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Research paper

Water retention and drainage in different brands of microcrystalline cellulose: Effect of measuring conditions

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Abstract

Interaction between water and microcrystalline cellulose (MCC) measured as retention and cumulative drainage of water (WR% and CDW%) is investigated for unmilled and micronized standard (Avicel and Emcocel) and silicified (Prosolv) MCC brands. A centrifuge method was applied with increasing duration and different porosity and thickness of cylindrical powder beds (specimens), in order to establish optimal determination conditions and quantify alterations in interaction between water and different MCC brands. Also, changes of specimen thickness due to presence of water (swelling) were followed. It was found that the effect of specimen porosity and thickness on water drainage (CDW%) appears to be opposite to that on water retention (WR%), while two patterns of WR% and CDW% change with specimen porosity and thickness can be distinguished depending on the centrifugation time. Also, WR% and CDW% are affected by the MCC brand and the micronization. Unmilled silicified MCC brand (Prosolv) shows significantly lower retention and higher drainage of water compared to standard unmilled brands (Avicel and Emcocel), while differences between the unmilled standard Avicel and Emcocel brands are not easily distinguished. Micronization, in general, increases greatly the WR% and decreases CDW% for all the tested MCC brands, and enhances their differences even between Avicel and Emcocel. Swelling of specimen due to presence of water was observed, which was significantly reduced with the micronization, the specimen porosity, and centrifugation as well, but showed slight variation between the different MCC brands. Values of specimen porosity between 60% and 70%, thickness/diameter ratio between 0.75 and 1.0, and centrifugation time between 5 and 20 min provide optimal measuring settings for comparison of MCC brands.

Keywords: Microcrystalline cellulose; Water retention; Water drainage; Centrifuge

1. Introduction

The interaction between water and powdered microcrystalline cellulose (MCC) is very much related to pharmaceutical formulation processes such as granulation, spheronization, and drying, because MCC is widely used as filler, disintegrant and binder of oral tablets, pellets, and capsules. For alteration of MCC behavior during formulation processes and particularly for elimination of some limitations to its use, it is manufactured as unsilicified (standard) and silicified grades, and in various particle size ranges. Particularly for extrusion-spheronization of pellets, the measurement of water retention capacity is considered as useful in characterizing and comparing the behavior of MCC and of other starch mixtures with dextrins as well as in selecting optimal amounts of wetting liquid for processing [1].

Importance of the interaction between water and MCC, besides its complexity and involvement of particle size and shape changes [2,3], is indicated by the numerous experimental methods employed for its study. Some of them are NMR [4], near-infrared spectroscopy [5,6], water-vapor sorption [7], dielectric response [8], thermal analysis [9], powder and mixer torque rheometry [10], as well as water movement in powder beds using pressure membrane [11] and centrifugation measurements [12]. In the last case, a

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simple centrifuge method was applied on wet-massed MCC samples using fixed centrifugation time and different centrifugation speeds and initial water levels as well and the ability to hold water was compared for MCC grades differing in their origin, polymer content, and particle size. Differences in water retention were found, which depended on water amount added initially and this dependency was diminishing at higher water addition [12]. Centrifugation technique has also been applied to standard and silicified MCC grades, in a manner similar to that applied in the paper industry [13], by adding relatively large water volumes and measuring its retention and drainage [14,15]. It was observed that in addition to the speed and time of centrifugation, both retention and drainage of water were affected by the packing of the particles or the porosity of the powder bed. The changes of specimen thickness due to swelling in the presence of water may be involved in the aforementioned effects and furthermore its consideration may contribute to optimization of the water retention and drainage testing method. Therefore, it was thought of interest to investigate in more detail the effects of specimen porosity and size (initial thickness, before water addition) on the retention and drainage of water, for standard and silicified MCC brands before and after micronization, in parallel with the specimen swelling due to water presence.

In the present work, cylindrical powder columns (specimens) of decreasing porosity and thickness were employed for two standard and one silicified MCC brands. Increasing centrifugation time was applied while the mass proportion of powder and water was fixed (1:3 w/w). This investigation is expected to be useful in establishing optimal conditions for the determination of retention and drainage of water by the centrifuge method, and hence for quantifying alterations in the interaction between water and MCC related to pharmaceutical processes like granulation and extrusion-spheronization.

2. Materials and methods

2.1. Materials

Powders of Avicel PH 101 (Batch no. 6950C, from FMC International, Cork Ireland) and Emcocel M50 (Batch no. 5L2670, from Penwest Pharmaceuticals, Nastola, Finland) were the standard unsilicified MCC brands and Prosolv SMCC50 (Batch no. P5S0010, from Penwest Pharmaceuticals, Nastola, Finland) was the silicified brand. The materials were used as received (unmilled) and after micronization, performed by milling twice on a fluid energy mill (Aljet, Plumsteadville, PA, USA), operated at 80–100 psi pressure of compressed air and a feed rate of 1–2 g of powder per minute.

2.2. Characterization of powder particles

Size and shape of particles were expressed as circle equivalent diameter (CED) by number and as aspect ratio. They were determined by using a particle sizing and image analysis program (Quantimet 500, Leica, UK) and processing data either selected from direct examination with a CCD camera (Sanyo VC-2512, Sanyo Electric, Japan) attached to an optical microscope (Leitz Laborlux S, Wild Leitz, Germany) or transferred after scanning electron microphotography (JSM 840A, JEOL, Japan) and storage in digital form. Representative SEM photographs are shown in Fig. 1.

