



## Assessing the potential of quartz crystal microbalance to estimate water vapor transfer in micrometric size cellulose particles



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### ABSTRACT

This study aims at assessing the use of a quartz crystal microbalance (QCM) coupled with an adsorption system to measure water vapor transfer properties in micrometric size cellulose particles. This apparatus allows measuring successfully water vapor sorption kinetics at successive relative humidity (RH) steps on a dispersion of individual micrometric size cellulose particles (1  $\mu\text{g}$ ) with a total acquisition duration of the order of one hour. Apparent diffusivity and water uptake at equilibrium were estimated at each step of RH by considering two different particle geometries in mass transfer modeling, i.e. sphere or finite cylinder, based on the results obtained from image analysis. Water vapor diffusivity values varied from  $2.4 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$  to  $4.2 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$  over the tested RH range (0–80%) whatever the model used. A finite cylinder or spherical geometry could be used equally for diffusivity identification for a particle size aspect ratio lower than 2.

### 1. Introduction

The use of biocomposites based on a fully biosourced and biodegradable polymer matrix combined with micrometric size cellulose or lignocellulose-based fillers is gaining more and more attention in the field of food packaging. They constitute an answer to both environmental and socio-economical concerns by reducing our dependence to oil resources, decreasing environmental pollution while displaying specific new functionalities allowing to better preserve food products (Berthet, Angellier-Coussy, Guillard, & Gontard, 2016). Considering this field of application, the key material properties that should be tailored and controlled are mass transfer properties. Mass transfers are characterized by two main phenomena, sorption and diffusion, characterized by the sorption coefficient, which is a thermodynamic parameter, and the diffusion coefficient or diffusivity, which is a kinetic parameter. In front of the diversity of the implied materials and keeping in mind the objective of designing in a reasoned way packaging material, the mathematical modeling of the link between structure and mass transfer properties in biocomposites is essential. However, there is still currently a gap of knowledge regarding the formalization of these relationships due to the difficulty to characterize mass transfer properties in two of the three compartments of composite structures, i.e. the filler/matrix interphase and the fillers themselves. Indeed, mass

transfer properties are well-known in neat polymer matrices and can be easily measured in the whole biocomposite material (Berthet, Gontard, & Angellier-Coussy, 2015; de Carvalho et al., 2016; Gouanvé, Marais, Bessadok, Langevin, & Métayer, 2007). Efforts have been made to characterize mass transfer properties in cellulose or lignocellulose-based materials and mainly focused on water vapor transfers. Many studies have been devoted to the study of water vapor sorption kinetics, for all kinds of cellulose or lignocellulose-based materials and even on micrometric size particles, as reported by Paes et al. for ball milled cellulose (Paes et al., 2010). However, measurements were all carried out on sample weights higher than 1 mg and/or stacks of particles, which may not be representative of phenomenon occurring at the level of an individual particle. Different gravimetric methodologies can be found in literature to measure water vapor sorption kinetics, i.e. isopiestic methods such as the use of salt saturated solutions (Mihiranyan, Llagostera, Karmhag, Strømme, & Ek, 2004), Dynamic Vapor Sorption (DVS) using a Cahn microbalance (Paes et al., 2010) or Intelligent Gravimetric Analyzer (IGA) (Gouanvé et al., 2006).

In the case of simple geometries, i.e. finite or infinite cylinders, spheres or infinite plates, analytical solutions of Fick's law allowed the estimation of the apparent diffusivity from sorption kinetics (Guillard, Broyart, Bonazzi, Guilbert, & Gontard, 2003; Marais et al., 2000). This requires an accurate evaluation of the particle morphology or to make

