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ORIGINAL PAPER

Fabrication of microfibrillated cellulose gel from waste pulp sludge via mild maceration combined with mechanical shearing

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Abstract This article describes a facile route, which combines mild maceration of waste pulp sludge and a mechanical shearing process, to prepare microfibrillated cellulose (MFC) with a high storage modulus. In the maceration, the mixture of glacial acetic acid and hydrogen peroxide was used to extract cellulose from never-dried waste pulp sludge. Then, two different mechanical processes including disc refining (DR) and ultrasonication plus homogenization (UH) were applied to the cellulose after maceration and resulted in MFC with a highly tangled fibril network. All of the resultant cellulosic suspensions (2 % w/w) exhibited a gel-like and shear-thinning behavior with storage moduli (G') ranging from 200 to 4000 Pa. Among them, the 30-min DR-treated MFC gels had the maximum G', which was much higher than for previously reported MFC gels at the same concentration. Additionally, after mechanical processing, specific surface areas and water retention values of MFC were accordingly increased with the enhancement of shear force, while the storage moduli (G') were not consistently increased. Finally, a strong MFC gel was successfully prepared from never-dried waste pulp sludge via a one-step disc refining process and using cost-effective chemicals. The obtained hydrogels will have potential as low-density reinforcing fillers or as a template for further surface modification.

Keywords Microfibrillated cellulose (MFC) · Disc refining · Ultrasonication plus homogenization · Storage modulus

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Introduction

Microfibrillated cellulose (MFC) has attracted significant interest because of its biocompatibility, biodegradability, strong mechanical properties, and highly porous network structure (Lavoine et al. 2012). Various applications of MFC can be found in composite materials (Iwamoto et al. 2007; Leitner et al. 2007; Medeiros et al. 2008; Siró and Plackett 2010), fire barrier materials (Liu et al. 2011), nanopapers (Henriksson et al. 2008; Wang et al. 2015b), and hydrogels (Czaja et al. 2006; Nair et al. 2014). Cellulosic fiber, the most abundant natural resource to produce MFC, has an elaborately hierarchical structure composed of cellulose chains, elementary fibrils, microfibrils, and macrofibrils (Meier 1962). In order to obtain MFC, cellulosic fibers are usually unraveled to expose smaller fibrils and microfibrils; the latter have diameters from 10 to 100 nm as observed by scanning electronic microscope (Herrick

et al. 1983; Wang et al. 2012a). When cellulosic material reaches the micro- or nano-scale, its surface area will be dramatically increased. The augmented surface area can significantly improve the interaction between cellulose and surrounding species, which will facilitate its chemical modification or dispersion in other polymer matrices. Therefore, fibrillating cellulose to MFC has considerably expanded the application of cellulose materials.

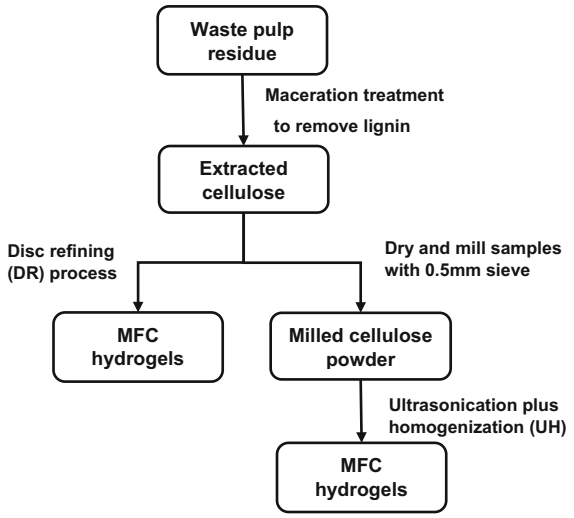
Various methods including chemical, biological, mechanical approaches or their combinations have been attempted to fibrillate cellulose into a nano- or micro-scale. For example, cellulose nanocrystals (CNCs) were produced by strong mineral acid hydrolysis and following mechanical treatments (Chen et al. 2015; Huntley et al. 2015; Pan et al. 2013; Wang et al. 2012b). In cellulose, there exist ordered and disordered regions (Osullivan 1997), and the latter is much easier to be hydrolyzed by strong acid. During hydrolysis, amorphous cellulose chains are easily broken, yielding CNCs with a low aspect ratio, which may not be favorable for polymer reinforcement. Strong acid could also result in the corrosion of devices. In addition, a solely mechanical shearing process was typically used to prepare MFC, which could yield final products with thixotropic viscosity and stable gel properties due to strong entanglement among relatively high-aspect-ratio fibrils or microfibrils. However, it has been greatly impeded by extensive energy consumption for solely mechanical fibrillation (Wang et al. 2012a). Various chemical or biological pretreatments like TEMPO-mediated oxidation (Saito and Isogai 2004), ionic liquid treatment (Li et al. 2012), and enzyme hydrolysis (Henriksson et al. 2007; Wang et al. 2015a) have been applied to reduce energy input. For example, mild enzyme treatment followed by homogenization was reported to not only preserve long fibrils, but also reduce total energy consumption (Paakko et al. 2007). The resultant MFC gels had high storage moduli (10^5 Pa at a 5.9 % w/w concentration and 10^3 Pa at a 2 % w/w concentration) and an extensively tangled network structure. Zhu et al. further studied the effects of different types of enzyme, and the results showed that the fiber length strongly depended on the enzyme type (Wang et al. 2015a). The introduction of appropriate chemical and enzyme pretreatment does assist the fibrillation and greatly reduced the energy input; however, the cost of chemicals or enzymes needs to be considered.