Volume specific surface area (S_v) was calculated from data of surface-volume mean particle diameter, d_{sv}, obtained using the air-permeability method (Fisher Sub-Sieve Sizer) and the equation:

$$S_v = 6/d_{sv}. \quad (1)$$

Values of d_{sv} were measured at different porosity between 75% and 55%, Fig. 2, and from these the plateau value was accepted and substituted in Eq. (1). Porosity represents the percentage of voids in the powder bed and is calculated from the expression: porosity $\% = [1 - m/(v \times p_s)] \times 100$ where m and v are the mass and volume, respectively, of the packed powder, and p_s its apparent particle density. The so-obtained S_v ($m^2\,cm^{-3}$) provides a measure of the envelope particle surface, excluding pores inside the particle [16].

Density of the experimental powders was measured as apparent particle density, on an air comparison pycnometer (Beckman, Model 930) and as bulk density according to the British Standards 1460:1967.

2.3. Determination of water retention and drainage

The experimental arrangement shown in Fig. 3 was placed in a centrifuge tube (1). The arrangement consisted of a plated cylindrical brass cup (2) of 50 mm height, 23 mm internal diameter, and perforated bottom (3), sitting on a plated brass tube (4) of the same internal diameter and 35 mm height. A membrane filter of 0.2 μm pore diameter was precisely cut to fit the perforated base of the cup (5), thus preventing any excipient particles from passing into the drained liquid.

For the specimen preparation, accurately weighed powder was transferred in the cup after the filter fitting and was packed to different specimen thickness and porosity using appropriate compressing lid and hydraulic press if necessary. The packed powder column was then saturated with 3× the powder weight distilled water, added with a pipette to the center of the specimen surface. This technique is similar to the one used in the paper industry [13] and is modification of that employed by Tomer and Newton [17]. The modification is expected to minimize the effects of the added water amount on the retention observed by Tomer et al. [12], because no wet mixing of the powder is done prior to placement in the cup and the water/powder ratio (×3) employed was fixed and relatively larger.

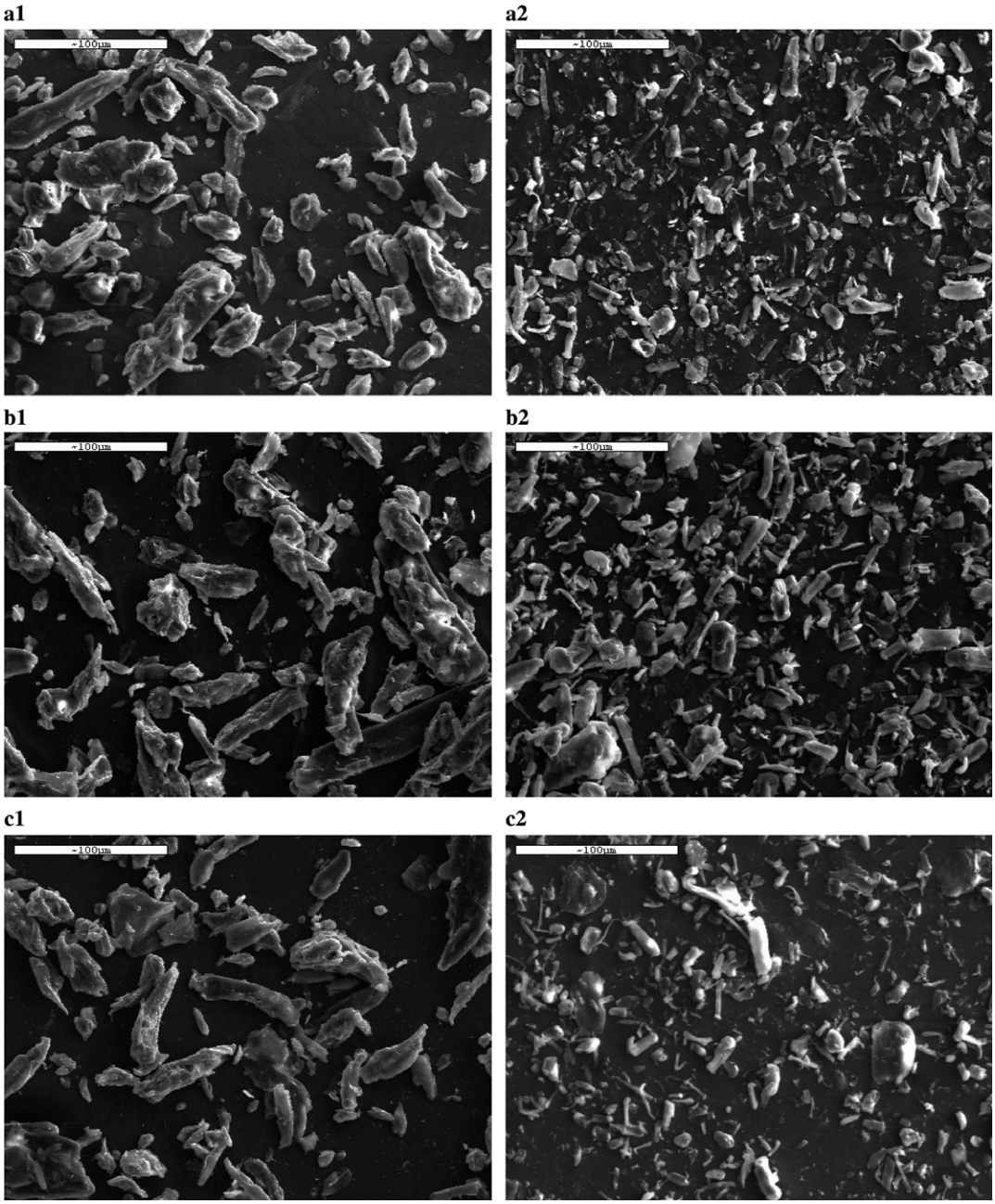

Fig. 1. SEM microphotographs of Avicel (a), Emcocel (b), and Prosolv (c), unmilled (1) and micronized (2).

