Physico-chemical Characterization and Comparison of Microcrystalline Cellulose from Several Lignocellulosic Sources

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The aim of this study was to investigate the influence of cellulose sources on the physico-chemical properties of microcrystalline cellulose (MCC) for various applications. The results showed that MCC prepared from non-wood resources including cotton stalk, bamboo, and sisal was comparable to MCC made from wood in α-cellulose content, pH, moisture content, crystallinity index (CrI), and moisture sorption capacity. However, the ash content, polymerization degree, thermal stability, and mechanical properties, including tablet hardness and tensile strength, of MCC were strongly dependent upon the cellulose sources. The crystalline size (002) had no effect on the mechanical properties of the prepared MCC. The order of the obtained mechanical properties was softwood > hardwood > cotton stalk > bamboo > sisal. Compared with the less obvious variation for bamboo and sisal, the tablet hardness for wood and cotton stalk MCC noticeably decreased in correlation with increased MCC particle sizes. In addition, compared to the polycaprolactone (PCL) neat film, the tensile strength and elastic modulus of PCL/MCC films were improved by 16.0% to 42.5% and 62.7% to 82.0%, respectively.

Keywords: Microcrystalline cellulose; Mechanical properties; Tablet; Polycaprolactone

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INTRODUCTION

Cellulose is the most abundant renewable raw material on the earth and there are many methods to convert cellulose into value-added derivatives. Microcrystalline cellulose (MCC) (Sun 2008; Dos Santos *et al.* 2017; Kambli *et al.* 2017) is one important cellulosic product obtained from cellulose or biomass-derived pulp. It is an white, odorless, rod-like or granular crystal obtained by hydrolyzing natural fibers under dilute mineral acid conditions. Generally, in addition to mineral acid hydrolysis (Adel *et al.* 2010), there are several methods that could be used to extract MCC, such as the use of hot water, steam explosion (Cherian *et al.* 2010), subcritical water/carbon dioxide, and biological treatment like enzyme hydrolysis (Trache *et al.* 2016; Kambli *et al.* 2017). The purest form of MCC is obtained from cotton, while other raw material requires extensive purification to remove lignin, hemicellulose, ash, and other impurities.

In industrial applications, MCC is mainly obtained from cotton or wood pulp due to a large number of suppliers in markets and the mature preparation process. It is usually utilized for pharmaceutical, food (Nsor-Atindana *et al.* 2017), cosmetics, reinforcing material, and functional material production. In the pharmaceutical industry, MCC is used as an excipient for the preparation of pellets due to its good compressibility and binding properties (Thoorens *et al.* 2014). Many approaches have been proposed for enhancing

MCC's ability to enhance the properties of pharmaceutical pellets. Chamsai and Sriamornsak (2013) studied the use of ethanolic solution with polysorbate 80, polyethylene glycol 400, and sodium croscarmellose, to produce a novel MCC with enhanced MCC-based pellet properties. In the food industry, MCC is an ideal health food additive and is commonly used in anti-caking agents, emulsifiers, stabilizers, dispersing agents, gelling agents, thickeners, *etc*. With the objective of replacing fat, Gibis *et al.* (2015) found that MCC resulted in a reduction of fat of approximately 50% in patties. Recently, bio-based functional composites of MCC are of interest to scientists. For example, Rashid *et al.* (2017) prepared magnetic MCC nanocomposite particles with application potential in biomolecule/water purification and oil recovery from water. The results indicated that the magnetically modified MCC/Fe_3O_4 nanocomposite particle possessed good paramagnetic properties and could be accumulated both in emulsion and dried states using an external magnetic field. Parveen *et al.* (2017) reported that MCC showed improvements of 106%, 31%, and 66% in flexural modulus, flexural strength, and compressive strengths in cementitious composites, respectively. Chartrand *et al.* (2017) synthesized low-density polyethylene-MCC composites with high mechanical strength *via* graft modification of ferulic acid, methacryl chloride, and oil acyl chloride on the surface of MCC. In addition, MCC could also be used as a reinforcing material. PCL is a polymer that can be degraded by microorganisms. Currently, there is much research in the biomedical field, including skin, blood vessels, and drug-delivery degrading suture material. The polymer PCL also has the ability to form biomaterials with other polymers. Neat PCL does not have the mechanical properties to be applied in high load bearing applications (Woodruff and Hutmacher 2010). The MCC used as an additive in PCL matrices can improve its mechanical behavior and biological performance significantly (Aleman-Dominguez *et al.* 2018). Dhakal *et al.* (2018) reported that lignocellulosic hemp fiber can enhance its properties (tensile, flexural, and low-velocity impact). To the best of the authors' knowledge, at present, there are few reports on the effect of MCC and its sources on the mechanical properties of PCL.

In recent years, researchers have investigated a variety of approaches to expand the sources of MCC due to an increasing emphasis on applying under-utilized lignocellulosis resources, for example, rice husk (Bae *et al.* 2017), jute (Jahan *et al.* 2011), tea waste (Zhao *et al.* 2018), bamboo, corn stover, bagasse, banana (Elanthikkal *et al.* 2010), oil palm (Xiang *et al.* 2016), roselle fibers (Kian *et al.* 2017), waste paper (Obumneme 2013), and so on. However, few studies have focused on the differences of MCC particles from woody and non-woody biomass, especially on the mechanical properties of MCC tablets in pharmaceutical applications. The particle properties are of critical importance not only as criterion to guide tablet production, but also as the standard for quality-control in drug tablet production in such processes as mixing, flow, and compression. Hardness is an important mechanical property of tablets in the field of pharmaceutical powder compaction (Kuentz and Leuenberger 2000). Solid tablets are the most commonly used dosage form, so tablet hardness is a principle parameter to indicate its capacity to resist stresses during transportation and storage. As reported, MCC made from bean hull, rice straw, and rice hull had different tablet properties (Adel and El-Shinnawy 2012) and the tensile strength of rice straw and rice hull MCCs were higher than bean hull MCC, which possibly indicated that rice straw and rice hull MCCs were more suitable to produce tablets. Furthermore, the ash content indicated to some extent the amount of care taken in the preparation of the substance, and the ash content of MCC prepared from groundnut husk was 0.38% (Ohwoavworhua *et al.* 2009), which was out of the range of pharmaceutical grade MCC.

