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Wheat gluten, a bio-polymer layer to monitor relative humidity in food packaging: electric and dielectric characterization

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Abstract: Thin wheat gluten protein film, largely investigated as eco-friendly material for food packaging, is investigated as a relative humidity monitoring polymer deposited on designed and manufactured interdigital capacitor (IDC) systems, on the frequency range from 30 MHz to 1000 MHz. The ability of wheat gluten to interact with water molecules was characterized and assessed in terms of electrical and dielectric properties with the IDC technique. When relative humidity increases from 20% to 95% RH at 25°C, the dielectric permittivity and loss change from 5.01 ± 0.04 to 9.79 ± 0.06 and from 0.39 ± 0.01 to 1.48 ± 0.02 respectively. The dielectric permittivity and loss are very sensitive to relative humidity and increase exponentially due to the comparable exponential increase of wheat gluten water content versus relative humidity. The accessibility of water molecules and the plasticization of

wheat gluten results in an increase in the water absorbed by the protein from 3.6% (at 20% relative humidity) reaching up to 33.6% (at 95% relative humidity) of the dry weight. The dependence of both dielectric permittivity and dielectric loss of wheat gluten on relative humidity offered the possibility to use the protein for monitoring relative humidity in packed food products. For this purpose, wheat gluten is foreseen to be coupled with Ultra High Frequency (UHF) Radio Frequency Identification (RFID) systems, giving a cost-effective, low-energy consuming and reliable solution for traceability and monitoring of food packed products.

Highlights

- Novel study based on wheat gluten development as relative humidity sensor.
- High coupling potential of wheat gluten with Ultra High Frequency Radio Frequency Identification systems.
- Retro-simulation for the determination of dielectric permittivity and loss.
- Exponential increase in dielectric permittivity and dielectric loss in controlled relative humidity conditions.
- Interaction of water molecules with wheat gluten network.
- Determination of the sensitivity of wheat gluten as a function of relative humidity.

Keywords: Dielectric properties, wheat gluten proteins, relative humidity monitoring, RFID.

1 Introduction

Modification of relative humidity in food products is highly impacting food quality and safety by inducing for example irreversible alteration of their texture, spoilage and/or pathogens microbial growth during storage. Due to the consumer's demand for high quality food products, many efforts are devoted to monitor and control the variation of relative humidity in food packages and in packed food products, giving precious information about the evolution of food quality in packages.

To reach this objective, a protein has been chosen as part of this work to mimic the behavior of food products and the evolution of relative humidity in packages. Wheat gluten being itself a wheat protein, usually found in dry food products such as cereals, bread or biscuits, has a hydrophilic behavior and is very sensitive to relative humidity. It has been broadly studied at high relative humidity for its gas properties [1] and increasingly investigated for its unique mass transfer properties [2–5]. The high permeability of wheat gluten to carbon dioxide and (to a lower extent) oxygen resulted in a high permselectivity (ratio of carbon dioxide permeability to oxygen permeability) of the material [1], making them interesting for packaging applications, such as fresh fruit and vegetable packages [5–7].

The complex combination of bonds (electrostatic interactions, van der Waals forces, salt bonding, hydrogen bonding and disulfide bonding) [8–11] in the wheat gluten network contribute to the stabilization of the protein structure and provide strong dipole-dipole interactions, sharing of electron pairs between atoms (stable electronic configuration) and electrical interaction of low intensity between atoms and molecules [12–15]. Wheat gluten is thus considered as a polarizable material, having dielectric properties (permittivity and dielectric loss). Most of the work carried on wheat gluten was performed on its gas transfer properties as aforementioned and on the electrical behavior of wheat gluten dough or powder

65 at 200 MHz, 915 MHz, 2000 MHz, 10000 MHz, 16000 MHz and at 20000 MHz [8,16–18], but
66 has never been studied as a potential film-based material for relative humidity monitoring,
67 relied on its dielectric property variations at 868 MHz.

68 The originality of the present study resides in the study of wheat gluten proteins for relative
69 humidity monitoring, at 868 MHz, in the perspective to be used with UHF RFID tags having
70 the aforementioned working frequency. Furthermore, wheat gluten (being a wheat protein)
71 mimics mechanisms induced in food products when exposed to relative humidity giving
72 therefore a close measurement of the state of food. Wheat gluten is probably one of the best
73 candidates for the monitoring of relative humidity in packed food products. Interdigital
74 capacitors (IDC), being widely used in chemical, humidity and biological sensing, as well as
75 for electrical and dielectric characterization of materials [19], have been used for electrically
76 characterizing wheat gluten, coated on the comb-like electrodes. The dielectric permittivity and
77 dielectric loss of wheat gluten have been determined by retro-simulation at the working
78 frequency of UHF passive RFID tags (868 MHz), for a foreseen coupling of both in an optimal
79 way. The impact of relative humidity on the dielectric properties of wheat gluten, as well as on
80 its sensitivity and hysteresis have been analyzed and discussed.