For the measurement, four supporting tube and cup arrangements were inserted into the tubes of a centrifuge (Heinz Janetzki, Engelsdorf-Leipzig, Germany) and rotated for time intervals from 0.5 min (shortest possible time) up to 120 min, at 2500 rpm. This speed corresponds to a relative centrifugal force of RCF = 700*g* (distance of perforated end of basket from the rotation axis is 10 cm) at which differences in retention or drainage of water between the MCC brands are better distinguished comparatively to lower RCF [14]. Centrifugation was interrupted at regular time intervals and the weight of the cylindrical brass cup containing the wet powder mass as well as the weight of drained liquid was measured. Also, the change in specimen thickness (swelling) was determined.

Experiments were performed at controlled room temperature 20 ± 1 °C and environmental relative humidity $50 \pm 5\%$, to reduce any effects on water evaporation and hence on retention and drainage. At least three replicated measurements of water retention and cumulative drained water were obtained for each unmilled or micronized brand. Water retention was expressed as percentage (WR%) on dry basis, calculated from the difference in the weight after each centrifugation time interval and after final overnight drying in a fan-fitted oven, at 105 °C. Drainage of water was expressed as cumulative drained

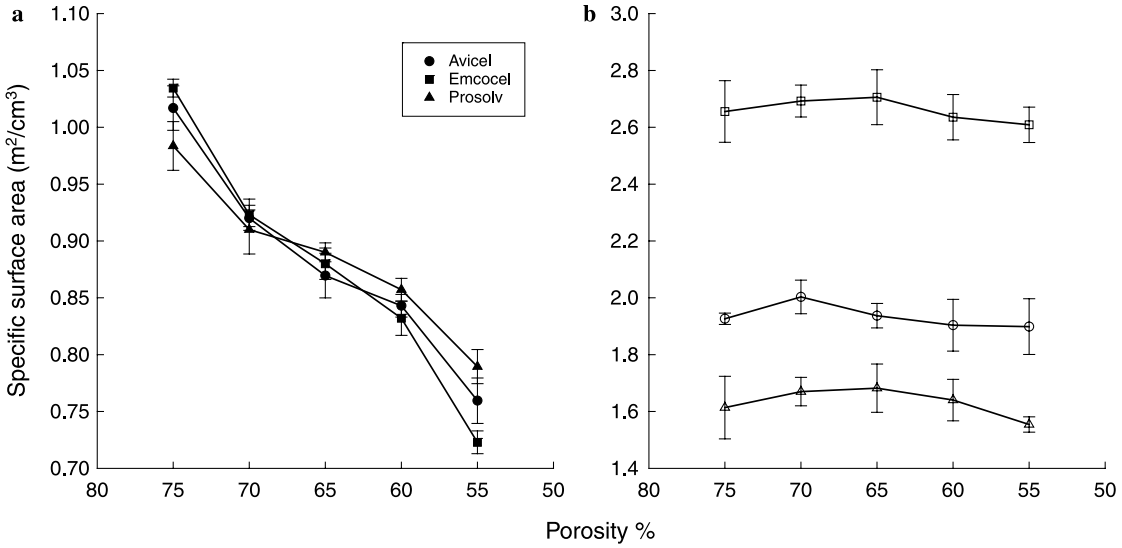

Fig. 2. Specific surface area of unmilled (a) and micronized (b) brands of microcrystalline cellulose vs porosity.

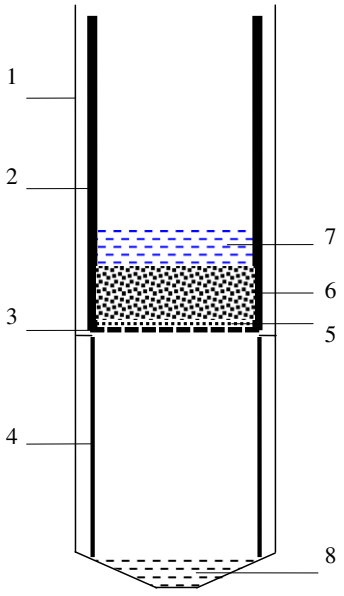

Fig. 3. Experimental arrangement used for the determination of water retention and cumulative drainage of water. (1) Centrifuge tube, (2) cylindrical cup, (3) perforated bottom, (4) supporting tube, (5) filter, (6) powder, (7) water, and (8) drained liquid.

water (CDW%), calculated from the weight of liquid collected at the bottom of centrifuge tube (Fig. 3), compared to that initially added.

The effect of porosity was studied at four levels, 75%, 70%, 60%, and 50%, and at a fixed intermediate thickness of the powder column (12.5 mm), obtained by packing 2–4 g of powder with the same lid (37.5 mm length). The effect of specimen thickness was studied at five levels (6.2, 12.5, 17, 23, and 29 mm) and at a fixed intermediate porosity 70%, obtained by packing 1.2–5.5 g of powder with different lids (21–43.8 mm penetration length).