In addition, currently reported MFC processes mainly used expensive bleached wood fibers as the feedstock. Therefore, it is important to seek an alternative and cost-effective feedstock for the preparation of MFC. In contrast to these processes, this study used never-dried waste fiber residues, which were treated by a mild maceration process and following two different mechanical shearing processes. These residues were gathered from the waste stream of the process to manufacture specialty wood cellulose or fluffy pulp. They had higher lignin content than bleached wood fibers. To remove lignin, we introduced a mild maceration method in this study, which was originally used in wood anatomy to characterize wood structure (Chamberlain 1905). Our rationale is that maceration using a mixed solvent containing acetic acid and hydrogen peroxide under mild conditions can effectively remove lignin from waste fiber sludge to extract cellulose and also minimize the size reduction of cellulosic fibers. The mixture of acetic acid and hydrogen peroxide yields peracetic acid (PAA), which has high delignification selectivity, but the least effect on most fibers (Nada et al. 1999). The maceration is expected to reduce the energy consumption of the subsequent mechanical treatment because it removes lignin and disintegrates fiber bundles into separate long fibers. After maceration, we applied two different mechanical shearing processes containing one-step disc refining (DR) and a typical ultrasonication plus homogenization (UH) process (Scheme 1). We investigated the effects of various mechanical shearing parameters such as refining time, pass number of homogenization, and ultrasonication time on the properties of corresponding MFC gels. The mild maceration method plus one-step disc refining is expected to prepare strong MFC hydrogels with tunable storage moduli by controlling the mechanical shearing conditions. The one-step disc refining in a short time consumes less energy than a complicated ultrasonification plus homogenization (UH) process since the UH process usually requires a size reduction process prior to it.

Materials and methods

Materials

The waste pulp sludge (32.42 % dry weight) was kindly provided by Georgia-Pacific Inc. and served as



Scheme 1 Schematic overview of two methods to prepare MFC gels

the feedstock. It was collected from the last screening step of the process to manufacture specialty wood cellulose or fluffy pulp. The residues were delignified by a modified maceration method (Franklin 1945). Briefly, the waste pulp sludge with 5 % dry weight was added into the solvent containing an equal volume of glacial acetic acid (Acros 99.7 %) and hydrogen peroxide (Ricca 30 %). Then, the mixture was transferred to an incubator shaker (Innova 4000 Benchtop Incubator Shaker, New Brunswick Scientific, USA), and the incubating condition was set at 60 °C, 150 rpm for 48 h. After maceration, the product was washed by deionized water for several times until neutral pH. The chemical composition of residues before and after maceration was analyzed according to the standard from the National Renewable Energy Laboratory (NREL) (Sluiter et al. 2008). Purified cellulose was directly used for the DR process, while further size reduction using a hammer mill (Model 4, Wiley Laboratory, USA) equipped with a 0.5-mm mesh sieve was applied before the UH process to avoid the blocking of the homogenizer by long fibers.

Gel preparation by a disc refining (DR) method

Macerated cellulose was dispersed in deionized (DI) water at 2 % (w/w) consistency, and then this suspension was refined using a Supermasscolloider ultra-fine grinder (disc refiner, model: MKZA6-2, Disk model: MKGA6-80#, Masuko Sangyo Co., Ltd., Japan) at 1500 rpm. When the cellulose suspension was forced to pass through the gap between the rotor and stator discs, repeated cyclic stress was applied to fibers for fibrillation. The gap setting was −100 microns after loading of fibers. Two discs were not in contact even with negative settings due to the presence of fibers. Three different disc refining time periods of 30, 60, and 120 min were used.

Gel preparation by an ultrasonication plus homogenization (UH) process

Cellulose after milling was prepared to 2 % (w/w) suspension and further treated by high-intensity ultrasonication at 80 % of the system's maximal power under a continuous mode for 10, 20, and 30 min. The ultrasonic processor (Model 1500 W, 20 kHz, Sonic, Newtown, CT) was directly applied to the suspension in a 250-ml beaker. After sonication, cellulosic suspensions were passed through a high-pressure homogenizer (Model APV-1000, Spx Flow Technology Rosista GMBH, Germany) at 80 MPa internal pressure. The passing numbers were set at 10, 20, 30, and 40, respectively.

Optical microscopy characterization

An optical microscope (Leica DMR, Leica microsystems, Germany) at differential interference contrast mode was used to characterize morphological changes of cellulose after maceration and mechanical processes, respectively. The testing sample was prepared by diluting 1 ml MFC suspension in 4 ml deionized water and then mixed by a vortex mixer (Standard vortex mixer, Fisher Scientific, USA). After that, one or two drops of suspension were transferred to a glass slide covered with a micro cover glass and observed under the microscope at a magnification of 400.