The MCC prepared from various raw materials has not been purposefully selected for various applications. Therefore, knowing the particle and mechanical properties of MCC could provide valuable information for the selection of MCC resources for manufacturers.

Hence, the objective of this study was to investigate the physical and chemical properties of MCC powders obtained from hardwood, softwood, bamboo, sisal, and cotton stalk and the influence of these cellulosic sources upon the mechanical properties of MCC tablets. The reinforcing capability of the different MCC powders was evaluated relative to the mechanical properties of a PCL matrix.

EXPERIMENTAL

Materials

The bleached pulp boards of softwood and hardwood were obtained from ANDRITZ AG (Foshan, China). Bamboo and sisal pulp boards were supplied by Zhongzhirenhe Company (Jinan, China). Raw cotton stalk was sourced from Aksu Prefecture, China. The cotton stalk pulps were cooked and bleached in the laboratory. Commercial MCC was purchased from Sinopharm Group (Beijing, China). Dichloromethane was supplied by Yongda Company (Tianjin, China). Hydrochloric acid was purchased from Guangzhou Chemical Reagent Factory (Guangzhou, China). The PCL was purchased from Perstorp AB (Malmö, Sweden).

Methods

Preparation of cellulose pulps

The pulp boards of softwood, hardwood, bamboo, and sisal were dispersed by a disintegrator for standardized disintegration of pulp suspensions (Aufschlaggerät disintegrator, Laborausrüstung Laboratory Equipment, Vorchdorf, Austria). Cotton stalks were chipped using a cutting-type grinding apparatus (CM 100; Beijing Grinder Instrument Co., Ltd., Beijing, China), and cotton stalk powders were sieved through a 40-mesh screen. Acetic acid (CH_3COOH) was used to pretreat cotton stalk powders at a solid-to-liquid ratio of 1:1 (w/v). The kraft cooking process for cotton stalk was completed in a laboratory digester as the following conditions: solid-to-liquid ratio of 1:15 (w/v), 23% active alkali, 25% sulfidity, temperature of 160 °C, and a duration of 3 h. The pulp obtained was then washed and screened. Stabilized chlorine dioxide was used to bleach cotton stalk pulp four times at pH 3 to 4 and at a temperature ranging from 95 °C to 100 °C for 1 h, and then washed with distilled water.

Preparation of MCC

Cotton stalk, softwood, hardwood, bamboo, and sisal pulps were hydrolyzed with 1 mol/L of HCl at 85 °C at a ratio of 1:10. Cotton stalk, softwood, hardwood, bamboo, and sisal pulps were hydrolyzed with agitation for 40 min, 60 min, 90 min, 120 min, and 120 min, respectively. The reaction was terminated with 300 mL of distilled water. Then, the samples were filtered and washed with distilled water to neutrality. Finally, the MCC samples were sprayed, dried, screened, and stored in a sealed plastic bag at room temperature until use.

Preparation of tablets

An aspirin tablet model was used to understand the impact of microcrystalline cellulose on tabletability, as shown in Table 2. Aspirin, MCC, and magnesium stearate were initially mixed, blended for 10 min, and then passed through a 60-mesh sieve to evenly disperse the samples. The tablets were prepared on a tablet compressing machine (FY-15; SCJS Co., Ltd., Tianjin, China). A consistent tablet weight close to 500 mg was compacted in a mold (ϕ = 10 mm) and the tablets were tested after 24 h.

Table 1. Chemical Composition of the Various Bleached Pulps Used

Pulp	α-cellulose (%)	Lignin (%)	Hemicellulose (%)	Ash (%)
Hardwood	82.63	1.82	15.34	0.21
Softwood	83.52	1.90	14.36	0.22
Bamboo	81.40	2.10	16.07	0.43
Sisal	80.56	2.16	16.31	0.97
Cotton stalk	92.40	1.14	6.28	0.18

Table 2. Composition of Aspirin Tablet Model

Component	Function	%
Aspirin	Active pharmaceutical ingredient	60.0
MCC	Binder	39.5
Magnesium stearate	Lubricant	0.5
Total		100.0

Preparation of PCL/MCC film

Two polymers were mixed using the solvent casting technique to prepare a blended PCL/MCC (PCL:MCC = 5:1) film. The PCL was dissolved and mixed with MCC in dichloromethane. The PCL/MCC solution was cast on a clean tetrafluoroethylene mold, and the solvent was evaporated at room temperature for 6 h in a fume hood.

Analytical methods

The determination of α-cellulose content, ash content, degree of polymerization, pH, moisture content, and moisture sorption capacity were completed following the methods set by the United States Pharmacopeial Convention (2012).

The hardness of the aspirin/MCC tablet and the tensile properties of the PCL/MCC film were determined at 5 mm/min using an Instron universal testing machine (Series 5560 Dual Column Table Top Models; Instron Corporation, Canton, MA, USA).

Tensile strength (Thoorens *et al.* 2015) was calculated using Eq. 1,

$$T = \frac{2F}{\pi DL} \quad (1)$$

where T is the tensile strength (MPa), F is the breaking force (N), D is the tablet diameter (mm), and L is the tablet thickness (mm).

The particle size and distribution analyses were performed using a Mastersizer 3000 (MAZ 3000; Malvern Panalytical, Malvern, UK). The statistics of the distribution were calculated using the derived diameters. The particle size D50 was the standard percentile reading from the analysis.

The Fourier transform infrared (FT-IR) spectra of the MCC samples were acquired using 32 scans on a Vector 33 spectrometer (Tensor 27; Bruker Corporation, Ettlingen,

Germany) in the range of 400 cm^{-1} to 4000 cm^{-1}. Potassium bromide was of spectral purity (Kermel, Tianjin, China), and the samples were mixed with KBr and pressed.

