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Article

Effect of silicification on the water sorption properties of microcrystalline cellulose II

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The aim of this study was to investigate the water sorption behavior of cellulose II:SiO_2 composites and to determine the influence of silicification on this property. These composites were prepared by spray-drying at a cellulose II:SiO_2 ratio of 98:2, 95:5, 90:10 and 80:20. The nonlinear models of Guggenheim-Anderson-de Boer (GAB), Generalized D'Arcy and Watt (GDW) and Hailwood & Horrobin (HH), were used for the characterization and analysis of the isotherms. The infrared and powder X-rays characterization showed no signs of chemical modification or change in the polymorphic form of cellulose II by SiO_2. The parameters derived from these models indicated that only a 20% level of silicification was able to hinder the water sorption properties of cellulose. Silicon dioxide was the most hydrophobic material since it had a lower ability to form hydrogen bonds with water than cellulose II. This finding was reflected in a delayed compact disintegration time when high levels of silicification (20%) and compression pressures higher than 120 MPa were used.

Uniterms: Cellulose II. Silicon dioxide. Silicification. Water sorption isotherms. Disintegration.

O objetivo deste estudo é investigar o comportamento de sorção de água a partir de misturas de celulose II e SiO_2 e determinar a influência da silicificação nesse processo. Estas misturas foram preparadas por nebulização (*spray-drying*) usando misturas de celulose II e SiO_2 nas proporções de 98:2, 95:5, 90:10 e 80:20. Os modelos não-lineares de Guggenheim-Anderson-de Boer (GAB), "Generalized" D'Arcy e Watt (GDW) e Hailwood & Horrobin (HH) foram utilizados para caracterização e análise das isotermas. As misturas foram caracterizadas por infravermelho e raio-X e os resultados não mostraram indicativo de modificação química ou polimórfica da celulose II em combinação com SiO_2. Os parâmetros derivados desses modelos indicaram que as propriedades de sorção de água da celulose foram prejudicadas apenas quando empregado um nível de silicificação de 20%. O dióxido de silício foi o material mais hidrofóbico, provavelmente por possuir uma menor capacidade de formar pontes de hidrogênio com a água quando comparado com a celulose II. Este resultado foi refletido em redução no tempo de desintegração, especialmente quando altos níveis de silicificação (20%) e força de compressão (acima de 120 Mpa) foram utilizados.

Unitermos: Celulose II. Dióxido de silício. Silicificação. Isotermas de sorção de água. Desintegração.

INTRODUCTION

The new microcrystalline cellulose II allomorph (UICEL®) was introduced as a new direct compression excipient (Reus, Kumar, 2002; 2006). It is compatible with other excipients and active ingredients, offers high dilution potential, is a good disintegrant and relatively inexpensive. Recently, co-processing of cellulose II with SiO_2 by spray-drying has resulted in a new material with mechanical properties comparable to those of Avicel PH102. SiO_2 reinforced the mechanical properties without detriment to the fast disintegrating properties of cellulose II (Rojas, 2010). It is known that these properties are related to the water uptake capacity of the material. In fact, this uptake depends on both the chemical structure of the polymer and also on its morphology. Knowledge of the moisture sorption behavior of this novel co-processed material is crucial to characterize, understand and predict its stability, resistance to hydrolysis and biodegradation, especially during stora-

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ge alone or combined with other materials in a dosage form under different ambient conditions. Studies of the water sorption ability of this composite material allow for comparing and establishing the appropriate storage conditions to maintain its quality requirements.

Equilibrium sorption refers to the equilibrium uptake of water as a function of water activity. Brunauer and collaborators proposed a classification of isotherms into five types according to their shape (Brunauer *et al.*, 1938; 1940). Type I is the typical Langmuir isotherm which is applicable to microporous solids. Type II and type III isotherms describe adsorption of gases on macroporous or non porous solids, while type IV and V isotherms are applicable to both mesoporous or microporous solids. It is known that type II isotherms are common in hydrophilic polymers such as silk and wool, whereas, less hydrophilic materials such as ethylcellulose present a type III isotherm (Van der wel, Adan, 1999). The goal of this study was to evaluate the role of SiO_2 in the water sorption properties of cellulose II:SiO_2 composites by using different mathematical models such as Guggenheim-Anderson-de Boer (GAB), Hailwood and Horrowin (HH), Darcy and Watt (GDW) models. The non-linear curve fitting and the resulting parameters were obtained using the Statgraphic software vs. 5 (Warrenton, VA). Currently, no studies investigating the effect of SiO_2 on the water sorption behavior of cellulose II are available.

MATERIALS AND METHODS

Materials

Cotton linter (grade # R270) was obtained from Southern Cellulose Products, Inc., Chattanooga, TN). Sodium hydroxide (97.5%; lot # 051758), was obtained from Fisher Scientific, Fair Lawn, NJ. Concentrated hydrochloric acid (37%; lot # 2612KLHV) was purchased from Mallinckrodt Specialty Chemicals Co. (St. Louis, MO). Amorphous silicon dioxide (Cab-o-Sil M5, lot I107) was obtained from Cabot Corp. (Billerica, MA).

Preparation of cellulose II powder (CII)

Cotton linter strips (~0.5x5 cm) were soaked in 7.5 N NaOH for 72 h (cellulose:NaOH ratio 1:6, w/v) at room temperature. The cellulose II strips were then washed with distilled water until reaching a neutral pH. Approximately 280 g of this material was hydrolyzed with 2 L of 1 N HCl for about 2 h at 105 °C. The cooled material was then filtered and washed with distilled water until neutralization. The material was then dried at room temperature.

