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AC impedance and microstructure of rye starch exposed to water vapour

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ABSTRACT

Purpose: The purpose of this paper was to record and analyse mass (m) changes of population of micro-granules of rye starch, effective alternative current (AC), (electric) complex impedance (EACI) of this system taking place during humidification as well as insight into microstructure evolution by X-ray diffraction (XRD).

Design/methodology/approach: Mass changes of biopolymeric micro-granular sample occurring during its exposition to saturated water vapour at room temperature, was recorded in time by means of precise torsional balance equipped with special chamber. The same was done in case of microstructure by XRD method. Monitoring of EACI was performed by means of interdigit comb capacitor and precise RLC meter equipped with PC software. Specially designed and constructed measuring chamber was applied to control temperature and relative humidity (RH %) in ambient sample atmosphere. Electric measurements were carried out for 5 selected frequencies.

Findings: Interdigit dielectric spectroscopy method turned out to be more sensitive technique to follow details of long lasting humidification than only mass changes recording. Correlation of changes of EACI with simultaneously occurring mass increase can be a way to describe the humidification stages processes involving water molecules adsorption and absorption by micro-granular biopolymeric sample. Frequency dependence of EACI gives insight into mechanism of water molecules inclusion, binding and immobilization on the starch granules surface as well as inside of its internal physical structure.

Research limitations/implications: The recording duration of m(t) was limited to ~10^4 s in case of humidification by balance resolution and character of the process. The whole range of measurements was limited to max ~23 RH % of water uptake in order to prevent over molecular structure irreversible changes. The above limitations enable us to collect data for modelling reversible water uptake and connected EACI micro-granular biopolymeric population sample.

Practical implications: EACI monitoring of humidification turned out to be much more selective than only gravitational measurement of mass change. Modelling purpose correlation of both can give new possibilities to modelling approach. Achieved data can contribute to better understanding of active adsorption and absorption centres in starch granules.

Originality/value: For the first time practically important humidification process was monitored in statu nascendi, without disturbing geometry of starch granules population by means of EACI evolution record. It was enabled by application of interdigit comb capacitor as a sensing unit. This is the first report of four stages for EACI evolution as well as the first XRD direct record of granular starch reversal swelling.

Keywords: Biopolymers; Micro–granular matter; Interdigit dielectrometry; Effective AC Impedance

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MATERIALS

1. Introduction

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

Water molecules behaviour within micro-granular biopolymeric matter which can be in the form of granular starch, plays a key role in many processes in character as well as in food, paper and pharmaceutical technology [4-6]. Enzymatically driven, biochemical synthesis within plants [7] and also within mammalian's liver is a main source of starch polymeric components: amylose and amylopectin or glycogen [7]. In plants, amylose and amylopectin are physically, precisely packed and form a physical structure called starch granules. Physical structure of starch granules was a subject of many, very long investigations [8-10]. Granules of many starches consist of many dense (crystalline) and amorphous (less dens) layers and remain externally out of the apple-like shape. Amylose and amylopectin polymers have a form of linear and branched polymers of glucose basic unit. Starch granules play a role of energy stores in plants seeds. Starch granules are also a final product for food industry and water behaviour in the individual granule structure, and in large granules population they are a very important phenomenon from practical point of view in flower for food storing. 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 supplied by Prof P. Tomasik from The University of Agriculture in Cracow. Portion of rye granules were heated up at 42°C in technical vacuum in order to remove adsorbed and capillary water, and then it was inspected under optical microscope, photographed and its granules diameters distribution of investigated population was measured. The outcome in a histogram form is presented in the Fig. 1.

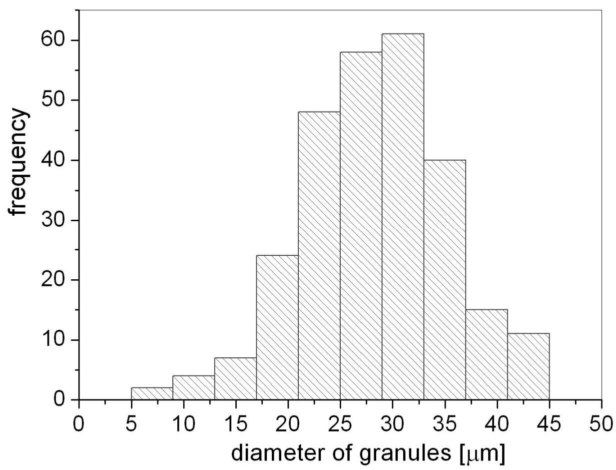

Fig. 1. Distribution of diameters sizes of the investigated rye starch granules population

It is unimodal distribution with maximum population frequency at about 30 μm, maximum diameter about 45 μm. The smallest granular diameter was about 5 μm. The half height width equals about 13 μm.