The crystallinity index (CrI) was analyzed using a D8 ADVANCE X-ray diffractometer (Bruker Corporation, Ettlingen, Germany) with CuKα radiation (λ = 1.54 Å) at 40 mA and 40 kV. The scattering angle (2θ) range was performed from 5° to 60°, and the step width was 0.02° with a scanning speed of 19.2 s per step. The CrI (Jahan *et al.* 2011) was calculated using Eq. 2,

$$CrI(\%) = \frac{I_{002} - I_{am}}{I_{002}} \times 100\% \quad (2)$$

where I_{002} is the peak intensity on the 002 lattice plane at 2θ of 22° and I_{am} is the peak intensity of the amorphous domain at a 2θ of 18°. The crystallite size was calculated from the Scherrer equation as shown in Eq. 3,

$$L = \frac{k\lambda}{\beta \cos\theta} \quad (3)$$

where L is the crystallite size (nm) of MCC, k is 0.94 (the Scherrer constant), λ is 0.15418 nm (X-ray wavelength), β is the full width half maximum of the lattice plane reflection (FWHM) in radian, and θ is the corresponding Bragg angle (reflection angle, °) (Trache *et al.* 2014).

A thermogravimetric analyzer (TGA Q500; TA Instruments, New Castle, DE, USA) was used to characterize the thermal stability. All samples runs were conducted under nitrogen flow, and temperature was heated at a constant heating rate of 10 °C/min from 30 °C to 700 °C.

RESULTS AND DISCUSSION

Different kinds of MCC were prepared by hydrochloric acid hydrolysis, as shown in Table 3. It was found that all raw materials used in this study were reduced to microcrystals *via* acid hydrolysis. Various lignocellulosic resources require different acid hydrolysis conditions due to the unique chemical constituents (cellulose, hemicellulose, and lignin) and structural organization.

Table 3. Properties of MCC Samples

Sample	Particle Size	MCC	
	D50 (μm)[a]	CrI (%)[b]	L_{002} (nm)[c]
Cotton stalk	56.4	80.29	5.09
Hardwood	52.9	80.33	4.43
Softwood	52.1	81.56	4.86
Bamboo	51.5	78.60	4.24
Sisal	48.2	81.13	4.83
Commercial MCC	54.6	80.60	5.34

[a] Average particle size; [b] Crystallinity index; [c] Crystallite size of 002 lattice plane

A possible explanation for the effects of acid hydrolysis was that the acid solution could easily penetrate the cell walls of pulp fibers at high temperatures and hydrolyze the weakest amorphous region of cellulose. The result of this experiment indicated that it was easier for the bamboo and sisal fibers to degrade than the cotton stalk, softwood, and hardwood fibers. One possible explanation for this was that the bamboo and sisal had lower crystallinity (Table 3) and a greater proportion of amorphous region than the woody resources.

The comparison of various physico-chemical properties of MCC isolated from cotton stalk, softwood, hardwood, bamboo, sisal, and commercial MCC are shown in Table 4. Most of them were well in agreement with the United States Pharmacopeial Convention (2012). The α-cellulose content of all MCC samples was higher than 97%. The ash contents of cotton stalk MCC and bamboo MCC were below 0.1%, while softwood MCC, hardwood MCC, and sisal MCC were higher. Generally, for lignocellulosic biomass, dilute acid pretreatment is an effective method to remove parts of the ash (Feng *et al.* 2004; Wang *et al.* 2011). However, the results showed that with acid hydrolysis pretreatment, the large amount of ash could not be efficiently removed. The number of β(1→4) linked D-glucose units is expressed as cellulose degree of polymerization and it is one of the most important and most frequently used parameters for MCC. The polymerization degrees of MCC are presented in Table 4.

Table 4. Physicochemical Analysis of MCC Powder Prepared from Cotton Stalk, Softwood, Hardwood, Bamboo, Sisal, and Commercial MCC

Property	MCC Samples						United States Pharmacopeial Convention (2012)
	Cotton Stalk	Hardwood	Softwood	Bamboo	Sisal	Commercial	
α-Cellulose content (%)	98.55	98.48	98.58	97.88	97.67	98.59	> 97
Ash content (%)	0.08	0.11	0.12	0.08	0.39	0.05	< 0.1
Degree of polymer-ization	148.34	180.65	169.83	124.23	108.25	137.53	< 350
pH value	6.65	6.37	6.76	6.77	6.78	6.77	5 to 7.5
Moisture content (%)	5.91	5.10	5.39	5.54	4.37	4.67	< 7.0
Moisture sorption capacity (%)	13.31	14.01	13.50	11.65	13.10	11.90	-

According to the United States Pharmacopeial Convention (2012) standard, the degree of polymerization should not be greater than 350. All MCC samples in this study met the criteria. However, the polymerization degrees of softwood and hardwood MCC were much higher than the others. In addition, the sisal MCC was much lower than bamboo, which indicated that cellulose sources affected the degree of polymerization. Moreover,

the pH values of all MCC samples ranged from 6 to 7 (Table 4), which was related to the frequency of washing.

The water content of MCC affected the compressibility and formability of the tablet. When the equilibrium moisture content was approximately 5%, most of the moisture would be present in the pore structure of the microcrystalline cellulose, and a considerable portion of the moisture could be bonded to the cellulose by hydrogen bonding in the cellulose particles. During plastic deformation, the water in the pores acted as an internal lubricant that promoted slip and flow in a single crystallite. Higher moisture content (above 3.3%) corresponded to an improved plasticity due to the plasticizing effects of water above the critical water content, consequently resulting in a larger interparticulate bonding area when compressed (Changquan Calvin Sun 2008). The MCC samples had various water absorption characteristics. Interestingly, the water absorption of bamboo MCC was lower than the rest of the MCC samples. Previous studies proposed that this moisture sorption capacity could be associated with surface area, pore volume, and crystallinity (Mihranyan *et al.* 2004).

