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Article

# Microstructure of Bio-Based Building Materials: New Insights into the Hysteresis Phenomenon and Its Consequences

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**Abstract:** Considering the current energy environment, both efficient and environmentally friendly solutions have to be developed for building construction. Bio-based building materials offer new perspectives through their insulating and natural humidity regulation capacities. Nevertheless, these materials are as complex as they are promising and grey areas still remain regarding their behavior. Their water sorption and desorption curves recorded in experimental work demonstrate a hysteresis phenomenon and, although plausible hypotheses have been formulated in the literature, there is currently no consensus on its causes. Furthermore, it is important to emphasize that no reference considers the hydrophilic nature of the resource. Yet this is a specificity of raw material coming from the plant world. In this context, this paper explores the microstructure and chemical composition of plant aggregates to propose a new explanation for the hysteresis. It is based on recent work demonstrating the existence of differentiated hydrogen bonds between the water sorption and desorption phase in cellulose. Obviously, hysteresis also has an origin at the molecular scale. Lastly, the hypothesis put forward here is supported by the swelling of bio-based materials that has been observed at high relative humidity and this study aims to identify a link between the mechanical (swelling/shrinking) of bio-based materials and their hygroscopic behavior. This leads to a better understanding of the hydro-mechanical coupling of these materials.

**Keywords:** bio-based building material; hysteresis; swelling; microstructure; cellulose

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## 1. Introduction

The study of bio-based materials is quite recent and works on these promising materials have increased over the past twenty years. This is probably due to their multiple advantages: local availability of resources, recovery of agricultural waste, low grey energy, limited environmental impact, and improvement of energy efficiency or even indoor air quality. Today, given the energy and climate upset facing humanity, large-scale development of these materials has become essential. Therefore, more and more authors are focusing on the experimental characterization of these materials, considering different binders and/or vegetal aggregates [1–6]. Those experimental data are fundamental. However, the literature is still limited concerning reflection on the phenomena underlying the macroscopic observables. So, this study aims to focus on the phenomenon of hysteresis. Although it is widely observed experimentally [7–11], its causes are still poorly understood. This article provides a new consideration of the microscopic origin of the phenomenon at the molecular level.

First, some specific characteristics of bio-based materials are recalled. In particular, experimental observations and recent results concerning these materials are highlighted. It is also stressed that, to date, there is no consensus on how hysteresis in bio-based materials can be understood and described. Then, the hydrogen bond is briefly defined in order to facilitate understanding of a recently conducted study on sorption-swelling coupling in nanoporous materials [12].

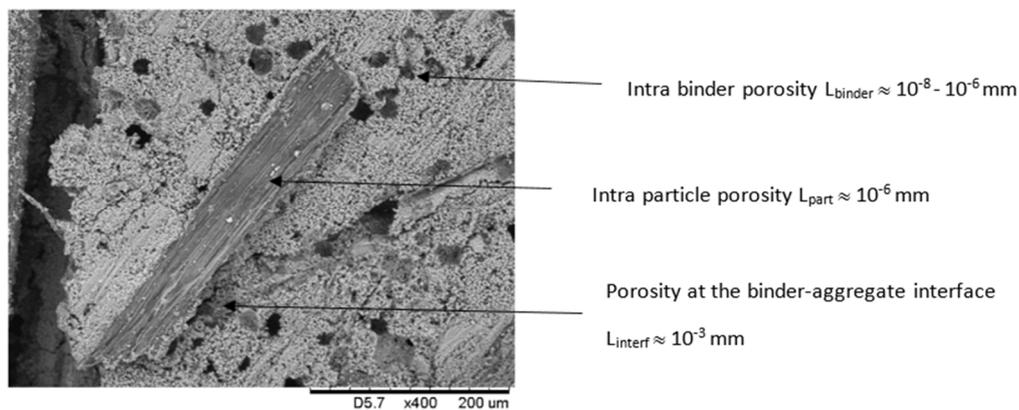
The results of this study are then applied to bio-based building materials. The interest and relevance of considering the hysteresis phenomenon differently are highlighted: first at the microscopic molecular scale so that the plant aggregate's specific nature can be considered, then by

exploring, one by one, the macroscopic consequences found in the literature. They are explained with the new theory put forward. This article thus proposes a new explanation, supported by numerous arguments, of hysteresis and its consequences.

## 2. Focus on Bio-Based Building Materials and Their Specificities

### 2.1. Microstructure

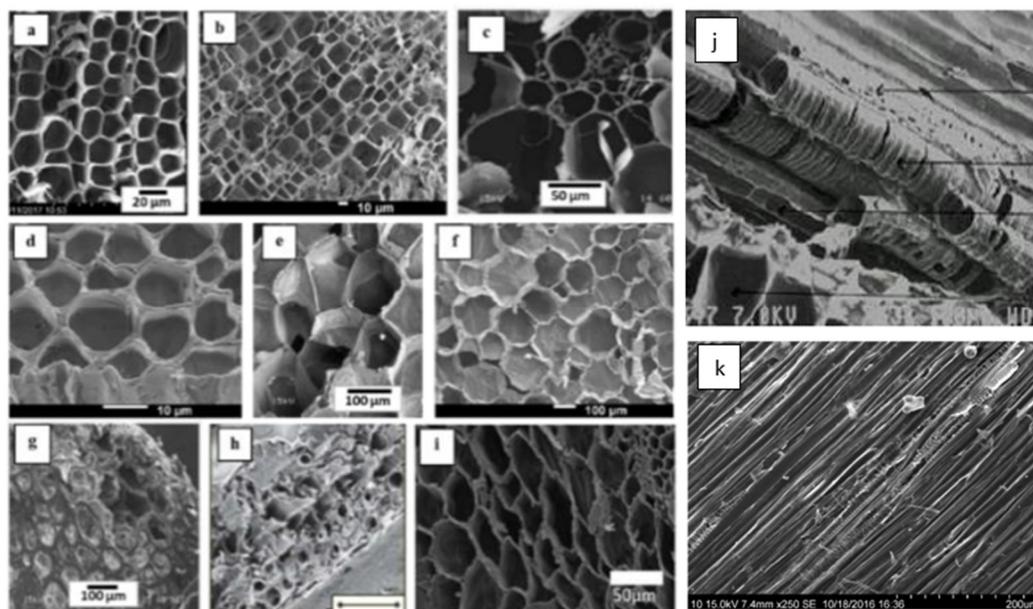
Bio-based building materials are made of agricultural by-products mixed with a binder (lime-based, metakaolin-based, clay, etc.). This leads to a microstructure that is both complex and variable, depending on the formulation, how the plant was grown, or even manufacturing [1,13]. A multi-scale porosity is also underscored by several studies [2–4,9]. Bio-based and conventional materials have comparable intrinsic binder porosity due to the arrangement of hydrates and trapped air. However, the final porosity values for bio-based materials also include the additional contributions of inter particulate and intra particulate porosity, and the porosity at the binder-aggregate interface (Figure 1).