2.4. Changes in specimen thickness on water addition (swelling)

The effect of water addition on thickness of packed powder beds and its dependence on initial porosity was estimated on specimens, prepared at a fixed initial thickness (12.5 mm) and three porosity levels 70%, 60%, and 50%. The same experimental arrangement and excipient/water quantities were employed as for the water retention and drainage determination. A linear variable displacement transducer (LVDT model D5-200AG, RDP Electronics UK) was used, which was attached to a metallic block and connected to a computer, through a signal conditioner and amplifier (model E309, RDP, UK), for the transfer of data in ASCII form [18]. A teflon plunger was placed between the LVDT and the packed powder bed (dry or wet). Several measurements of thickness were taken with an accuracy of 0.5 μm when centrifugation was interrupted at regular time intervals.

2.5. Statistical analysis

For the statistical analysis of the data the SPSS 12.0 statistical software was used (SPSS Inc. Chicago, IL, USA).

3. Results and discussion

3.1. Physical properties

In Table 1 are summarized the results of particle characteristics for all the experimental powders. Differences in circle equivalent diameter (CED) between the optical and scanning electron microscope (SEM) determination may be attributed to the ability to distinguish the individual MCC particles from agglomerate [19]. All unmilled or micronized brands have similar mean CED, aspect ratio,

Table 1
Particle characteristics of microcrystalline cellulose experimental powders (mean ± SD)

Powder	CED[a] (μm)		Aspect ratio		Specific surface area S_v ($m^2\ cm^{-3}$)	Particle density p_s ($g\ cm^{-3}$)	Bulk density p_b ($g\ cm^{-3}$)
	Optical	SEM[c]	Optical	SEM[c]			
Avicel	41 ± 22	19 ± 10	2.04 ± 0.6	2.14 ± 0.7	0.87 ± 0.01	1.55 ± 0.01	0.31 ± 0.00
Emcocel	31 ± 27	22 ± 12	2.13 ± 0.7	2.33 ± 0.8	0.92 ± 0.02	1.54 ± 0.00	0.31 ± 0.00
Prosolv	41 ± 33	20 ± 9	2.09 ± 0.7	2.31 ± 0.9	0.93 ± 0.01	1.56 ± 0.01	0.32 ± 0.00
Avicel m[b]	8 ± 6	9 ± 6	1.99 ± 0.7	2.21 ± 0.8	1.94 ± 0.03	1.53 ± 0.02	0.25 ± 0.00
Emcocel m[b]	8 ± 5	11 ± 5	1.97 ± 0.7	2.34 ± 0.9	2.71 ± 0.08	1.52 ± 0.01	0.19 ± 0.01
Prosolv m[b]	9 ± 6	12 ± 6	1.96 ± 0.7	2.32 ± 0.9	1.68 ± 0.02	1.54 ± 0.01	0.28 ± 0.00

[a] CED, circle equivalent diameter.
[b] m, micronized.
[c] SEM, scanning electron microscopy.

air-permeability volume specific surface area (S_v), apparent particle density (p_s), and bulk density (p_b) except of micronized Emcocel, for which S_v and p_b values are very different from those of micronized Avicel and Prosolv. The specific surface area is higher while the bulk density is lower and therefore they can both be attributed to higher surface roughness of micronized Emcocel.

The higher surface roughness of micronized Emcocel than that of Avicel can be attributed to the source of cellulose and the fibril characteristics or the crystallinity [20]. This is supported by previously published values of specific surface area of unmilled MCC brands measured by nitrogen adsorption, which were always higher for Emcocel 1.33–1.35 $m^2\ g^{-1}$, compared to Avicel 0.98–1.14 $m^2\ g^{-1}$ [21–23]. They can be considered as evidence of the higher surface roughness of Emcocel fibrils, because nitrogen due to small molecular cross-sectional area (16 $Å^2$) has the ability to penetrate fine pores inside the MCC particles and thus provide information about the fibril surface texture besides that of particles. The difference in the surface roughness between Emcocel and Prosolv should be attributed to the incorporation of SiO_2 probably resulting in different fracturing during micronization, since both Prosolv and Emcocel have the same origin and micronization is expected to have minimal effect on crystallinity [24].

From the above discussion it may be concluded that the cellulose source together with silicification is responsible for alterations in the MCC surface resulting in the improved packing and slightly higher bulk density of micronized Prosolv compared to both Avicel and Emcocel and therefore eliciting possible differences with water interaction.

3.2. Changes in specimen thickness on water addition (swelling)

From the results presented in Table 2 it can be seen that the specimen thickness increases due to the water addition for all the experimental powders. Also it can be seen that this increase (swelling) was reduced with the micronization, the specimen porosity, and the centrifugation time as well. The differences in thickness increase (swelling) between the different MCC brands were slight and not characteristic.