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an assumption in order to select the appropriate analytical solution. Most published studies on diffusivity estimation are focusing either on long fibre bundles with a length higher than 1 cm, such as flax, hemp, jute, sisal (Céline, Fréour, Jacquemin, & Casari, 2013) or agave fibres (Bessadok et al., 2009), sheets of associated fibres such as papers or films (Li, Henriksson, Klason, & Ödberg, 1992; Minelli et al., 2010), or pieces of raw biomasses such as wheat straw (Wolf, Guillard, Angellier-Coussy, Silva, & Gontard, 2016), raffia (Tiaya Mbou, Njeugna, Kemajou, Sikame, & Ndapeu, 2017) or wood (Khazaei, 2008; Simpson, 1993), but never on individual micrometric size particles. Furthermore, it is worth noting that for a given material, a large range of water vapor diffusivity values have been reported. As an example, water vapor diffusivity of a paper sheet could vary from  $3.10^{-12}$  to  $4.10^{-7} \text{ m}^2 \text{ s}^{-1}$  (Bedane, Huang, Xiao, & Ei, 2012; Hashemi, Comes, Crotogino, & Douglas, 1997; Nilsson, Wilhelmsson, & Stenstrom, 1993), depending on the paper composition, chosen methodology and modeling approach. As another example, water vapor diffusivity of lignocellulosic fibres (agave fibres with length of the order of centimeter) could vary from  $8.10^{-10}$  to  $2.10^{-8} \text{ m}^2 \text{ s}^{-1}$  according to modeling approach and relative humidity (Bessadok et al., 2009). This highlights the complexity of accurately assessing mass transfer properties in cellulose or lignocellulose-based particles and the lack of reference method. Furthermore, for all these studies, identified diffusivities were only estimated for either macroscopic samples or beds of particles that never represent the diffusion within one micrometric size particle.

Quartz crystal microbalance (QCM) is an extremely sensitive technique able to detect a mass of  $7.10^{-7} \mu\text{g}$  in the best case (Stockbridge, Warner, & Behrndt, 1963), mostly depending on the frequency stability. This minimal detection load has to be compared with that of the most sensitive classical balances, i.e.  $0.1 \mu\text{g}$  (Mecea, 2006). This technique is well known to follow the thickness of a deposited layer during its growth in a vacuum deposition technique, knowing the mass density of the deposited material. During the last years, the QCM has been extensively used as a sensor devoted to the study of the detection of numerous biomolecules (Villares, Moreau, Dammak, Capron, & Cathala, 2015), to analyze selective membranes and sensors to a specific gas (Caron et al., 2014; Jia, Yu, Zhang, Dong, & Li, 2016; Michalzik, Wilke, & Büttgenbach, 2005; Passamano & Pighini, 2006) and to evaluate interfacial polymer behavior (Ahola, Myllytie, Österberg, Teerinen, & Laine, 2008; Marx, 2003; Tammelin et al., 2015). QCM with dissipation monitoring (QCM-D) could be useful to investigate viscoelastic properties of the adsorbed layer and take into consideration energy dissipation effects (Hakalahti, Faustini, Boissière, Kontturi, & Tammelin, 2017; Kontturi, Kontturi, & Laine, 2013; Niinivaara, Faustini, Tammelin, & Kontturi, 2015; Niinivaara, Faustini, Tammelin, & Kontturi, 2016). Up to now, QCM has mainly been used for thin films, generally deposited by spin coating (Kushner & Hickner, 2017; Rouessac, van der Lee, Bosc, Durand, & Ayril, 2008; Thomas, Rudich, Trakhtenberg, & Ussyshkin, 1999). A study has been carried out on the use of QCM-D to determine the equilibrium water content inside cellulose nanofibers prepared by electrospinning by regenerating cellulose to obtain a thin cellulose film (to keep fibers of QCM sensor) (Roemhild et al., 2016). However, no work has been yet proposed to measure mass variations of dispersed micrometric size powders or fibres.

In this context, the aim of this work is to explore the potential of using the QCM coupled with a water vapor adsorption/desorption system as a reliable methodology to evaluate water vapor transfer (apparent diffusivity and sorption) in individual micrometric size cellulose particles from water vapor kinetics recorded at different relative humidities, which is never possible with classical methods. For this purpose, pure cellulose was selected. After having discussed the suitability of the QCM system, the paper focuses on evaluating the impact of the hypothesis for sample geometry on the estimation of water vapor diffusivity by a comparison of two analytical solutions. This choice was critically done based on the characterization of particle morphology (size and shape-through both laser diffraction granulometry and image analysis).