81 2 Materials and Methods

82 2.1 Interdigital capacitor (IDC) sample

83 The design of the IDC system was performed using ANSOFT® software, which is a high
84 performance electromagnetic simulation software. The IDC system design technique was
85 already developed in a previous study [20]. In order to have an IDC system (figure 1 (a)) having
86 the desired frequency range (up to 1000 MHz), the following geometrical dimensions were
87 used: $W_2=0.4$ mm, $E_2=0.4$ mm, $L_2=10$ mm, $C_2=2$ mm, $I_2=1$ mm, $J_2=7.4$ mm, $G_2=12.4$ mm,
88 number of fingers (N)=8 and with a substrate (FR4) dielectric permittivity of 4.8.

The designed IDC systems were manufactured by CIRLY, France (figure 1 (b)), in order to have homogeneity on all samples. The IDC system electrodes are made of copper metal deposited on a prefabricated circuit board made of a composite of glass fiber reinforced epoxy resin (thickness 1.6 mm). The thickness of the electrode fingers (17 μm) being fixed by the manufacturer, were also kept fixed in the design process.

Figure 1: Designed interdigital capacitor (a), manufactured interdigital capacitor system casted with wheat gluten having a capacitive behavior up to 1000 MHz (b).

2.2 Wheat gluten sample

2.2.1 Solution preparation

Wheat gluten (amygluten 110) powder (7.2 wt % of moisture and 76.5 wt % of protein, 14.2%, 8.1% and 1.2% dry weight of carbohydrates, lipids and ashes respectively) was provided by Amylum (Mesnil St Nicaise, France). Sodium sulfite and acetic acid were obtained from Sigma-Aldrich (St Quentin, France). The wheat gluten solution was prepared at room temperature (25°C) and humidity (50% RH). 30 g of wheat gluten powder was dispersed under shaking in 50 ml of a sodium sulphite solution (0.06 g sodium sulphite for 50 ml of distilled water) to reduce disulfide bonds in the wheat gluten protein. The mixture was left to settle for 30 minutes. The pH of the solution was adjusted to 4 by adding 3.4 ml of 50/50 v/v solution of acetic acid. The mixture was stirred. The solution was finally adjusted to 130 ml by adding deionised water and mixed. The prepared wheat gluten solution was left degassing under vacuum for one night [21,22] and used within one week.

2.2.2 Sample preparation – Solvent Casting method

Sample preparation: 1 ml of wheat gluten solution was cast onto IDC systems using an E409 blade coater from Erichsen (France), in order to cover the whole comb-like structure. The coater was equipped with the **number 4** blade having spires of 0.51 mm, in order to create a humid film deposit having a thickness of 40 μm . The speed was set to **1 mm/s**. The sample was left to dry for 24 hours at room temperature and at 50% of relative humidity.

Self supported wheat gluten: The wheat gluten solution was cast onto glass panes and left to dry under a constant flow of air, at room temperature and 50% of relative humidity. After drying, circular samples were cut from the wheat gluten layer.

Thickness measurement of wheat gluten layer: The average thickness of the layer deposited onto IDC systems and glass panes was measured at room temperature and humidity with a profilometer. 5 measurements were performed at 10 random positions. The thickness of the wheat gluten layer is equal to $9.37 \pm 1.10 \mu\text{m}$.

2.2.3 Structural characterization

Dynamic Vapor Sorption (DVS): Water vapor sorption measurements were carried out at 25°C over a wide range of relative humidity from 0% to 95%, making use of a microbalance apparatus (Surface Measurement System Ltd, London, UK). **The relative humidity range on which the experiment was conducted was made possible due to the precision of the apparatus (microbalance) used. Relative humidity was controlled in a hermetically closed chamber.** The process is described in another publication [23]. The self supported wheat gluten layers were used and left for equilibrium at 0% RH in a dessicator for 72 hours. They were then inserted into the microbalance and left for equilibrium at 0% RH for 12 hours to establish a dry mass. The layers were then exposed to different relative humidity values by a continuous air flow having a specific relative humidity value. The different relative humidity values were

135 programmed in the software controlling the microbalance. Mass equilibrium was reached at
 136 each relative humidity level by measuring the mass change over time, $dm/dt < 0.002\text{ mg/min}$,
 137 of wheat gluten or by imposing a time frame for each relative humidity step. Once equilibrium
 138 was achieved, the apparatus shifted to the next programmed RH stage, and so forth. Sorption
 139 and desorption cycles were performed to determine the reversibility of the wheat gluten
 140 material. The sorption and desorption isotherms were built, as well as the sorption and
 141 desorption kinetic curve. The experiment was performed as triplicates.

142 2.3 Electrical measurements

143 2.3.1 Measurement of the impedance (real and imaginary parts) with interdigital 144 capacitor systems

145 Impedance measurements were performed using a vector network analyzer (VNA) (Hewlett-
 146 Packard 8753D) with an open-ended coaxial cable fitted with a coaxial connector (SMA
 147 connector), calibrated prior to connection with IDC systems, using three different types of
 148 loads: open circuit, short circuit and a $50\ \Omega$ load, over a frequency range up to 1000 MHz.