Scanning electronic microscopy (SEM) characterization

The SEM (FEI XL 40 FEG SEM, FEI Instruments, USA, operating voltage 30 kV) was employed to examine the morphology of MFC at a higher magnification. First, the MFC suspension was diluted to 0.02 % (w/w), and then one drop of diluted suspension was placed on a SEM mount covered with a carbon tab. Samples were frozen by liquid nitrogen and

immediately vacuum dried by a freeze dryer (Freeze dryer 8, Labconco, USA). The lyophilization process was applied to avoid possible aggregation during a normal drying process, which preserved the morphology of MFC in a wet state (e.g., suspension or gel). Finally, freeze-dried samples were coated with Au–Pd (~10 nm) before SEM imaging.

Water retention value (WRV) measurement

The water retention value (WRV) is defined as the ratio of water remaining in the sample after centrifugation to its dry weight. In this study, water retention values (WRVs) of MFC at different mechanical shearing conditions were measured according to Method UM256 from the Technical Association of the Pulp and Paper Industry (TAPPI) with a slight modification. In brief, a stainless steel centrifuge holder was prepared in our laboratory, which had a membrane filter thimble with filter paper and 0.5-mm metal mesh located on the perforated bottom. First, the holder was pre-weighed (W_1). Then, the MFC suspension was uniformly poured into the holder, which was placed inside a 50-ml centrifuge tube and subjected to centrifugation for 30 min at 2600 rpm. After centrifugation, each holder containing the sample was re-weighed (W_2) immediately to prevent water evaporation. Finally, the holder containing the sample was dried in an oven at 105 °C overnight, and the dry weight (W_3) was measured. The WRV of each sample was calculated according to the following equation:

$$\mathrm{WRV} = (W_2 - W_3)/(W_3 - W_1)$$

A total of three replicates were performed for each sample.

Specific surface area (SSA) measurement

The specific surface areas (SSAs) of MFC gels were determined by N_2 sorption isotherms using a NOVA 1200 series volumetric gas adsorption instrument (Quantachrome, FL, USA) according to the Brunauer-Emmett-Teller (BET) theory (Brunauer et al. 1938). In a typical procedure, lyophilized MFC gels were first degassed in an outgas station at 40 °C overnight to remove moisture. Then, samples were loaded in a specific glass cell, which was submerged in liquid nitrogen, and the BET analysis was carried out in a relative vapor pressure range from 0.01 to 0.3 P/P_0 at −196 °C. The SSA was calculated from 6-recorded values.

Dynamic rheology measurement

The rheological properties of different MFC gels were characterized by a controlled strain rheometer (AR 2000, TA instrument, USA) equipped with a 40-mm steel plate geometry. The gap was set at 1 mm between the plate and plate geometry. First, the linear viscoelastic region of each sample was determined by a 0.1–100 % strain sweep at 1 Hz, and 2 % strain was chosen for all tested samples. Under this condition, frequency sweeps were carried out in a range of 0.1–100 Hz, and the corresponding moduli were recorded. In addition, the effect of shear rate on viscosity was also examined by a stepped flow method with the shear rate ranging from 0.1 to 100 1/s.

Results and discussion

Chemical composition analysis for the waste pulp sludge before and after maceration

Waste pulp sludge was treated by a modified maceration method to remove lignin. After maceration, a dramatic color change could be easily distinguished (Fig. 1), and composition analysis showed that the lignin radically dropped from 8.47 to 1.61 % (Table 1). The cellulosic content was increased from 80.35 to 94.81 %, while the hemicellulose content was reduced from 10.37 to 3.48 %. After maceration, as shown in Fig. 2, cellulosic fibers are composed of long fibers with a width ranging from 20 to 50 μm and a length of several hundred micrometers. In the maceration process, the mixture of acetic acid and hydrogen peroxide could yield peracetic acid (PAA). The above results indicated that the yielded PAA could effectively remove lignin and partially hydrolyze hemicelluloses and meanwhile retain the original cellulose morphology.

Water retention values (WRVs) of MFC hydrogels

Typically, WRV is an important parameter to characterize the degree of cellulose fibrillation (Hu et al. 2015). In the present study, the WRVs of DR-treated MFC hydrogels were plotted as a function of refining