Preparation of CII-SiO_2 composites by spray-drying

Aqueous dispersions (5%, w/v) containing 98:2, 95:5, 90:10, and 80:20 weight-by-weight ratios of CII and SiO_2 were prepared with a homogenizer (Biospec products, Inc, Bartlesville, OK) for 10 min at 10,000 r.p.m. The dispersions were spray-dried on a Yamato Pulvis spray-drier (Model GB-22, Yamato Scientific, Co. Tokyo, Japan). The operational conditions used were: inlet air temperature of 195 °C; atomizing air pressure of 1.0 kg-f/cm^2; drying air rate of 0.44 m^3/min; feed flow rate of 2.0 mL/min and nozzle diameter of 0.7 mm. Samples with silicon dioxide levels higher than 20% were not employed in this study since high levels of silicon dioxide rendered weak compacts showing signs of chipping and capping independent of the compression force used.

Fourier-Transform Infrared Spectroscopy (FT-IR) characterization

Approximately 1.5 mg of sample was mixed with about 300 mg of dry Potassium Bromide (dried at 110 °C for 4 hours before use) with an agate mortar and pestle. The powdered sample was compressed into a pellet using a 13 mm flat-faced punch set and a die on a hydraulic press (Pasadena press, Pasadena Hydraulics, Inc, El Monte, CA) at ~15,000 lbs. The dwell time was five minutes. A Nicolet 210 FT-IR spectrophotometer (Nicolet Corp, Madison, WI), equipped with Ommic software (Nicolet Corp, Madison, WI), was used to obtain the spectrum between 650 to 4000 cm^{-1}.

Powder X-Rays (PXRD) characterization

Powder X-ray diffractions (PXRD) measurements were conducted over a 5 to 45º 2θ range using a Siemens diffractometer (Model D5000, Siemens Energy and Automation, Inc., Madison, WI), equipped with monochromatic CuKα (α_1=1.5460 Å, α_2= 1.54438 Å) X-ray radiation. The step width was 0.020º 2θ /min with a time constant of 0.5 sec. The Difrac® plus Eva software, version 2.0 (Siemens Energy and Automatization, Inc, Madison, WI) was used for calculation of the areas.

Water sorption isotherms

Water sorption isotherms were conducted on a VTI® Symmetric Gravimetric Analyzer (Model SGA-100, VTI Corporation, Hialeah, FL), equipped with a chilled mirror dew point analyzer (Model Dewprime IF, Edgetech, Milford, MA) at 25 °C. The water activity range employed was between 0 and 0.9. Water uptake was considered at equilibrium when the sample weight change of no more than 0.01% was reached. Samples were analyzed in triplicate.

Moisture sorption models

The Guggenheim-Anderson-de Boer (GAB) model

This model was derived independently by Guggenheim (1966), Anderson (1946), and de-Boer (1953). It has been adopted widely among scientists (Koskar, Kmetec, 2005) since it fits data of non-ideal water sorption at water activities from 0 to 0.95 (Jonquieres, Fane, 1998).

The GAB model is based on the sorption theory of water on the surface of solids developed by BET (Brunauer, Emmet, and Teller) (Brunauer *et al*., 1940). This model assumes that the partition functions for the secondary and higher layers of sorbed water to be energetically the same, but different from that of liquid water, as well as different from the primary sorbed water (Villalobos *et al.*, 2006). The model assumes that the heat of adsorption in the multilayer system is less than the heat of liquefaction. The GAB model is expressed as depicted in equations 1-3 (Vega-Mercado, Barbosa-Canovas, 1993):

$$m = \frac{ka_w m_0 C}{(1-ka_w)(1-ka_w+Cka_w)} \qquad \text{Equation 1}$$

$$C = De^{(H_m - H_c)/RT} \qquad \text{Equation 2}$$

$$k = Be^{(H_C - H_n)/RT} \qquad \text{Equation 3}$$

Where, m is the fractional moisture content, a_w is the water activity, and m_o is the monolayer moisture content. This value can be used to estimate the optimum moisture content for the stability and preservation of food and pharmaceutical additives (Oliveira *et al.,* 2009). H_M, H_N and H_C are the molar sorption enthalpies of the monolayer, multilayer and heat of condensation of water, respectively. R is the gas constant (8.31 J/Kmol), T is the absolute temperature, and D and B are entropic accommodation factors, respectively. K is the energy constant related to the multilayer properties. Thus, it represents the partition function of the secondary sorbed molecules to that of external condensed liquid. This constant is usually less than 1 (Perrin *et al*.., 1997). The C constant is related to the energetic properties of the monolayer. It is the ratio of the partition function of the primary molecules to that of the external condensed water (Kachrimanis *et al.*, 2006).

Generalized D'Arcy and Watt (GDW) Model

This model assumes the existence of monolayer and multilayer adsorption sites on the solid surface and the possibility that one water molecule attached to a primary center can give rise to more than one secondary adsorption site (Furmaniak *et al.*, 2007). This means that not all water molecules adsorbed on the primary sites will create secondary centers. Thus, the number of secondary sites created from primary molecules will be different, making the multilayer coverage non-homogeneous. This model is expressed as shown in equation 4:

$$m = \left(\frac{a_w m_0 K}{1+a_w K}\right)\cdot\left(\frac{1-C(1-w)a_w}{1-a_w C}\right) \qquad \text{Equation 4}$$

where: m is the total fractional moisture content , m_0 the monolayer capacity, a_w the water activity, w a parameter determining what fraction of water molecules adsorbed on primary sites convert into secondary adsorption sites, and K and C have the same meaning as mentioned in the GAB model (Vieira, Rocha, 2006).