149 The coaxial cable was fixed to the extent possible in order to avoid stray capacitors due to cable
 150 movements after calibration and connected to IDC system located in a chamber where relative
 151 humidity and gases were controlled. Relative humidity was increased from 20% to 95% ($\pm 1\%$)
 152 using a two-pressure process. The equipment consists of two chambers maintained at the same
 153 temperature. In the saturator chamber, air is saturated with water vapor at high pressure. The
 154 air then passes through to the test chamber (containing the IDC system), which is at a lower
 155 pressure, thus reducing the air pressure, and consequently its relative humidity with a precision
 156 of ± 1 at 95% RH. Relative humidity value extremities such as 0% RH and 100% RH being non-
 157 stable were avoided due to experimental and material limitations.

The impedance real and imaginary component, as well as frequency were acquired at fixed time intervals and saved by a program developed on Labview software using a host computer. The IDC system is represented by an equivalent resistance-capacitance (RC) circuit used in other studies [24,25]. The associated real and imaginary parts are represented by equation 1 and equation 2 respectively, where both are frequency dependent.

$$Z_r = \frac{R}{1 + (RC\omega)^2} \quad \text{Equation 1}$$

$$Z_{img} = -\frac{R^2 C \omega}{1 + (RC\omega)^2} \quad \text{Equation 2}$$

where R represents the resistance, C the capacitance and ω the angular frequency.

Electrical measurements were performed in triplicate using the IDC systems in air, coated with wheat gluten, at 433 MHz, 868 MHz and 960 MHz after stabilization was reached.

2.3.2 Identification of dielectric permittivity and loss of wheat gluten by retro-simulation of IDC systems

The identification of the dielectric properties of wheat gluten was performed by simulation with ANSOFT® software using geometrical and substrate (FR4) parameters of the designed IDC system. The identification procedure was developed in a previous study [20] where the permittivity and dielectric loss were obtained by comparing the simulated impedance values to the measured values at the specified frequency. The only modification performed to the IDC system was the addition of the wheat gluten layer on top. This layer represented the dielectric whose permittivity and loss were varied and re-injected in the simulation procedure. By comparing the simulated impedance values to the measured ones at the specified frequency and upon matching, the dielectric permittivity and loss of the wheat gluten layer were obtained.

3 Results and discussion

3.1 Dynamic Vapor Sorption measurements

3.1.1 Moisture sorption kinetics

As wheat gluten is known to be very sensitive to humidity, dynamic vapor sorption measurements were performed, at 25°C, on a wide range of humidity values (from 0% to 95% of relative humidity). The necessary time for wheat gluten to be in equilibrium with the surrounding atmosphere was determined using water vapor sorption isotherms plots of the self-supported wheat gluten layers. The water content on a dry basis (d.b) was calculated using equation 3.

$$\text{Water content (\%)} = \left(\frac{M_w - M_d}{M_d} \right) \times 100\% \quad \text{Equation 3}$$

where M_w is the mass of the wet wheat gluten sample at equilibrium and M_d the dry mass of the wheat gluten sample.

The results are presented in figure 2, giving the stabilization time for the capacitance value and the mass intake for each humidity step when a sorption and desorption process was performed. For each humidity value, when a change in mass with respect to time (dm/dt) was recorded and remained constant, the experiment proceeded to the next programmed humidity stage. In the present study, this information is important to know the necessary conditioning time of wheat gluten at each humidity level and the stabilized electrical measurement (capacitance). Fundamentally speaking, at low relative humidity (0% to 50% RH), the net change in mass was up to 8.03% d.b and the capacitance value increased from 6.46 pF to 6.53 pF. In this state, few bind water molecules are present in the wheat gluten network, where a short delay is necessary for equilibrium (~1 hour). At medium relative humidity (50%-70% RH), the net mass increased

from 8.03% to 10.2% d.b and the capacitance from 6.53 pF to 6.72 pF. In that phase, the water content of the wheat gluten layer is still low but present under the form of a monolayer (at 25°C). Within this monolayer, water molecules present are directly linked with hydrophilic groups. A delay of approximately 4h30 is necessary for the monolayer formation and equilibrium. With increase in relative humidity, the amount of water content increases, forming clusters with the present monolayer. This linking takes place around 70%-90% of relative humidity increasing consequently the net mass from 10.2% to 23.09% d.b, the capacitance from 6.72 pF to 7.66 pF and the necessary time for equilibrium is approximately 5 hours. Another phenomenon occurs at even higher relative humidity (90%-95% RH), with the settling of free water in the wheat gluten network with an increase in the net mass from 23.09% to 33.6% and the capacitance from 7.66 pF to 8.47 pF, but a longer delay is required for equilibrium (~8h30). In spite of this, the protein is one of the best candidates for monitoring food quality change within packages because:

- i) As it was specified, wheat gluten mimics the behavior of food products and would give a close measure of what is actually taking place within the food material. Moreover, the stabilization of the capacitance value at each relative humidity level is promising to electrically monitor the packed food products.
- ii) Foreseen food packages containing fresh food (~95% RH) have a shelf life of approximately 1 week, which is much more than the required equilibrium time. It can thus be concluded that wheat gluten would give an accurate measurement of relative humidity within the packed food product.