**Figure 1.** Multi-scale porosity of hemp concrete observed with SEM and  $L_i$ , order of magnitude [4].

Thus, this large, interconnected and complex porosity allows the mass transfer of water within the microstructure.

A large porosity can be observed more closely at the intra particulate scale (Figure 2).

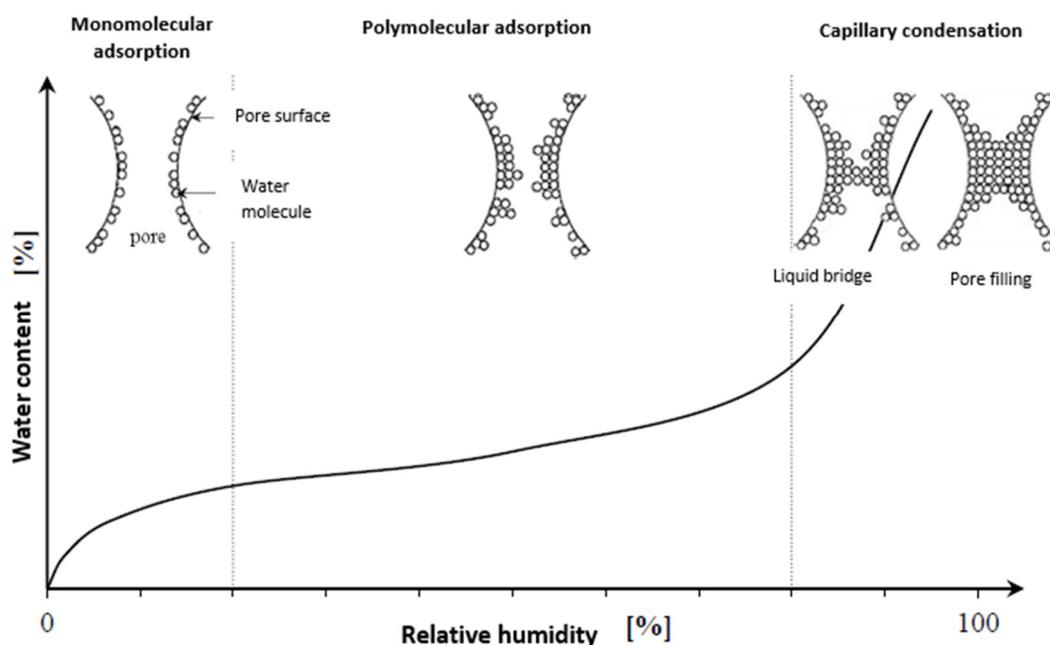


**Figure 2.** SEM cross-sectional images of (a) hemp shiv, (b) flax shiv, (c) barley straw, (d) wheat straw, (e) sunflower pith, (f) rape straw, (g) corn cob, (h) rice husk, (i) miscanthus stem [7], longitudinal (j) and transversal (k) images of hemp shiv [8,9].

These tubules allow the sap to circulate when the plant is growing. After drying, they fill with air, which causes intra-particle porosity, explaining, in particular, the insulating capacity of bio-based building materials. It is useful to note that a tubular morphology exists in a wide range of plant aggregates.

## 2.2. Hygroscopic properties

Hygroscopic material is able to fix and store water depending on moisture conditions. This capacity is governed by the pore size distribution [14]. According to many studies, both binder and plant particles are hygroscopic materials [3,9,13,15–17]. This means that they are able to adsorb excess water from the environment (in the form of vapor that condenses under certain conditions) and desorb this water when the environment is drier. This natural humidity regulation capacity is a major asset as it contributes to healthier indoor conditions. Sorption effects are widely described in the literature by Van der Waals interactions between water and the pore walls. The type of binding that causes poly-molecular adsorption and capillary condensation are not specified. Thus, three different mechanisms schematically describe how water is adsorbed in the pore network of bio-based building materials (Figure 3) [18–22].



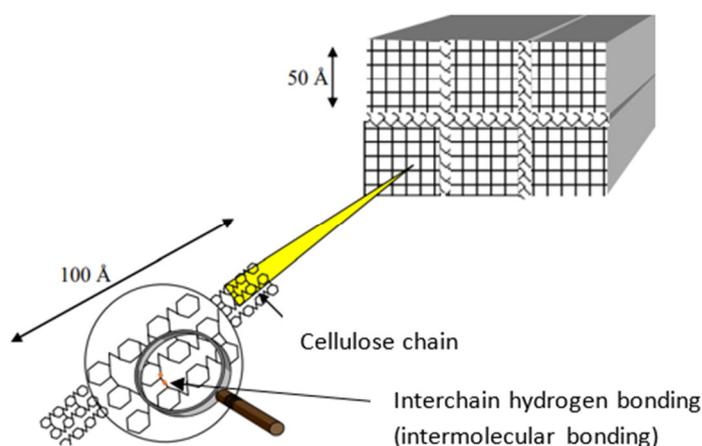
**Figure 3.** Modes of water fixation in a pore [22].