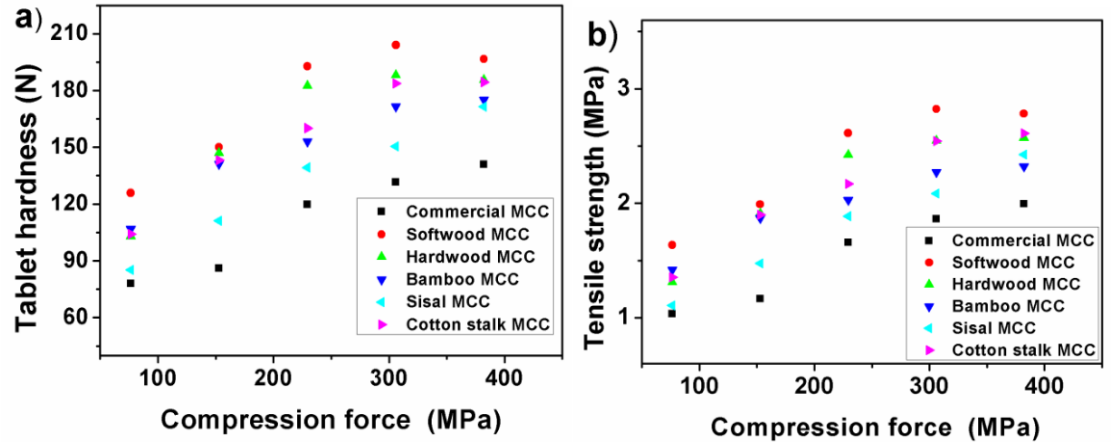

Fig. 1. Typical mechanical properties of tablet hardness and tensile strength under different compression forces (MCC particle size/D50 ≈ 52 ± 4 μm; dwelling time = 2 min)

The compression of MCC powders included the following processes: (1) the rearrangement of particles; (2) the elastic deformation of particles; (3) the plastic deformation of particles; (4) the breakup of particles; and (5) the combination of particles. When the MCC powder layer was compressed, the contact area between the particles increased with the elimination of some gases in the powder layer, which enhanced the bonding strength of the powder layer and eventually caused it to form into a solid tablet.

When the tablets were prepared from different materials under the same prescriptions, if the tensile strength (hardness) of tablet was higher, or the strength of the tablets prepared under lower pressure was higher, the material had a strong binding force and good compression formability. Normally, if the hardness of the MCC tablet is high at a lower pressure, the binding strength would be stronger, which would be economically advantageous for a pharmaceutical company. Based on the results presented in Fig. 1, the tablet hardness of commercial MCC was lower than the others that were derived from different cellulose sources and preparation processes.

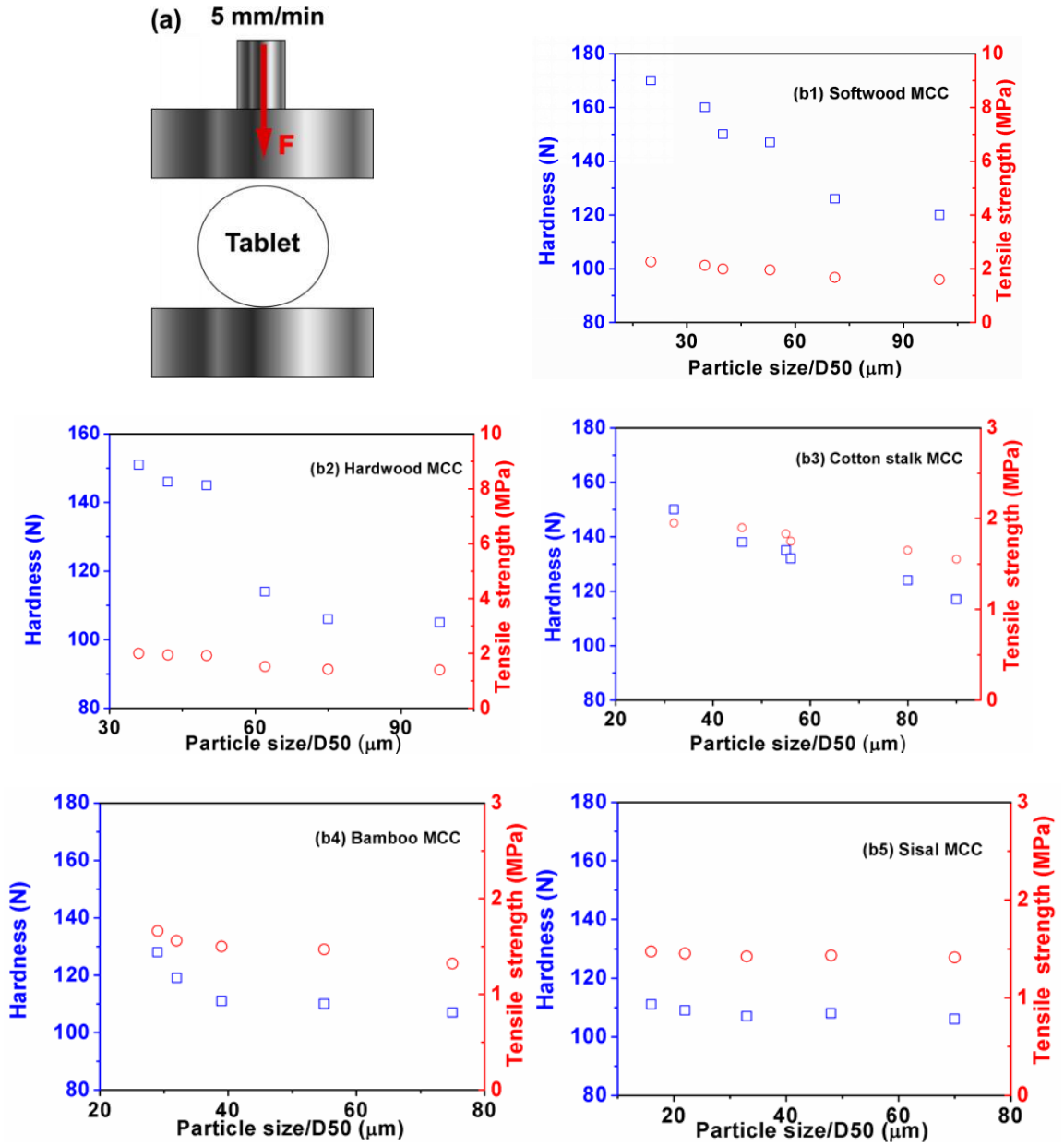

Fig. 2. Mechanical properties of tablet hardness and tensile strength on different MCC particle sources (compression force = 152 MPa; dwelling time = 0 min)