Figure 2 : Net change in mass (+) and capacitance (▲) of wheat gluten layer as a function of relative humidity (—) and time.

3.1.2 Sorption and desorption isotherms

The sorption and desorption isotherms of wheat gluten are represented in figure 3 which clearly highlights the hydrophilicity of wheat gluten. The results are in the range of those reported by several authors for wheat gluten and zein films [18,26]. The water sorption and desorption isotherms displayed a sigmoid evolution on the complete studied relative humidity range, which is specific to hydrophilic materials, and is also reported by both authors. In addition, sorption isotherms of food materials generally have a sigmoid shape and are useful for the determination of the shelf life and to access background operation such as drying, conditioning, mixing, packaging and storage [27]. Wheat gluten isotherm curve, having precisely the same shape, indicates its close behavior to food materials. The sorption isotherm curve also gives information about the specific interaction between water molecules and the products since it directly relates the thermodynamic potential of water on the system to its mass fraction. If it is considered that hydration of wheat gluten occurs by successive layers, the isotherm curve in figure 3 can be divided into several regions related to a decrease in the intensity of interactions among proteins in the wheat gluten matrix:

- i) RH 0% - 50% corresponds to few bind water molecules with strong hydrogen and hydrophobic bonds among wheat gluten proteins (strong protein-protein interactions).
- ii) RH 50% - 70% coincides with increasingly bind water molecules with the wheat gluten network to high energy sorption sites (monolayer formation).

iii) RH 70% - 90% corresponds to successive adsorption of monolayers (water molecule monolayers) interacting mainly by hydrogen bonds. It can also be seen at this stage as cluster formation with increasing movement of the molecular chain.

iv) RH 90% - 95% is related to the presence of free water within the wheat gluten network due to their accumulation by capillary. In this region, interactions among proteins of the wheat gluten network are very weak at the expense of interactions with and between water molecules themselves.

Figure 3: Absorption and desorption isotherms of wheat gluten conditioned at different relative humidity values.

3.2 Swelling of wheat gluten layer

The ability of a material to swell is a property of polymers induced by their macromolecular structure, caused by the sorption of liquids or vapors from the surrounding environment. Fruits and vegetables are known to swell or lose water the same way as wheat gluten. A 90% to 95% relative humidity atmosphere is needed for the proper conservation of fruits and vegetables and to prevent shrinking of the materials. On the other hand, a low relative humidity environment around food produce causes their shriveling and causes crack formation resulting in aesthetically displeasing products. According to authors who worked on wheat gluten coated on paper substrate, micro-fractures on the material surface were revealed at low relative humidity and were reduced as relative humidity increased [28]. At 60% RH some of the cracks disappeared completely. It can be assumed that at 95% RH, a defect-free surface was obtained. The disappearance of the fractures is due to the swelling of the wheat gluten layer. It should be made clear that the fractures do not completely penetrate the layer down to the electrodes or the substrate. At high relative humidity, the swelling of the layer increases its integrity (continuous

layer at the surface). It can also be considered that at high humidity, bigger cracks are filled with water (free water) due to capillarity.

3.3 Wheat gluten electrical performances

3.3.1 Physical characterization

Prior to coating of wheat gluten on IDC systems, the verification of the physical parameters of the manufactured IDC systems was performed using a profilometer. There was a good agreement between the measured physical parameters and the design parameters. Furthermore, the measured electrical properties of the uncoated IDC systems were close to the simulated electrical properties (table 1) indicating their correct manufacture. These measurements were performed at 25°C and at 20% of relative humidity.

Table 1: Comparison of experimental and simulated electrical properties of uncoated IDC systems.

3.3.2 Impedance measurements

Impedance measurements were performed between 20% and 95% of relative humidity, where each humidity step was maintained constant until the impedance reached a steady state value. The impedance real component is represented in figure 4 (a) and the impedance imaginary part in figure 4 (b). As illustrated in figure 4 (a), the real part increases from $0.15 \pm 0.05 \, \Omega$ to $2.06 \pm 0.21 \, \Omega$ when relative humidity increases from 20% to 95% at 868 MHz, with a sharp rise noted as from 70% of relative humidity. The impedance imaginary component (figure 4 (b)) has negative values, confirming the capacitive behavior of the IDC system. The imaginary component increases from $-29.12 \pm 0.36 \, \Omega$ to $-21.28 \pm 0.61 \, \Omega$ for the same conditions as for the real component that is, 20% to 95% of relative humidity at 868 MHz. Similarly, the rise becomes significant as from 70% of relative humidity, due to the increasing water content in

the wheat gluten film. It is also clear that the sensitivity of wheat gluten is very low at low relative humidity values and that the sensitivity becomes significant as from 70% RH. This is convenient for the foreseen applications with fresh food products where relative humidity within the packaging is estimated to be at approximately 95% RH. Moreover, if dry foods such as cereals are monitored, an alarm for threshold relative humidity value overrun can be programmed. In that case, if the package is accidentally opened, integrity is lost resulting in an increase in the headspace relative humidity, activating the alarm. Wheat gluten is therefore a good candidate for these types of applications.