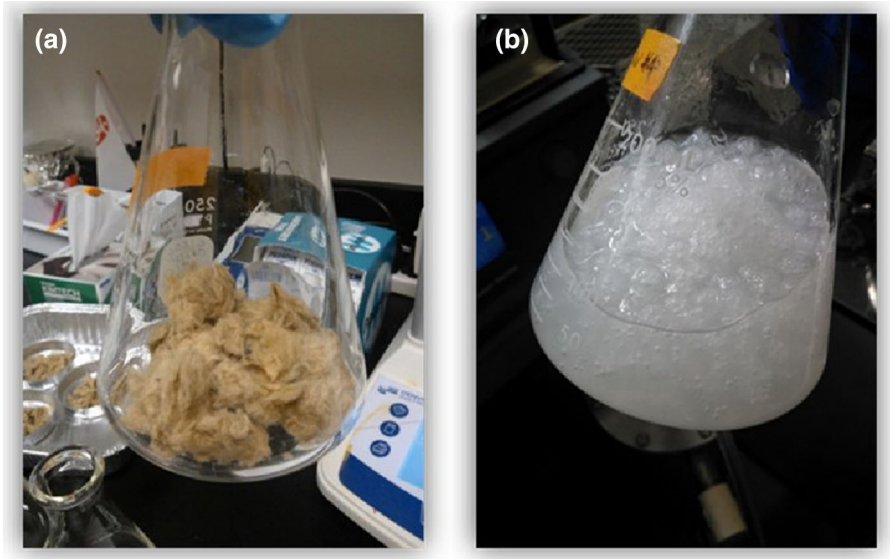


Fig. 1 Waste pulp sludge before (**a**) and after (**b**) maceration treatment

Table 1 Composition of waste pulp sludge before and after maceration

Material	Lignin (%)	Cellulose (%)	Hemicelluloses (%)	Ash (%)
Before maceration	8.47 ± 0.00	80.35 ± 2.36	10.37 ± 0.60	0.80 ± 0.02
After maceration	1.61 ± 0.05	94.81 ± 0.11	3.48 ± 0.18	0.10 ± 0.02

Error bar is represented by standard deviation

time in Fig. 3a. It was demonstrated that 120-min DR-treated MFC could retain water almost 16 times its own weight. We also found its WRV was 2.5 times higher than that of the 30-min DR-treated sample. Figure 3b shows the effects of homogenizer pass numbers on WRVs of UH-treated MFC gels under three different ultrasonication time periods. Ultrasonication is a mechanical technique that applies cavitation effects to generate intense shear force for the rupture of materials, such as fibers (Suslick 1990). In the UH process, ultrasonication was expected to break down fibers to facilitate the subsequent homogenization process. However, it was found that the duration of ultrasonication had almost no influence on WRVs, while the pass number through the homogenizer was a dominant factor. Taking all samples under 5-min ultrasonication as an example, the WRV of MFC was increased from 1.72 g/g without homogenization to 5.15 g/g after 40 passes. In addition, the WRVs of MFC after DR (Fig. 3a) were greater than those after UH processes (Fig. 3b). Even the minimum WRV of DR-treated MFC (6.3 g/g, 30 min DR treatment) was greater than the maximum WRV of UH-treated MFC (5.15 g/g, 5-min ultrasonication plus 40 passes). Therefore, we can conclude that the DR process is capable of preparing MFC with higher water retention values than the UH process. The water retention feature of cellulose is correlated with its surface area. The greater the surface area of cellulose, the more available hydroxyl groups could be exposed to form more hydrogen bonds with water (Herrick et al. 1983; Spence et al. 2010).

Specific surface areas (SSAs) of MFC hydrogels

The specific surface areas (SSAs) of MFC hydrogels from the two different aforementioned mechanical processes as well as solely macerated cellulose were investigated. For all UH-treated samples, the ultrasonication time was set for 5 min. As shown in Fig. 4, the SSA of cellulosic fiber after maceration was only 0.4 m^2/g, while the SSAs of MFC gels were

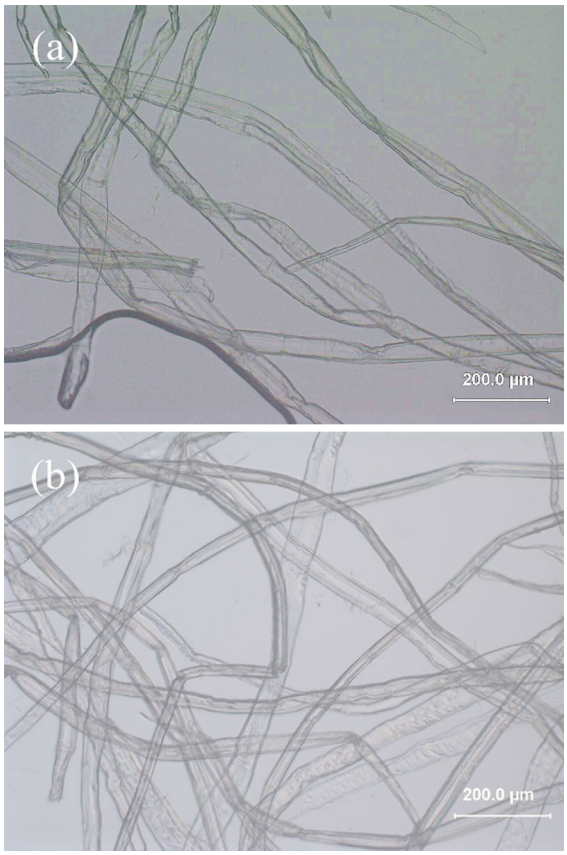


Fig. 2 Morphology of cellulose after maceration: **a** optical micrograph and **b** differential interference contrast micrograph