Table 2
Changes in initial thickness (12.5 mm) due to presence of water (swelling) for three porosity levels of specimen during the centrifugation (mean, $n = 4$)

Powder	Porosity (%) of dry specimen	Swelling (mm)[a] at centrifugation time	
		5 min	120 min
Avicel	50	4.55	4.51
Emcocel	50	4.07	3.89
Prosolv	50	4.61	4.37
Avicel m[b]	50	2.44	2.40
Emcocel m[b]	50	2.27	2.18
Prosolv m[b]	50	2.16	2.09
Avicel	60	3.60	3.32
Emcocel	60	3.45	3.28
Prosolv	60	3.32	3.18
Avicel m[b]	60	1.78	1.73
Emcocel m[b]	60	1.50	1.38
Prosolv m[b]	60	1.55	1.45
Avicel	70	2.22	1.98
Emcocel	70	2.23	1.98
Prosolv	70	2.84	2.52
Avicel m[b]	70	0.82	0.67
Emcocel m[b]	70	0.60	0.42
Prosolv m[b]	70	0.30	0.11

[a] SD = 0.05–0.1.
[b] m, micronized.

The reduction of specimen swelling due to micronization may be attributed to the greater number and strength of interparticle bonds resulting in increased resistance for interparticle separation when the particle size increases in the presence of water. Also, the reduction may be attributed to the smaller size and size distribution of the interparticle voids (pores) for the case of micronized brands resulting in expanded MCC–liquid water interface and reduced interaction between water molecules and intraparticle cellulose polymer chains. Similarly, the increase in swelling with the porosity reduction may be attributed to greater proportion of internal cellulose polymer chains comparatively to those on the particle surface. This is also

indicated by the remarkable decrease of specific surface area in the packed powder with the porosity, as shown in Fig. 2a for the unmilled brands. Finally, the swelling reduction with centrifugation time, which may be due to elimination of the interaction between liquid water and MCC on the particle surface, is relatively small compared to the changes due to micronization and porosity. Therefore, it confirms the predominance of interaction between water molecules and intraparticle cellulose polymer chains at extended centrifugation, and suggests the possibility of distinguishing the two aforementioned MCC–water interactions or in other words described as capillary, funicular or pendular (under quick centrifugation) and as sorbed state (under extended centrifugation).

3.3. Effect of measuring conditions on water interaction

3.3.1. Specimen porosity and centrifugation time

In Fig. 4 are presented plots of water retention (WR%) and drainage (CDW%) vs porosity of the dry specimen, for all the powders studied, at a fixed specimen thickness (12.5 mm) and increasing centrifugation time (0.5, 2.5, and 5 min). Plots at longer centrifugation time (not shown) were similar to those of 5 min.

Fig. 4 shows that irrespective of the centrifugation time, the effect of porosity on water drainage (CDW%) change appears to be opposite to that on water retention, while two patterns of WR% and CDW% change with porosity can be distinguished depending on the centrifugation time. One pattern with 0.5 min of centrifugation (the shortest possible, Figs. 4a1 and b1), which is characterized by slight initial decrease of WR% with porosity decrease followed by remarkable increase at the lower porosity, corresponding to initial increase followed by decrease of CDW%. Another pattern obtained with 5 min centrifugation (Figs. 4a3 and b3) is characterized by decrease of WR% for all the range of porosity examined and by increase of CDW% with porosity decrease. For intermediate centrifugation time (2.5 min) the changes of WR% and CDW% with porosity (Figs. 4 a2 and b2) have similarities either with the first or the second pattern depending on the MCC brand and the micronization. Particularly, for the micronized standard MCC brands the changes are similar to those seen after 0.5 min centrifugation, but for the unmilled powders and for the micronized Prosolv as well, the changes are similar to those seen after 5 min centrifugation.

Alteration in the patterns of WR% and CDW% vs porosity plots with the centrifugation time should be connected to the proportion of water kept by the columns of the compacted powder as capillary, funicular or pendular (under quick centrifugation) and as sorbed state (under extended centrifugation).

The initial slight decrease of WR% and increase of CDW% with porosity decrease, observed with quick centrifugation, may be explained due to particle packing interactions, which seem to be responsible for similar increased

