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Humidification and drying of granular matter – correlation of mass change and effective dielectrometry

F. Starzyk*
Institute of Physics, Cracow University of Technology,
ul. Podchorążych 1, 30-084 Kraków, Poland
* Corresponding author: E-mail address: fstarzyk@ifpk.pk.edu.pl

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ABSTRACT

Purpose: The purpose of this paper was to record and mutualy correlate mass changes of population of micro-granules of rye starch and effective dielectric permittivity of this system taking places during humidification and drying processes.

Design/methodology/approach: Mass changes of biopolymeric mirco-granular sample occuring during its exposition on saturated water vapour at room temperature, was recorded in the time by means of precise torsional balance equipped with special chamber. The same was done in case of drying. Monitoring of effective dielectric permittivity was performed by means of interdigit comb capacitor and precise RLC meter equipped with PC program. Specially designed and constructed measuring chamber was applied to control temperature and relative humidity (RH %) of ambient sample atmosphere.

Findings: Interdigit dielectric spectroscopy method turned out to be more sensitive technique to follow details of humidification as well as drying processes. Correlation of changes of effectife dielectric permittivity with simultaneously occurring mass increase or decrease can be a way to describe the humidification and drying processes of micro-granular biopolymeric sample.

Practical implications: Effective dielectric permittivity monitoring of humidification and drying processes turned out to be much more selective than only gravitational measurement of mass change. For modeling purpose correlation of both is giving new possibilities of modelling approach.

Originality/value: For the first time practically important humidification and drying processes were monitored in statu nascendi, without disturbing geometry of granules starch by means of ε' values evolution record. It was enabled by application of interdigit comb capacitor as sensing unit.

Keywords: Biopolymers; Micro–granular matter; Water uptake; Interdigit dielectrometry

MATERIALS

1. Introduction

Many types of biopolymers, biocompatible materials [1-3] and starch among them [4-6] are subject of modern technological investigations.

Water molecules behavior within micro-granular biopolymeric matter which can be in the form of granular starch, plays key role in many processes in nature as well as in food, paper and farmaceutical technology [4-6]. Enzymatically driven, biochemical synthesis witin plants [7] and also within mammalian's liver main starch polymeric components amylose and amylopectine or glicogen [7] occurs. In plants, amylose and amylopectine are physically, precisely packed and form a physical structure called starch granules. Physical structure of starch granules were very long a subject of many investigations [8-10]. Granules of many starches consist of many dense (crystallic) and

amorphous (less dens) layers and remains extremely of the apple-like shape. Amylose and amylopectine polymers have a form of linear and branched polymers of glucose basic unit. Starch granules plays a role a energy stores in plants seeds. Starch granules are also final product of food industry and water behavior in the indyvidual granule structure and in the large granules population is a very important phenomenon. Among others, humidification and drying are very important from practical point of view. The change of water molecules content in granular starch can be a source of single granule and also granules set dielectric properties evolution.

2. Sample preparation

Granular rye starch samples were kindly supplyed by prof. P. Tomasik from University of Agriculture in Krakow. Portion of rye granules were heated at 42 ^{0}C in technical vacum in order to remove a adsorbed and capillary water and next it was inspected under optical microscope, photograph and its granules diameters distribution of investigated population was measured. The outcome in the histogram form is presented in the Fig.1.

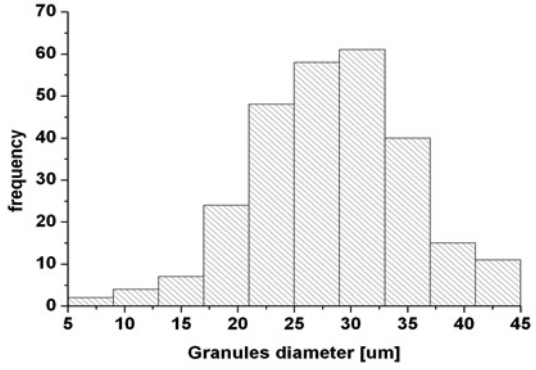

Fig. 1. Distribution of granules diameters for rye starch sample

It is unimodal distribution with maximum population at about 30 μm, maximum about 45 μm. The smallest granular had about 5 μm size. Half width equal about 13 μm.