As shown in Fig. 1(a), the hardness of sisal MCC and commercial MCC tablets exhibited a noticeable upswing in the range of 76 MPa to 382 MPa, while the hardness of the rest of the MCC tablets increased in the range of 76 MPa to 306 MPa and decreased slightly in the range of 307 MPa to 382 MPa. The curves of tensile strength in Fig. 1(b) were similar to the curves for tablet hardness. It was clear that tablets made from softwood MCC had higher hardness than the others. Overall, the tablets made from wood MCC had superior mechanical properties compared to the non-wood tablets. Moreover, the cotton stalk MCC had more excellent mechanical properties than the bamboo MCC and sisal MCC. A possible explanation for this might be that the internal structure of cellulose and hydrogen bonds led to the differences in mechanical properties. Another explanation was

that the various degrees of polymerization, moisture content, particle size, and distribution affected the tablet hardness of MCC (Adel and El-Shinnawy 2012). Taken together, the results could also help to understand the correlation between cellulose resources and mechanical performance for MCC application in the production of drug tablets.

The effect of MCC particle size on mechanical properties is shown in Fig. 2. Changes in particle size not only affected the external surface area of particles, but also affected the bonding strength of particles. As shown in Fig. 2, the tablet hardness for wood MCC and cotton stalk MCC exhibited a downswing with increases the MCC particle size, which was consistent with previous findings (Khan and Pilpel 1986). This is because with larger particles, there are fewer potential sites in a given cross-sectional area of powder for pendular bonds to form between the particles (Khan and Pilpel 1986). However, bamboo MCC and sisal MCC showed no evident changes in their mechanical properties. This finding indicated that the influence of MCC particle size was also associated with lignocellulosic sources.

Table 5. Effect of MCC Samples Reinforcement on Tensile Strength and Elastic Modulus Values of PCL/MCC Film and PCL Neat Film

Sample	Tensile Strength at Break (MPa)	Elastic Modulus (MPa)
PCL/20% Cotton stalk	1.93	255.99
PCL/20% Hardwood	2.09	266.99
PCL/20% Softwood	2.13	270.90
PCL/20% Bamboo	1.88	242.18
PCL/20% Sisal	1.99	251.36
PCL Neat	1.62	148.84

A blended PCL/MCC was prepared. As can be seen from Table 5, overall, compared with PCL neat film, the tensile strength and elastic modulus of PCL/MCC films were improved by 16.0% to 42.5% and 62.7% to 82.0%, respectively. This increase was attributed to the good cellulose reinforcement effects and cellulose matrix interfacial compatibility (Dhakal *et al.* 2018). There was a remarkable improvement in tensile stress from 1.72 MPa for neat PCL to 2.13 MPa for the softwood MCC/PCL film. The elastic modulus increased from 148.8 MPa for neat PCL to 270.9 MPa for softwood MCC/PCL film. Overall, the reinforcing effect of MCC prepared from woody resources was stronger than the others. In addition, cotton stalk MCC also enhanced the elastic modulus of PCL film more effectively than bamboo MCC and sisal MCC.

The FT-IR spectra of the MCC samples are shown in Fig. 3. All MCC samples had a typical cellulose I structure. There were two main typical cellulosic absorbance regions presented in the ranges from 3500 cm^{-1} to 2800 cm^{-1} and 800 cm^{-1} to 1700 cm^{-1}. The peaks at 3320 cm^{-1} to 3445 cm^{-1} are attributed to the O-H stretching vibration of hydrogen-bonded hydroxyl groups (Mirmohamadsadeghi *et al.* 2016). The peaks in the range of 2901 cm^{-1} to 2903 cm^{-1} were attributed to -CH_2 and -CH_2OH. The peaks in the range of 1637 cm^{-1} to 1644 cm^{-1} were related to the absorbed water and C=O stretching vibration (Adel and El-Shinnawy 2012). The spectra showed a strong band at 1430 cm^{-1} to 1432 cm^{-1} presented in the -CH or- CH_2 vibration and it was a typical crystallinity band in MCC that indicated the crystallinity degree. The band at 896 cm^{-1} to 898 cm^{-1} was attributed to the C-O-C vibration at β-(1-4)-glycosidic and linkages between the sugar units. The results showed that no

major differences in FT-IR spectra were observed between the commercial MCC and MCCs isolated from various sources.

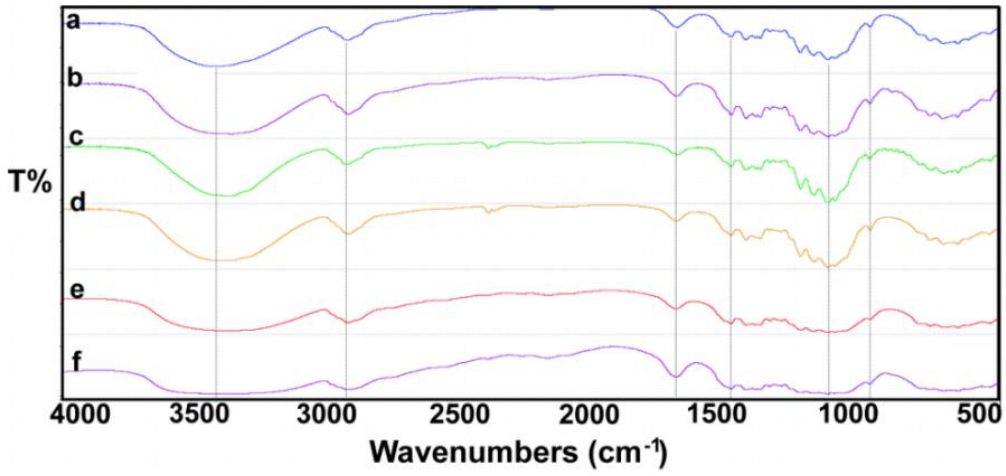

Fig. 3. FT-IR spectra of cotton stalk MCC(a), softwood MCC(b), hardwood MCC(c), bamboo MCC (d), sisal MCC, (e) and commercial MCC(f)