Up to now, the nature of the solid skeleton surrounding the pores has not been differentiated. The same fixing modes are suggested for both the organic and the mineral parts of bio-based materials.

## 2.3. Chemical Composition

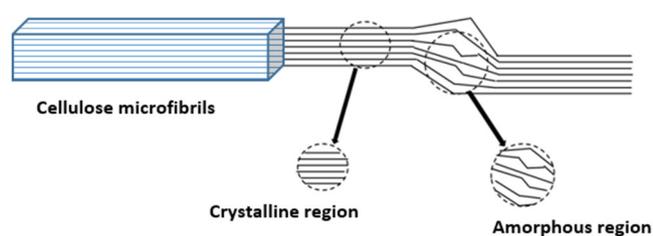
Bio-aggregates are mainly composed of cellulose, hemicellulose, and lignin [23–26]. Because cellulose is the major component [27,28], it is interesting to take a closer look at its microstructure. This bio-polymer is organized into chains of glucose. They are linked together by hydrogen bonds (interchain or intermolecular bonds) [12,29]. The cellulose chains are organized in the form of

microfibrils, the arrangement of which determines the deformation capacity of the plant particle [30] (Figure 4).



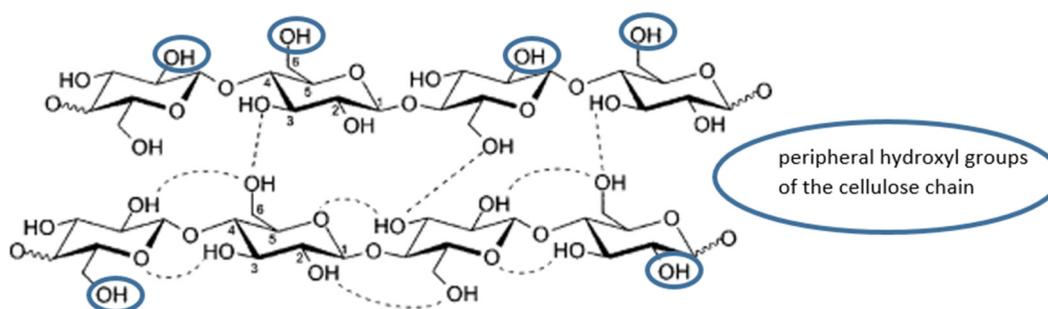
**Figure 4.** Cellulose microfibrils and inter-molecular hydrogen bonding [30].

In reality, cellulose chains are not always perfectly aligned (crystalline part) and amorphous regions are present, especially in natural cellulose [31] (Figure 5). Some authors indicate that cellulose is mainly crystalline in agro-resources [32], while dosages on hemp shiv have shown very low crystallinity levels [33]. However, the sources agree that amorphous and crystalline zones coexist within plant walls. The proportion of each part is variable and depends on the harvesting zone, the method of extracting the fibers from the plant, and the treatments applied [34].



**Figure 5.** Semi-crystallinity of cellulose, adapted from [35].

Cellulose chains have both intra- and inter-molecular hydrogen bonds. The hydroxyl groups on the surface of the chains are more accessible to create hydrogen bonds with other molecules than those located inside (Figure 6).

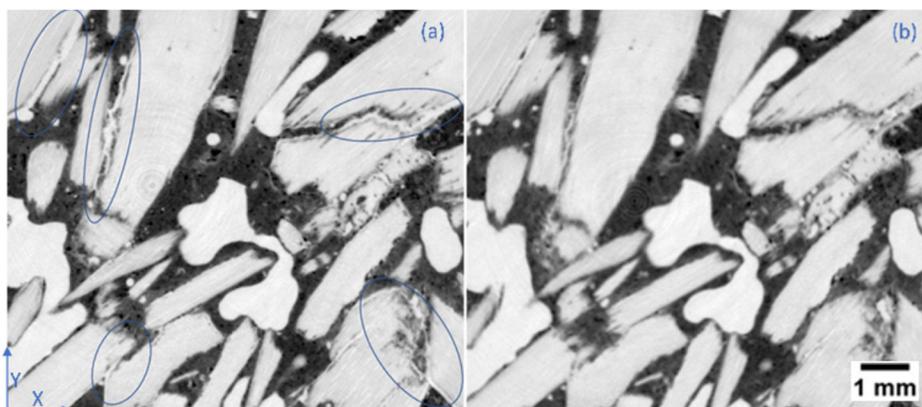


**Figure 6.** Intra- and inter-hydrogen bonds in cellulose (dotted lines), adapted from [36].

Thus, the reactivity of cellulose, i.e. its ability to create hydrogen bonds with its environment (with another cellulose molecule or a different molecule), is facilitated by its semi-crystallinity. This means that the steric hindrance is weaker in amorphous portions; space between cellulose chains increases the possibilities of hydrogen bonds with other potential molecules. Consequently, amorphous cellulose is a particularly favorable site for the creation of hydrogen bonds with its environment [37]. This is not the case for mineral or clay binders, as they do not contain cellulose [5,38–40].

#### 2.4. Swelling and Shrinkage

Cracking due to plastic shrinkage of composites is well known and is explained by mechanical stresses during drying [41,42]. Furthermore, other swelling and shrinkage phenomena are reported in the literature, whether at a young age or after a period of accelerated aging [9,21,43]. This is observed at the particulate scale under increasing or decreasing relative humidity conditions (Figure 7). The result is a significant change in the aggregate interface, which alters its porosity. This modification of microstructure in bio-materials is simply attributed to the presence of plant particles by the authors and has not been explained to date.



**Figure 7.** X-ray tomography images of hemp concrete showing the swelling phenomenon between dry and wet states ( (a) 0% RH (b) 85% RH ) [9].

Swelling and shrinkage impact the porosity of bio-materials [21,44,45] and can therefore have effects on their thermal, hydric, and mechanical properties in the more or less long term.