In order to have a better illustration of the increase in electrical properties, the relative variation of the impedance imaginary part is shown on figure 5 at different frequencies (433 MHz, 868 MHz and 960 MHz) and as a function of relative humidity. **It has to be specified that 433 MHz, 868 MHz and 960 MHz are frequency values corresponding to RFID systems working at these different frequency values.** As it can be observed, the impedance increases drastically with relative humidity. Comparing the impedance values at each humidity step, one can observe the small change in the impedance value from 20% to 50% of relative humidity for 960 MHz and 868 MHz. A slightly greater change is recorded for 433 MHz. But for higher relative humidity values, the change in impedance is different for 433 MHz than the other two frequencies (868 MHz and 960 MHz), particularly at 95% of relative humidity where the delta change is twice for 433 MHz than at 868/960 MHz. This is because more elements (interface, dipoles and charges) are under the influence of the electromagnetic field at low frequency. As such, at high relative humidity, the effect of water on those elements is more pronounced, increasing the significance of the change in the electrical properties due to water molecules. One can thus find the lower frequency range very attractive for developing the material.

However, in the present study, the target RFID system is 868 MHz based justifying the pursuit of this study at 868 MHz.

Figure 4: Impedance real (a) and imaginary (b) component as a function of frequency from 20% to 95% of relative humidity (RH), at 25°C.

Figure 5: Relative variation of the impedance imaginary component with increase in relative humidity, at 433 MHz, 868 MHz and 960 MHz.

3.3.3 Identification of dielectric parameters

The identification of the dielectric loss at a frequency of 868 MHz (figure 6 (a)) was performed by FEM (finite element method) simulation, using the impedance real component, which represents the energy loss in the wheat gluten layer. The dielectric permittivity was also simulated at 868 MHz (figure 6 (b)) using the impedance imaginary component. Both simulations were performed for increasing and decreasing relative humidity values at 25°C to further evaluate the hysteresis. The dielectric loss increases exponentially from 0.39 ± 0.01 to 1.48 ± 0.02 and back to 0.401 ± 0.006 . As it can also be noticed, the increase in dielectric loss becomes more significant starting from 70% of relative humidity in the same way as the impedance real part. Regarding the dielectric permittivity, an exponential increase is illustrated from 5.01 ± 0.04 to 9.79 ± 0.06 and back to 5.02 ± 0.01 , being more significant as from 70% of relative humidity. For relative humidity values less than 70%, the rise is weak, from 5.01 ± 0.04 to 5.76 ± 0.03 , indicating that the dielectric permittivity is not impacted by the amount of water sorbed within the wheat gluten layer. As from 70% of relative humidity, the permittivity increases significantly to higher values, illustrating that an increasing amount of water is sorbed and participate in the dielectric behavior of the polymer. If figure 7 is considered, it can be

observed that the dielectric permittivity increases linearly as from 8% of water content (~50% relative humidity). Under these 8%, all few water molecules present are directly linked to the hydrophilic groups of the wheat gluten network. These water molecules are not mobile and are not available for any kind of chemical reaction. Consequently, they can neither participate to degradation reactions within food materials, nor to the dielectric permittivity of wheat gluten. With increase in water content, water accumulates in successive layers which are more and more mobile and thus available for a participation in degradation reaction in food products and in the measurement of the dielectric properties. Therefore, dielectric property measurement also gives a measure of the availability of water molecules in the protein network.

Figure 6: **Simulated** dielectric loss (a) and **simulated** dielectric permittivity (b) of wheat gluten as a function of relative humidity (RH) at 868 MHz, at 25°C.

Figure 7: **Simulated** dielectric permittivity of wheat gluten layer as a function of water content at 868 MHz, at 25°C.

Effects of relative humidity: Wheat gluten, in the present case, is in contact with surrounding relative humidity, which increases from 20% to 95%. Phenomena taking place at these relative humidity values are diverse. At low relative humidity (20%), the water content in the film is 3.6% dry basis (figure 3), indicating that wheat gluten is in its dry state. The small percentage of water is considered to be bound water to the highest energy sorption sites, and has little contribution to the dielectric properties of wheat gluten. In addition, the high cross-linking of glutamine (content: 45%) is probably responsible for protein-protein interactions, not favoring protein-water interactions, forming a dense network and a cohesive, unplasticized gluten film. The same phenomenon on the flexibility of native wheat gluten at low relative humidity was

also observed [29]. When the latter increased, more water molecules are adsorbed on the surface of wheat gluten and absorb through the protein layer. The sorption process increases the water content in the wheat gluten layer, where 8.03% of water content on a dry basis is obtained for 50% and 10.2% d.b at 70% of relative humidity. At this stage, it can be stated that all the polar sites are occupied by water molecules with the formation of the monolayer. When relative humidity is more than 70%, additional water concentrates within the layer forming clusters (accumulation of layers) which continuously increase in size with water addition. Once clusters are increasing, changes such as protein conformation, internal protein mobility and mobility of water molecules take place. These water molecules are then considered as free water at more than 90% RH, able to move within the network, and even more under the influence of an electric field, due to their polarity. As it was specified in section 3.1.2 and figure 3, different types of binding between water molecules and wheat gluten are formed:

