WATER RETENTION VALUE MEASUREMENTS OF CELLULOSIC MATERIALS USING A CENTRIFUGE TECHNIQUE

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A centrifugal method has been modified and applied to the assessment of water retention value (WRV) in cellulosic materials. Microcrystalline cellulose (MCC), small particles/fibrils isolated from MCC using high-pressure homogenizer, and pulp fibers saturated in water were centrifuged at different speeds and times with filter paper and/or a membrane acting as the filter in the WRV measurement setup. As centrifugal speed, time, and filter pore-size increased, lower WRVs were obtained. Smaller MCC particles/fibrils retained more water than the as-received MCC and pulp fibers. The results are useful for WRV measurements of cellulosic materials, especially for microfibrillated cellulose and small cellulosic fibrils.

Keywords: Biomass; Cellulose; Water retention value; Centrifuge; Microfibrillation

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INTRODUCTION

Cellulose, isolated from biomass, especially woody biomass, is renewable, biodegradable, and the most abundant natural biopolymer. There are about 100 billion metric tons of cellulose produced naturally every year in the world, while the total biomass is about 280 billion metric tons. Natural cellulosic fibers are synthesized mainly in plants such as grasses, reeds, stalks, and woody vegetation (Lima and Borsali 2004). For example, there are about 2.41 million dry tons of wood residues produced per year as a result of manufacturing processes in West Virginia, which can be used for bio-material and biofuel productions (Wang et al. 2006). The applications of cellulosic materials, such as pulp fibers, microfibrillated cellulose (MFC), microcrystalline cellulose (MCC), and fibril aggregate include paper, foods, cosmetics, paints, nonwoven textiles, oil field services, medicine, and polymer reinforcements (Turbak et al. 1983; Yano and Nakahara 2004; Zimmermann et al. 2004; Cheng et al. 2007; Cheng et al. 2009).

Several approaches have been explored to characterize cellulosic materials, including physical and chemical procedures. Cellulose is a high-molecular-weight linear homopolymer, consisting of repeating β-D-glucopyranosyl units joined by (1-4) glycosidic linkages in a variety of arrangements. Due to interaction of its hydroxyl groups with water molecules and the supramolecular structure of different cellulose with different available inner surface (e.g. less ordered amorphous regions, void structure) where sorption processes take place, cellulose has a high hygroscopicity. The interaction between cellulose and water plays a significant role during the chemical and physical process and isolation of cellulose (Klemm et al. 1998). Water retention value (WRV) is a useful reference to evaluate the performance of cellulosic materials relative to moisture behavior. The TAPPI UM 256 is a standard test method for pulp WRV to measure the performance of pulps relative to dewatering behavior on paper machine (TAPPI 1981). Water retention value is a measure of water retained by a material after centrifuging under standard conditions. The WRV of many materials has been investigated, especially cellulosic samples, such as pulp fibers (Stana-Kleinschek et al. 2002; Hubbe and Heitmann 2007), microfibrillated cellulose (MFC) (Turbak et al. 1983; Herrick et al. 1983), microcrystalline cellulose (MCC) (Tomer and Newton 1999), and cellulosic fibril aggregates (Cheng et al. 2007; Wang and Cheng 2009). WRV can be used to indirectly evaluate the degree of fibrillation of the fibers for the MFC and cellulosic fibril aggregates isolations.

The WRV of cellulosic materials can be measured under different conditions. For pulp fibers, the standard conditions from TAPPI used for WRV measurement include a representative specimen with 1400 g/m^2 on an oven-dry fiber basis, a relative centrifugal force (RCF) of 900 G, and a centrifuge duration time of 30 min (TAPPI 1981). A similar European standard DIN 53 814 for assessing the water retention capacity of cellulosic fibers is based on a determination of the quantity of water that fibers can absorb and retain under strictly controlled conditions (fiber soaking for 2 hours and centrifuging for 20 min with 3000 rpm) (Stana-Kleinschek et al. 2002). For smaller cellulosic materials (e.g. MFC, MCC, cellulosic fibril aggregates), however, there is no standard WVR measurement method. Glass filtering crucibles or metal cups with fine wire screens are not suitable for very fine cellulosic particles/fibrils. Furthermore, the RCFs and centrifugal times vary in different references, such as 2000 G and 15 min for pulp fibers (Rom et al. 2007), 3600 RPM and 10 min for MFC (Herrick et al. 1983), 900 G and 30 min for cellulosic fibril aggregates (Cheng et al. 2007; Wang and Cheng 2009).