#### 2.5. Functional Properties with Age

According to recent studies, thermal and hygric properties of bio-based materials change with age [6,46]. Thus, whether aging is accelerated or not, several authors show that age reduces the adsorption and desorption rate and the water vapor permeability. However, some authors indicate an increase with age for thermal conductivity while others show the opposite [6,9].

#### 2.6. Temperature Effects

The thermal conductivity of bio-based materials is temperature dependent [47]. Moreover, several studies have demonstrated the temperature dependence of sorption curves [11,17,48,49]. Thus, the effects of temperature on the sorption process have been promisingly modeled but no explanation of this phenomenon has been proposed so far.

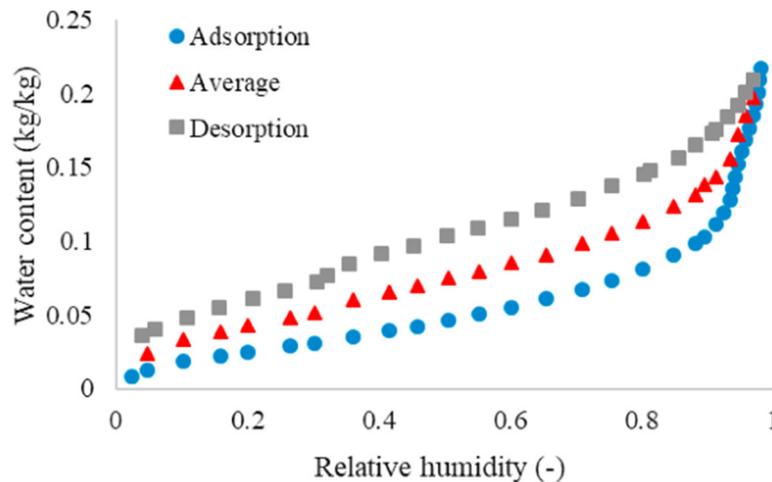
#### 2.7. Local Kinetic Sorption

Recent work has highlighted the relevance of considering local sorption kinetics in bio-based materials, especially when coupled with hysteresis [50,51]. This was motivated by the observation that these materials take a long time to stabilize when the environment changes (more or less humid). The consideration of local kinetics is very relevant to describe the transformation of water from vapor

to liquid (and vice versa). This has been experimentally validated. Thus, the fixation of liquid water in hemp concrete would be conditioned by a very slow diffusion of water molecules.

### 2.8. Sorption Hysteresis

Sorption hysteresis observed on bio-based materials is widely reported in the literature [7,11,14,21,26,50,52–57]. At a given relative humidity, the eco-material does not have the same water content (after stabilization), depending on the sorption or desorption phase (Figure 8).

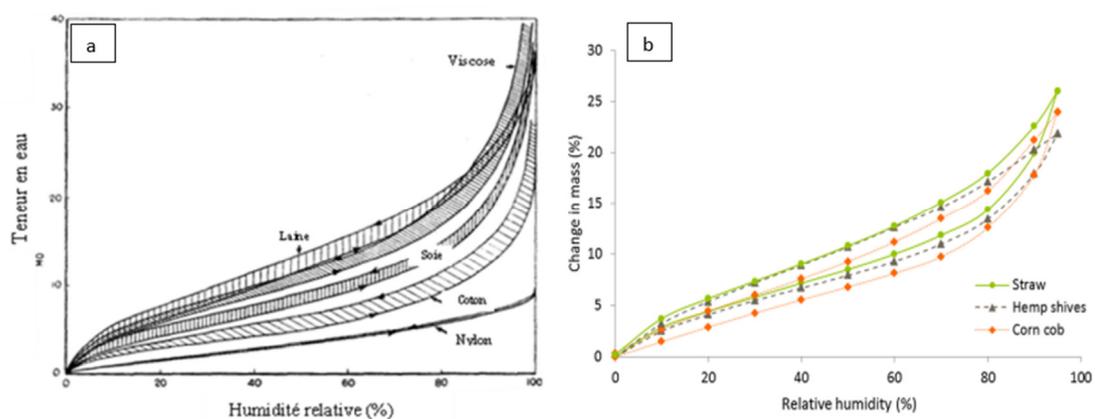


**Figure 8.** Hysteresis in the case of hemp concrete [7].

This fundamental point must be considered to assess the hygrothermal behavior of bio-based walls. Thus, the following items have been experimentally demonstrated:

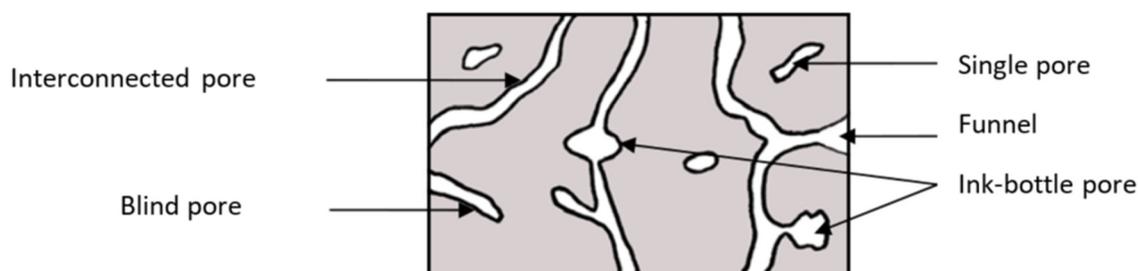
- The sorption mechanism is reversible since the original state is obtained at a dry state [56]
- Hysteresis is more pronounced for plant-based concrete materials than for aggregates [24,54,56,58]
- Aging reduces the rate of adsorption and desorption for hemp concrete [59]
- Temperature can influence hysteresis [11] [60], or not [61]
- Swelling of the plant particles or fibers during hysteresis is irreversible [43,60]
- Hysteresis increases while crystallinity decreases [60]
- Water content is always higher in the desorption than in the adsorption phase for the same relative humidity.