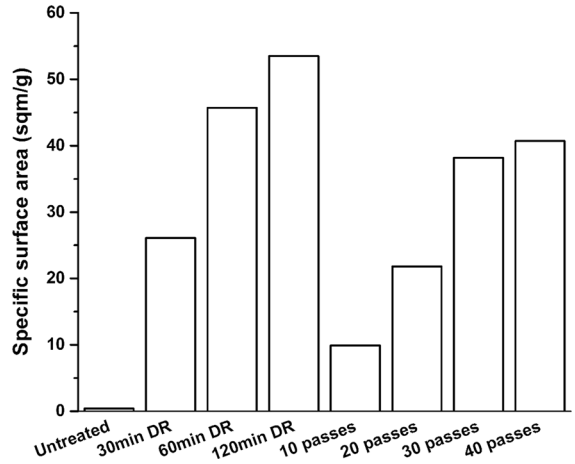


Fig. 4 Specific surface areas (SSAs) of freeze-dried MFC gels after disc refining (DR) and ultrasonication plus homogenization (UH), where 5-min ultrasonication was applied

significantly enhanced to the range from 10 to 55 m^2/g. The SSAs of MFC gels in this study were comparable to those from previously reported cellulose aerogels (Paakko et al. 2008) and foams (Sehaqui et al. 2010), which possessed 20–66 and 10–40 m^2/g specific surface area, respectively. In all MFC gels, 120-min DR-treated samples possessed the highest SSA, while the 10-pass UH sample had the lowest value. Moreover, it is worth noting that, although the

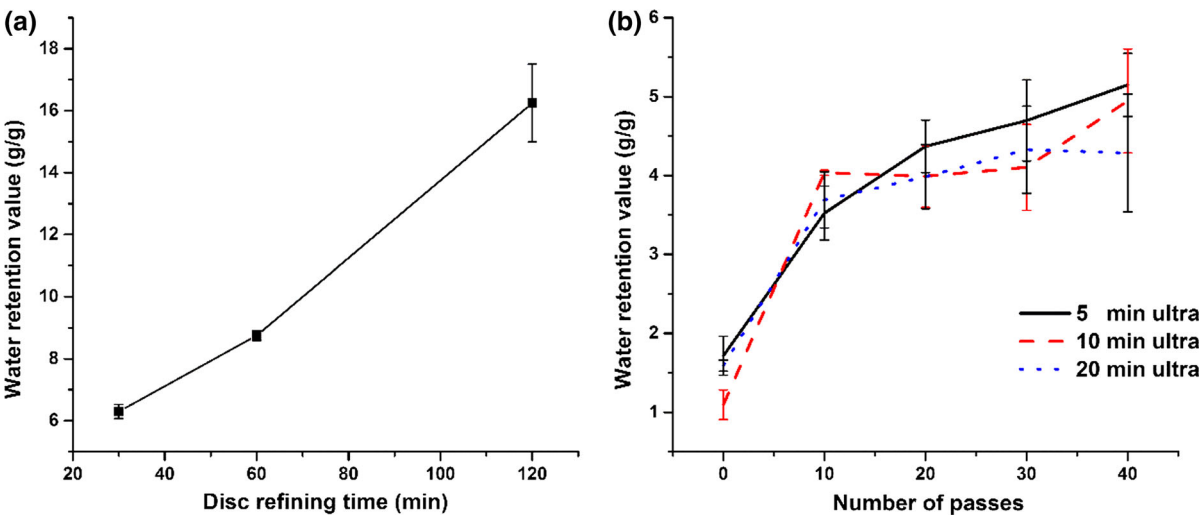


Fig. 3 Water retention values (WRVs) of MFC gels after disc refining (DR, **a**) and ultrasonication plus homogenization (UH, **b**)

SSAs of MFC after 30- and 40-pass homogenization (40 m^2/g for 40 passes and 38 m^2/g for 30 passes) were slightly greater than that by a 30-min DR treated sample (27 m^2/g), the latter had a higher WRV. This inconsistency implies that besides SSA, some other factors such as the entanglement degree, hydrogen bonding numbers, and aspect ratio may also affect the WRV of MFC (Herrick et al. 1983).

