

# Cellulose Non Freezing Bound Water and Activation Energy of Desorption by Thermogravimetric Analysis

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## Research Article

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# Abstract

Understanding water-cellulose interaction is a key factor in cellulose processing strategies and to achieve the best properties for each application. The emergence of new advanced materials based on nanocelluloses calls for more precise methods to study these systems. In this work, we described the study of water-cellulose interaction by thermogravimetric analysis (TGA), comparing dynamic and auto stepwise methods. The auto stepwise method was able to identify with precision the different species of water: i) the free water or freezing water, ii) the freezing bound water and iii) the non-freezing bound water. The Ozawa-Flynn-Wall method was used to estimate the activation energy of bound water desorption,  $E_a$  average = 50.45 kJ.mol<sup>-1</sup> and the cellulose degradation energy,  $E_a$  average = 143.18 kJ.mol<sup>-1</sup>. The results obtained given a new knowledge on the interaction between water and cellulose since other techniques such as DSC are not sensitive to non-freezing bound water increasing the range of water content that can be studied.

## Introduction

Water is present in all aspects of our life and is a key factor in determining the properties of materials from biomass such as cellulose. In its cold and noncrystalline state it shows non predictable behavior and understanding its properties is fundamental for several aspects of science and technology of materials (Debenedetti and Stanley 2003). Polymers capable of strong interaction with water in its non crystalline state are influenced in its mechanical, thermal and biological properties. This is especially relevant for polymers in which intra and intermolecular interactions due to hydrogen bonds determine its properties (Hoeve 1980). Kuo (Kuo 2018) classified hydrogen bonds for practical reasons, such as "strong", "moderate" and "weak" bonds. Energy between 16.7 to 41.8 kJ.mol<sup>-1</sup> is related to moderate strength and determine the frontier between strong and weak interactions. Cellulose is the most important polysaccharide biopolymer and several studies were performed to investigate the cellulose-water interactions (Weise et al. 1996; Prusov et al. 2014; Stenqvist 2015). Such interacting water is generally classified into two forms; free and bound water (Hatakeyama and Hatakeyama 1998; Hatakeyama et al., 2008). The water for which the temperatures of melting and crystallization and the respective enthalpies are not significantly different from the normal water is called free or unbound water (Park et al. 2006), while bound water display an unusual behavior. The common feature of this interacting water is the fact that it is associated with the substrate.

Nakamura (Nakamura et al. 1981) classified these associated or bound water into two types, non-freezing and freezing-bound water. The non-freezing-bound water (NFBW) is strongly associated with polymer matrix and it did not display crystallization exothermic or melting endotherms and is attributed to one or few layers of absorbed water. Water trapped in nano-sized pores can also behave as non-freezing water (Park et al. 2007). For large pores or cracks freezing-bound water (FBW) exists being held by capillary forces. This water is not strongly associated with cellulose, presenting peaks of crystallization and melting that are not significantly different from free water. The reduction in its melting observed is

due to the greater pressure created in the micropores and microcracks and this phenomenon is named freezing point depression.

During the complete process of water evaporation or drying of cellulose, first the free water was eliminated and then trapped water in pores and the freezing bound water. Finally, the non-freezing bound water is eliminated at conditions of high energy. (Park et al. 2006, 2007). Mono-layers of non-freezing water absorbed on microcrystalline cellulose corresponds to a concentration of 3.3 wt% which is very below the non-freezing water for cellulose pulp that is of the order of 25 wt% (Park et al. 2007).

Due to the importance of from water in biopolymers several new approaches have been adopted for the study of bound water interactions in biopolymers by techniques such as differential scanning calorimetry (Maloney 1998), nuclear magnetic resonance spectroscopy (Capitani et al. 2009), nuclear magnetic resonance pulsed field gradient (Perkins and Batchelor 2012), spectroscopic techniques (Švedas 2000), thermal analysis (Vyas et al. 2004), impedance spectroscopy at low temperatures (Moreira 2009), dielectric measurements (Hatakeyama et al. 1988). Another relevant aspect is the determination of the activation energy of desorption of bound water on polymers the method commonly chosen is the Ozawa-Flynn-Wall (Ozawa 1965). This method is based on multiples thermogravimetric curves that are held at different rates of dynamic heating and to consider the activation energy of a material in a certain weight loss (conversion) corresponding to a linear dependence between the logarithms of the heating rate with the inverse of Kelvin temperature. The process of weight loss due to water evaporation can be described by the following kinetic equation:

$$\log \beta = \log \left[ \frac{\Delta E}{Rg(\alpha)} \right] - 2.315 - 0,4567 \left( \frac{\Delta E}{R} \right) \quad (1)$$

$$\log \beta = - 0,4567 \left( \frac{\Delta E}{R} \right) \left( \frac{1}{T_i} \right) + \text{constant} \quad (2)$$

If  $1/T_i$  is plotted on a graph in function of  $\beta$ ,  $\Delta E$  can be obtained as from the gradient (Method Ozawa-Flynn-Wall).