Moreover, the hysteresis phenomenon can be observed on binders alone, whether they are mineral or geo-sourced [8,14,62–64]. It can also be demonstrated on plant fibers or aggregates (Figure 9) used both in the textile and the building industries [22,60].



**Figure 9.** Hysteresis for a wide range of plant fibers and aggregates used in the textile industry (a) [60] or in the building industry (b) [10].

The offset between the sorption and desorption curves is commonly explained by an ink-bottle effect (Figure 10), capillary condensation and/or the contact angle difference [18,21,54,56,64,65]. No distinction is made according to the nature of the material where hysteresis is observed.



**Figure 10.** Schematic diagram of the porous network [18].

To date, the explanations remain open since there is no real consensus on this subject [53,66].

### 3. From Hydrogen Bonding to Hysteresis

#### 3.1. Hydrogen Bonding

Hydrogen and Van der Waals bonds are modelled by dipole-dipole interactions [67,68]. Although they both result from electrostatic interaction, hydrogen bonds have a higher binding energy due to the strong polarization of the hydroxyl groups. On the other hand, a covalent bond results from the pooling of valence electrons between two atoms. It involves a chemical reaction that is not reversible. Consequently, the binding energies differ since they result from different phenomena (Table 1). Finally, the greater the binding energy, the more difficult it is to break the bond. Thus, hydrogen bonds can break or change form easily at ambient temperature (300 K) due to their low bonding energy [67]. Nevertheless, for the same type of bond, the binding energy may differ according to the nature of the atoms and molecules involved.

**Table 1.** Order of size of different bonds [67].

Type of bonding	Bonding energy [kJ.mol <sup>-1</sup> ]
Covalent	≈ 100
Hydrogen	≈ 10
Van der Waals	≈ 1

It should be noted that Van der Waals interactions, mentioned to explain the first step of water fixation in bio-based materials (cf. Section 2.2), are about 10 times weaker than the hydrogen bonds. Moreover, it is well known that water, a polar molecule, forms hydrogen bonds [69]. It establishes hydrogen bonds rather than Van der Waals bonds as far as possible. The two interactions are different and should not be confused [68].

In addition, cellulose is a host polymer concerning hydrogen bonding, due to its hydroxyl groups [70]. Recent work highlights the potential of hydrogen bonding in porous molecular materials [71]: they condition the spatial organization of the microstructure [72].

#### 3.2. Microscopic Understanding of Hysteresis

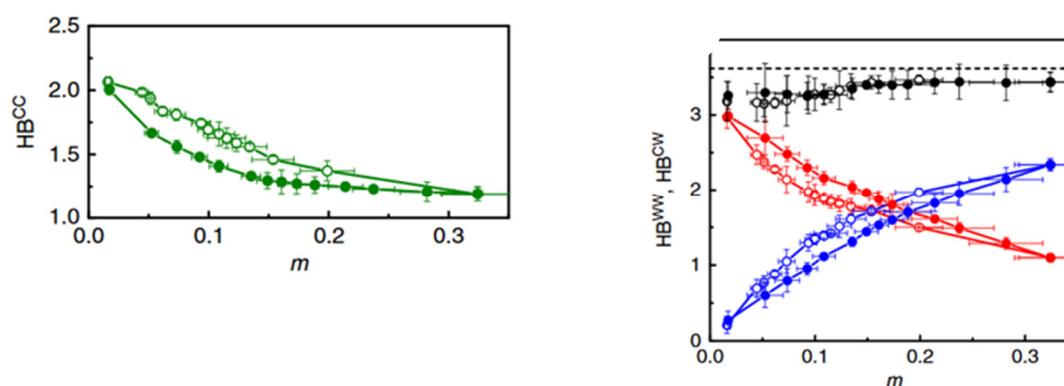
A recent study has demonstrated a molecular-scale coupling mechanism to explain the sorption hysteresis and swelling of polymers such as cellulose [12]. The authors explain that three types of hydrogen bonds coexist within cellulose:

- Inter molecular hydrogen bonds between water molecules (HB<sup>WW</sup>)
- Inter molecular hydrogen bond between water molecules and cellulose (HB<sup>CW</sup>)

- Inter chain Hydrogen bonds in cellulose ( $HB^{CC}$ )

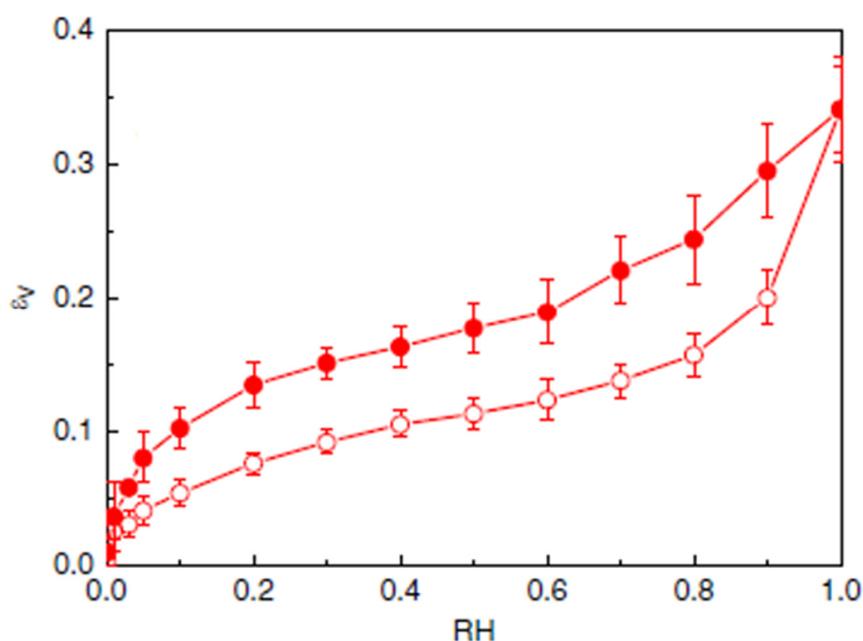
The sequence of creation/breakage of these hydrogen bonds is conditioned by the phase observed: sorption or desorption.