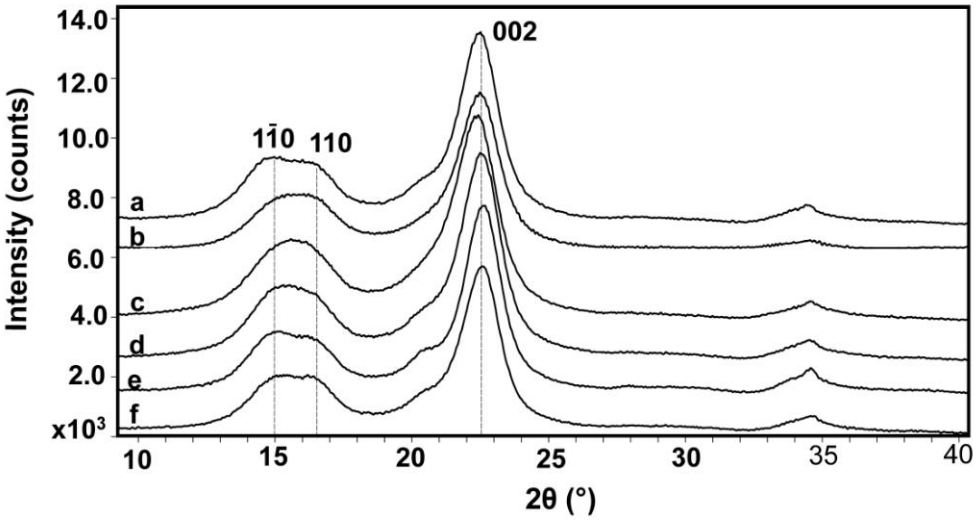

Fig. 4. X-ray diffraction patterns of hardwood MCC (a), softwood MCC (b), bamboo MCC (c), sisal MCC (d), commercial MCC (e), and cotton stalk MCC (f)

According to Thoorens *et al.* (2014, 2015), the degree of crystallization relative to microcrystalline cellulose is important due to its effect on a variety of properties, including the stabilizing capacity for suspension and emulsion, thermal properties, and hydration capacity of the MCC particles. The X-ray diffraction spectra of cotton stalk MCC, hardwood MCC, softwood MCC, bamboo MCC, sisal MCC, and commercial MCC are shown in Fig. 4, and the main reflections were at 15.0°, 16.6°, and 22.6°, which originated from cellulose I. The CrIs of the pulps and MCC samples are shown in Table 3. Excluding bamboo, the crystallinity of the other five MCCs reached approximately 80% through appropriate hydrochloric acid hydrolysis. Furthermore, the crystalline size (002) was noted in Table 3, and the crystalline size (002) of cotton stalk MCC (5.092 nm) was close to

commercial MCC (5.341 nm), which had the largest crystallite size. Generally, the crystalline size had no effect on the mechanical properties of the prepared MCC.

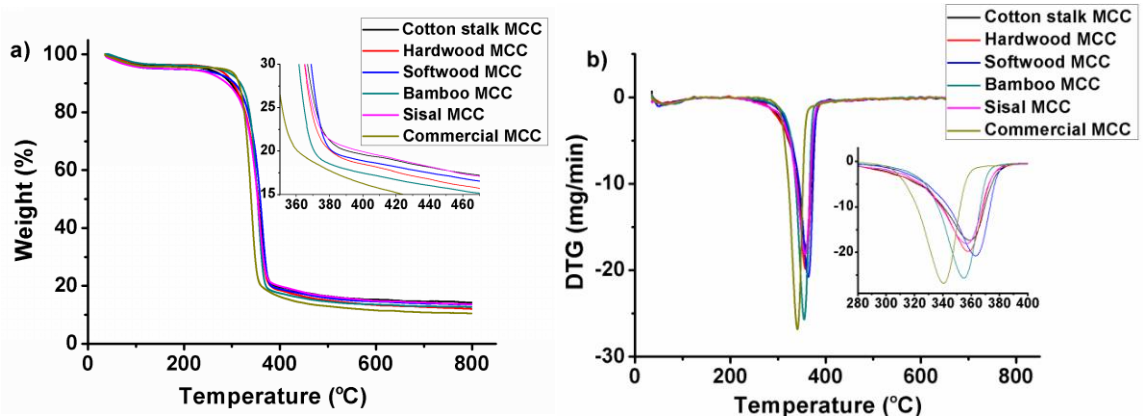

Fig. 5. Typical TGA (a) and derivative thermogram (DTG) (b) curves of MCC samples

The thermal properties of MCC, a type of polymer material, are critical for adaptability to high temperature. The typical TGA and DTG data of the MCC samples in thermal degradation processes are shown in Fig 5. Overall, as shown in Fig. 7(a), there were four stages based on weight. In the first stage, the weight was from 100% to 94% due to the evaporation of water and other volatile substances at the range of 36 °C to 140 °C. In the second stage, the weight remained at approximately 90% under the range of 290 °C to 317 °C. In the third stage, there was a sharp reduction in the range of 320 °C to 380 °C, which indicated that chemical bonds, such as C-C, C-O, and C-H were broken. Moreover, this stage mainly involved the thermal cracking process of the MCC samples due to degradation processes of cellulose, such as the decarboxylation, depolymerization, and decomposition of glycosyl units. In the fourth stage with the process of ash formation, the solid residues of the MCC samples were approximately 10% to 15% in the temperature range of 380 °C to 600 °C. Furthermore, as shown in Fig. 5b and Table 6, the DTG peak temperatures of cotton stalk MCC, hardwood MCC, softwood MCC, bamboo MCC, sisal MCC, and commercial MCC were 359.2 °C, 356.7 °C, 361.1 °C, 353.0 °C, 357.2 °C, and 337.6 °C, respectively. The thermal stability of softwood MCC was higher than the other samples. The TGA temperature of the MCC samples at 10% weight loss (T10) are shown in Table 6.