Here we determine the activation energy of desorption of bound water on cellulose by dynamic thermogravimetric analysis and we determined the kind of water interacting by the auto stepwise thermogravimetric method.

In the auto stepwise TGA method, the sample is heated at a constant heating rate until it is detected a previously set value of weight loss, due to water removal. The experiment keeps the temperature constant (isotherm condition) until the rate of weight loss is negligible or reaches a least preset threshold, returning

to the dynamic heating, keep until the next event of weight is detected. The values of thresholds were determined from the height of derivative ( $d\%/dt$ ) of thermogravimetric curve. The method showed a high resolution with separation of the non-freezing water event in two events and determined the amount of water to saturate the interacting sites for these events. Three non-freezing water in total amount below 13 wt% were detected by ASW method being one weak bounded, eliminated at room temperature one medium bounded removed at temperature between 25 °C and 40 °C and one high bounded, which was eliminated above 40 °C, up to 120/180 °C. These three events appear as one single event for dynamic scanning method.

## Experimental

### Material

Microcrystalline cellulose Avicel PH101 from Sigma Aldrich was used as cellulose model material. The inorganic salts utilized in the experiments were: LiCl (Mallinckrodt), MgCl<sub>2</sub> (Panreac), Mg(NO<sub>3</sub>)<sub>2</sub> (Panreac), NaCl (Synth) and K<sub>2</sub>SO<sub>4</sub> (Sigma Aldrich).

Prior use, cellulose Avicel was dried in a vacuum oven at 80 °C for 24 hours and kept in a vacuum desiccator. Three conditions were used for cellulose preparation, dry in which the previously dried cellulose with approximately 5% of moisture, conditioned samples ambient with relative humidity of 11.3, 32.8, 43.2, 75.3 and 97.3%, which were obtained with saturated salt solution of respectively LiCl, MgCl<sub>2</sub>, Mg(NO<sub>3</sub>)<sub>2</sub>, NaCl and K<sub>2</sub>SO<sub>4</sub> at 25 °C in accordance with ASTM E104 (ASTM 2014) and with excess water added using a microsyringe.

### Measurements

#### Thermogravimetric analysis (TGA)

Cellulose samples of approximately 5mg were analyzed in a Pirys1 Perkin-Elmer thermogravimetric analyzer. For dynamic method, the experiments were carried out with different heating rates of 3, 10, 20, 3 and 40 °C/min. For Auto Stepwise method, at a heating rate of 3, 5, 7 and 10 °C /min. The Auto Stepwise method settings were 10 min maximum for the isothermal step with a maximum loss in dynamic mode of 0.5 wt% in which the dynamic mode was changed to isothermal mode and kept up to a loss of 0.2 wt%. When 0.2wt% loss was reached the modes was changed to dynamic and keeps until reach 0.5 wt% again. For both methods, dry nitrogen gas was used as inert atmosphere at a flow rate of 20 mL/min, from room temperature at 180 °C.

#### Differential scanning calorimetry (DSC)

DSC measurements were conducted in a Perkin-Elmer DSC 8000 Differential Scanning Calorimetric analyzer. The samples mass were approximately 10 mg and were carried out with open type aluminum

samples pans. The scanning rate was 10°C/min for all samples and nitrogenous gas flow rate 20mL/min. The temperature was varied from -50 to 200°C.

## Result And Discussion

### Differential Scanning calorimetry

Differential scanning calorimetry is one most used methods to investigate the interactions of water with cellulose and other hydrophilic polymers. For purpose of comparison, we use this method to characterize microcrystalline cellulose Avicel with approximately 5 to 6 wt% of equilibrium absorbed water and with excess water at around 50wt%. DSC curves of pure water and cellulose Avicel with excess added water of 50wt% and 5 wt% absorbed are shown in Figure 1.