3. Mass evolution during humidification and drying of granular sample

The portion of freely stacked granules of initial value of 21 mg, formed into rectangular shape sized as 7 x 11 x 0.4 mm^3 was placed in moisturizing chamber (~100 RH %) equipped with precision torsional balance. The mass evolution of the starch sample was monitored in time up to about 10000 s. The resulting m(t) curve is shown in the Fig.2. Above this time, the changes of sample mass exceeded balance resolution and were very slow.

The mass behavior in time m(t) was fitted as a superposition of constant component and two exponential form with time constants and amplitudes specified in the Fig.2. Final water uptake of about 5.2 mg was observed after 10^4 s time. During exposition on water vapours the geometry of granules stack was not disturbed. The repetition of moisturized granules microscope inspection under polarized light showed that the over molecular structure of granules was not disturbed [11]. It means that maltese cross was of the same undisturbed shape.

Mass monitoring in time of drying of similarly formed rye population granules of $m_o \approx 22.8$ mg is presented in the Fig.3. The fitted curve parameters are also presented there. It is of the form of superposition of constant and two exponent components. Physically, the drying run m(t) is a mass of the sample response on the step of relative humidity from 100 % RH to 30 % RH.

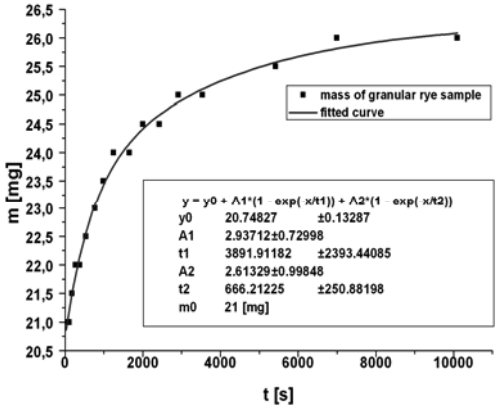

Fig. 2. Sample mass increase along the exposition time on saturated water vapour at 23 ^{0}C

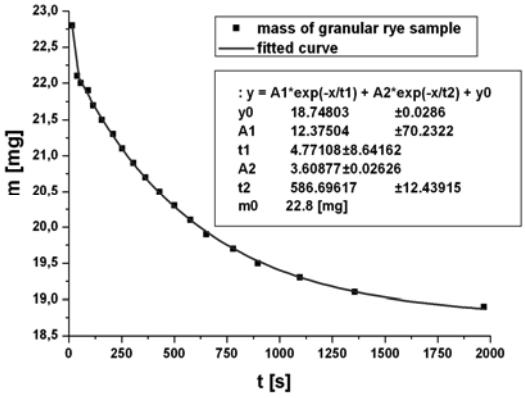

Fig. 3. Sample mass decrease along the time of drying

4. Monitoring of effective dielectric permittivity evolution during humidification of rye starch population sample

The method of effective dielectric permittivity relayed on application of interdigit comb capacitor as a sensing unit. The precise RLC meter Agilent 4284A was applied to measurement together with Novocontrol WinDeta program. Details of calibration and measurement method were described elsewhere [6, 12].

5. Dielectric permittivity evolution during humidification and drying of granules population for selected frequencies

Effective dielectric permittivity of granular rye sample as function of time of its exposition on saturated water vapour at room temperature is presented in the Fig.4.