Factors that may influence WRV measurements include sample weights, centrifugal time and force, pore size of filters used in the measurement setup, and cellulosic particle/fibril sizes. The objectives of this study were to investigate the effects of these factors on WRV of cellulosic materials, to determine an appropriate setup for the WRV measurements of smaller cellulosic particles/fibrils.

EXPERIMENTAL

Materials

Two cellulose sources were used as raw materials: microcrystalline cellulose (MCC, Avicel PH-101, supplied by FMC BioPolymer) and pulp fiber (supplied by Kimberly-Clark Worldwide, Inc.). The size of MCC air jet particles in wt % was ≤ 1.00 of +60 mesh and ≤ 35 of +200 mesh. The loose bulk density was 0.26-0.31 g/cc, and the degree of polymerization of MCC was ≤ 350. The pulp fibers were about 30 μm in width and 2 to 5 mm in length. Small cellulosic particles and fibrils were isolated from MCC by using a high-pressure homogenizer (NanoDeBee, Bee International Inc., South Easton, MA, USA) with 138 MPa pressure and 5 and 20 passes. Whatman filter paper #3 (particle retention: 6 μm), #42 (particle retention: 2.5 μm), and membrane (pore size: 0.2 μm, Whatman Nuclepore) were used to detect the influence of different pore sizes of filters on WRVs. The scanning electron microscope images (SEM, Hitachi S-4700) of pulp fiber, MCC, and homogenizer treated cellulosic particles/fibrils are shown in Fig. 1. The dimension and structure varied differently among the three tested materials. The pulp fibers (~30 μm in width and 2~5 mm in length) were much bigger than the MCC (~50 μm) and treated MCC particles/fibrils (most < 10 μm).

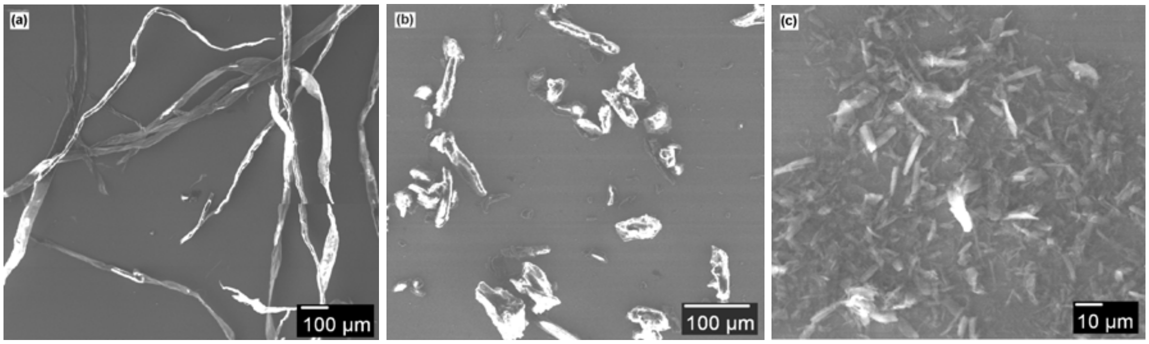

Fig. 1. SEM images of pulp fibers (a), MCC (b), and treated MCC using a homogenizer with 138 MPa pressure and 20 passes (c)

Methods

The water retention value measurement is based on subjecting a sample of aqueous slurry or water-saturated pulp to a standard centrifugal force with standard conditions of time, temperature, and apparatus. WRV is defined as the percent ratio of water contained in the sample after centrifuging at a certain force and time relative to the dry weight of the sample. A 25-mm diameter stainless steel cap with diameter of 1 mm holes (D) and a filter (E) were used to hold the wet sample (G) (Fig. 2). Two or four caps were filled with wet sample of designated weight and placed inside the carriers. After centrifuging (AccuSpin 400, Fisher Scientific) for a designated time and a designated relative centrifugal force (RCF) at room temperature, the samples were removed and placed onto aluminum foil, the “wet weights” were measured, and then the samples were oven dried at approximately 103 °C until they reached constant mass (dry weights). The WRV was calculated from Equation 1 (Cheng et al. 2007; Wang and Cheng 2009),

$$\mathrm{WRV} = \frac{\mathrm{W_{Wet}} - \mathrm{W_{Dry}}}{\mathrm{W_{Wet}}} \times 100\% \tag{1}$$

where, $\mathrm{W_{Wet}}$ is the weight of the sample after centrifuging and W_{Dry} is the absolute dry weight of the sample.