Hailwood & Horrobin model (HH)

This solid-solution model was created to describe the water sorption properties of cotton and can be used to determine the sorption properties of cellulosic materials. This model considers that water can be absorbed as a multilayer and monolayer (hydrated) form. It assumes that unhydrated polymer, hydrated polymer and multilayer water are in equilibrium (Hill *et al.*, 2009). The HH model is expressed as shown in equation 5 and 6:

$$A = m_h + m_s \qquad \text{Equation 5}$$

$$m = \frac{W}{18g/mol} * \left(\frac{a_w K_1 K_2}{1+a_w K_1 K_2}\right) + \frac{W}{18g/mol} * \left(\frac{a_w K_2}{1-a_w K_2}\right) \qquad \text{Equation 6}$$

Where, m is the total fractional moisture content, m_h and m_s are the fractional moisture contents of the monolayer, and multilayer water, respectively. W is the molecular weight of polymer per sorption site, a_w is the water activity, 18 g/mol is the molar mass of water and K_1 and K_2 are the equilibrium constants for the formation of monolayer and multilayer, respectively. In contrast to the GAB model, it assumes that the monolayer is evolving during the dynamic sorption process in the whole range of water activities. This model does not explain the hysteresis phenomena of microporous materials. M_h is related to the number of primary sorption sites (OH groups) in the polymer. This value can be used to determine the number of accessible OH groups in each material (Hartley *et al.*, 1992).

Compact disintegration studies

Approximately 500 mg of powder was compressed on a hydraulic press (Model C, Carver Press, Menomonee Falls, WI) at pressures ranging from 10 to 260 MPa using a round flat-faced 13 mm punch and die set at a dwell time of 30 seconds. The upper punch was equipped with a load cell (Model: LCGD-10K, Serial No. 188578, Range 0-10000 lbs, Omega Engineering, Inc., Stamford, CT) and a strain gauge meter (Model: DP25B-S, Serial No. 033252291, Omega Engineering, Inc., Stamford, CT). Tablets were kept in a dessicator over Drierite for 48 h before analysis. The disintegration test was performed in five replicates in distilled water at 37 ºC employing an Erweka GmbH disintegration apparatus (type 712, Erweka, Offenbach, Germany) at 30 strokes/min.

RESULTS AND DISCUSSION

FT-IR characterization

As seen in Figure 1, the incorporation of silicon dioxide had no effect on the cellulose II infrared bands. These results are not surprising since it is well known that co-processing does not cause any change in the chemical structure of cellulose (Tobyn *et al.,* 1998). Cellulose II samples showed the following characteristic vibration peaks: 3445 cm^{-1} corresponding to intramolecular OH stretching, including hydrogen bonds, 2893 cm^{-1} due to CH and CH_2 stretching, 1642 cm^{-1} corresponding to OH from absorbed water, 1427 cm^{-1} due to CH_2 symmetric bending, 1379 cm^{-1} due to CH bending, 1330 cm^{-1} due to OH in plane bending, 1255 corresponding to C-O-H bending, 1161 due to C-O-C asymmetric stretching (β-glucosidic linkage), 1061 due to C-O/C-C stretching and 895 cm^{-1} due to the asymmetric (rocking) C-1 (β-glucosidic linkage) out-of-plane stretching vibrations. This band is associated to the cellulose II lattice (Carrillo *et al.*, 2004; Zhbankov, 1964). Amorphous silicon dioxide showed vibration bands at: 3445 cm^{-1} due to OH stretching (sylanol moieties), 1080 cm^{-1} and 810 cm^{-1}due to the asymmetric stretching and symmetric stretching modes of Si-O-Si, respectively (Wang *et al.,* 1999).

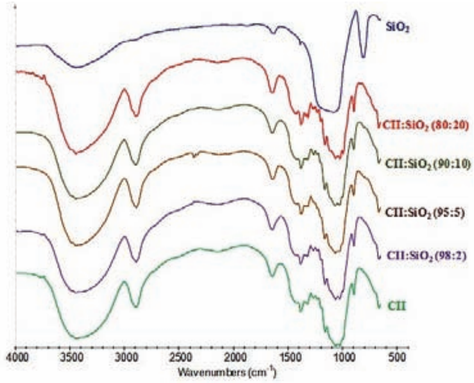

FIGURE 1 - FT-IR spectra of the $CII:SiO_2$ composites.

PXRD characterization

The PXRD of CII, SiO_2, and $CII:SiO_2$ composites are shown in Figure 2. Independent of the silicification level, all the cellulose II materials showed peaks at 12, 20 and 22° 2θ corresponding to the $1\,\bar{1}\,0$, 110 and 200 reflections, respectively, confirming the presence of the cellulose II lattice (Klemm *et al.*, 1998). In contrast, SiO_2 showed a diffused halo indicating its amorphous nature. It is clear that silicification had no effect on the polymorphic nature of cellulose II.

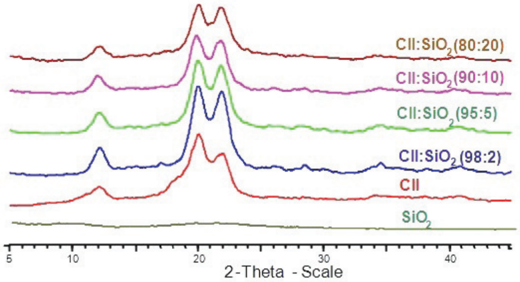

FIGURE 2 - PXRD Characterization of the $CII:SiO_2$ composites.

The Guggenheim-Anderson-de Boer (GAB) model

Figure 3 shows the fitting curves for water sorption of the materials and Table I shows the parameters derived from the GAB model. Figure 3 also shows that SiO_2 was the least hydrophilic material compared to the $CII:SiO_2$ composites. Except for SiO_2, correlation coefficients were higher than 0.9967 indicating a good fit of the data to the experimental model. Since CII is highly hydrophilic, the monolayer sorption capacity (m_0) indicates that the affinity of CII for water decreased by 20% (0.04 g water/g cellulose) only at the 20% silicification level. In other words, the surface area covered by a monolayer of water molecules decreased by 20%. This means that the primary sites of CII are already interacting via hydrogen bonding with the sylanol groups of SiO_2 leaving few hydroxyl groups of CII available for hydrogen bonding with water molecules. The energy constant of multilayer sorption (k) and the H_m-H_c difference did not change with silicification (0.8 and 0.6 kJ/mol, respectively). By contrast, the energy constant of monolayer sorption (C) only increased significantly at the 20% silicification level (35.6). Similarly, at this level the largest H_m-H_c difference was observed (8.9 kJ/mol).