It is possible to see in Figure 1a that the free water in Avicel with 50 wt% shows a crystallization peak at -18 °C, a melting peak between near 0 °C and vaporization peak after 100 °C. The melting and crystallization peaks are very similar to the peaks observed for pure milli-Q water (Figure 1b) which is in accordance with literature for samples of cellulose with more than 20 % of water. These peaks correspond to free water or freezing water.

For 5 wt% water content (Figure 1c), no peak was observed in DSC because in this case the water absorbed is bounded to cellulose as described by Hatakeyama, et.al. (Hatakeyama and Hatakeyama, 1998). According to Park et al 2007 (Park et al., 2007) the non-freezing bound water content of microcrystalline cellulose reported is 3.3 wt% and 25 wt% for wood pulp fiber. This lower value for MCC is attributed to the higher crystalline index of MCC than wood pulp fiber and the lower accessibility of water to sites of absorption. It is also reported that for cellulose fiber with water content below 19.6% all water is bounded and DSC did not show any transient due to melting or crystallization (Nakamura et al. 1981). This data shows that DSC is not adequate to characterize water interactions below such values and the need for other tools to characterize bound water in cellulose and other hydrophilic polymers. Since thermogravimetric analysis detect water up to very low concentration its use has been considered, however in dynamic mode a single event is usually observed for a large interval of temperature, making it difficult to characterize different kind of non-freezing bound water in a material. The results reported in Figure 1 shows that DSC shows that free water can be detected in samples with 50 wt% of water and that for samples of microcrystalline cellulose water content up to 5/6 wt% cannot be detected by DSC since it corresponds to non-freezing bound water as reported in literature (Park et al., 2007).

### Experimental setup for TGA conditions for cellulose analysis

In order to determine the general conditions for the TGA experiments, cellulose Avicel with 5wt% humidity was analyzed by TGA using dynamic heating program at 3, 10, 20, 30 and 40 °C.min<sup>-1</sup> and by the auto stepwise method with heating rate of 3, 5, 7 and 10 °C.min<sup>-1</sup>, from room temperature to 200°C.

Figure 2a shows the dynamic experiments. It is clear from TGA plots there are only one desorption process during the heating, with a curve shift to higher temperatures as the heating rate were increased. The interval of loss was from the start at 25 °C to 120 – 160 °C depending on the heating rate.

The auto stepwise results are shown in figure 2b and the total water desorption was very close to dynamic method, but without such appreciable temperature shift of the curve as the heating rate was changed.

The results obtained with the auto stepwise program suggests that two process of water loss occur, one up to approximately 50 °C (loss of about 3.4 %) and a second from 50 up to 120 °C with a loss of about 2 %. These loses of absorbed water will be analyzed in detail in the next section

#### Effect of different water content absorbed in cellulose Avicel on the loss profile

For a more accurate determination of the different kind of absorbed water the auto stepwise program was followed by an isothermal step at room temperature in order to detect the loosely bounded water. Figures 3 shows TG curves of conditioned samples in environments with 11.3, 32.8, 43.2, 75.3 and 97.3% of relative humidity using dynamic and auto stepwise program at a heating rate of 10 °C.min<sup>-1</sup>. The amount of absorbed water in the samples varies from 4 to 13 wt%, depending on the condition of conditioning.

The curves obtained in the dynamic heating (Fig. 3a) showed a single loss of mass being difficult to distinguish different types of water. By other hand, the curves obtained by the auto stepwise program showed clearly three steps of water losses, the first one starting immediately after the sample was placed in the balance at isothermal conditions and two others at higher temperatures.

The first event shows an abrupt loss and begins immediately after the sample was placed in the thermoanalyzer. In this stage, purge gas drag the free water absorbed onto cellulose at constant temperature of approximately 25 °C. A second heating starts at 25 °C and goes up to 40 °C. The third loss step starts after 40 °C and proceeds with continuous heating up to 120-150 °C. The events observed above 40 °C were attributed the non-freezing bound water.

The data for water loss determined by dynamic and auto stepwise methods are presented in Table 1.

Water losses at first step at isothermal conditions increase with the relative humidity of conditioning, while the losses from bound water that occur above 25 °C are almost constant and independent on the initial absorbed water content. This behavior indicates that the level of saturation of the two non-freezing bound water are achieved for all samples being of around 1.4% for the first loss between 25 °C and 40 °C and 2.2 % after 40 °C. Those results indicate that bound water is limited by the sites of absorption available in cellulose as described in literature (Park et al., 2006; 2007). Non-freezing bound water can be distinguished in two types, one easy to be removed and one hard to be removed. This is a valuable information that can help in understand the structure of absorbed water onto cellulose substrates.