Morphologies of the MFC hydrogels

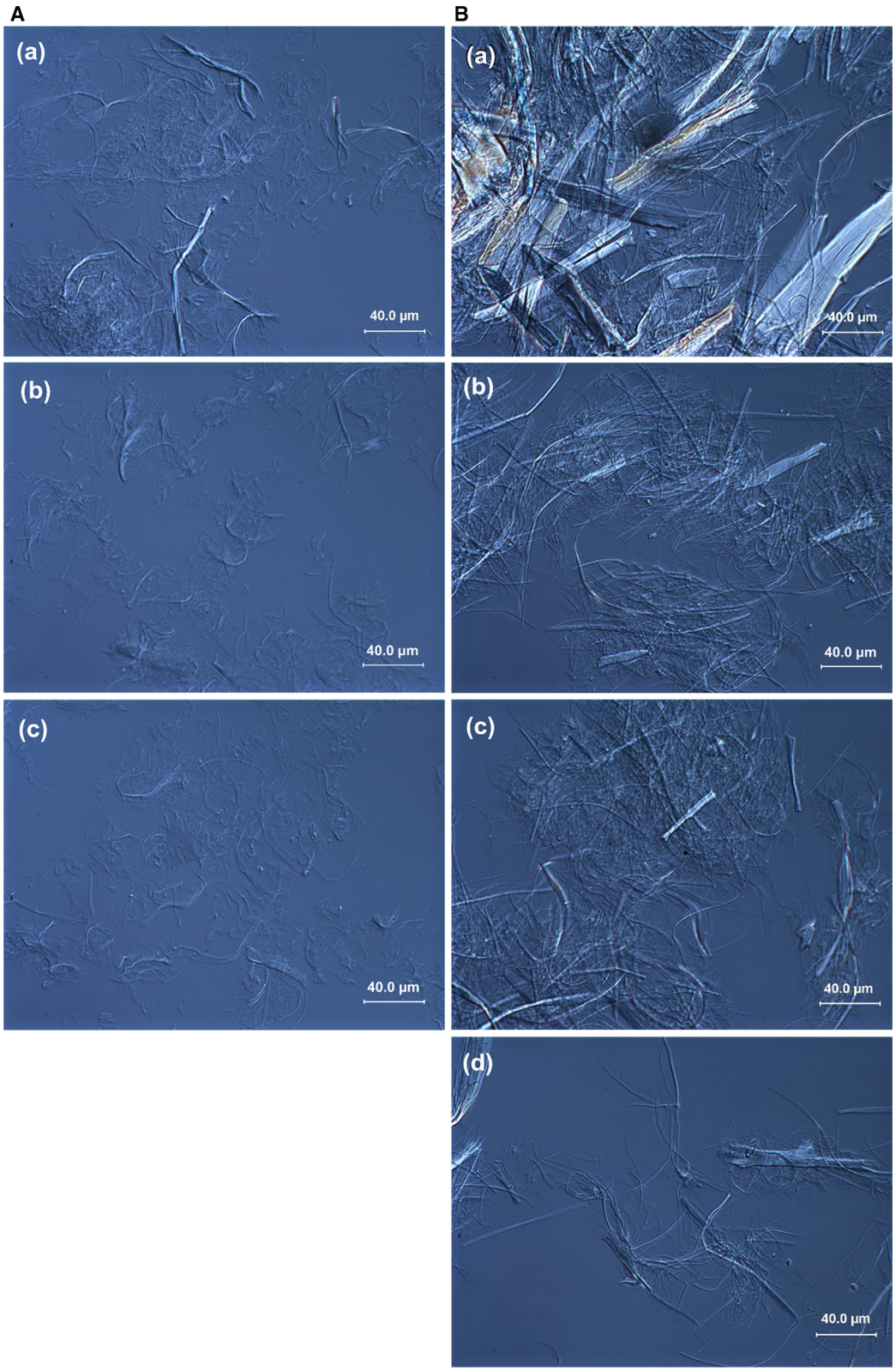
The morphologies of MFC hydrogels were examined by both differential optical microscopy and scanning electron microscopy (SEM). Figure 5A (a) shows that the 30-min DR sample is mainly composed of fibrils and fibril bundles. With the increase of refining time, the number of large bundles gradually reduced, and a more uniform size distribution can be observed in Fig. 5A (b–c). The 60- and 120-min DR-treated samples include a majority of entangled fibrils and a small portion of fibril bundles. Among them, the 120-min DR-treated sample has a greater number of short fibrils, indicating a higher surface area. Figure 5B also shows the micrographs of MFC gels after different UH treatments (5-min ultrasonication and various homogenizer pass numbers). The 10-pass UH sample mainly consisted of large fibers with diameters ranging from 10 to 40 μm and a few disintegrated fibrils [Fig. 5B (a)]. With the increase of homogenization passes, large fibers were substantially fibrillated. In the 30- and 40-pass treated UH samples, a number of fibril bundles and some fibrils with an entangled network existed. It is worth mentioning that when the pass number was increased to 40, the suspension became very viscous, which resulted in the blocking problem of the homogenizer. In a word, both DR and UH mechanical processes can effectively reduce the size of cellulosic fibers, and the DR process is more efficient than the UH process, because DR leads to smaller and more uniform fibrils with fewer steps.

In order to elucidate the morphologies of MFC hydrogels at a higher resolution, we further characterized these samples by SEM. Figure 6 shows the structures of corresponding MFC gels after 30- and 120-min DR treatment and 5-min ultrasonication plus 40-pass homogenization. The SEM image shows that the 30-min DR sample is mainly composed of a highly entangled network of fibrils and fibril bundles (Fig. 6a), which agrees well with the previous optical microscopy result. With a significant extension of refining time, the 120-min DR treatment led to numerous short microfibrils with an approximate average diameter of 60 nm (Fig. 6b), indicating a high degree of fibrillation. However, the 120-min DR sample possesses a lower degree of entanglement. This phenomenon can be ascribed to the over-cutting of fibers in transverse dimension by extensive mechanical processing, which results in the formation of fibrils with low aspect ratio. Thus, a high-intensity mechanical treatment does lead to better fibrillation, but greatly reduces the entanglement degree by producing more fibrils with low aspect ratio. In addition, the UH-treated sample shown in Fig. 6c has a looser fiber matrix and some large fibril bundles.