Water is first physisorbed (through  $HB^{CW}$ ) in the sorption phase (to the cellulose chains). The cellulose swells and the number of  $HB^{CC}$  decreases with increasing water content. Consequently, the intermolecular bonds in cellulose ( $HB^{CC}$ ) break: more and more hydroxyl groups are accessible to form  $HB^{CW}$ . Simultaneously, the number of  $HB^{WW}$  increases, reflecting the formation of water clusters within the polymer pore space (Figure 11).



**Figure 11.** Number of  $HB^{CC}$  (on the left) /  $HB^{WW}$  and  $HB^{CW}$  versus moisture content ( $m$ ) from Chen et al. [12].

In the desorption phase, lower energy bonds break first. As  $HB^{CW}$  is stronger than  $HB^{WW}$ , water molecules are first removed from pore water clusters. Thus, there are more  $HB^{CW}$  in the desorption than in the sorption phase for the same relative humidity since more “host sites” are accessible in the polymer. This microscopic phenomenon leads to an observable hysteresis in the sorption-induced swelling of cellulose (Figure 12).



**Figure 12.** Hysteresis in sorption-induced swelling, case of cellulose [12].

The existence of differentiated hydrogen bonds between the water sorption and desorption phases in amorphous cellulose has been clearly demonstrated. It causes macroscopic hysteresis within the polymer. This leads us to consider these results while analyzing the behavior of bio-based materials.

In addition, Chen et al. point out that the moisture content first increases rapidly (low relative humidity) and then less rapidly (higher relative humidity). This inflection point in the adsorption isotherm can be explained by an initial rapid and easy adsorption of water molecules into the initially available host sites of cellulose. Subsequently, the cellulose chains open up and more water molecules are adsorbed but the process is slower. Finally, the authors indicate that the pore size prevents the phenomenon of capillary hysteresis in nanoporous media (with pores smaller than 2 nm). Thus, in cellulose, where the pores are smaller than 1 nm, capillary hysteresis cannot take place.

#### 4. Discussion: New Insights into Hysteresis in Bio-Sourced Materials

##### 4.1. A Necessary New Approach

The explanations for hysteresis provided in the literature are open to criticism. First, SEM images show that the plant aggregates have a tubular morphology. No pronounced narrowing or widening is visible. The hypothesis of ink-bottle shaped pores is not justified at this scale. It is more relevant at the scale of the material, due to a multi-scale complex and tortuous porosity. However, in the case of plant aggregates, the pore size is measured in tens of micrometers [73], so capillary hysteresis is founded.

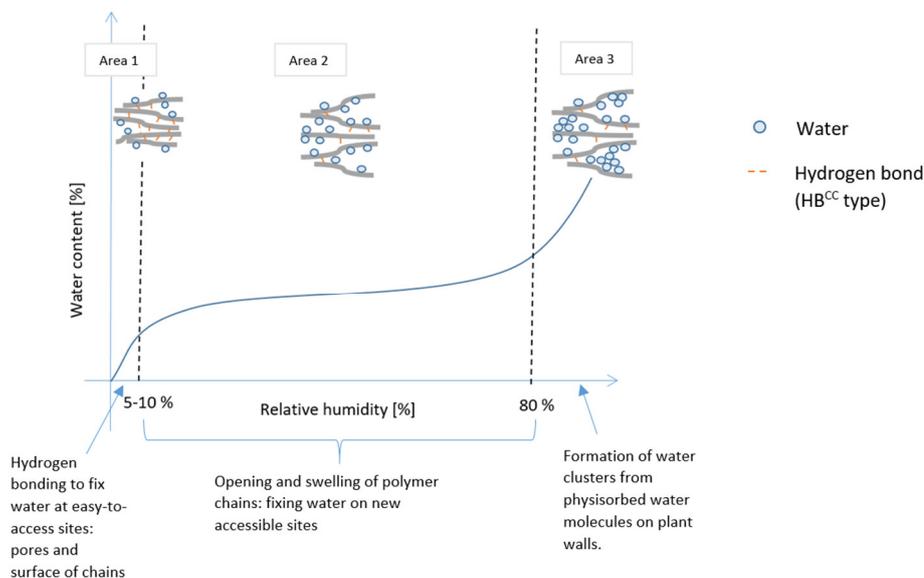
Furthermore, covalent bonds cannot explain the sorption mechanism, since sorption is reversible. In contrast, it seems appropriate to regard weaker bonds as Van der Waals or hydrogen bonds to explain water sorption and desorption.

In addition, whether it is through the ink-bottle effect, the capillary condensation and/or the contact angle difference, the hypotheses mentioned assume that the condensed state of the water is reached. However, capillary condensation occurs from 80% RH (cf. Figure 3). The sorption and desorption curves do not overlap, even at low relative humidities. Moreover, while the smallest pores can contain liquid water, they probably cannot account for the entire shift between the curves at low humidity values. Finally, no assumption made so far can explain other observables such as swelling, sorption kinetics and temperature effects.

##### 4.2. Hysteresis: From the Aggregate Scale to the Material One

###### i) A new water fixation mechanism

It is now possible to differentiate the modes of water fixation between the pore network of the plant aggregate and that of the material (vegetal concrete or lightened earth). This means that the plant aggregate's lignocellulosic nature is considered. Nevertheless, as most sorption sites for hydrogen bonds have been found in the hemicellulose followed by cellulose and lignin [74], this study does not consider the nature of the polymers in the plant aggregate. Only the scale of the plant particle and the material will be differentiated. A new water fixation mechanism is thus proposed (Figure 13).