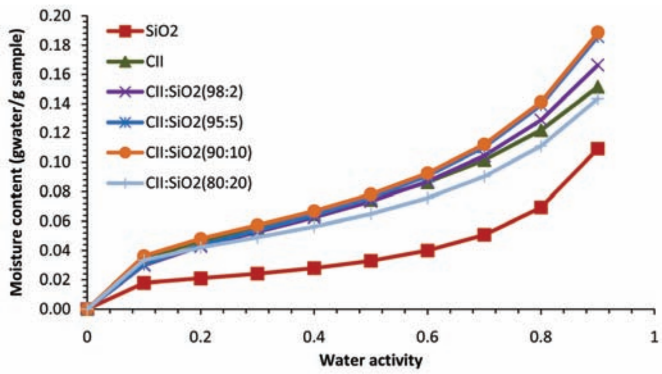

FIGURE 3 - Moisture sorption behavior of the CII:SiO_2 composites fitted by the GAB models.

In all cases, the enthalpy difference found for the monolayer was higher than that for the multilayer (H_m-H_c > H_c-H_n) indicating that the energetic for the formation of a monolayer is more prevalent than that of the multilayer. The enthalpy difference for the monolayer (H_m-H_c) was the highest at a silicification level of 20% and for SiO_2. As CII becomes less hydrophilic, water molecules are sorbed more tightly in the active sites and thus, the formation of a monolayer is energetically more favored than the formation of multilayer. Conversely, the enthalpy difference (H_c-H_n) remained unchanged indicating that silicification influences the affinity of cellulose II for water mainly by inducing changes in the monolayer enthalpy.

The low affinity of SiO_2 for water was reflected in the lowest m_o value (0.02 g water/g polymer). This indicates that the material has only 40% of the hydrophilicity shown by CII. As SiO_2 contains fewer hydroxyl groups than CII, it is inferred that the better affinity of water for CII is due to its stronger interaction with the hydroxyl groups compared to the interaction with the sylanol groups of SiO_2.

SiO_2 presented the lowest H_c-H_n and the highest H_m-H_c enthalpy values among all the samples (0.2 kJ/mol and 11.4 kJ/mol, respectively). This indicates that the formation of a monolayer is more likely to occur and remain in this state than to form secondary and on-going water layers. In this case, the multilayer formation is less favored since its energetic is very low indicating a very weak interaction.

Figure 4 and Table II show the data obtained from the desorption isotherms according to the GAB model. Correlation coefficients were higher than 0.9938 indicating a good fit to the experimental data.

As seen for the sorption isotherms, the energetic for the multilayer sorption (k and H_c-H_n values) was not affected by silicification (0.7 and 0.8 kJ/mol, respectively), but the C and H_m-H_c values increased with silicification. The enthalpies of the multilayer adsorption were 25% lower than the enthalpies of desorption, indicating that the multilayer formation is more favorable during adsorption than the desorption stage. Conversely, there were no significant differences among the monolayer enthalpies of adsorption and desorption, respectively.

The monolayer capacity (m_0) of the desorption isotherms decreased 29% at a SiO_2 level of 20%. In general, m_0 values were 40% higher than the those obtained from the adsorption isotherms, except for SiO_2 in which it remained constant (0.02 g water/g SiO_2). Results proved that desorption isotherms of CII:SiO_2 composites were larger

TABLE I- GAB parameters obtained from sorption isotherms of CII:SiO_2 composites

Sample	K (SD)	m_0 (SD)	C (SD)	H_c-H_n	H_m-H_c	R^2
CII	0.8 (0.0)	0.05 (0.00)	21.3 (1.7)	0.6	7.6	0.9988
CII:SiO_2(98:2)	0.8 (0.0)	0.05 (0.00)	14.9 (0.6)	0.6	6.7	0.9993
CII:SiO_2(95:5)	0.8 (0.0)	0.05 (0.00)	14.9 (6.6)	0.6	6.7	0.9987
CII: SiO_2 (90:10)	0.8 (0.1)	0.05 (0.01)	24.3 (13.7)	0.6	7.9	0.9967
CII: SiO_2 (80:20)	0.8 (0.0)	0.04 (0.00)	35.6 (1.8)	0.6	8.9	0.9967
SiO_2	0.9 (0.1)	0.02 (0.00)	100 (0.0)	0.2	11.4	0.9842

SD = standard deviation of three replicates; K= energy constant of multilayer sorption; C= energy constant of monolayer sorption; H_c-$H_{n,}$ = enthalpy for multilayer sorption, H_m-$H_{c=}$ enthalpy for monolayer sorption; m_o= monolayer capacity; R^2= correlation coefficient than the desorption isotherms, indicating hysteresis in the water uptake behavior. It has been reported that hysteresis is a common phenomenon in highly hydrophilic materials due to the ink drop theory. This phenomenon is less evident for SiO_2.

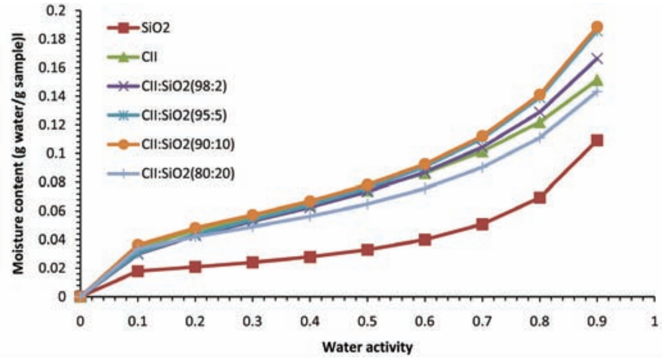

FIGURE 4 - Moisture desorption behavior of the CII:SiO_2 composites fitted by the GAB models.