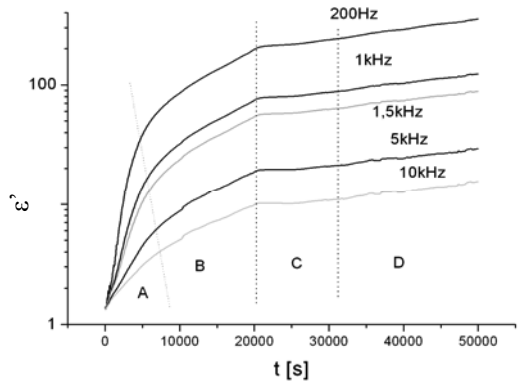

Fig. 4. Effective dielectric permittivity of granular rye sample as function of its exposition time on saturated water vapours at room temperature

Independently on measuring frequency, one can infer minimum four stages of ε'(t) dependence assigned as A, B, C and D in the Fig.4. One can postulate the following processes participating in the ε'(t) changes originating from water molecules uptake:

A: initial substitution of dry air present in between micro-granular spaces by air with saturated water vapour. As secondary process involved, one can specify initiation of immobilization and adsorption of water molecules by active centers on starch granules free surfaces. Time period 0 s ÷ 10^4 s can be correlated precisely with independently recorded mass increase demonstrated in the Fig.2. Up to $2 \cdot 10^4$ s one can postulate the correlation by means of fit equation for m(t) written in the frame on the Fig.2. Stage B (Fig.4) ranges from about 10^4 s to $2 \cdot 10^4$ s. It represents slower ε'(t) increase leading to saturation of all active surface centers of adsorption with tendency to saturation and equilibration between free surface adsorption and desorption of water molecules.

Again, independently on frequency at about $2 \cdot 10^4$ s begins the stage assigned as C in the Fig.4. It involves a threshold type of slowing down of further ε'(t) grow. It can be treated as surface adsorption saturation and beginning of diffusion of water molecules into inter-granular contacts spaces. This diffusion (C) is followed by further slow and long lasting increase of ε'(t) also independent on frequency which can be attributed to capillary water condensation with in deeper areas of inter-granular contacts and within structural channels present in individual granules structures [13]. Further water content increase can initiate not reversible changes of granules physical structure (over molecular chains movements) and they are out of this work scope. This last slow process turned out to be recordable when interdigit-comb-capacitor dielectric spectroscopy was applied. Simultaneously, mass change monitoring (for time greater than ~$2 \cdot 10^4$ s) is very difficult to perform. It should be treated as great advantage of interdigit dielectrometry application. C and D stages are running with very slow uprising of sample mass but the ε'(t) increase connected with them is quite substantial. It is possible that main component of them is of secondary character and involve rearrangement of formerly adsorbed and absorbed or bonded water molecules. The outcome is polarizability increase with almost frequency independent dynamics.

As it is known from literature, moisturizing of granular starch of different origin is very long lasting process leading finally to granules structure destruction [14]. In this work only reversible humidification was monitored.

In the Fig.5 effective dielectric permittivity of formerly humidified granular rye sample as a function of drying time is shown for selected frequencies of measuring field. The frequency dependence vanishes within 100 s ÷ 1000 s decade of time almost completely. Population of rye starch granules is coming back to permittivity value between 1and 2. Drying occurring much faster than humidification and both these processes will be subject of more detailed modeling.

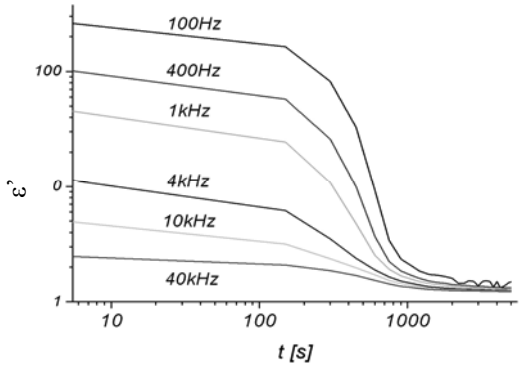

Fig. 5. Effective dielectric permittivity of granular rye starch sample as function of time of drying

6. Correlation between E'(t) and water molecules content

The effective dielectric permittivity for selected frequencies correlated with current mass of granules population during humidification process is demonstrated in the Fig.6.

