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Plant polymer as sensing material: Exploring environmental sensitivity of dielectric properties using interdigital capacitors at ultra high frequency

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An interdigital capacitor (IDC) system was designed in order to provide a controlled high exposure (high surface/thickness ratio) to the environmental atmosphere of a sensing layer of which the dielectric properties were identified by a finite element method simulation and validated using a common parallel plate capacitor technique. The dielectric properties of one of the most sensitive and widely available plant polymers in nature: wheat gluten (WG) proteins were determined at ultra high frequency (500 MHz–1000 MHz) at 25 °C and at two different values of relative humidity (RH). Increasing relative humidity from 20% RH to 80% RH increased the dielectric loss and permittivity of wheat gluten from 0.39 ± 0.01 to 0.84 ± 0.02 and from 5.01 ± 0.06 to 7.07 ± 0.18, respectively. This effect was discussed in the light of wheat gluten composition (constituting amino acids), structure (high molecular weight, proteins unfolding and mobility) and water content (adsorbed water-bonding state). In addition to RH, two other analytes known as food quality markers, carbon dioxide (CO_2) and ethanol were studied in terms of sensitivity. The sensitivities of 10.0 ± 0.4 fF/%RH, 31.38 ± 0.06 fF/%CO_2 and 25.50 ± 0.05 pF/%ethanol obtained should pave the way for the development of innovative green radio frequency identification (RFID) tags using renewable, cheap and biodegradable plant polymers as gas and vapor sensors. The sensors are intended to be interfaced to low-cost, ultra high frequency, passive, RFID tags for monitoring food quality and freshness volatile markers in packaging headspace.

1. Introduction

Wasting food is not only an ethical and economical issue, it also depletes the environment of its limited natural resources. Confusion by consumers about food date labels ("best before", "sell by" and "display until") is a principal issue in household food waste prevention and is responsible for over 20% of avoidable (food thrown away while still edible) food waste [1]. To avoid the issues of margin of safety and misunderstanding of conventional food date labels, a new generation of "self-adjusting" date labels was developed and named smart, intelligent packaging or indicators. They represent a key tool to prevent food waste and to improve food logistics, traceability and safety. Currently, the most promising area is about direct indicators, which aim to monitor in situ the quality and safety of packed food by reacting in a tailored manner with target markers of food degradation, such as ethanol and carbon dioxide. Ethanol is a precursor and a naturally occurring substance of food fermentation and its content increases during the fermentation process. Regarding carbon dioxide, the latter is formed as a result of food degradation also due to fermentation, and respiration reactions within the food products [2–6]. Both of them are food degradation markers and an indication of their concentration values in food packages would be essential information for the preservation of food products.

An important advance in the area of indicators has been the integration of time-temperature and gas or vapor sensors to RFID devices. These allow in situ, continuous and wireless tracking of the food temperature [7] and surrounding oxygen concentration [8]. They can also detect the threshold content of targeted gases

Abbreviations: FEM, finite element method; IDC, interdigital capacitor; PS, polystyrene; RC, resistance capacitance; RH, relative humidity; RFID, radio frequency identification; SEM, scanning electron microscopy; THF, tetrahydrofuran; TTI, time temperature indicator; VNA, vector network analyzer; WG, wheat gluten.

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using a metal oxide sensor [9], as well as gas sensors and chemical sensors [10], throughout the entire food chain.

RFID tags use radio-frequency electromagnetic waves to communicate real-time information of the product for automatic product identification and traceability [11]. The tags consist of an integrated circuit (chip) attached to an antenna for the transmission of the information stored in the chip to a reader. Depending on the types of RFID tag, they may not require any power supply, have a long reading range, they are low cost and have a long operational life.

In the context of intelligent packaging and direct monitoring, sensors coupled to RFID tags are able to monitor the quality and safety of packed food. A sensor enables the detection of analytes such as humidity, vapors, gases, temperature, pH-level and light exposure [12], and can interface differently with RFID tags. They can be potentiometric, conductometric or resistive [13]. Resistance and reflectance changes are induced by the sensitivity of the sensor to analytes, impacting the RFID tag output signal, such as frequency and amplitude [14]. In other cases, the sensor resistance is converted to a voltage suitable to be read by the RFID chip due to the effects of analytes such as humidity and volatile amines. There are different types of sensors like polytriarylamine, which is sensitive to trimethylamine [15] or metal oxides, used for discriminating ethylene, acetaldehyde, ethanol and ammonia [16,17]. Oprea et al. [18] coupled sensing layers (cellulose acetate, poly cellulose-acetate-butyrate, poly methylmethacrylate and polyvinylypyrrolidone) to interdigital capacitors made of copper based electrode fingers on different substrates (polyethylene-naphthalate and polyimide), intended to be used with RFID tags. Among the large portfolio of existing and studied sensing materials (synthetic polymers, carbon allotrope based materials, metal nano-particles, etc.), almost no attention has been paid to plant polymers, although their complexity could be counterbalanced by their sustainability and their natural ability to interact to gases and vapors, as food degradation markers (mainly known, CO_2 and ethanol) that sensors are often expected to monitor.