One possible explanation is that the first bound water removed at lower temperature is the second layer of water absorbed and the bound water eliminate at higher temperature is the first layer directed link to cellulose. This result can be used to evaluate the number of sites for the different species of bound water on cellulose and can give an idea of its nature. A sketch showing the three kind of water observed is presented in the Figure 4.

#### Determination of activation energy of bound water desorption and cellulose degradation

The Ozawa Flynn-Wall non-isothermal method (Ozawa 1965) was used to estimate the activation energy of bound water desorption and thermal degradation of cellulose. The cellulose degradation energy was also estimated with the purpose of comparison with water desorption. The thermograms showing the water desorption (5.5% at 25-150 °C) followed by cellulose degradation (88.0% at 270-550 °C) performed at several heating rates are shown in Figure 5a. The residue from the pyrolysis of cellulose was approximately 6% of the initial weight.

Figure 5b showed the plots of  $\log \beta$  vs  $1/T$  for both water desorption and cellulose degradation, where  $\beta$  is the heating rate, according to Equation 1. The data shows a linear behavior with R-square higher than 0.990 for the water desorption and higher than 0.970 for cellulose degradation.

The activation energies for water desorption and for cellulose degradation obtained from the plots of Fig. 5b are presented in Table 2.

The activation energies of water desorption did not vary appreciable with the degree of conversion and was about  $50 \text{ kJ.mol}^{-1}$  and was associated to bound water (Kuo 2018; Hatakeyama and Hatakeyama 1998) The activation energy of bound water can be considered high since the activation energy for cellulose degradation was in the range of  $150$  to  $170 \text{ kJ.mol}^{-1}$  when measured for between 12 and 60% conversion.

## Conclusion

The study of water-cellulose interaction provides information about the physic/mechanical properties of materials and the type of bounds can be investigated through thermogravimetric analysis. In this work we demonstrate that the thermogravimetric auto stepwise technique yields the highest possible resolution between desorption and decomposition events and was able to detect different kinds of water-cellulose interactions than the dynamic thermogravimetric method and differential scanning calorimetry, identifying both unbound and bound water. It was observed that the non bound water shows a dependence on the conditioning conditions of the samples while nonfreezing-bound water had no significant variation in water weight with the different levels of humidity in the cellulose, suggesting a saturation of water for the type bound in the bulk of Avicel. Two distinct non-freezing water were observed, one weakly bounded and one hardly bounded to cellulose suggestion the first is the outer layer and the second a layer linked directly to cellulose. The energy of freezing-bound water desorption was

35% of energy degradation of cellulose approximately, demonstrating the high bound energy of the hydrogen bound.

## Declarations

### AUTHOR CONTRIBUTIONS

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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### COMPLIANCE WITH ETHICAL STANDARDS