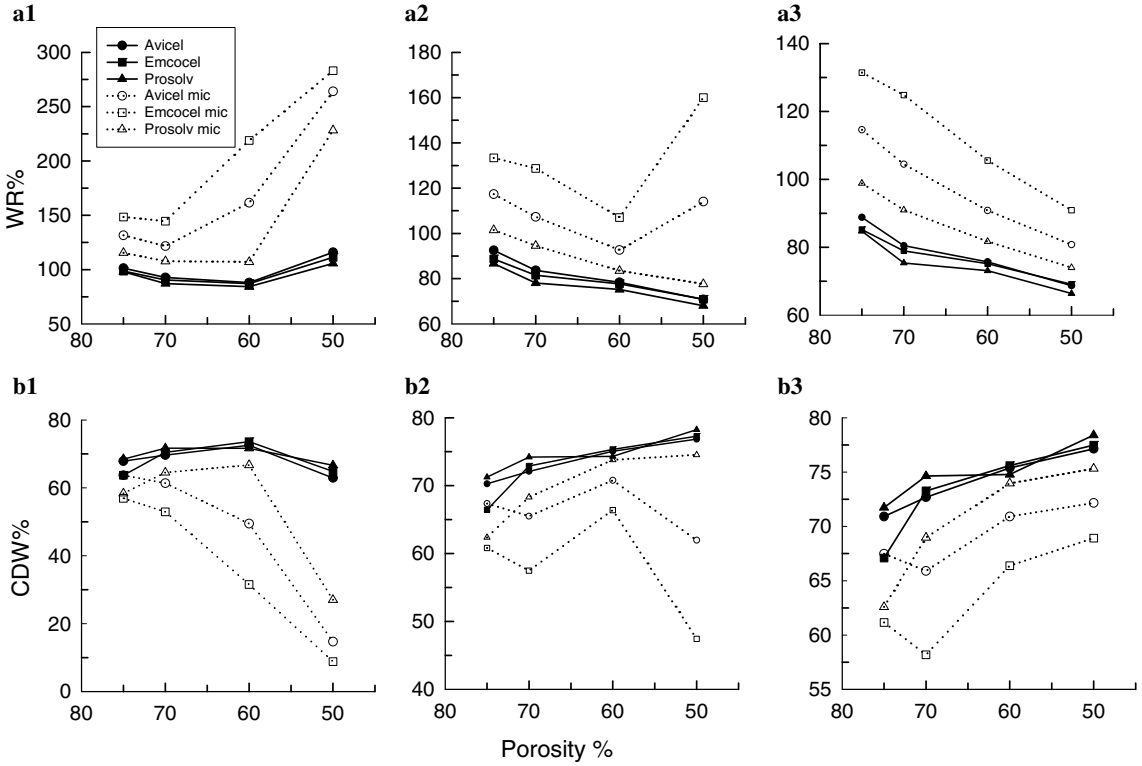

Fig. 4. Water retention (a) and cumulative drainage of water (b) vs porosity, at fixed specimen thickness (12.5 mm) and different centrifugation time (1 = 0.5 min, 2 = 2.5 min, 3 = 5 min).

negative slope in the plots of S_v vs porosity of unmilled brands, in Fig. 2a, for porosity higher than 70%. The following increase of WR% or decrease of CDW% seen in Figs. 4a1 and b1 should be due to the reduction in the pore size and to the increased capillarity, which hinder passage of water through the powder bed and increase retention of water as capillary and funicular state. However, the increase of WR% or decrease of CDW% with porosity decrease, seen after 5 min centrifugation for all powders and after 2.5 min for the micronized Prosolv and all the unmilled brands, should be ascribed to increased interparticle contacts, resulting in reduction of surface available for solid–liquid interaction. With 2.5 min centrifugation, WR% does not increase and CDW% does not decrease, at porosity lower than 60%, for the case of micronized silicified brand (Prosolv) as it does for the micronized standard brands (Avicel and Emcocel). This should be attributed to reduced proportion of funicular water due to different particle–particle or cellulose–water interactions caused by the presence of SiO_2.

In conclusion, the interaction between water and MCC measured as WR% and CDW% except for the specimen's porosity depends on the MCC processing (micronization and silicification). Also, porosity of powder specimen between 70% and 60% provides optimal comparison of different MCC brands and more than 2.5-min centrifugation time is necessary to avoid water retention in capillary and funicular state.

3.3.2. Specimen thickness and centrifugation time

The plots of water retention and drainage vs thickness of dry specimen, Fig. 5, also show two different patterns; one for 0.5 min and another for 2.5 min centrifugation. Plots obtained at longer centrifugation time (not shown) were similar to those of 2.5 min. For 0.5 min centrifugation, Fig. 5a1, WR% decreases remarkably with the specimen thickness up to 12.5 mm, then remains more or less unchanged up to 23 mm, and finally increases greatly at a higher thickness. For 2.5 min centrifugation, Fig. 5a2, WR% decreases up to 17 mm and remains unchanged thereafter. The changes of CDW% with specimen thickness for all the centrifugation times are seen to be opposite to those of water retention. The above results show that WR% and CDW% are less dependent on thickness in the range between 17 and 23 mm. This thickness is close to specimen diameter (thickness/diameter ratio between 0.75 and 1) and may indicate relation to possible variation of powder packing and liquid distribution within the specimen (powder column).

The relatively high WR% and the low CDW% seen in Fig. 5 with the lowest specimen thickness or powder weight (1.2 g) studied, although fixed water/powder ratio was used, should be due to the relatively short duration of water flow in the powder bed. Other possible reasons may be the easier airflow that is developed during the centrifugation as well as the different porosity of the powder adjacent to the wall of the cup [25]. The increase of