Relative centrifugal force (RCF) is given in multiples of the earth gravity G. It is a dimensionless number that allows one to compare the efficiency of separation or sedimentation of diverse instruments because it is independent of the instrument used. RCF is only related to radius and speed of the centrifugation (Equation 2) (Fisher Scientific 2003).

$$\mathrm{RCF} = 11.18 \times \left(\frac{n}{1000}\right)^2 \times r \tag{2}$$

where, r is the radius of centrifugation in cm from the centrifuge center to sample mass center and n is the speed in rpm.

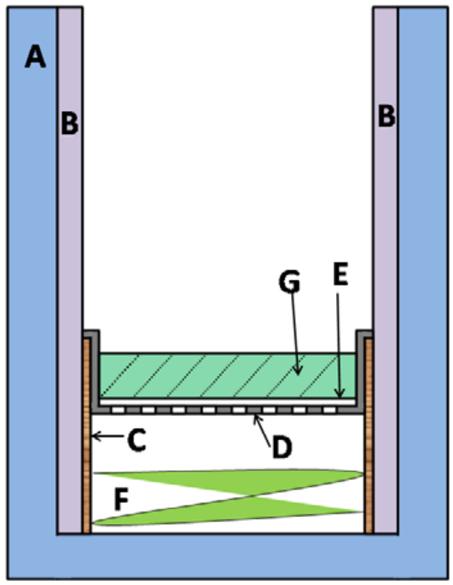

Fig. 2. Scheme of water retention value measurement setup for centrifuge, A: Centrifuge bucket, B: Adapter, C: Spacer, D: Stainless steel cap with holes, E: Filter paper/Membrane, F: Tissue for water absorption, G: Sample

Untreated MCC was used to investigate how sample weight, centrifugal time, centrifugal force, and filters with different pore sizes influence the WRVs of cellulosic materials. Samples of certain weight were immersed in distilled water for 2-3 days to make sure that the material was fully saturated before centrifuging. For the sample weight test, five weight levels of each specimen were used: 0.25, 0.5, 0.75, 0.1, and 1.25 grams for MCC, and 0.06, 0.12, 0.18, 0.24, and 0.3 grams for treated MCC using a NanoDeBee homogenizer at 138 MPa and 5 passes (MCC were saturated in distilled water for 2-3 days before homogenization). Three RCF levels: 900, 1350, and 1800 G, and four centrifugal time levels: 5, 10, 20, and 30 min. were used. The Whatman filter paper #3 (particle retention: 6 µm), #42 (particle retention: 2.5 µm), and membrane with 0.2-µm pore-size (Whatman Nuclepore) were used for examining the effects of filters of different pore sizes on WRV measurements. The pulp fiber and treated MCC using a homogenizer at 138 MPa and 20 passes were also used to detect the effects of cellulosic particle/fibril sizes on the WRV measurements. Six to eight replicates of each test were conducted to examine the variation of the WRVs. Single parameter test of analysis of variance (ANOVA) was used to examine the influence significance of the measurement conditions on WRVs (α=0.05).

RESULTS AND DISCUSSION

Effects of Specimen Weight

Figure 3 shows the WRVs of MCC (Fig. 3a) and treated MCC (Fig. 3b) at varied specimen masses. Only the effect of lower specimen weight (between 0.25 g to 0.5 g) on WRVs of MCC was significant (p=0.0058) (Fig. 3a). Although there was about 12% reduction in WRVs when specimen weight changed from 0.25 g to 0.5 g, the difference of WRV change was not dramatic, as shown by the error bar overlap. There were no significant differences among the WRVs of other different weight specimens (from 0.5 g to 1.25 g) (p values from 0.06 to 0.91). The higher standard deviation for lower weight samples may be attributed to the scale and drying processes. The WRV is independent of the surface area and hence that the centrifuge is effectively removing surface water in some weight range for large cellulosic materials, such as filter paper fibers (Kato and Cameron 1999). For MCC, a higher specimen weight could be better due to smaller influences and lower standard deviations. A sample weight of 0.5 grams was used for most of the following experiments. For treated MCC (138 MPa and 5 passes using a homogenizer), the results showed that all the sample weights (from 0.06 g to 0.3 g) did not significantly influence the WRVs (p values from 0.05 to 0.88) (Fig. 3b), which indicates that WRV is independent to the sample weights. However, it is notable that higher standard deviations for smaller mass samples were mainly attributable to the lower masses. More care should be taken during the sample weight measurements for small samples.