**Conflict of interest.** The authors declare no competing financial interest.

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## Tables

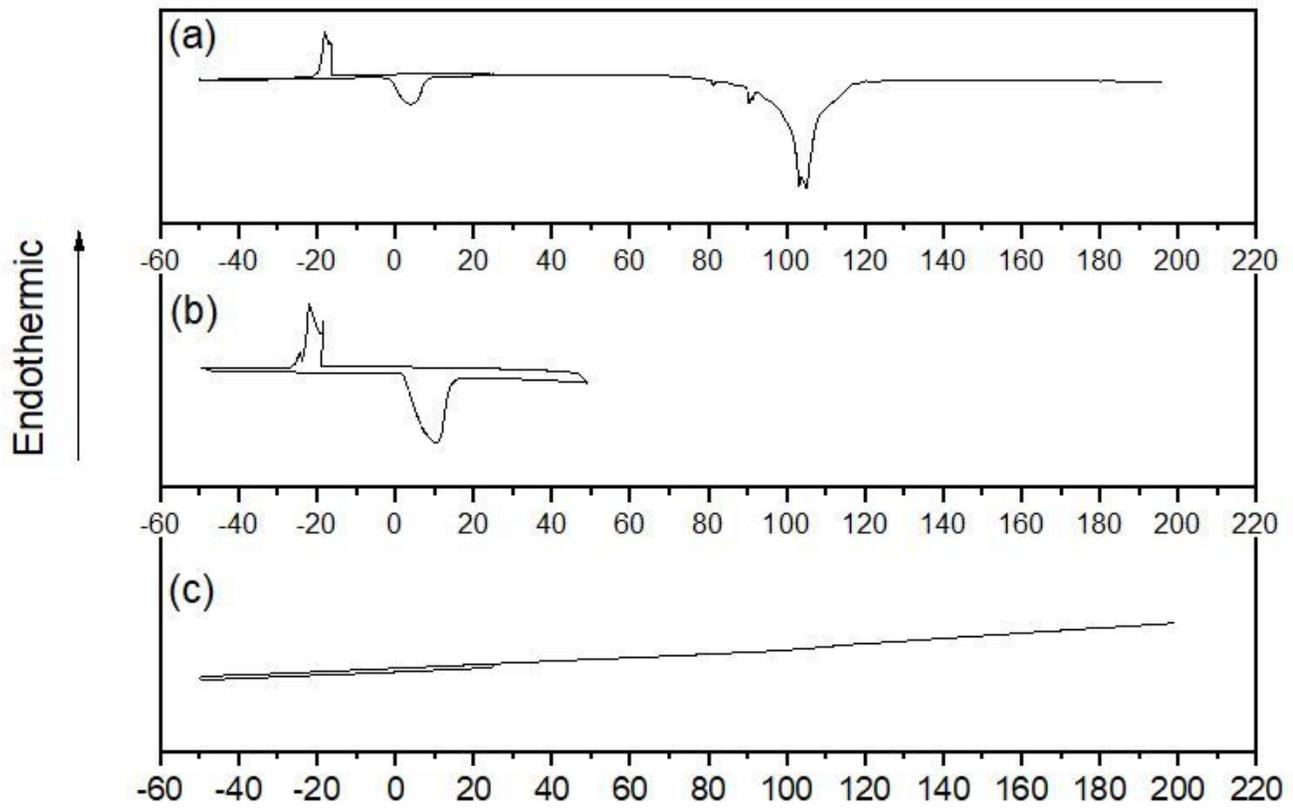
**Table 1.** Water losses by dynamic TGA at 10 °C/min and by auto stepwise method for samples with different moisture content obtained by conditioning in different relative humidity conditions.

Conditioning humidity (RH %)	Temperature and water losses in each step of auto stepwise analysis (%)			Cumulative water loss in ASW (%)	Dynamic method (%)
	1 (~ 25 °C)	2 (~ 40 °C)	3 (40– 20/150 °C)		
11.3%	1.1	1.2	1.9	4.2	3.9
32.8%	1.5	1.1	2.2	4.8	5.0
43.2%	1.5	1.6	2.1	5.3	5.5
75.3%	3.4	1.7	2.4	7.5	7.3
97.3%	8.8	1.5	2.4	12.7	12.4