- i) 20%-50%: Few bind water molecules.
- ii) 50%-70%: Bind water molecules to high energy sorption sites (monolayer formation).
- iii) 70%-90%: Cluster formation with formation of hydrogen bonds to water molecules, with increasing movement of the molecular chain.
- iv) >90%: Presence of free water.

According to the water sorption measurements, the water content in the film at 95% of relative humidity is equal to 33.6%. It was demonstrated that the glass transition temperature (T_g) was related to relative humidity and temperature. Other authors state that below 22% of water content, wheat gluten is considered dry in a glassy state and that the T_g is up to 110°C at 25°C [17,30–32]. Increasing relative humidity up to 82.5% (water content: 20% dry basis) results in

a T_g around 25°C (current experiment temperature). Therefore, increasing water molecules plasticizing the polymer matrix lowers T_g of the polymer, so that the transition from glassy to rubbery state takes place at a lower temperature value. This change in the protein conformation gives freedom to mobility of macromolecular chain and to a further extent, smaller elements such as amino acids and water molecules.

Effects of relative humidity on dielectric loss: The dielectric loss is characterized by energy dispersion of the relaxation phenomena of dipoles taking place in the network, produced at microwave and radio frequencies. The dielectric loss can be modeled by equation 4, representing the different contribution phenomena. Conduction in the network is ionic based, obtained from residual free charges found in the network, such as residual salts in the present case [33].

$$\varepsilon'' = \varepsilon''_d + \frac{\sigma}{\varepsilon_0 \omega} \quad \text{Equation 4}$$

where ε''_d represents the loss factor due to dipolar orientation and relaxation, and $\sigma/\varepsilon_0 \omega$ represents the loss factor caused by ionic conductivity with σ , ε_0 and ω representing the conductivity of the material, the dielectric constant of vacuum and the angular frequency respectively.

It is important to specify that the relaxation phenomena are slow processes and are not produced instantaneously, and that ionic conductivity only introduces losses into the polymer when exposed to electromagnetic energy. Loss due to dipolar relaxation results from the movement and frictional motion of the constituent dipoles (dipole-dipole interactions) which is transformed into heat energy [34,35]. At low water content, mainly relaxation phenomena contribute to dielectric loss instead of ionic conduction in dry wheat gluten under the influence of the electromagnetic field. As the level of hydration increases, wheat gluten becomes

413 plasticized with more freedom for the motion of its different constituents, resulting in a rise in
414 the extent of charge movement, bringing electrical conduction within the layer [16,27]. At this
415 high hydration level, dielectric loss is mainly due to ionic conduction [36] and are facilitated
416 by free water retained by capillarity within the wheat gluten layer. Ionic conduction could hide
417 the dipolar losses effect [33]. The overall result remains that the effective dielectric loss ε''
418 increases with relative humidity.

419 **Effects of relative humidity on dielectric permittivity:** The charged network of wheat gluten,
420 the hydrogen bonds linking the protein chains, the dipolar interactions of amino acids confer
421 wheat gluten its dielectric permittivity under the influence of an electromagnetic field. At low
422 hydration level (20% of relative humidity), few water molecules bind to the wheat gluten
423 network. This binding is progressive up to 70% of relative humidity. At this point, the maximum
424 water content in the wheat gluten layer is 10.2% on a dry basis. The charged network and
425 hydrogen bonds of water molecules with the side chains of amino acids participate in the
426 dielectric permittivity. Increasing relative humidity (to more than 70% RH) results in a
427 considerable increase in water content within the wheat gluten layer. Between 70% and 90%
428 of relative humidity, the water content increases from 10.2% to 23.09% on a dry basis, and an
429 increase of 23.09% to 33.6% of water content for a rise in relative humidity of 90% to 95% is
430 recorded. When plasticizers such as water molecules bind to the wheat gluten, under an
431 isothermal process, the effect is the same as an increase in temperature on the molecular
432 mobility. Water, being a low molecular weight component, increases free volume and hence
433 increases backbone chain segmental mobility [30], as well as elements such as dipoles and
434 amino acids under the influence of an electromagnetic field.

435 The rise in water content has a significant impact on the permittivity of the wheat gluten layer,
436 as free water, being a dipole with a strong dipolar moment [27,37,38], having a high permittivity

of approximately 80 [39–42] drastically increases the effective dielectric permittivity of the wheat gluten layer.