Generalized D'Arcy and Watt (GDW) model

The GDW model assumes the existence of primary (Langmuir-type) adsorption sites on the surface. Each site adsorbs one water molecule, which could serve as secondary adsorption sites for the consecutive molecules. Figure 5 shows that the CII:SiO_2 composites were more hygroscopic than SiO_2 alone. The high water affinity of these composites is due to the large number of hydrophilic groups (binding sites) present in their structure. Table III shows the parameters obtained from the GDW model. All samples presented an excellent fit to the sorption data (>0.9984).

The water sorption capacity decreased as the amount of SiO_2 increased. This effect could be attributed to possible hydrogen bond interactions between hydroxyl groups of cellulose and sylanol groups of SiO_2, reducing the number of active sites for water adsorption. As water activity increases, changes in the supra-molecular structure of CII may occur, modifying the CII-SiO_2 interactions.

Table III shows the parameters derived from the GDW model for the sorption data. Except for SiO_2, correlation coefficients were higher than 0.9984, indicating a good fit to the experimental data. Even though CII materials are highly hydrophilic, the fraction of primary sites which became centers for secondary sorption (W) was less than 1, ranging from 0.38 to 0.87. This indicates that the secondary centers were not energetically the same. In this case, the lowest fractions were obtained at SiO_2 levels greater than 10% and for pure SiO_2. This implies that silicification hinders the formation of secondary and higher levels of water layering. In fact, for pure SiO_2 only 25% of the strongly bound water molecules become centers for the formation of a multilayer. It is plausible that the surface of water molecules become rough since the thickness will not be constant throughout the entire surface.

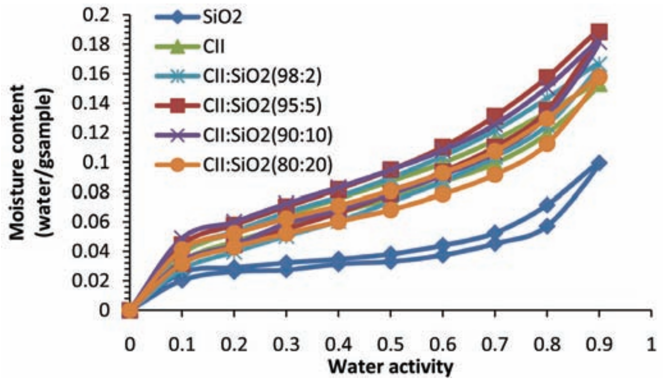

FIGURE 5 - Moisture sorption and desorption behavior of the CII:SiO_2 composites fitted by the GDW model.

TABLE II - GAB parameters obtained from desorption isotherms of CII:SiO_2 composites

Sample	K (SD)	m_0 (SD)	C (SD)	H_c-H_n	H_m-H_c	R^2
CII	0.7 (0.0)	0.07 (0.00)	15.2 (2.4)	0.8	6.8	0.9994
CII:SiO_2(98:2)	0.7 (0.0)	0.07 (0.00)	15.6 (4.4)	0.8	6.8	0.9989
CII:SiO_2(95:5)	0.7 (0.0)	0.07 (0.00)	18.7 (2.6)	0.8	7.2	0.9991
CII: SiO_2 (90:10)	0.7 (0.1)	0.07 (0.01)	26.3 (7.9)	0.8	8.1	0.9996
CII: SiO_2 (80:20)	0.7 (0.0)	0.05 (0.00)	31.2 (11.6)	0.8	8.5	0.9998
SiO_2	0.8 (0.1)	0.02 (0.01)	110.3 (17.9)	0.5	11.7	0.9938

SD= standard deviation of three replicates; K= energy constant of multilayer sorption; C= energy constant of monolayer sorption; H_c-$H_{n,}$ = enthalpy for multilayer sorption, H_m-$H_{c=}$ enthalpy for monolayer sorption; m_o= monolayer capacity; R^2= correlation coefficient

The monolayer constant (m_0) ranged from 0.06 to 0.08 g water/g polymer and was not correlated to the silicification level. However, for pure SiO_2 the maximum sorption on the primary sites was very low (0.03 g water/g SiO_2) showing the most hydrophobic properties among all materials.

The monolayer energy constants (C) were higher than the multilayer energy constants (k). This indicates that the monolayer water molecules are strongly attached to the surface of the polymer whereas the secondary and further water molecules are weakly attached. The values of C and k indicate that silicification had virtually no affect on the energetic of the system. SiO_2 exhibited the highest C value indicating the prevalence of energetic for the formation of a monolayer. This high value is reflected in the high monolayer enthalpy obtained (7.7 kJ/mol). In contrast, this model predicts an enthalpy for multilayer formation (H_m-H_c) of 0.0 kJ/mol for SiO_2. This indicates that the formation of secondary and further sorption sites is not favored in this material.

Table IV shows the desorption parameters obtained from the GDW model. The model fits to the data very well (R^2>0.9983). The desorption isotherms showed that the C energy value increased with silicification (from 9.2 to 21.1). This observation was also reflected in the enthalpy values of monolayer (from 5.5 to 7.6 kJ/mol). In other words, silicification eased the formation of a monolayer as opposed to a multilayer. However, the k value remained virtually unchanged and was the highest for SiO_2. The fraction of primary sites which became centers for secondary sorption (W) was equal to one for all cellulosic materials. This indicates that all primary sites serve as centers for the creation of secondary sites independent of SiO_2 content.

The monolayer constant (m_0) was 0.07 g water/g polymer and decreased at the 20% silicification level. This means that the high concentration of SiO_2 on the surface of CII hindered the formation of hydrogen bonds between cellulose and water. However, for pure SiO_2, the maximum sorption on primary sites was the same as that shown by the sorption isotherm (0.03 g water/g SiO_2) thus demonstrating its hydrophobic property.