Rheology properties of MFC hydrogels

The rheological properties of MFC hydrogels prepared under different mechanical shearing conditions were characterized at 2 % w/w consistency. Figure 7 shows the plot of storage moduli (G') and loss moduli (G'') as the function of frequency. It is observed that all MFC aqueous suspensions are relatively independent of the angular frequency. For a typical viscous fluid, G' and G'' are dependent on frequency and $G' \ll G''$, while in an ideal gel, G' and G'' are relatively independent and $G' \gg G''$ (Tenijenhuis and Mijs 1998). Based on this rationale, all tested MFC samples exhibited a gel-like behavior, even for the 10-pass suspension, since its G' (10^3–10^4 Pa) were much greater than G'' (10^2–10^3 Pa), and both G' and G'' were relatively insensitive to frequency. The entangled network formed by topological interaction of cellulose contributes to the gel-like behavior for all suspensions (Paakko et al. 2007; Picout and Ross-Murphy 2003).

As shown in Fig. 7, the 30-min DR-treated MFC had the maximum storage modulus, which was greater than G' of the 60- and 120-min DR-treated MFC gels as well as all UH-treated samples. Regarding UH-treated MFC, the storage moduli of 20- and 30-pass MFC gels were greater than those of the 40-pass sample. The ten-pass MFC gel exhibited the weakest mechanical property, which could be attributed to the least entanglement of large fibers. It is worth noting that excessive shear force (60-min DR, 120-min DR, 40-pass UH) did not facilitate the fabrication of strong hydrogel, but reduced the G' instead. Under intensive


A
B
(a)
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40.0 µm
(d)
40.0 µm

◀**Fig. 5** Differential interference micrographs of **A** DR-treated MFC and **B** UH-treated MFC at different processing conditions in (**A**) *a* 30 min, *b* 60 min, and *c* 120 min; in (**B**) *a* 10 passes, *b* 20 passes, *c* 30 passes, and *d* 40 passes

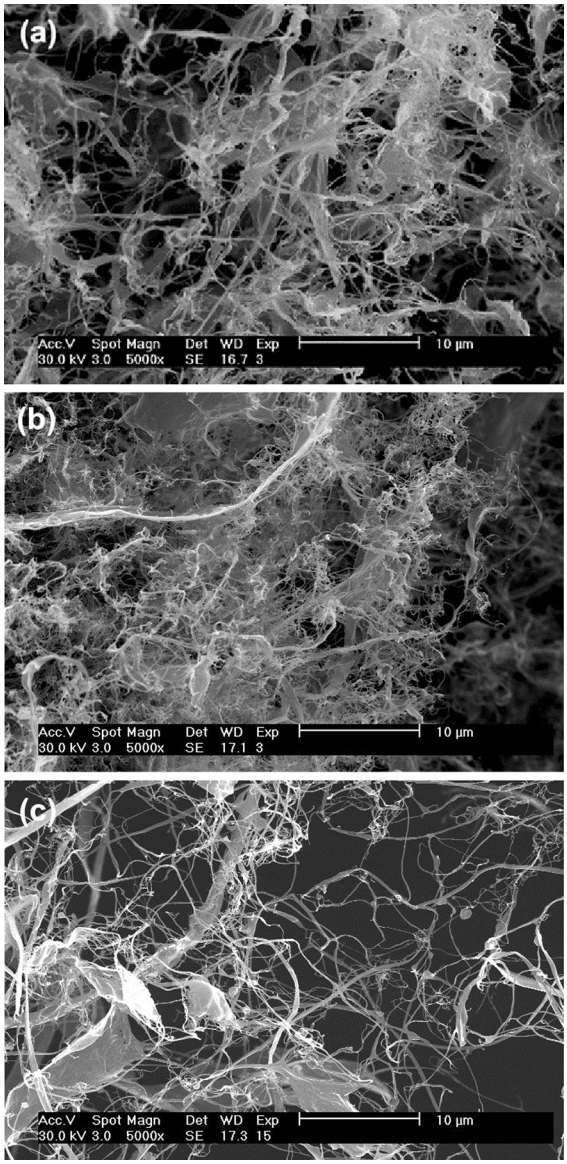

Fig. 6 SEM images of freeze-dried MFC gels after different shear force treatments: **a** 30-min DR, **b** 120-min DR, and **c** 40-pass UH

shear force, fibers were more susceptible to be broken down in the transverse dimension yielding fibrils with lower aspect ratio, which are detrimental to form