Table 6. TGA and DSC Data Obtained from MCC Samples

Sample	TGA Analysis				Residual Weight (%)[e]
	T_{on} (°C)[a]	T_{10} (°C)[b]	T_{peak} (°C)[c]	W_{loss} (%)[d]	
Cotton stalk MCC	312.6	297.4	359.2	80.6	14.24
Hardwood MCC	315.0	302.2	356.7	83.0	12.08
Softwood MCC	321.2	305.6	361.1	80.2	13.60
Bamboo MCC	328.6	317.6	353.0	82.7	12.70
Sisal MCC	310.4	289.4	357.2	80.0	13.72
Commercial MCC	320.2	314.2	337.6	84.0	10.49

[a] TGA onset decomposition temperature; [b] TGA temperature at 10% weight loss; [c] DTG peak temperature; [d] TGA maximum weight loss; and [e] TGA char residue weight

One unanticipated finding was that the T10 of bamboo MCC was the highest. Prior studies have noted that these differences derived from different sources of raw materials. The decomposition temperatures of MCC isolated from Sago seed shell were in the range of 250 °C to 340 °C (Naduparambath and Purushothaman 2016). Furthermore, the maximum weight loss of tea waste MCC was at 334 °C (Zhao *et al.* 2018). The thermal property of cotton stalk MCC was comparable to that of hardwood MCC.

CONCLUSIONS

1. All MCC samples showed typical cellulose I structures. The properties of α-cellulose content, pH, moisture content, CrI, and moisture sorption capacity were similar with each other and in agreement with the US pharmacopoeia standard. However, the ash contents of wood MCC and sisal MCC did not meet the standards of food and pharmaceutical application.
2. In this study, MCC isolated from woody materials obtained a higher degree of polymerization than that of non-woody materials, and softwood MCC was more stable at high temperatures. The tablets made from softwood MCC had higher tablet hardness than the others. Meanwhile, MCC powder effectively reinforced PCL film and the MCC samples obtained from woody sources were more suitable for use as reinforcing agents for PCL.
3. Cotton stalk MCC was most similar to woody MCC, especially in terms of its mechanical properties. In general, the wood MCC had better mechanical and reinforcing properties compared to non-wood MCC. The sources of cellulose should be thoroughly considered when manufacturing MCC for pharmaceutical and reinforced agent fields.

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REFERENCES CITED

Adel, A. M., and El-Shinnawy, N. A. (2012). "Hypolipidemic applications of microcrystalline cellulose composite synthesized from different agricultural residues," *International Journal of Biological Macromolecules* 51(5), 1091-1102. DOI: 10.1016/j.ijbiomac.2012.08.003

Adel, A. M., El-Wahab, Z. H. A., Ibrahim, A. A., and Al-Shemy, M. T. (2010). "Characterization of microcrystalline cellulose prepared from lignocellulosic materials. Part I. Acid catalyzed hydrolysis," *Bioresource Technology* 101(12), 4446-4455. DOI: 10.1016/j.biortech.2010.01.047

Aleman-Dominguez, M. E., Giusto, E., Ortega, Z., Tamaddon, M., Benitez, A. N., and Liu, C. (2018). "Three-dimensional printed polycaprolactone-microcrystalline cellulose scaffolds," *Journal of Biomedical Materials Research Part B: Applied Biomaterials* 107(3), 521-528. DOI: 10.1002/jbm.b.34142

Bae, D. H., Choi, H. J., Choi, K., Nam, J. D., Islam, M. S., and Kao, N. (2017). "Fabrication of phosphate microcrystalline rice husk based cellulose particles and their electrorheological response," *Carbohydrate Polymers* 165, 247-254. DOI: 10.1016/j.carbpol.2017.02.037

Chamsai, B., and Sriamornsak, P. (2013). "Novel disintegrating microcrystalline cellulose pellets with improved drug dissolution performance," *Powder Technology* 233, 278-285. DOI: 10.1016/j.powtec.2012.08.019

Cherian, B. M., Leão, A. L., De Souza, S. F., Thomas, S., Pothan, L. A., and Kottaisamy, M. (2010). "Isolation of nanocellulose from pineapple leaf fibres by steam explosion," *Carbohydrate Polymers* 81(3), 720-725. DOI: 10.1016/j.carbpol.2010.03.046

Chartrand, A., Lavoie, J., and Huneault, M. A. (2017). "Surface modification of microcrystalline cellulose (MCC) and its application in LDPE-based composites," *Journal of Applied Polymer Science* 134(1), Article No. 4438. DOI: 10.1002/app.44348

Dos Santos, F. A., Valle Iulianelli, G. C., and Bruno Tavares, M. I. (2017). "Development and properties evaluation of bio-based PLA/PLGA blend films reinforced with microcrystalline cellulose and organophilic silica," *Polymer Engineering and Science* 57(4), 464-472. DOI: 10.1002/pen.24447

Dhakal, H. N., Bourmaud, A., Berzin, F., Almansour, F., Zhang, Z., Shah, D. U., and Beaugrand, J. (2018). "Mechanical properties of leaf sheath date palm fibre waste biomass reinforced polycaprolactone (PCL) biocomposites," *Industrial Crops and Products* 126, 394-402. DOI: 10.1016/j.indcrop.2018.10.044

Elanthikkal, S., Gopalakrishnapanicker, U., Varghese, S., and Guthrie, J. T. (2010). "Cellulose microfibres produced from banana plant wastes: Isolation and characterization," *Carbohydrate Polymers* 80(3), 852-859. DOI: 10.1016/j.carbpol.2009.12.043

Feng, Q., Yamamichi, H., Shoya, M., and Sugita, S. (2004). "Study on the pozzolanic properties of rice husk ash by hydrochloric acid pretreatment," *Cement and Concrete Research* 34(3), 521-526. DOI: 10.1016/j.cemconres.2003.09.005

Gibis, M., Schuh, V., and Weiss, J. (2015). "Effects of carboxymethyl cellulose (CMC) and microcrystalline cellulose (MCC) as fat replacers on the microstructure and sensory characteristics of fried beef patties," *Food Hydrocolloids* 45, 236-246. DOI: 10.1016/j.foodhyd.2014.11.021

Jahan, M. S., Saeed, A., He, Z., and Ni, Y. (2011). "Jute as raw material for the preparation of microcrystalline cellulose," *Cellulose* 18(2), 451-459. DOI: 10.1007/s10570-010-9481-z

Kambli, N. D., Mageshwaran, V., Patil, P. G., Saxena, S., and Deshmukh, R. R. (2017). "Synthesis and characterization of microcrystalline cellulose powder from corn husk fibres using bio-chemical route," *Cellulose* 24(12), 5355-5369. DOI: 10.1007/s10570-017-1522-4