Hysteresis is defined as the difference between the amount of water desorbed and sorbed, respectively. This difference creates a loop in the isotherm and is very common in hydrophilic materials. Figure 6 shows the relationship between percentage of hysteresis formation

TABLE III- GDW parameters obtained from the sorption isotherms of CII:SiO_2 composites

Sample	C (SD)	m_0 (SD)	K (SD)	W (SD)	H_c-H_n	H_m-H_c	R^2
SiO_2	22.1 (1.4)	0.03 (0.00)	1.0 (0.0)	0.25 (0.14)	7.7	0.0	0.9986
CII	8.1 (1.4)	0.07 (0.00)	0.8 (0.0)	0.47 (0.07)	5.2	0.4	0.9997
CII:SiO_2(98:2)	7.7 (4.1)	0.06 (0.01)	0.8 (0.0)	0.87 (0.10)	5.1	0.5	0.9994
CII:SiO_2(95:5)	7.0 (1.5)	0.07 (0.01)	0.9 (0.0)	0.56 (0.07)	4.8	0.3	0.9992
CII: SiO_2 (90:10)	6.1 (2.3)	0.08 (0.04)	0.9 (0.0)	0.38 (0.10)	4.5	0.2	0.9988
CII: SiO_2 (80:20)	8.9 (1.0)	0.06 (0.00)	0.9 (0.0)	0.38 (0.05)	5.4	0.2	0.9984

SD= standard deviation of three replicates; k= energy constant of multilayer sorption ; C= energy constant of monolayer sorption; H_c-H_n = enthalpy for multilayer sorption; H_m-H_c= enthalpy for monolayer sorption; m_o= monolayer capacity; w= fraction of primary sites which become centers for secondary sorption; R^2= correlation coefficient.

TABLE IV - GDW parameters obtained from the desorption isotherms of CII:SiO_2 composites

Sample	C (SD)	M_0 (SD)	K (SD)	W (SD)	H_c-H_n	H_m-H_c	R^2
CII	9.2 (2.0)	0.07 (0.00)	0.7 (0.0)	1.00 (0.0)	5.5	1.0	0.9997
CII:SiO_2(98:2)	9.8 (5.4)	0.07 (0.00)	0.7 (0.0)	1.00 (0.2)	5.7	0.9	0.9997
CII:SiO_2(95:5)	12.9 (2.4)	0.07 (0.00)	0.7 (0.0)	1.00 (0.2)	6.3	0.8	0.9997
CII: SiO_2 (90:10)	20.3 (3.4)	0.07 (0.01)	0.7 (0.0)	1.00 (0.2)	7.5	0.8	0.9997
CII: SiO_2 (80:20)	21.1 (6.8)	0.06 (0.00)	0.7 (0.0)	1.00 (0.1)	7.6	0.8	0.9997
SiO_2	204.0 (1.8)	0.03 (0.00)	0.9 (0.0)	0.64 (0.2)	13.2	0.2	0.9983

SD= standard deviation of three replicates; k= energy constant of multilayer sorption; C= energy constant of monolayer sorption; H_c-H_n = enthalpy for multilayer sorption; H_m-H_c= enthalpy for monolayer sorption; m_o= monolayer capacity; w= fraction of primary sites which become centers for secondary sorption; R^2= correlation coefficient with water activity of the CII:SiO_2 composites. In all cases, the percentage of hysteresis was the lowest at a water activity of 0.9 and the highest at a water activity of 0.1. The degree of hysteresis remained virtually unchanged from 0.2 to 0.7. Results indicate that hysteresis occurred throughout the sorption range and not just in the capillary condensation region as reported previously (Parker *et al.*., 2006). It is well known that the higher moisture content obtained when a polymer is desorbing from a saturated state is due to microcapillary deformation accompanied by the creation of more permanent hydrogen bonds which are no longer attainable in subsequent re-wetting processes. This phenomenon is known in cellulose as hornification. Thus, when cellulose sorbs water it swells slightly because microcapillaries expand due to the thermal motion of incoming water molecules forming new internal surfaces. Once water is removed, relaxation of the matrix to the original state is prevented. As a result, microcapillaries become greater on desorption compared to the adsorption step.

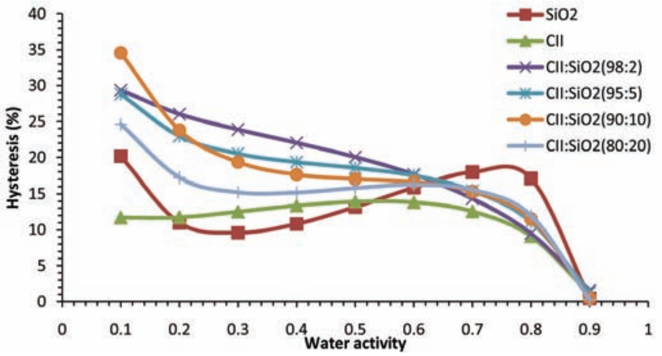

FIGURE 6 - Degree of hysteresis for the CII:SiO_2 composites.

Hailwood & Horrobin model (HH)

The HH model assumes the formation of three species in equilibrium (anhydrate polymer, polymer with a monolayer and polymer with a multilayer). The HH is a solution-based theory and is not based on the layering method as described in the GAB model.

Figures 7 and 9 show the fitted HH models and Figures 9 and 10 show the deconvoluted curves in which the monolayer and multilayer are shown as saturation and exponential curves, respectively. The formation of a monolayer starts at a water activity of 0.1 for both the sorption and desorption curves. The shape of these monolayers resembles the Brauner type I isotherms. Silicon dioxide presented the lowest amount of water necessary to form a monolayer. It reached a plateau at a water activity of 0.1 and then remained constant. This indicates a low affinity for water since the formation of hydrogen bonds occur only through the sylanol groups. Thus, all the sylanol groups available for binding are occupied rapidly at a water activity of 0.1. Conversely, all CII:SiO_2 composites exhibited a great affinity for water molecules. This is explained by the great number of hydroxyl groups of the polymer which can form hydrogen bonds with these water molecules. In this case, there is a steady increase of sorbed water up to a water activity of 0.5. Further water sorption only accounts for around 7% of the whole monolayer coverage.