3.4 Sensitivity

A better insight of the wheat gluten response can be obtained using partial sensitivities. The capacitance sensitivity has been calculated in order to be compared in an easier manner to the literature. The capacitance was calculated using a resistance capacitance model and the sensitivity was calculated using equation 5.

$$S = \left(\frac{C^u - C^i}{X^u - X^i} \right) \quad \text{Equation 5}$$

where S represents the sensitivity of wheat gluten coated IDC. C represents the capacitance value. X represents the concentration of relative humidity. u represents the final values and i the initial values.

The change in the capacitance values occurs between 20% and 95% of relative humidity. Figure 8 reveals four distinct regions: one between 20% and 50% of relative humidity where the sensitivity is low equal to 2.14 ± 0.03 fF/%RH, the second between 50% and 70% relative humidity where the sensitivity is equal to 9.65 ± 0.23 fF/%RH, the third region between 70% and 90% of relative humidity with a sensitivity value of 46.84 ± 0.05 fF/%RH and finally the fourth region between 90% and 95% with a much higher sensitivity value of 162.0 ± 0.6 fF/%RH. The graph pattern (exponential behavior) is not common to synthetic relative humidity sensors (usually having a linear behavior) found in literature [43,44]. The pattern intrinsic to wheat gluten is closer to food material behavior and is in a better way adapted for the monitoring of packed food products, which is advantageous over synthetic humidity sensors. For example, the region above 90% RH gives a particularly high sensitivity indicating that wheat gluten can

458 be ideally used for monitoring food packages with high relative humidity products (fruits and
 459 vegetables). The sensitivity can be intelligently optimized in order to adapt wheat gluten to the
 460 focused application.

461 Table 2 summarizes results of sensitivity and hysteresis of a natural polymer, synthetic
 462 polymers and oxide based sensors. Most of the presented materials are meant for RFID
 463 applications and for humidity sensors in general, foreseen to be applied in RFID technology.
 464 The results obtained in the present study are in the range of those presented in the table. The
 465 sensing material of high performance giving the best sensitivity (111 pF/%RH) is Cerium (IV)
 466 oxide [44], which is 10000 folds higher than the present study. The study, performed at low
 467 frequency (10 kHz), may explain this high sensitivity. The other types of sensor developed are
 468 porous aluminum oxide based, having sensitivities of 483 fF/%RH and 4200 fF/%RH [45,46].
 469 The porous aluminum oxide layer contain nano-pores on the sensitive layer, able to absorb large
 470 amounts of water, increasing considerably the permittivity, and thus the sensitivity [24].
 471 Moreover, this effect is optimized with an increase in the thickness of the film, as the volume
 472 of the nano-pores increased as well [45]. Materials with a lower but honorable sensitivity are
 473 wheat gluten (162.0±0.6 fF/%RH) (present study), polyethylene-naphthalate and polyimide
 474 foils (21 fF/%RH) [47] and polyphenylacetylene (PPA) (10 fF/%RH) [48]. With the exception
 475 of wheat gluten developed in the present work which is a natural polymer, the other two are
 476 synthetic polymers. The sensors with the lowest sensitivity values are polyimide [43] and
 477 cellulose acetate butyrate [49], which are synthetic polymers and thermoplastic based on
 478 cellulose acetate. Their sensitivity values are 4.5 fF/%RH and 1.5 fF/%RH respectively.

479
 480 Figure 8: Sensitivity of wheat gluten coated IDC system as a function of relative humidity.

3.5 Hysteresis

Hysteresis is an important design parameter. It can be defined as the difference in the output signals when measured for the up-trace and down-trace of the input signal. Comparing between the increasing and decreasing permittivity values, a weak hysteresis can be noticed between the up-trace and down-trace. The maximum hysteresis equal to 7% at 90% of relative humidity was calculated using equation 6.

$$Max\ Hysteresis = \frac{\max |C_{dec} - C_{inc}|}{C_{max} - C_{min}} \times 100\% \quad \text{Equation 6}$$

where C_{dec} represents the decreasing capacitance value, C_{inc} the increasing capacitance value, C_{max} and C_{min} the maximum and minimum capacitance values.

With increasing water content, modification in the protein film conformation occurs, particularly unfolding and exposure of polar residues, favoring water uptake within the layer, and resulting in the swelling of the layer. Upon desorption (decrease in water content), the slow shrinkage of the wheat gluten layer resulted in a hysteresis due to conformational changes involving structural relaxation (coming from clusters of absorbed water), noticeable on the dielectric permittivity and loss of wheat gluten (figure 6). This phenomenon is also observed on various polymers [49,50] and humidity sensors [36,45]. The swelling/shrinkage process of the wheat gluten matrix is often time dependant. At the end of the desorption process, the layer is brought back to its original state, where it is considered that no free water is present within the layer, but only bound water, with the same structure as at 20% RH, indicating its reversibility. Table 2 gives an overview of the hysteresis for the different materials, where only 1% of maximum hysteresis is obtained for cerium(IV) oxide at 45% of relative humidity. The hysteresis obtained in the present study is in the range of the other materials, being equal to 7%

for wheat gluten and 16% for anodic aluminum oxide [46], 20% for cellulose acetate butyrate [49], 10% for polyimide films [43] and a maximum of 30% for anodic aluminium oxide [45].