**Figure 13.** Water fixation mechanism in bio-based materials at the molecular scale in plant particle.

The bonds involved in the process are likely to be hydrogen bonds, although Van Der Waals bonds (induced dipole) may occur at the margin. Only hydrogen bonds are considered here. Thus, different regions of the curve and the corresponding slopes show the existence of 3 processes with different kinetics:

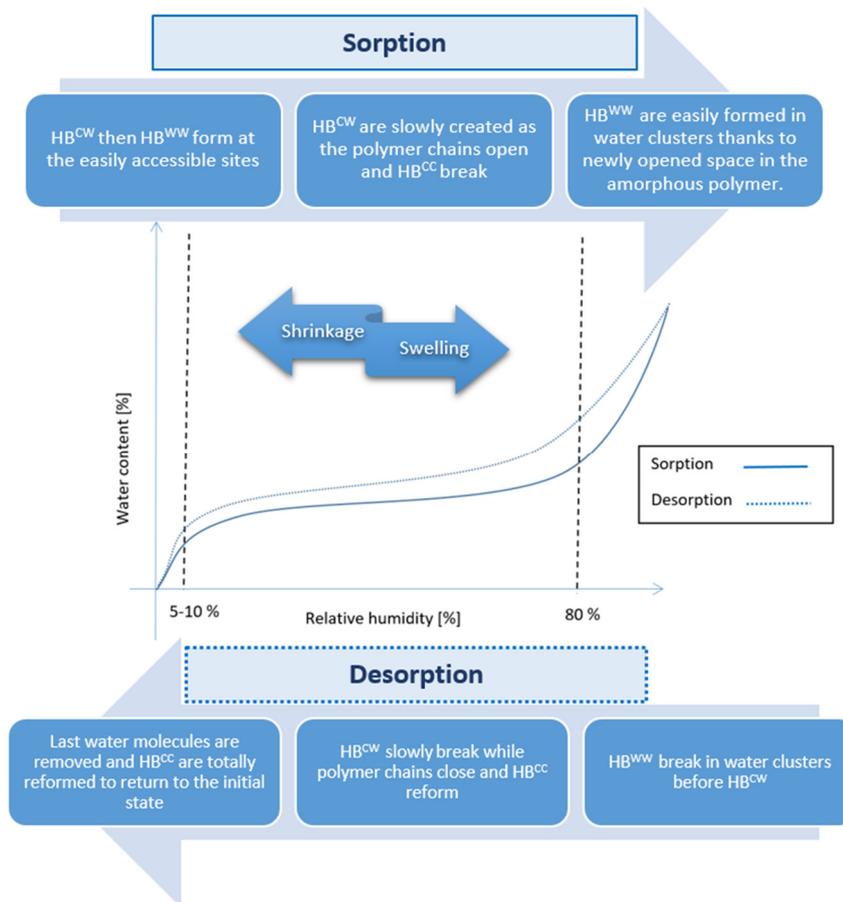
- Area 1: Water fixation on a pore surface is relatively fast because the host sites are easily accessible:  $HB^{CW}$  bonds form on polymer surface chains or in pores of an amorphous region then  $HB^{WW}$  form easily until the initial pores are filled.
- Area 2: Polymer chains open up, freeing new host sites to create  $HB^{CW}$  bonds. In parallel,  $HB^{CC}$  bonds break.
- Area 3: At high relative humidity, hydrogen bonds mostly form between water molecules because many host sites are occupied on polymer chains. This leads to water clusters in the new pore spaces created by the swelling of the polymer chains. Because host sites are very accessible, the associated kinetics is quite fast, as in area 1.

#### ii) A new description of hysteresis

Furthermore, from the results presented in Section 2.2, it is assumed that, when plant aggregate is subjected to an increase in relative humidity, more and more new “host sites” become available to create  $HB^{CW}$  bonds. Those bonds are not broken at the same relative humidity level during the desorption phase. This is assumed to be the only cause of hysteresis at the particulate scale up to 80 % RH. First, this phenomenon has been proven, and, second, the microstructure of the plant aggregates is inconsistent with the other assumptions made in the literature so far.

In addition, the richer the plant aggregate is in amorphous polymers (cellulose, hemicellulose, and lignin), the likelier it is that the mechanism will occur.

In contrast, at the material level, the ink-bottle effect, capillary condensation and/or the contact angle difference probably coexist—especially at high humidity when water is mostly liquid. Consequently, a new description of hysteresis in bio-based building material can be proposed (Figure 14).



**Figure 14.** Hysteresis mechanism in bio-based building materials explained thanks to differentiated hydrogen bonds in plant particle.

#### 4.3. Macroscopic Effects

The theory put forward in the previous section is supported by a wide range of macroscopic observations. Thus, it is possible to connect and explain all these points—raised in Section 2—through sorption-swelling coupling (Table 2).

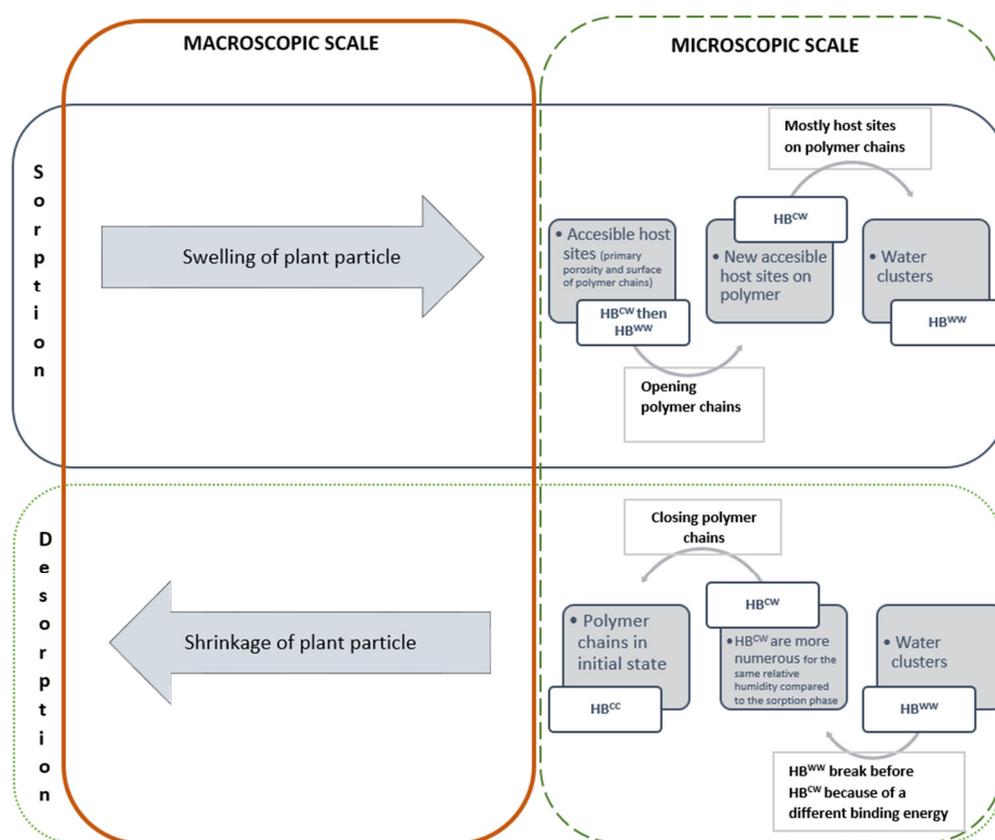
**Table 2.** Macroscopic observations of sorption-swelling coupling that causes hysteresis in bio-based building materials.