Khan, F., and Pilpel, N. (1986). "The effect of particle size and moisture on the tensile strength of microcrystalline cellulose powder," *Powder Technology* 48(2), 145-150. DOI: 10.1016/0032-5910(86)80073-0

Kian, L. K., Jawaid, M., Ariffin, H., and Alothman, O. Y. (2017). "Isolation and characterization of microcrystalline cellulose from roselle fibers," *International Journal of Biological Macromolecules* 103, 931-940. DOI: 10.1016/j.ijbiomac.2017.05.135

Kuentz, M., and Leuenberger, H. (2000). "A new model for the hardness of a compacted particle system, applied to tablets of pharmaceutical polymers," *Powder Technology* 111(1-2), 145-153. DOI: 10.1016/S0032-5910(00)00250-3

Mihranyan, A., Llagostera, A. P., Karmhag, R., Strømme, M., and Ek, R. (2004). "Moisture sorption by cellulose powders of varying crystallinity," *International Journal of Pharmaceutics* 269(2), 433-442. DOI: 10.1016/j.ijpharm.2003.09.030

Mirmohamadsadeghi, S., Chen, Z., and Wan, C. (2016). "Reducing biomass recalcitrance *via* mild sodium carbonate pretreatment," *Bioresource Technology* 209, 386-390. DOI: 10.1016/j.biortech.2016.02.096

Naduparambath, S., and Purushothaman, E. (2016). "Sago seed shell: Determination of the composition and isolation of microcrystalline cellulose (MCC)," *Cellulose* 23(3), 1803-1812. DOI: 10.1007/s10570-016-0904-3

Nsor-Atindana, J., Chen, M., Goff, H. D., Zhong, F., Sharif, H. R., and Li, Y. (2017). "Functionality and nutritional aspects of microcrystalline cellulose in food," *Carbohydrate Polymers* 172, 159-174. DOI: 10.1016/j.carbpol.2017.04.021

Obumneme, O. O. (2013). "The effect of pulping concentration treatment on the properties of microcrystalline cellulose powder obtained from waste paper," *Carbohydrate Polymers* 98(1), 721-725. DOI: 10.1016/j.carbpol.2013.06.039

Ohwoavworhua, F., Adelakun, T., and Okhamafe, A. O. (2009). "Processing pharmaceutical grade microcrystalline cellulose from groundnut husk: Extraction methods and characterization," *International Journal of Green Pharmacy* 3(2), 97-104. DOI: 10.4103/0973-8258.54895

Parveen, S., Rana, S., Fangueiro, R., and Paiva, M. C. (2017). "A novel approach of developing microcrystalline cellulose reinforced cementitious composites with enhanced microstructure and mechanical performance," *Cement and Concrete Composites* 78, 146-161. DOI: 10.1016/j.cemconcomp.2017.01.004

Rashid, M., Gafur, M. A., Sharafat, M. K., Minami, H., Miah, M. A. J., and Ahmad, H. (2017). "Biocompatible microcrystalline cellulose particles from cotton wool and magnetization *via* a simple *in situ* co-precipitation method," *Carbohydrate Polymers* 170, 72-79. DOI: 10.1016/j.carbpol.2017.04.059

Sun, C. C. (2008). "Mechanism of moisture induced variations in true density and compaction properties of microcrystalline cellulose," *International Journal of Pharmaceutics* 346(1-2), 93-101. DOI: 10.1016/j.ijpharm.2007.06.017

Trache, D., Donnot, A., Khimeche, K., Benelmir, R., and Brosse, N. (2014). "Physico-chemical properties and thermal stability of microcrystalline cellulose isolated from alfa fibres," *Carbohydrate Polymers* 104, 223-230. DOI: 10.1016/j.carbpol.2014.01.058

Trache, D., Hussin, M. H., Chuin, C. T. H., Sabar, S., Fazita, M. R. N., Taiwo, O. F. A., Hassan, T. M., and Haafiz, M. K. M. (2016). "Microcrystalline cellulose: Isolation, characterization and bio-composites application—A review," *International Journal of Biological Macromolecules* 93(Part A), 789-804. DOI: 10.1016/j.ijbiomac.2016.09.056

Thoorens, G., Krier, F., Leclercq, B., Carlin, B., and Evrard, B. (2014). "Microcrystalline cellulose, a direct compression binder in a quality by design environment—A

review," *International Journal of Pharmaceutics* 473(1-2), 64-72. DOI: 10.1016/j.ijpharm.2014.06.055

Thoorens, G., Krier, F., Rozet, E., Carlin, B., and Evrard, B. (2015). "Understanding the impact of microcrystalline cellulose physicochemical properties on tabletability," *International Journal of Pharmaceutics* 490(1-2), 47-54. DOI: 10.1016/j.ijpharm.2015.05.026

United States Pharmacopeial Convention (2012). "Microcrysatlline cellulose," in: *The United States Pharmacopoeia National Formulary 30*, Rockville, MD, USA, pp. 1746-1747.

Wang, H., Srinivasan, R., Yu, F., Steele, P., Li, Q., and Mitchell, B. (2011). "Effect of acid, alkali, and steam explosion pretreatments on characteristics of bio-oil produced from pinewood," *Energy & Fuels* 25(8), 3758-3764. DOI: 10.1021/ef2004909

Woodruff, M. A., and Hutmacher, D. W. (2010). "The return of a forgotten polymer - polycaprolactone in the 21st century," *Progress in Polymer Science* 35(10), 1217-1256. DOI: 10.1016/j.progpolymsci.2010.04.002

Xiang, L. Y., Mohammed, M.A.P., and Baharuddin, A. S. (2016). "Characterisation of microcrystalline cellulose from oil palm fibres for food applications," *Carbohydrate Polymers* 148, 11-20. DOI: 10.1016/j.carbpol.2016.04.055

Zhao, T., Chen, Z., Lin, X., Ren, Z., Li, B., and Zhang, Y. (2018). "Preparation and characterization of microcrystalline cellulose (MCC) from tea waste," *Carbohydrate Polymers* 184, 164-170. DOI: 10.1016/j.carbpol.2017.12.024

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