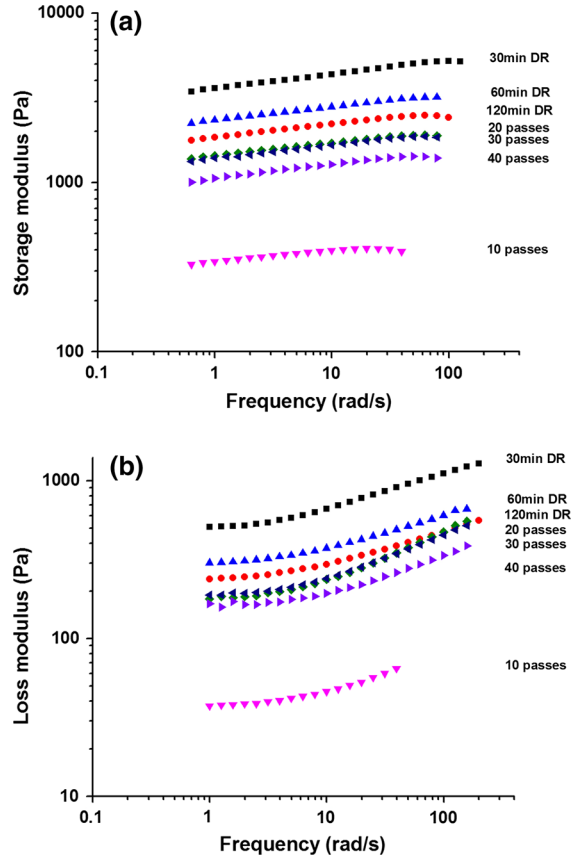

Fig. 7 The storage moduli (G's) (**a**) and the loss moduli (G''s) (**b**) as a function of frequency for all MFC gels

entangled networks, so MFC gels with low G' were obtained (Liimatainen et al. 2012; Stelte and Sanadi 2009). This phenomenon agrees well with the morphological observation in previous SEM images, in which a large number of fibrils with low aspect ratio exist in the 120-min DR-treated sample (Fig. 6). The G' value of the MFC gel by 30-min DR treatment is almost four times that of previously reported MFC gels at the same concentration (Paakko et al. 2007). In addition, the values of storage moduli of the entire MFC gels prepared in this study are higher than previously reported nanoscale cellulose crystallites (Ono et al. 2004; Rudraraju and Wyandt 2005; Tatsumi et al. 2002).

Moreover, the viscosities of MFC gels were investigated as a function of shear rate and are plotted in Fig. 8. The viscosities of all MFC gels decreased with the rise of shear rate indicating a pseudoplastic (shear thinning) behavior. The shear thining occurred

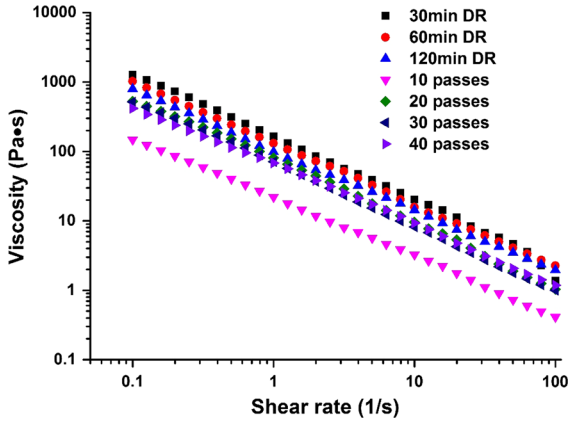

Fig. 8 Influence of the shear rate on the viscosity of different MFC gels

when the rate of imposed motion by external shear force was gradually higher than the rate needed for the formation of new entanglement (Picout and Ross-Murphy 2003). MFC gels presented a viscous property at low shear rate, and a fluid characteristic at high shear rate, in accordance with Herrick's report (Herrick et al. 1983). The shear viscosities provide the evidence of structure variance among differently fibrillated MFC hydrogels. For example, at the shear rate of 0.1 1/s, the viscosity of highly entangled 30-min DR-treated MFC hydrogel was about 1000 Pa s, which was one order of magnitude larger than ten-pass UH-treated sample. The degree of entanglement plays an important role on shear viscosity. With the increase of external shear force, weakly entangled fibrils with low aspect ratio were easily driven apart, while more entangled fibril networks could maintain higher viscosity. The result indicates that the higher the entanglement degree of MFC hydrogel is, the more difficult it is to disrupt MFC hydrogels by external shear force.

Conclusion

This study presented the production of strong microfibrillated cellulosic (MFC) gels through a mild maceration followed by a one-step disc refining process, which was compared with an ultrasonication plus homogenization process, for the aspects of SSAs, WRVs, morphologies, and rheological properties. It was demonstrated that the mild maceration (1:1 v/v of acetic acid and hydrogen peroxide) effectively removed lignin from never-dried waste pulp sludge. The macerated product had a cellulosic content up to 95 % and the most retained original cellulose morphology. In addition, the morphological results illustrated that maceration plus one-step disc refining could produce MFC with a high degree of entanglement. Furthermore, the rheological characterization results indicated that all prepared MFC suspensions at low concentration (2 % w/w) exhibited a typical gel-like and shear thinning behavior. Particularly, the 30-min DR treatment resulted in a strong MFC gel with G' as high as 4000 Pa, which was much higher than previously reported MFC gels. The strong MFC gel in this study may open a door for future widespread use as reinforcing fillers for low-density polymer composites, templates for further functionalization, and immobilization.

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