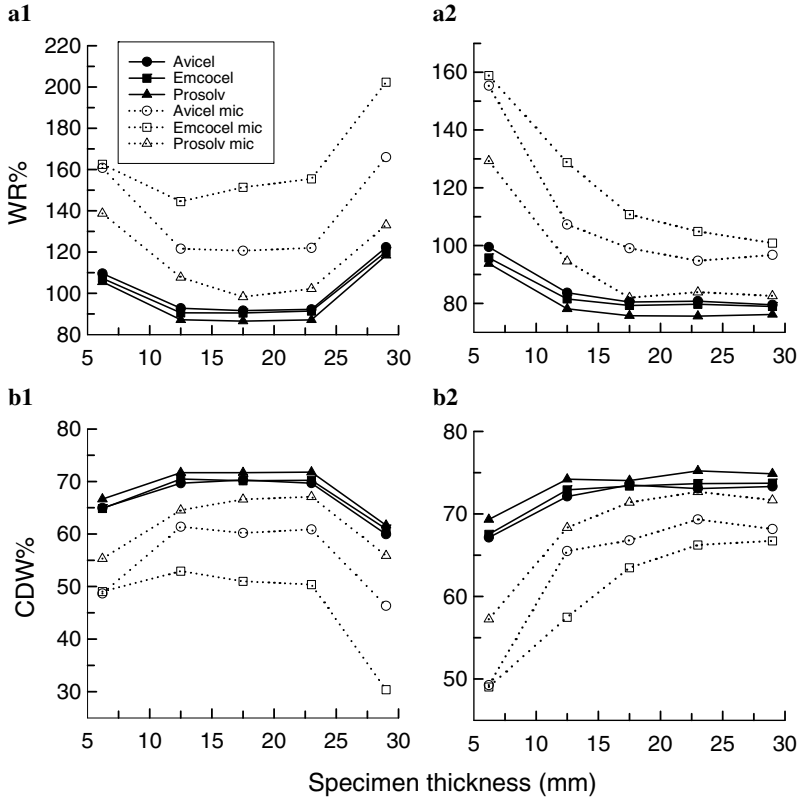

Fig. 5. Water retention (a) and cumulative drainage of water (b) vs specimen thickness, at fixed porosity (70%) and different centrifugation time (1 = 0.5 min, 2 = 2.5 min).

WR% and decrease of CDW% after quick centrifugation (0.5 min) at high specimen thickness (Figs. 5a1 and b1) should be due to the longer path that the liquid needs to travel through the powder and inadequacy of time to drain out. This increase of WR% and decrease of CDW% at high thickness is not seen however after 2.5 min centrifugation, probably due to sufficiency of time for water uptake and swelling of the powder particles, resulting in equilibrated alteration of their dimensions, total porosity, and tortuosity. Therefore, values of specimen thickness/diameter ratio between 0.75 and 1 should be used for comparison of the water retention capacities and water drainage of MCC powders and centrifugation time above 2.5 min should be applied.

3.4. Effects of MCC processing on water interaction

3.4.1. Micronization

From Figs. 4 and 5, it can be seen that WR% of the micronized samples is much greater and CDW% much lower than that of the corresponding unmilled samples. This should be attributed to the larger surface area of the micronized powders in contact with water, leading to immobilization of larger water amounts, and also to the smaller pore size or pore capillarity. It is also seen that the differences between the brands are greatly enhanced due to micronization, and that for WR% the results follow the order Emcocel > Avicel > Prosolv, which is the same with that of specific surface area (Table 1). For drainage the order is: Prosolv > Avicel > Emcocel, which is reverse from that of specific surface area. Therefore, since micronization is expected to have minimal effects on the crystallinity of MCC [24], the surface roughness or the source of cellulose or the fibril characteristics, together with silicification, should be responsible for the observed marked differences in the retention and drainage of water between the micronized brands.

However, from Figs. 4 and 5 the differences in water retention and drainage between the unmilled brands are not easily distinguished. To make these clearer, specimens corresponding to the plateaus, as they appear in Figs. 4 and 5, indicating reduced dependence of water retention and drainage on specimen's porosity and thickness, were used (porosity = 70% and thickness = 17 mm). The obtained results, Fig. 6, show that there are considerable differences in the WR% or CDW% values between the silicified and the standard MCC brands, at centrifugation time between 5 and 90 min, but very small differences at short (<5 min) and long (>90 min) centrifugation. On the contrary, no differences in retention and drainage can be seen between the two unmilled standard MCC brands of different cellulose source (Avicel and Emcocel), at any centrifugation time.

3.4.2. Silicification

The statistical significance of the overall effect of MCC brand and centrifugation time on retention and drainage, and their possible interaction, were tested employing a mixed factorial or split-plot ANOVA experimental design (General Linear Model – repeated-measures procedure, SPSS Advanced statistics 1997). It included two independent variables, one qualitative and one quantitative. The qualitative variable (within factor) had three levels (Avicel, Emcocel and Prosolv) and the quantitative variable (between factor) had nine levels (0.5, 2.5, 5, 10, 20, 40, 60, 90, and 120 min).

The effects of cellulose brand on WR% and CDW% were found significant, with $p = 0.008$ (df = 2, $F = 8.042$) and $p = 0.013$ (df = 2, $F = 6.994$), respectively. Also the interactions between the cellulose brand and centrifugation time were also significant, with $p = 0.011$ (df = 16, $F = 2.213$) and $p < 0.001$ (df = 16, $F = 4.140$). These interactions were further analyzed by comparing separately the differences in the WR% and CDW% values between each of the standard MCC brands (Avicel and Emcocel) and the silicified Prosolv, at all centrifugation times, using the Bonferroni test adjusted for multiple comparisons. The results are summarized in Table 3.

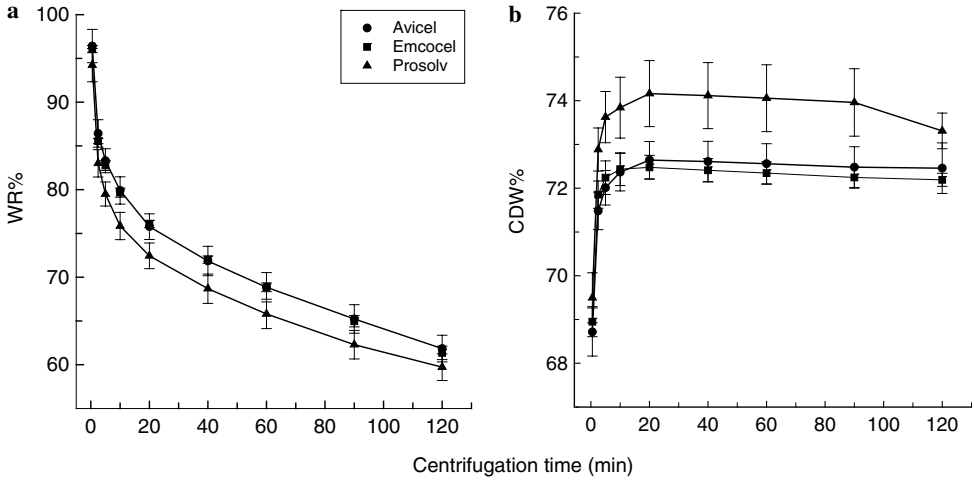

Fig. 6. Water retention (a) and cumulative drainage of water (b) vs centrifugation time, at fixed specimen porosity (70%) and thickness (17 mm).