**Table 2.** Activation energy for water desorption and cellulose degradation.

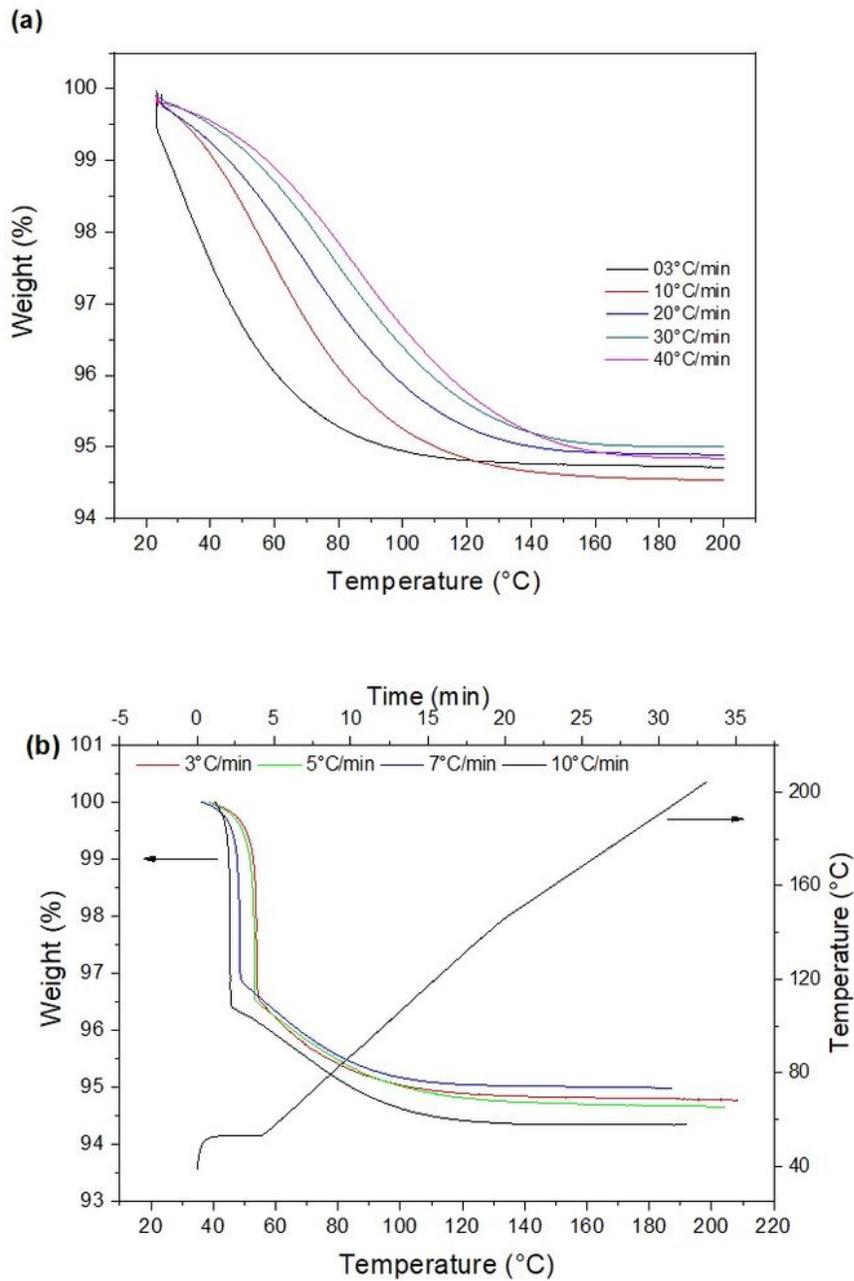
Events	Conversion (%)	Activation energy (kJ/mol)	Deviation ± (kJ/mol)
	2	52.65	2.81
Water desorption	3	47.84	1.49
	4	46.45	1.95
	12	172.55	25.86
	20	167.86	23.21
Cellulose degradation	30	160.83	21.18
	40	156.55	20.87
	50	152.53	20.48
	60	148.82	20.53

## Figures



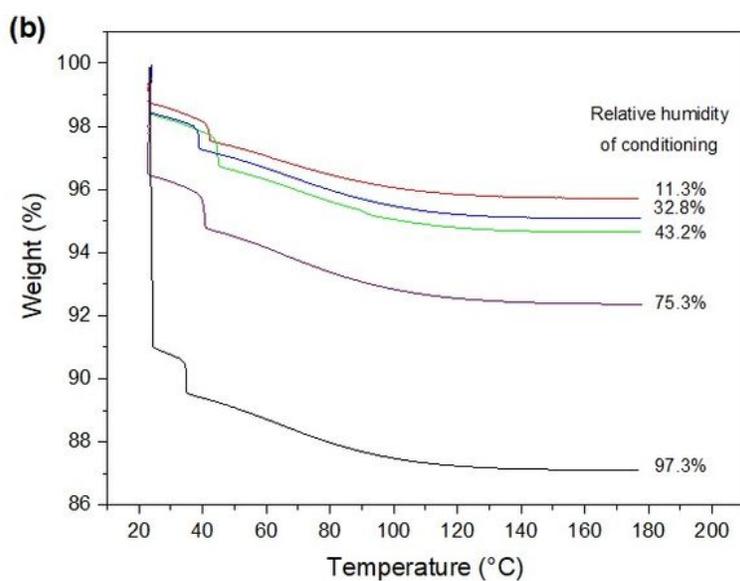
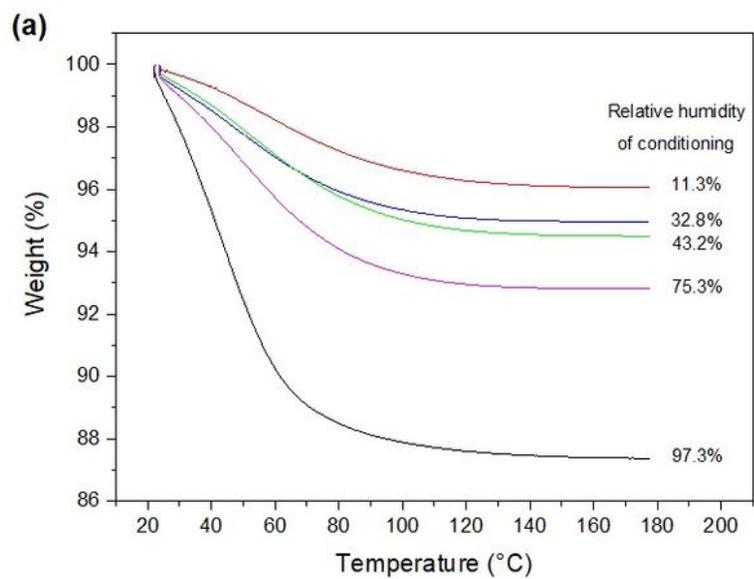
**Figure 1**