In this study wheat gluten, which is the water insoluble protein fractions of wheat, was selected. It was studied because it is widely available, inexpensive, renewable and biodegradable. It was studied as a gas and vapor sensor in the perspective of developing self adjusted date labels by coupling wheat gluten bio-sensors with RFID tags. A complex combination of electrostatic interactions, van der Waals forces, salt bonding, hydrogen bonding and disulfide bonding [19,20] contribute to the stabilization of the 3D structure of wheat gluten. The wheat gluten network is a dynamic system which is highly sensitive to vapors, gases and temperature [21,22], which displays dielectric properties [23,24] evolving as a function of environmental conditions [25].

The present study aims to gain in situ knowledge of the impact of environmental conditions on the dielectric properties of wheat gluten proteins, i.e. the dielectric permittivity (ε') defined as the ability of the material to store energy due to polarization phenomena, and the dielectric loss (ε'') defined as its ability to dissipate energy into heat by the frictional motion of the element carrying charges [26]. Such knowledge is missing in literature and will permit to explore the feasibility of designing innovative cheap sensor coated passive RFID tags to monitor food quality and freshness, operating at high frequency (e.g. 868 MHz) for long reading range and fast data transfer rate. The objective of this study is to develop and validate a strategy for determining in appropriate conditions of geometry and environment, the dielectric properties (dielectric permittivity and dielectric loss) of a plant polymer: wheat gluten proteins, as a function of its atmospheric environment. Interdigital capacitors (IDC) were first designed in order to allow electrical measurements on the targeted frequency range and environmental conditions. Dielectric permittivity and loss of wheat gluten were then identified by simulation and clarified relating to wheat gluten composition, structure and dynamic, as a function of environmental gas (carbon dioxide) and vapor (water and ethanol), which were selected as typical food freshness markers.

2. Materials and methods

To develop and validate an innovative strategy to assess dielectric permittivity and loss of wheat gluten proteins, interdigital capacitors (IDC) were preferred to conventional characterization methods (parallel plate capacitors) due to their versatile use in different environmental conditions and on a large scale of frequency (by adjusting the IDC geometry). The drawback of using IDC is that the dielectric permittivity and/or loss cannot be directly measured, and then a simulation procedure is needed to identify those parameters. This procedure required validation steps carried out as follow: (i) identification of dielectric parameters of air and standard polymer (polystyrene films) deposited onto IDC in comparison with literature, and (ii) measurements of dielectric parameters of wheat gluten films with the parallel plate capacitor technique when possible (i.e. in particular RH conditions only). The sensing ability of wheat gluten films was explored for two kinds of possible applications:

(i) Monitoring quality of packed food, by choosing two common RH conditions, i.e. low, 20%, to mimic dry products such as biscuits, and high, 80%, to mimic moist products such as fruits and vegetables.
(ii) Monitoring safety of packed food by mimicking the fermentation process in the case of moist food, e.g. CO_2 (at 40%) and ethanol (at 0.1%) at high relative humidity only (80%).

2.1. Wheat gluten 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 and humidity. 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 min. 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 [27,28] and used within one week.

2.2. Polystyrene (PS) solution preparation

Polystyrene pellets were purchased from PolyOne (France) having a glass transition temperature of 105 °C, a density of 1.05 g/cm^3 and a molecular weight of 285,000 g/mol. 2 g of polystyrene pellets were dissolved in 10 ml tetrahydrofuran (THF) using magnetic stirring. The container was covered to prevent solvent evaporation while stirring [29].

2.3. Sample preparation—solvent casting method

2.3.1. Sample preparation

1 ml of wheat gluten solution was cast onto interdigital capacitors (IDC) systems using an E409 blade coater from Erichsen (France), in order to cover the whole comb-like structure (i.e. active