Table 3
Pairwise comparisons of water retention (%) and cumulative drained water (%) mean values obtained at different centrifugation time for each of the standard MCC brands (Avicel and Emcocel) and the silicified brand (Prosolv)

Centrifugation time (min)	Brand compared to Prosolv	Water retention (%)			Cumulative drained water (%)		
		Mean difference	Std. error	p	Mean difference	Std. error	p
0.5	Avicel	2.180	0.936	0.126	0.709	0.340	0.190
2.5		3.411	0.884	0.010	1.165	0.286	0.007
5.0		3.802	0.969	0.009	1.273	0.320	0.008
10.0		4.057	1.018	0.008	1.246	0.361	0.019
20.0		3.337	1.026	0.026	1.143	0.370	0.034
40.0		3.162	1.053	0.040	1.118	0.375	0.041
60.0		3.048	1.024	0.042	1.106	0.377	0.045
90.0		2.944	0.985	0.041	1.088	0.380	0.051
120.0		2.123	0.740	0.050	0.459	0.354	0.673
0.5	Emcocel	1.831	0.936	0.237	0.473	0.340	0.581
2.5		2.531	0.884	0.051	0.794	0.286	0.058
5.0		3.262	0.969	0.022	1.042	0.320	0.026
10.0		3.816	1.018	0.011	1.178	0.361	0.026
20.0		3.650	1.026	0.016	1.308	0.370	0.016
40.0		3.326	1.053	0.031	1.318	0.375	0.017
60.0		3.044	1.024	0.042	1.318	0.377	0.017
90.0		2.681	0.985	0.064	1.322	0.380	0.018
120.0		1.630	0.740	0.157	0.725	0.354	0.204

From the pairwise comparisons presented in Table 3, it can be seen that Prosolv shows significantly lower retention ($p < 0.05$) compared to Avicel, from 2.5 to 90 min centrifugation, and significantly higher drainage ($p < 0.05$) from 2.5 to 60 min centrifugation. Compared with Emcocel, Prosolv shows significantly lower retention ($p < 0.05$) from 5 to 60 min and significantly higher drainage ($p < 0.05$) from 5 to 90 min. Maximum of mean difference in water retention and drainage between Avicel and silicified Prosolv, significant at $p < 0.01$, is noticed for centrifugation time of 10 and 5 min, respectively. Between Emcocel and Prosolv the maximum mean difference is noticed at 10 min centrifugation time for water retention ($p = 0.011$), but at 90 min for cumulative drainage ($p = 0.018$). This retarded drainage may be indicative of higher water affinity for Emcocel compared to Avicel, which is expressed clearly after micronization as higher WR% or lowered CDW% (Figs. 4 and 5).

Since the specific surface areas of the unmilled standard MCC brands and silicified Prosolv were similar (0.87–0.93 $m^2\,cm^{-3}$), the lower WR% and higher CDW% of Prosolv shown in Fig. 6 should be due to the silicification process. Presence of SiO_2 on the particle surface may affect the solid–liquid interaction and cause reduction in wetting and penetration of water into the particles of unmilled Prosolv, as that found for the environmental moisture uptake [26].

In the plots of CDW% vs centrifugation time, Fig. 6, three phases can be distinguished, a rapidly increasing initial phase at <5 min followed by a slower increasing phase between 5 and 20 min, and a nearly constant phase after 20 min centrifugation. These phases are probably related to the distribution state of retained water in the MCC powder (capillary, funicular or pendular and sorbed) and its reflection on drainage. The slight decrease of CDW% for the silicified Prosolv with centrifugation longer than 100 min, seen in Fig. 6, may be attributed to extended evaporation of water, resulting from the strong airstream developing inside the centrifuge during rotation.

4. Conclusions

Retention and drainage of water in different brands of microcrystalline cellulose powder (standard Avicel or Emcocel and silicified Prosolv) measured by the centrifuge method depend on the porosity of the specimen used, its thickness, and on the centrifugation time. Significant change of specimen thickness due to presence of water (swelling) was observed, which was reduced with the micronization, the specimen porosity, and centrifugation as well, but was slightly different between the various MCC brands. Porosity between 60% and 70%, specimen thickness/diameter ratio between 0.75 and 1.0, and centrifugation time between 5 and 20 min provide optimal settings for comparison of the different brands.

Unmilled silicified MCC (Prosolv) shows significantly lower retention and higher drainage of water compared to standard unmilled brands (Avicel and Emcocel), while differences between the unmilled standard Avicel and Emcocel brands are not easily distinguished. Micronization, in general, increases greatly the water retention and decreases drainage of water for all the tested powder and enhances their differences even between the standard brands (Avicel and Emcocel).

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