Observation	Origin	Explanation
Sorption mechanism is reversible.		Hydrogen bonds form and break easily, even at ambient temperature, due to their low binding energy.
Hysteresis is more pronounced for plant-based concrete materials than for aggregates.	sorption-swelling coupling at molecular scale in vegetal aggregate	Because of additional origins of hysteresis in material than in aggregate. Effects are cumulative.
Aging reduces the rate of adsorption and desorption.		Residual water masks “host sites”: they are no longer accessible, as inhibited by the first sorption phase.
Swelling of the plant particles or fibers during hysteresis is irreversible.		Returning to a dry state allows the last physisorbed water to be extracted. The intercellulosic chains seem to return to their original state. In any case, there is no (or negligible)

	macroscopic manifestation of swelling.
Hysteresis increases while crystallinity decreases	The more amorphous the cellulose is, the more important is sorption-swelling coupling. Interchain bonds cannot open in crystalline regions due to high stability.
Swelling and shrinkage is observed at a young age or after a period of accelerated aging.	Swelling and shrinkage are possible as soon as HB <sup>CW</sup> replaces HB <sup>CC</sup> . This potential decreases with age (inhibited sites) but remains possible given the large number of host sites in the plant aggregate.
Temperature dependence of sorption curves.	Hydrogen bonding is temperature dependent.
Relevance of considering local sorption kinetics in bio-based materials, especially when coupled with hysteresis.	The opening/closing of the cellulose chains is probably a rather slow process that needs a kinetic factor to be taken into account, both in sorption and desorption phases.
Swelling is observed between dry state and 80 % RH	The opening of the cellulose occurs from 5-10 % to 80 % RH ( cf. Figure 13)
Water content is always higher in desorption than in sorption phase for the same relative humidity	More water molecules are physisorbed during desorption because they do not have the same chemical potential.

All these elements allow us to establish the relevance of taking this recently demonstrated sorption-swelling coupling effect into account. It improves our understanding and description of hysteresis and its consequences in bio-based building materials.

In view of all the elements discussed above, a new multi-scale schematization of bio-based materials' behavior is proposed (Figure 15).



**Figure 15.** Sorption-Desorption of water: summary diagram of the coupling reversible process at the plant particle scale that causes hysteresis in bio-based building material.

This makes the link between molecular-scale phenomena their consequences at the macroscopic scale. It thus highlights the hydro-mechanical multi-scale coupling of these materials.

## 5. Conclusions

This study demonstrates the need to reconsider the description of water sorption in bio-based building materials. The explanations put forward in the literature are not to be totally discarded but are not sufficient. Indeed, recent work has shown how water adsorbed at the cellulose scale can induce both hysteresis and swelling of cellulose chains. The lignocellulosic nature of the plant aggregates incorporated should therefore be taken into account.

Thus, a new description of sorption hysteresis in the case of bio-based materials is proposed. It is based on the existence of hydrogen bonds that are differentiated between the water sorption and desorption phases in cellulose. These bonds are stronger than the Van der Waals bonds commonly reported in the literature until now.

It is thus possible to better understand the hysteresis phenomenon widely observed in the literature for bio-based materials. A new scale of porosity, that has been ignored so far, is to be considered: nanoporosity (in the amorphous polymers constituting the plant aggregate). This molecular-scale hydro-mechanical coupling explains many observations at the macroscopic scale. We matched this new consideration with a set of macroscopic observables widely reported in the literature. This lends support to the new hypothesis suggested and to shows how it is relevant.

Finally, this study opens up new perspectives:

- (i) A better understanding of macroscopic swelling makes it possible to anticipate and to predict. It is important to leave a corresponding gap in the wall to avoid any disorder. In addition, swelling effects impact the porosity of the material and therefore probably affect its mechanical properties and durability.

- (ii) It would be interesting to investigate whether, as in the case of hysteresis in electromagnetism, the area of the hysteresis curve gives additional information but, here, on the sorption/desorption phenomenon.

To conclude, this work combines the fields of chemistry, civil engineering and applied physics. It underlines the interest of conducting interdisciplinary studies to understand the full complexity of bio-based materials.

**Author Contributions:** Conceptualization, S.R.L.; methodology, S.R.L.; software, S.R.L.; validation, S.R.L, V.S and A.A.C; formal analysis, S.R.L; investigation, S.R.L; resources, S.R.L.; data curation, S.R.L; writing—original draft preparation, S.R.L; writing—review and editing, S.R.L; visualization, S.R.L.; supervision, A.A.C; project administration, S.R.L; funding acquisition, S.R.L. All authors have read and agreed to the published version of the manuscript.

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