The fraction of water molecules which are part of the multilayer are shown in Figure 7. This shape is similar to the Brauner type III isotherm. These curves exhibit an exponential increase with water activity. In contrast, water molecules in the multilayer presented the lowest increasing tendency for silicon dioxide. It is also observed that, initially at a low water activity, molecules of water prefer binding to an empty site rather than to an already monomolecular occupied site. Nevertheless, at a 0.5 water activity an incoming water molecule has the same probability of binding a monomolecular occupied or an empty

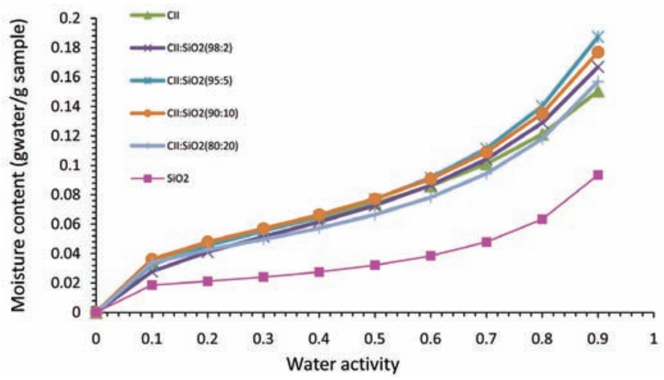

FIGURE 7 - Moisture sorption behavior of the CII:SiO_2 composites fitted by the HH model.

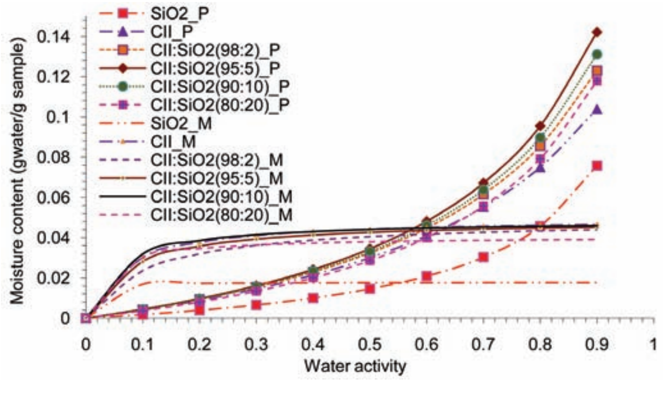

FIGURE 8 - Deconvoluted sorption curves of the CII:SiO_2 composites fitted by the HH model.

site. Further, at water activities higher than 0.55, incoming water molecules are more likely to be attracted to already occupied sites than to the few remaining empty centers.

Table VI shows the parameters of the HH fitting. Except for SiO_2, the correlation coefficients from the non-linear fitting were higher than 0.9967, indicating a good fit of the experimental data to the model. Silicification increased the k equilibrium constant, while the C constant remained unchanged. This indicates that the presence of SiO_2 favors the formation of a monolayer and makes no contribution to the formation of a multilayer. In fact, a surface formed by sylanol groups is more likely to form almost a complete monolayer with incoming water molecules (~90% coverage) at a very low water activity (0.1) than the hydroxyl groups of cellulose. The w value indicates the grams of water per mole of sorption sites. It is clear that the amount of water which binds to the sorption sites decreases with the presence of SiO_2. This means that SiO_2 occupies part of the surface area of cellulose, consuming part of the hydroxyl groups available for binding water molecules. As a result, a low amount of hydroxyl groups of cellulose will be able to bind water molecules. Silicon dioxide is able to bind only ~ 1/3 of the water molecules which cellulose II alone binds.

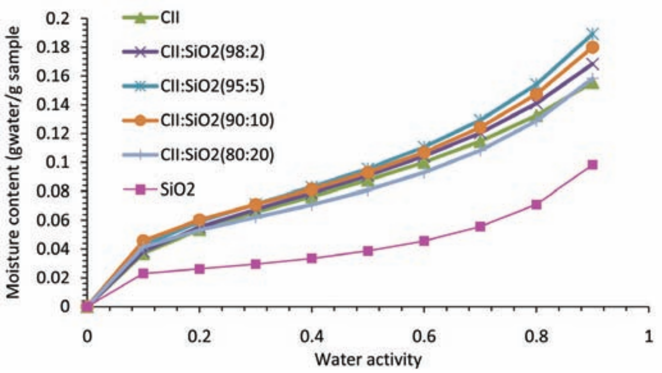

FIGURE 9 - Moisture desorption behavior of the CII:SiO_2 composites fitted by the HH model.

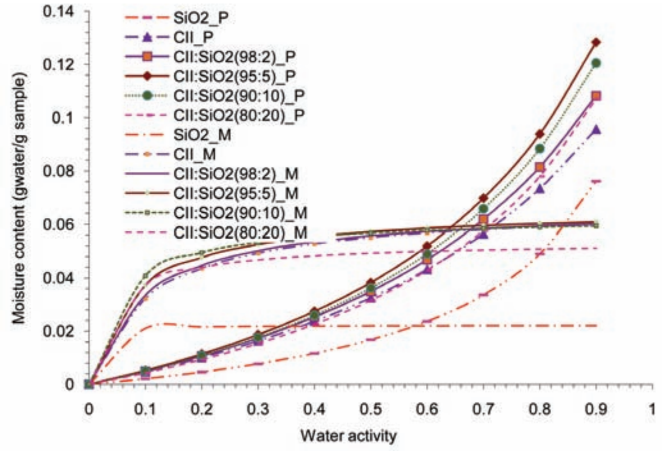

FIGURE 10 - Deconvoluted desorption curves of the CII:SiO_2 composites fitted by the HH model.