DSC curves: (a) Avicel with excess water(50wt%), (b) pure Milli-Q water and (c) Avicel with 5wt % water absorbed in atmosphere with 50% relative humidity at 25 °C



**Figure 2**

TGA curves for cellulose Avicel with 5% moisture (a) dynamic program at heating rate of 3, 10 20, 30 and 40 °C.min<sup>-1</sup> and (b) auto stepwise program at heating rates of 3, 5, 7 and 10 °C.min<sup>-1</sup>



**Figure 3**

TGA curves for cellulose Avicel (a) dynamic heating rate of 10 °C.min<sup>-1</sup> and (b) auto stepwise program at heating rate of 10 °C.min<sup>-1</sup> for samples conditioned in 11.3, 32.8, 43.2, 75.3 and 97.3% relative humidities.

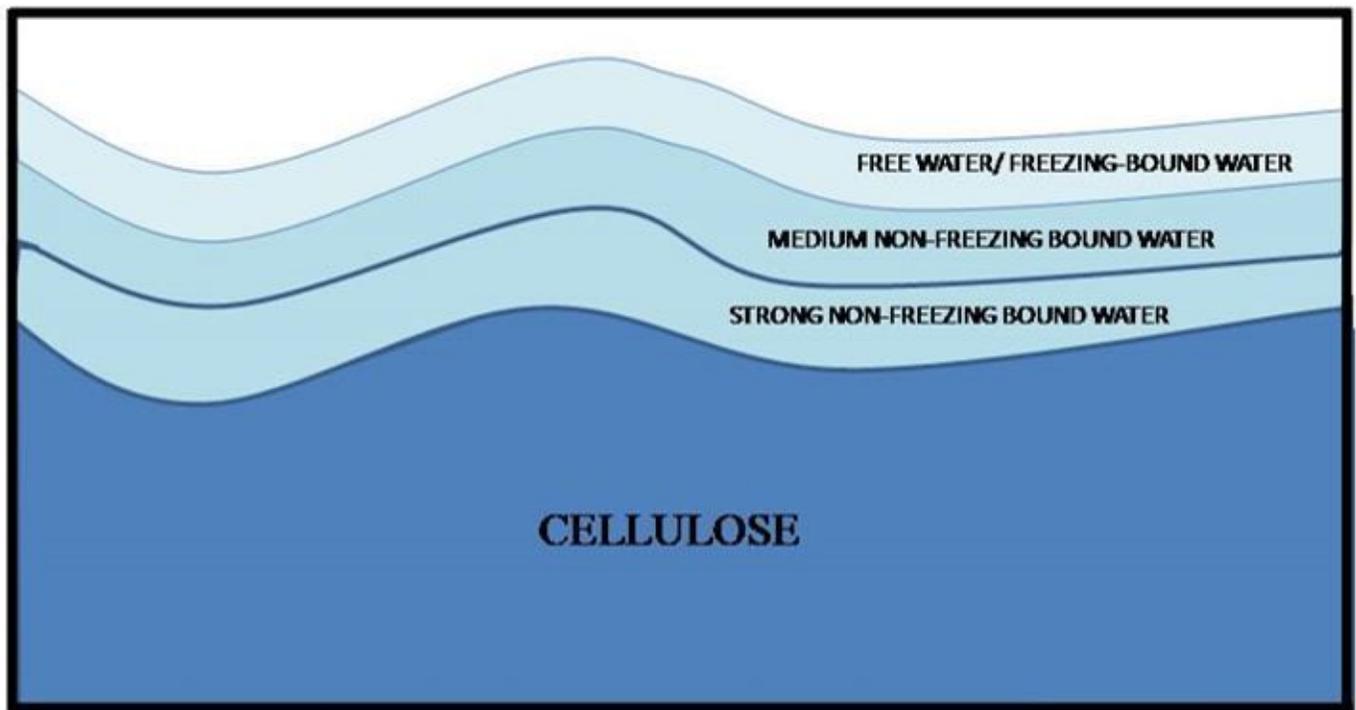
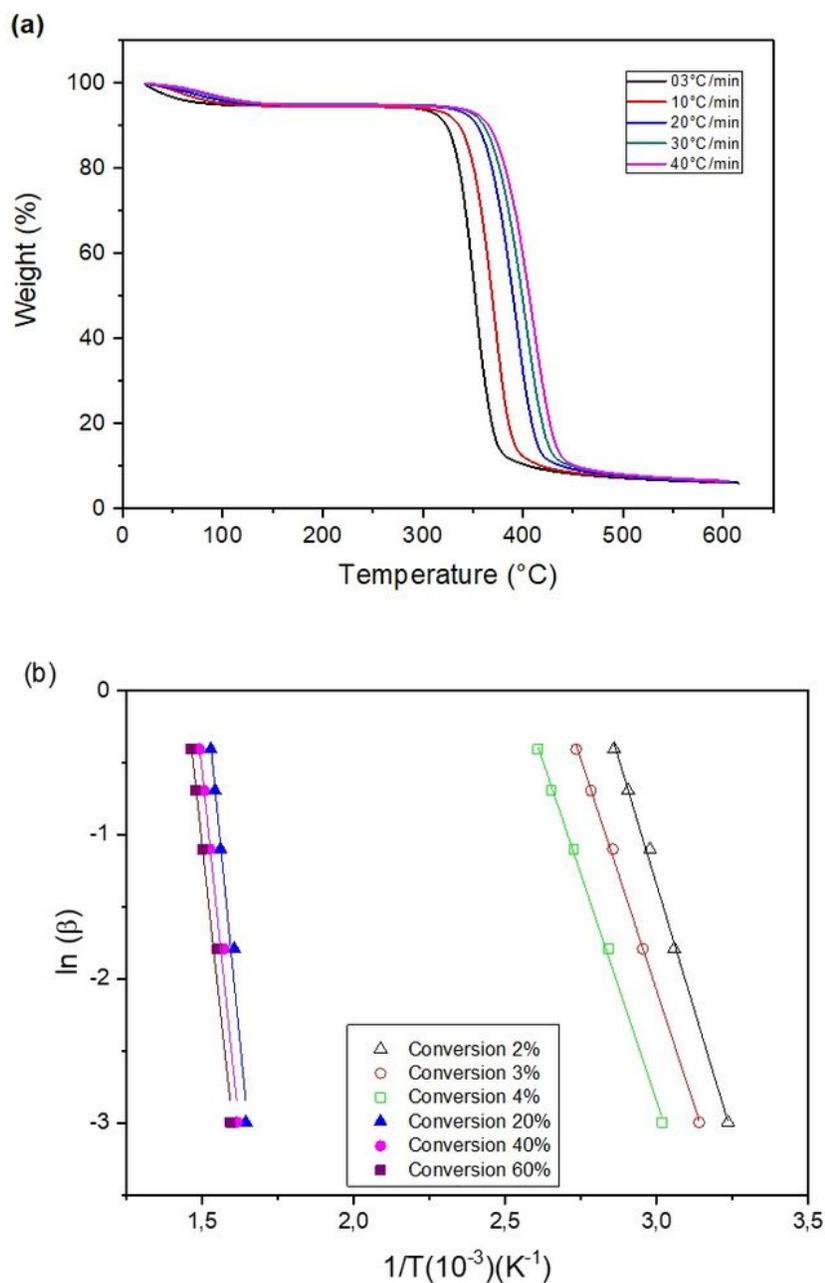


Figure 4

Scheme of different water absorbed on cellulose surface.



**Figure 5**

(a) TG curves at different heating rates of cellulose and (b) Kinetic curves for Ozawa-Flynn-Wall method for water desorption with conversion of 2, 3 and 4% (right curves) and cellulose degradation with conversions of 20, 40 and 60%(left curves).

## Supplementary Files

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