, 2010), less mechanical energy may be required to dissociate microfibrils and hence less fiber degradation may have occurred. It should also be noted that rheological data were measured for the corn cob cellulose 2 pass sample in Table 1 at 0.5% only. Thus, comparison of viscoelastic properties of higher concentrations with literature results could be different due to changing interparticle hydrogen bonding with particle size, separation distance and surface area.

4. Conclusions

In summary, corn cob cellulose gels having a wide range of elastic moduli (10^0–10^4 Pa) were prepared by varying the degree of shear and cellulose concentration. Moduli and viscosity of 0.5% cellulose in water dispersions showed a maximum after 2 passes through the high pressure homogenizer and this was likely due the presence of microfibril aggregates. Such swollen aggregates may account for the much higher moduli measured for these gels than for well-dispersed MFC gels previously reported although other factors such as cellulose microfibril length and composition could also be involved. Due to the abundance and low cost of corn cobs, cellulose gels made from this source could well be suitable for many applications in food, cosmetics, etc.

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