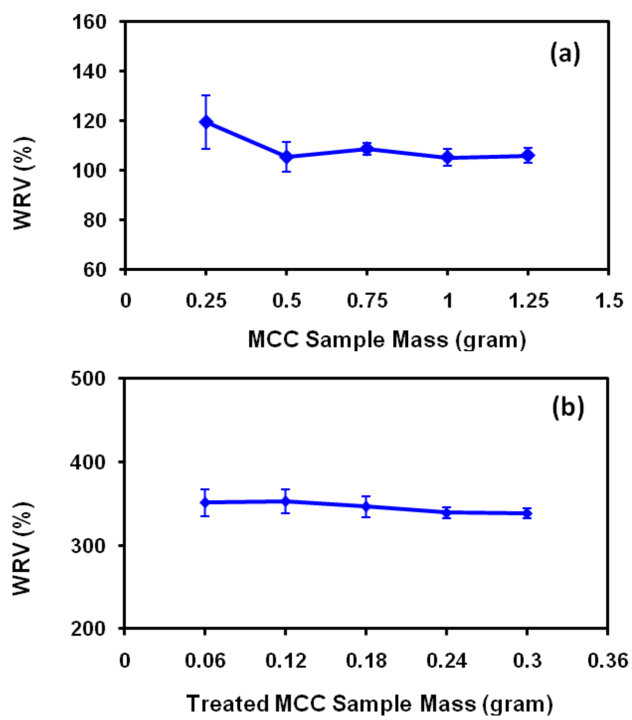

Fig. 3. WRVs with standard deviations of MCC with centrifugal force of 900 G and time of 5 min (a) and treated MCC with centrifugal force of 900 G and time of 20 min (b) at varied specimen masses

Effects of Centrifugal Time and Force

Generally, WRVs of MCC decreased with the increase of centrifugal time and RCFs (Fig. 4). For RCF of 900 G, the WRV reduction trend was somewhat linear, while there were no significant differences between 20 min and 30 min for both RCFs of 1350 G ($p=0.121$) and 1800 G ($p=0.087$), respectively, which indicates that no more water could be forced out from materials under these forces after 20 min. At higher centrifugal speeds (higher RCFs), due to higher pressure forced to the materials, it caused lower WRVs than those of lower RCFs. Similar results showed that increasing centrifugal speed can decrease the measured WRVs of the kenaf core material because higher forces can force out more water from the material than low forces (Lips et al. 2009).

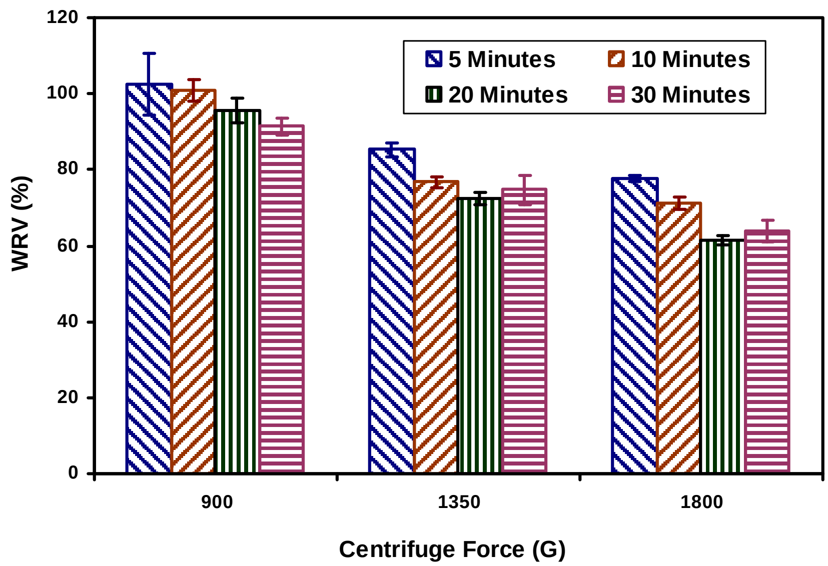

Fig. 4. Water retention values of MCC (0.5 g) with varied centrifugal times and varied relative centrifugal forces