Table 2: Humidity sensors characteristics found in literature and in this study.

4 Conclusion

Wheat gluten protein has been investigated for relative humidity monitoring. Interdigital capacitors have been used for performing electrical measurements, and the dielectric loss and permittivity of wheat gluten were determined by retro-simulation at 868 MHz. The electrical and dielectric characterization of the wheat gluten layer showed that the natural polymer is hydrophilic with significant changes at high relative humidity values ($>70\%$), rather than at lower relative humidity values. The permittivity increased from 5.01 ± 0.04 to 9.79 ± 0.06 and the dielectric loss from 0.39 ± 0.01 to 1.48 ± 0.02 when relative humidity increased from 20% to 95%. This rise, mainly due to water molecules, was confirmed by the net mass intake of water reaching up to 33.6% d.b in the wheat gluten film. The results indicated a good sensitivity of wheat gluten at high relative humidity values, ideal for foreseen applications related to the monitoring of packed food products. The different phases of water interaction between water dipoles and the wheat gluten molecular structure have been presented, at low, medium and high hydration level, with the material response depending mainly on the percentage of linked and free water present.

To a further extent, optimization of the sensor could be performed in order to adapt its sensitivity to targeted applications. Plasticizers, such as glycerol, may be used as additives to increase the mobility of the elements in the network and be used for food products having a lower water activity. Another modification that can be considered is the manufacture of a

526 porous wheat gluten layer, able to absorb water molecules through its nano-pores, increasing
527 even more the sensitivity of the layer. According to the generally high accuracy of results
528 obtained, wheat gluten sensors could be used in cost-effective passive UHF RFID tags, with
529 humidity monitoring capabilities.

530

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537 smooth progress of the study.

538 7 Abbreviations

539 FEM, finite element method; IDC, interdigital capacitor; RC, resistance capacitance; RH,
540 relative humidity; RFID, radio frequency identification; WG, wheat gluten; d.b, dry basis; UHF,
541 ultra high frequency; DVS, dynamic vapor sorption; **VNA, vector network analyzer.**

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Captions for figures

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Figure 1: Designed interdigital capacitor (a), manufactured interdigital capacitor system casted with wheat gluten having a capacitive behavior up to 1000 MHz (b).

Figure 2 : Net change in mass (+) and capacitance (▲) of wheat gluten layer as a function of relative humidity (—) and time.

Figure 3: Absorption and desorption isotherms of wheat gluten conditioned at different relative humidity values.

Figure 4: Impedance real (a) and imaginary (b) component as a function of frequency from 20% to 95% of relative humidity (RH), at 25°C.

Figure 5: Relative variation of the impedance imaginary component with increase in relative humidity, at 433 MHz, 868 MHz and 960 MHz.

Figure 6: **Simulated** dielectric loss (a) and **simulated** dielectric permittivity (b) of wheat gluten as a function of relative humidity (RH) at 868 MHz, at 25°C.

Figure 7: **Simulated** dielectric permittivity of wheat gluten layer as a function of water content at 868 MHz, at 25°C.

Figure 8: Sensitivity of wheat gluten coated IDC system as a function of relative humidity.

Table 3: Comparison of experimental and simulated electrical properties of uncoated IDC systems.

	Impedance real component (Ω)	Impedance imaginary component (Ω)	Capacitance (pF)
Measured values	1.54 $\pm$ 0.05	-28.29 $\pm$ 0.93	6.41 $\pm$ 0.04
Simulated values	1.46 $\pm$ 0.12	-28.20 $\pm$ 0.22	6.45 $\pm$ 0.02

Table 2: Humidity sensors characteristics found in literature and in this study.

Material	Type	Max. Sensitivity	Max. Hysteresis	Application	References
Wheat gluten (film)	Natural polymer	162.0 $\pm$ 0.6 fF/%RH between 90% and 95% RH	7% at 90% RH	Agrifood sector-Passive RFID	Present study
Anodic aluminum oxide	Oxide	483 fF/%RH	30% at 92% RH	Humidity sensors	[45]
Polyethylene-naphthalate and polyimide foils	Synthetic polymer	21 fF/%RH	-	Intelligent RFID	[47]
Polyimide	Synthetic polymer	4.5 fF/%RH	10% at 50% RH	Humidity sensor for RFID for monitoring environmental humidity	[43]
Cellulose acetate butyrate	Synthetic polymer	1.5 $\pm$ 0.03 fF/%RH	20% at 20% RH and 30% RH	Low cost sensor arrays and disposable sensing platforms	[49]

Porous aluminum oxide	Oxide	312.5 fF/%RH	-	-	[24]
Polyphenylacetylene (PPA)	Synthetic polymer	10 fF/%RH	-	-	[48]
Anodic Aluminum oxide	Oxide	4200 fF/%RH	16.5% at 70% RH	Humidity sensors	[46]
Cerium(IV) oxide	Oxide	111 pF/%RH	1% at 45%RH	Humidity sensors	[44]

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