## 2. Materials and methods

### 2.1. Materials

Arbocel® BE 600-10 Tg cellulose was provided by J. Rettenmaier & Söhne (JRS). According to the manufacturer, it was highly pure cellulose (cellulose content of 99.5 wt%) with an average fibre length of  $18 \mu\text{m}$ , an average fibre thickness of  $15 \mu\text{m}$  and a bulk density around  $0.23\text{--}0.30 \text{ g cm}^{-3}$ , obtained after successive grinding and sorting steps from pine cellulose pulp. The true density of cellulose, measured by pycnometry, was  $1.56 \text{ g cm}^{-3} \pm 0.08$ . Crystallinity of cellulose was determined using a Philips PW3830 generator, results shown that cellulose is quasi amorphous (crystallinity less than 5%). Absolute ethanol (purity of 99.9%) was purchased from Meridis (France). Gold sensor crystals with nominal frequency equal to 6 MHz were supplied by Neyco (France).

### 2.2. Methods

#### 2.2.1. Water vapor sorption kinetics using a quartz crystal microbalance coupled with adsorption system

**2.2.1.1. Quartz preparation.** First, the peripheral unusable surface of a golden AT-cut quartz resonator was masked by putting a tape. Then,  $15 \mu\text{L}$  of a suspension of cellulose in absolute ethanol at a concentration of  $0.07 \text{ g L}^{-1}$  was deposited on the usable surface ( $S = 0.5 \text{ cm}^2$ ) of the quartz resonator in order to obtain a total weight of cellulose ranging from 1 to  $1.5 \mu\text{g}$ . Ethanol was then evaporated under vacuum. The goal of this preparation was to achieve the best repeatability of data. The weight of one cellulose particle being around  $5.7 \times 10^{-4} \mu\text{g}$  (value deduced from the true density of particles and the average size given by the supplier), it was calculated from the total deposited weight that around 2000 particles were deposited on each quartz.

**2.2.1.2. Water vapor sorption kinetics.** Water vapor sorption kinetics were carried out using a QCM apparatus (Maxtek TM-400). Frequency variation  $\Delta f$  was measured by this apparatus.  $\Delta f$  is the difference between the frequency of the quartz at time  $t$  and the frequency of the quartz at time  $t_0$ , in MHz. This frequency variation was linked to mass variation due to water vapor sorption or desorption.  $\Delta f$  is proportional to the mass variation of quartz  $\Delta m$  according to Sauerbrey equation Eq. (1) (Rouessac et al., 2008):

$$\Delta f = -\frac{f_q^2 \cdot \Delta m}{C \cdot \rho_q \cdot S} \quad (1)$$

where  $f_q$  is the nominal frequency (6 MHz) of the quartz, value depending on its size,  $\rho_q = 2.65 \text{ g cm}^{-3}$  the quartz density,  $S$  the usable area ( $0.5 \text{ cm}^2$ ) of quartz where cellulose particles were deposited and  $C$  an apparatus constant ( $1.67 \times 10^5 \text{ cm s}^{-1}$ ).

Initial sample weight was determined by measuring the frequencies difference between the pristine dry quartz and the quartz loaded by the cellulose. In this paper, knowing that mass of quartz and cellulose were constant,  $\Delta m$  corresponded to the water mass uptake  $m_{\text{sorbed}}$  ( $\mu\text{g}$ ) of cellulose particles. Cellulose particles were adsorbed on a golden AT-cut quartz resonator (6 MHz) placed in a closed chamber in which the pressure of water vapor can be set in a range from vacuum ( $< 100 \text{ Pa}$ ) up to 80% of water steam at  $25^\circ\text{C}$  ( $P_0 = 31.7 \text{ mbar}$ ). Eq. (1) becomes:

$$m_{\text{sorbed}}(\text{RH}\%) = -\frac{\Delta f}{f_q^2} C \cdot \rho_q \cdot S \quad (2)$$

Data acquisition consisted in collecting the frequency variation due to the sorption of water on cellulose particles adsorbed on the gold surface of the quartz as a function of water vapor pressure and time. Cellulose particles were dried and desorbed at  $25^\circ\text{C}$  during 30 min before sorption kinetics by using a vacuum pumping system composed of a primary dry pump and a turbomolecular pump. Eight successive

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