Effects of Filters with Different Pore Sizes

The pore size of the filter paper/membrane was found to dramatically influence the MCC's WRVs for all four centrifugal times tested (Fig. 5). The bigger pore-size filters are used, the lower WRVs are possible to obtain. For example, at the centrifugal time of 5 min, the WRV from filter paper #3 (particle retention 6 µm) was 24% and 40% lower than those from filter paper #42 (particle retention: 2.5 µm) and membrane (0.2 µm pore-size), respectively. Larger pore-size resulted in lower WRVs because water is easily forced out through bigger pore-size filters, and cellulosic fine particles may not block the filter pores easily during the centrifuging process. This indicates that choosing filters of appropriate size is important for the setup of WRV measurements. When filter paper #3 was used, there was no significant difference between the WRVs of centrifugal times of 5 and 10 min ($p=0.601$). Approximately a 5% decrease was exhibited gradually from 10 min to 20 min, and then to 30 min. However, for the membrane, centrifugal time influenced the WRVs drastically due to the small pores that made the water passing the filter much slower. Meanwhile, it is worthy of note that the materials of filter paper (cellulose fiber) and the membrane (polycarbonate) were different, which may affect the WRV measurements because they have different hydrophilic properties.

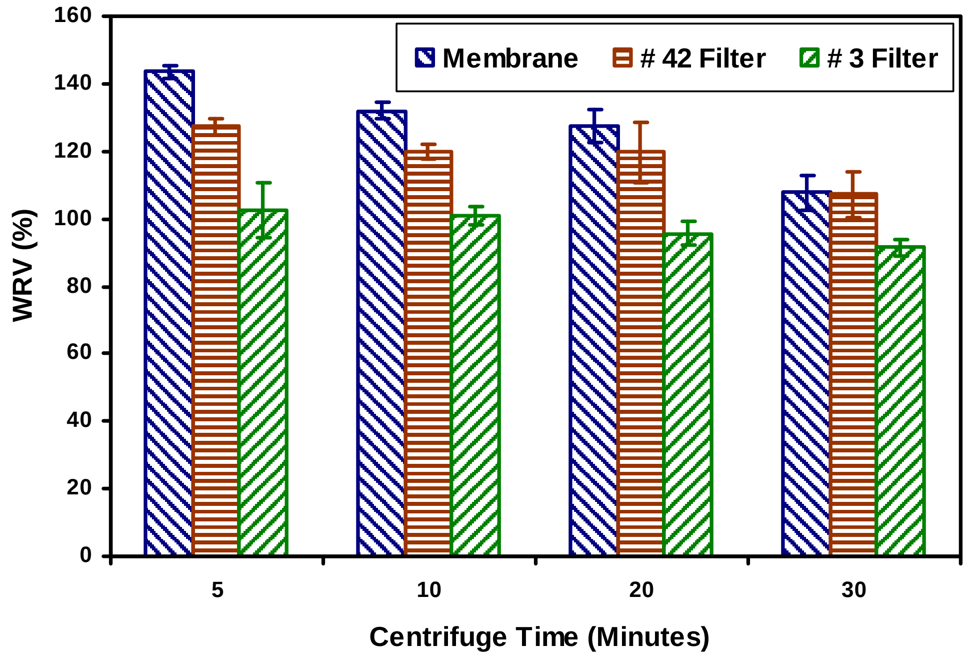

Fig. 5. Water retention values of MCC (0.5 g) with different filter paper/membranes at varied centrifugal times (relative centrifugal forces: 900 G).

Effects of Cellulosic Particle/Fibril Sizes

The WRVs of pulp fiber samples and homogenizer treated MCC particles/fibrils (138 MPa and 20 passes) were derived at varied centrifugal time, force, and filter paper/membrane (Tables 1 and 2). As shown in Fig. 4 for the MCC, the WRVs of pulp fiber decreased with the increasing of centrifugal times and RCFs (Table 1). Also, the filters with different pore sizes were found to drastically influence the pulp fiber's WRVs as well. When the centrifugal time is 5 min, the WRV using membrane was 40% higher than that of filter paper #42, and 43% higher than that of filter paper #3.