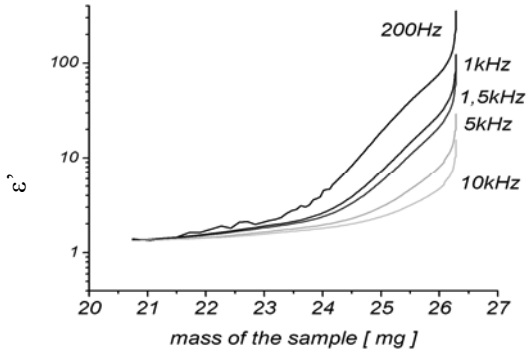

Fig. 6. Effective dielectric permittivity of granular rye sample as function of current mass (number of water molecules) in statu nascendi, during humidification in saturated water vapour at room temperature

The evolution of ε'(m) function becomes strongly frequency selective after about Δm ~ 3 mg of water uptake (21 mg to ~ 24 mg shift). For saturated state of water content (~ 6 mg) increase of sample mass), the vertical (almost) parts of ε'(m) curves, represent rearrangement of water dipoles, contributing to increase of effective ε' occurring in formerly described as C and D stages.

One should take into consideration that water vapour behavior in contact areas between granules may contribute substantially to ε' increase. Contact areas are working as semi-closings micro- or nano-vacancies. Inside them, the interaction between vapour dipoles and semi-closing walls can slow down vapour dipoles dynamics very slightly. This can explain effective permittivity values above 100 for lowest frequency used. Rescaling of ε'(t) from the Fig.5 into ε'(m) on Fig.7 does not change importantly the character of frequency dependence of ε' during drying process.

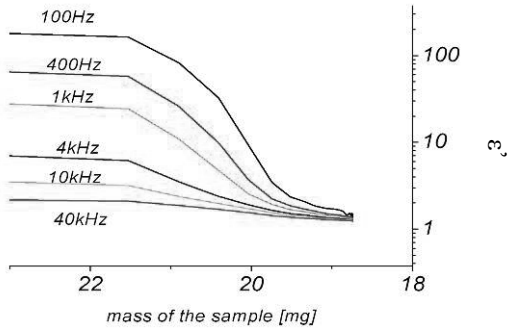

Fig. 7. Effective dielectric permittivity of granular rye sample as a function of current mass in statu nascendi, during drying at room temperature

This is connected with the fact of drying formerly wet sample without transition to vacuum but to lower vapour pressure only. Thus, water molecules localized in granular system in places where they were stronger bonded were not taking part in drying evacuation from the structure.

7. Conclusions

Population of about 2000 micro-granules of rye starch, with average diameter about 25 μm, initially dryed in at 42 ^{0}C and technical vacuum was humidified and mass increase in time was monitored. Fitting to m(t) curve points out on constant component and two exponential processes.

Wet population of granules was dryed and m(t) curve was recorded as a mass response to step change of relative humidity of ambient air from ~100 % to 30 % at 23 ^{0}C. Fit to experimental curve involves constant component and two exponential decays. Practically available range of mass change detection was limited to about 10^4 s in case of humidification and to about 2000 s for drying case.

Application of interdigit dielectric spectroscopy turned out to be much more sensitive when applied to both processes, than only mass recording. In the case of humidification of rye starch granules population it was possible to infer about 5 stages of water molecules uptake and rearrangement within the time scale up to $5 \cdot 10^4$ s and ~6 mg mass increase. The effective permittivity rises up from ~1,3 value to 100 and more in case of 100 Hz measuring frequency. Humidification process seen via ε' values is frequency sensitive and it will be a subject of further quantitative analysis.

Correlation of ε'(t) and m(t) runs recorded during water molecules uptake and location within the granular, mechanically undisturbed sample will enable to express ε'(ν) function as ε'(ν, N(t)), where ν – frequency, N – number of water molecules as function of time. Geometrical parameters describing sample of granules population have to be of fractal nature [15] and will be geometrical base of effective polarizability model for bio-organic micro – granular matter.

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