Figure 10 shows the deconvoluted desorption curves according to the HH model. This model shows that the monolayer formation of most materials starts as early as 0.1 water activity. Thus, at a water activity of 0.1, nearly 90% of most materials are already covered by a monolayer. However, it is possible that secondary sorption centers start emerging before the monolayer is complete.

Table VI shows the fitting parameters obtained from the desorption isotherms. Except for SiO_2, the correlation coefficients from the non-linear fitting were higher than 0.9938, indicating a good fit of the experimental data to the model. Table VI also shows the k and C equilibrium constants for the formation of a monolayer and multilayer, respectively. Silicification favored the formation of a monolayer over a multilayer, particularly at a 20% silicification level. In fact, the w values for the desorption isotherms showed a significant reduction (0.97 g water/mole polymer) at this level of silicification. Silicon dioxide is considered the most hydrophobic material among all samples since it had the lowest w value (0.4 g water/mole polymer). Comparison of w parameters from

TABLE V - HH parameters obtained from sorption isotherms of CII:SiO_2 composites.

Sample	K (SD)	w SD	C (SD)	R^2
CII	20.3 (1.7)	0.90 (0.02)	0.8 (0.0)	0.9988
CII:SiO_2(98:2)	11.6 (4.2)	0.89 (0.03)	0.8 (0.0)	0.9993
CII:SiO_2(95:5)	16.3 (2.8)	0.88 (0.02)	0.8 (0.0)	0.9986
CII: SiO_2 (90:10)	23.3 (3.7)	0.88 (0.16)	0.8 (0.0)	0.9967
CII: SiO_2 (80:20)	34.6 (1.8)	0.73 (0.03)	0.8 (0.0)	0.9967
SiO_2	200.0 (0.00)	0.32 (0.06)	0.9 (0.0)	0.9842

SD= standard deviation of three replicates; k= monolayer equilibrium constant ; C= multilayer equilibrium constant; w= grams of water per mole of sorption sites; R^2= correlation coefficient

TABLE VI - HH parameters obtained from desorption isotherms of CII:SiO_2 composites

Sample	K (SD)	w (SD)	C (SD)	R^2
CII	14.2 (2.4)	1.2 (0.1)	0.7 (0.0)	0.9994
CII:SiO_2(98:2)	14.6 (4.4)	1.2 (0.0)	0.7 (0.0)	0.9989
CII:SiO_2(95:5)	17.7 (2.6)	1.2 (0.0)	0.7 (0.0)	0.9991
CII: SiO_2 (90:10)	25.3 (7.9)	1.1 (0.1)	0.7 (0.1)	0.9996
CII: SiO_2 (80:20)	30.2 (11.5)	1.0 (0.1)	0.7 (0.0)	0.9998
SiO_2	200 (0.1)	0.4 (0.0)	0.9 (0.0)	0.9938

SD= standard deviation of three replicates; k= monolayer equilibrium constant; C= multilayer equilibrium constant; w= grams of water per mole of sorption sites; R^2= correlation coefficient

Table V and VI clearly illustrates that more water molecules are able to interact through hydrogen bonding with the substrate during the desorption than the sorption phase (0.4 vs 0.32 g water/g SiO_2, respectively).

COMPACT DISINTEGRATION

This test was conducted to determine how silicification could affect the fast disintegrating properties of cellulose II. As seen in Figure 11, the fast disintegrating properties of cellulose II were not affected (~18 sec.) by silicification up to 120 MPa. However, at compression pressures higher than 150 MPa, compacts disintegrated slowly and disintegration times were inversely related to the silicification level. In other words, at 260 MPa, cellulose II alone showed the fastest disintegration (70 sec) whereas the sample with a 20% silicification level showed the slowest disintegration ability (270 sec.). These results agreed with the trend observed in the water sorption ability of cellulose II with silicification. This means that high levels of amorphous silicon dioxide (20%) hinder the interaction of cellulose II, with water delaying the water accessibility into the compact necessary for rapid tablet disintegration.

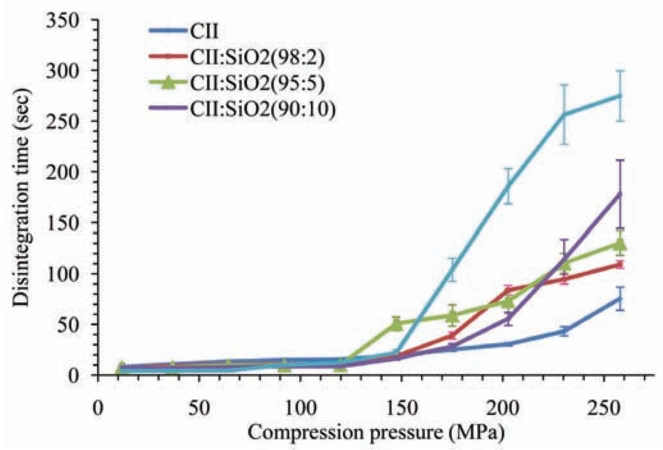

FIGURE 11 - Compact disintegration of the CII:SiO_2composites.

CONCLUSION

The water sorption and desorption property of the cellulose II:SiO_2 composites was affected only at the 20% silicification level. In this case, cellulose II became more hydrophobic. All the models employed had an excellent fit to the data, showing a type II Brunauer isotherm. These composite materials showed a hysteresis loop which is characteristic of cellulosic materials when the capillaries shrink during desorption. In contrast to the GAB model, the GDW and HH models assume sorption and desorption as a dynamic process in which the primary centers are filled up throughout the whole water activity range and do not require the formation of a monolayer to form a multilayer as shown by the GAB model. Only compacts made with the sample that had a 20% silicification level presented a delayed disintegration time at high compression pressures. Silicification had no effect on the fast disintegrating properties of cellulose II at compression pressures lower than 120 MPa.

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