Table 1. WRV of Pulp Fiber Samples with Varied Centrifugal Time, Force, and Filter Paper/Membrane (mass: 0.5 g)

Centrifugal Time (Min.)	Centrifugal Force (G)	Filter	WRV ± STD* (%)
30	900	#3	142.3 ± 3.8
30	1350	#3	104.6 ± 6.1
30	1800	#3	90.7 ± 0.8
20	1800	#3	90.5 ± 4.1
10	1800	#3	97.4 ± 3.1
5	1800	#3	105.7 ± 2.2
5	1800	#42	112.3 ± 1.1
5	1800	Membrane	185.8 ± 95.4

* STD: standard deviation.

Table 2. WRVs of Homogenizer Treated MCC (HPH: 138 MPa & 20 passes) Particles/Fibrils Samples with Varied Centrifugal Time, Force, and Filter Paper/Membrane (mass: ~ 0.08 g)

Centrifugal Time (Min.)	Centrifugal Force (G)	Filter	WRV ± STD* (%)
30	900	#3	523.0 ± 25.2
30	1350	#3	452.9 ± 54.4
30	1800	#3	360.0 ± 33.0
30	1800	#42	380.0 ± 22.9
30	1800	Membrane	548.1 ± 58.3
20	1800	Membrane	767.1 ± 187.2
10	1800	Membrane	---**

* STD: standard deviation; ** Not centrifuged completely, and with some water on the top of the samples.

Again, the WRVs of homogenizer-treated MCC particles/fibrils also decreased along with the increase of centrifugal time and forces (Table 2). The filters with different pore sizes influenced the WRVs of the smaller cellulosic particles/fibrils much more than the big particles/fibers. For example, when the membrane was used, the free water could not be easily forced out through the membrane filter completely at lower centrifugal time (10 min), so that water on the top of the samples could be left and observed after centrifuging. The possible reasons for water remaining in the samples include; that the small cellulosic fibrils with sizes under 1 μm may completely block the filter pores and/or a very dense thin film just above the filter may be formed and may also block the water passing the filter pores during the centrifugation. Several mechanisms may be used to explain this phenomenon, such as sealing mechanism (Hubbe and Heitmann 2007). Furthermore, much higher standard deviations were obtained when the membrane, shorter centrifugal time, and/or lower centrifugal force were used, especially for treated MCC with larger passes (e.g. 20 passes) (Table 2), while the standard deviations were much smaller for the treated with fewer passes (e.g. 5 passes) (Fig. 3b), which included less very fine cellulosic particles/fibrils. All of these results reveal that higher centrifugal time and/or higher force should be used for smaller cellulosic particles/fibrils when a very small pore-size membrane is used as the filter in the WRV measurement setup. For example, for the MCC treated with homogenizer with 138 MPa and 20 passes, a centrifugal force of 1800 G or higher and time of 30 min. or longer should be used (Table 2).

It is apparent that the WRVs varied depending on materials such as pulp fiber (Table 1), MCC (Figs. 3 and 4), and homogenizer-treated cellulosic particles/fibrils (Table 2). The WRV of cellulosic particles/fibrils was about six times of that of MCC. These cellulosic materials showed different WRVs because the WRV depends on surface properties of fibers/particles, and water content of cellulosic fibers/particles contained on surface and bulk water (Maloney et al. 1999; Forsstrom et al. 2005). The homogenizer-treated cellulosic particles/fibrils, also called MFC, were much smaller than the original MCC material and highly microfibrillated. The cellulosic particles/fibrils or MFCs had higher surface area and volume than big size pulp fibers and MCCs. So MFCs could retain higher WRVs because of the fibril and microfibril surface and volumetric phenomena (Herrick et al., 1983). The smaller the particles/fibrils isolated from raw materials, the higher the WRVs obtained.

CONCLUSIONS

1. A modified centrifuge setup with stainless steel cap and filters can be used to measure water retention values (WRVs) of cellulosic materials, especially for small cellulosic particles/fibrils or microfibrillated cellulose.
2. Lower specimen weight may result in higher standard deviations of WRVs.
3. Lower WRVs of cellulosic materials could be obtained through using higher centrifugal speed, longer time, and larger pore size of filters.
4. Smaller MCC particles/fibrils can retain more water than untreated MCC and pulp fibers.
5. Filter membranes with very small pore sizes are not suitable for small cellulosic particles/fibrils or MFC for the WRV measurement setup if the centrifugal force is not high enough and/or the centrifugal time is not long enough. Higher forces such as more than 1800 G for more than 20 min are recommended for these cellulosic materials.
6. Same filter or membrane should be used for WRV measurement in this setup.