3. Mass evolution during humidification of rye starch granular sample

A portion of freely stacked granules of initial value 21 mg, formed into rectangular shape sized as 7 x 11 x 0.4 mm^3 was placed in moisture chamber (~100 RH %) equipped with precision of 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, changes of sample mass exceeded balance resolution and they were very slow.

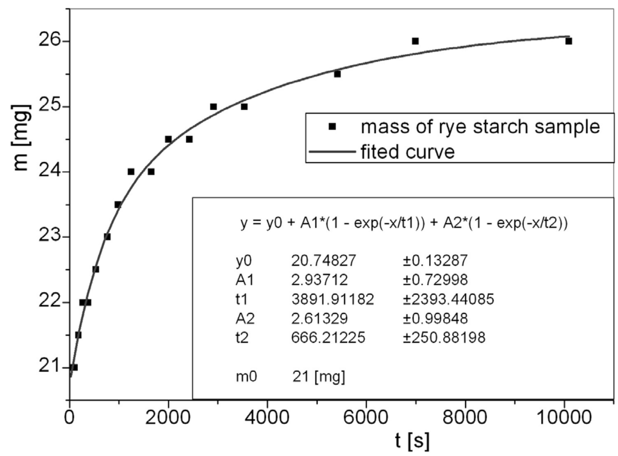

Fig. 2. Rye starch granular sample mass increase in time induced by saturated water vapour adsorption and absorption at room temperature, initial period in time

The mass behaviour in time m(t) was fitted as a superposition of constant component and two exponential forms 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 to water vapours the geometry of granules stack was not disturbed. 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. Physically, a humidification run m(t), is a mass of a dry sample response to a step of relative ambient atmosphere humidity up to about100 % RH at room temperature.

4. Monitoring of effective AC electric complex impedance evolution during humidification of rye starch population sample

The method of EACI measurement was relayed on application of interdigit comb capacitor as a sensing unit. The precise RLC meter Agilent 4284A was applied for measurement together with Novocontrol WinDeta software. Details of calibration and measurement method were described elsewhere [6, 12]. EACI measurements outcomes are presented here in the form of impedance modulus as a function of time for five selected frequencies in Fig. 3 and with phase angle of complex impedance vector dependence on the same variables, in Fig. 4.

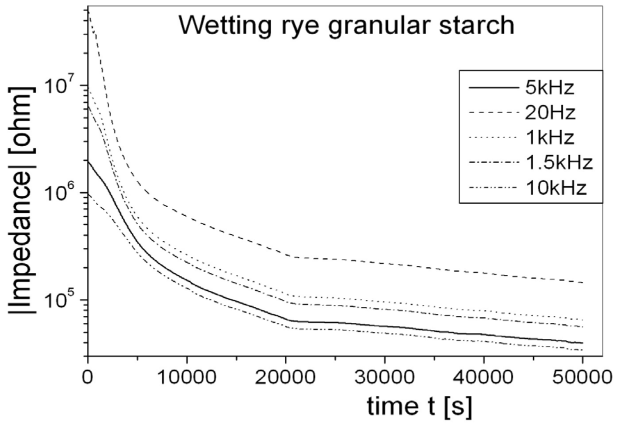

Fig. 3. AC effective electric impedance (modulus) of rye granular starch sample exposed to saturated water vapour at room temperature and its frequency dependence

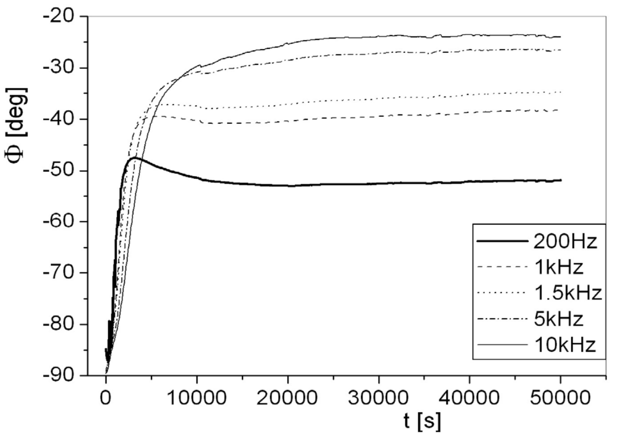

Fig. 4. Time evolution of the phase angle of electric ac impedance for dry rye granular sample exposed to saturated water vapour at room temperature

Closer analysis of the Fig. 3 shows that EACI value reacts almost instantly on the relative humidity step of ambient atmosphere. It is seen as a rapid fall of EACI for all frequencies applied during first ~5000 s. For time above ~500 s the dependence on frequency has the same form for all used frequencies. The second stage involves the time period up to ~21000 s with a discontinuity /breaking region at the end.

The origin of EACI dependence on time and frequency will be a subject of separate work. The last slower decline of EACI occurs with the same slop for all frequencies up to the end of measurement. The initial fast increase of phase angle takes place within about 5000 s and transient maximum is frequency dependent up about 1.5 kHz. For higher frequencies only slower increase takes place and subsequent declination seems to be reflected as further increase. The origin of such behaviour is to be studied separately. As a working hypothesis one can point to possibility of relaxation process in the form of asymmetric charging and discharging of non-linear capacities present in the form of inter-granular contacts. The distribution of granules sizes may be a source of effective capacities of these contacts.

5. XRD - detected microstructure evolution during humidification of rye granules population

The XRD measurements outcomes for dry and wet rye starch granules population are compared in the Fig. 5.

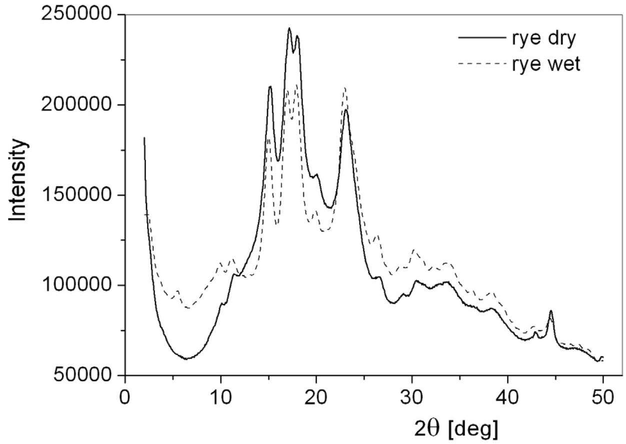

Fig. 5. The X-ray diffraction pattern for dry and wetted rye granular starch population sample

For 2θ angles values in central part of diffraction pattern (~13 – 23 deg) introducing water molecules damped down XRD intensity. Also peaks heights are changed. Out of this range, XRD intensity undergoes elevation with a new peak appearance at about 5 deg. Thus the action of water molecules inclusion on granules surface and inside of granules volume seems to be not only plasticization as it is described in the literature but also surface and interior physical structure may be locally altered as a primary process, and the global swelling may be postulated as a secondary one. Because these XRD data are probably the first ones published of this quality, one should wait for further confirmation before deeper concluding.

6. Conclusions

Independently on measuring frequency, one can infer minimum three stages of EACI evolution taking place during rye granular starch humidification. One can postulate the following processes participating in these 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 centres on starch granules free surfaces. Time period $0\ s \div 10^4\ s$ can be correlated precisely with independently recorded mass increase demonstrated in the Fig. 2. Up to $5{\cdot}10^4$ s one can postulate the correlation by means of fit equation for m(t) written in the frame on the Fig. 2. Stage B ranges from about $5{\cdot}10^3$ s to $22{\cdot}10^4$ s. It represents slower EACI decrease leading to saturation of all active surface centres of adsorption with tendency to saturation and equilibration between free surface adsorption and desorption of water molecules.

Again, independently on frequency at about $22{\cdot}10^4$ s begins the stage of constant and the slowest fall. It involves a threshold type of slowing down for further EACI decrease. It can be treated as surface adsorption saturation and beginning of diffusion of water molecules into inter-granular contacts spaces. This diffusion is followed by further slow and long lasting decrease of EACI also with a speed independent on frequency which can be attributed to capillary water condensation within 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 scope of this work. This last slow process turned out to be recordable when interdigit-comb-capacitor dielectric spectroscopy was applied. Additionally, mass change monitoring (for time greater than $\sim 2{\cdot}10^4$ s) is very difficult to perform. It should be treated as great advantage of interdigit dielectrometry application. Further stages are running with a very slow rise of sample mass. It is possible that main component of theirs is of secondary character and involve rearrangement of formerly adsorbed and absorbed or bond 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 a very long lasting process leading finally to granules structure destruction [14]. In this work only reversible humidification was monitored. The EACI of formerly dried granular rye sample as a function of moisturizing time for selected frequencies of measuring field evolves from $1\ M\Omega$ - $50\ M\Omega$ range to about $100\ k\Omega$ value. The frequency dependence is established almost completely within the first ~5000 s of time. One should take into consideration that water vapour behaviour in contact areas among granules may contribute substantially to EACI and phase angle dependencies on time. Contact areas work as semi-closed micro- or nano-vacancies. Inside of them, interaction between vapour dipoles and semi-closed walls can slow down vapour dipoles dynamics very slightly. Population of about 2000 micro-granules of rye starch, with average diameter about 25 μm, initially dried up at $42\ ^0C$ and technical vacuum was humidified and mass increase in time was monitored. Fitting to m(t) curve, it points out on constant component and two exponential processes. Practically available range of mass change detection was limited to about 10^4 s in case of humidification. Application of interdigit dielectric spectroscopy turned out to be much more sensitive when applied in both processes, than only mass recording. Humidification process seen via speed of impedance values is frequency sensitive only during initial period of time and it will be a subject of further quantitative analysis. Geometrical parameters describing sample of granules population have to be of fractal character [15] and will be a geometrical base for an effective polarizability model for bio-organic micro–granular matter.

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