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REFERENCES CITED

Cheng, Q., Wang S., and Rials, T. G. (2009). "Poly(vinyl alcohol) nanocomposites reinforced with cellulose fibrils isolated by high intensity ultrasonication," *Composites Part A: Appl. Sci. Manufact.* 40, 218-224.

Cheng, Q., Wang, S., Rials T., and Lee, S. H. (2007). "Physical and mechanical properties of polyvinyl alcohol and polypropylene composite materials reinforced with fibril aggregates isolated from regenerated cellulose fiber," *Cellulose,* 14(6), 593-602.

Fisher Scientific (2003). Centrifuge AccuSpin 400, *"Operating Instruction*," p. 31.

Forsström, J., Andreasson, B., and Wågberg, L. (2005). "Influence of pore structure and water retaining ability of fibers on the strength of papers from unbleached kraft fibers," *Nord. Pulp Pap. Res. J.* 20(2), 176-185.

Herrick, F. W., Casebier, R. L., Hamilton, J. K., and Sandberg, K. R. (1983). "Microfibrillated cellulose: morphology and accessibility," *J Appl. Polymer Sci.: Appl. Polymer Symp.* 37, 797-813.

Hubbe, M. A., and Heitmann, J. A. (2007). "Review of factors affecting the release of water from cellulosic fibers during paper manufacture," *BioRes.* 2(3), 500-533.

Kato, K. L., and Cameron R. E. (1999). "Structure-property relationships in thermally aged cellulose fibers and paper," *J Applied Polymer Sci.* 74, 1465-1477.

Klemm, D., Philipp, B., Heinze, T., Heinze, U. and Wagenknecht, W. (1998). "*Comprehensive Cellulose Chemistry. Fundam. Anal. Methods,"* Wiley-VCH, Weinheim, New York, Chichester, Brisbane, Singapore, Toronto.

Lima, M. M. D. and Borsali, R., 2004. "Rodlike cellulose microcrystals: Structure, properties, and applications," *Macromolecular Rapid Communications* 25(7), 771-787.

Lips, S. J. J., de Heredia, G. M. I., den Kamp, R., and van Dam, J. E. G., (2009). "Water absorption characteristics of kenaf core to use as animal bedding material," *Industrial Crops and Products* 29(1), 73-79.

Maloney, T. C., Jaine, J. E., and Paulapuro, H. (1999). "Comments on the measurement of cell wall water," *Tappi. J.* 82(9), 125-127.

Stana-Kleinschek, K., Ribitsch, V., Kreze T., and Fras L. (2002). "Determination of the adsorption character of cellulose fibres using surface tension and surface charge," *Mat. Res. Innovat.* 6, 13-18.

TAPPI. (1981). TAPPI useful method UM256. "Water retention value (WRV)," *TAPPI Useful Methods*, TAPPI Press, Atlanta, USA.

Tomer, G., and Newton, J. M. (1999). "A centrifuge technique for the evaluation of the extent of water movement in wet powder masses," *Int. J. Pharm.* 188, 31-38

Turbak, A. F., Snyder, F. W. and Sandberg, K. R. (1983). "Microfibrillated cellulose, new cellulose product: Properties, uses, and commercial potential," *J. Appl. Polymer Sci.: Appl. Polymer Symp.* 37, 815-827.

Wang, S., and Cheng, Q. (2009). "A novel method to isolate fibrils from cellulose fibers by high intensity ultrasonication. Part I: Process optimization," *J. Appl. Polymer Sci.* 113: 1270-1275.

Wang, J., Grushecky, S., and McNeel, J. (2006). *Biomass Resources, Uses, and Opportunities in West Virginia*, West Virginia University Biomaterials Center, Division of Forestry and Natural Resources, Morgantown, WV, 103 pp.

Yano, H., and Nakahara, S. (2004). "Bio-composites produced from plant microfiber bundles with a nanometer unit web-like network," *J. Mat. Sci.* 39(5), 1635-1638.

Zimmermann, T., Pohler, E., and Geiger, T. (2004). "Cellulose fibrils for polymer reinforcement," Adv. *Engin. Mat.* 6(9): 754-761.

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