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Water induced evolution of dielectric and micro-structural properties of rice starch

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ABSTRACT

Purpose: The purpose of this paper was to record and correlate mass (m) changes of population of rice starch micro-granules and their effective dielectric permittivity(ε′), as well as X-ray diffraction (XRD) changes observed in this system during humidification.

Design/methodology/approach: Changes of mass of bio-polymeric-granular sample occurring during its exposition on saturated water vapour at room temperature, was recorded in the time. The ε′ evolution was recorded by means of fringe-field-interdigit-dielectric spectroscopy (FFIDS) method. The temperature and relative humidity (RH %) of ambient atmosphere were controlled. Microstructure changes induced by water absorption were recorded by means of XRD diffractometer.

Findings: The FFIDS method turned out to be sensitive technique to follow details of humidification process. Correlation between changes of ε′ with simultaneously occurring mass increase can be a way to describe the humidification and drying processes of micro-granular bio-polymeric sample. The changes observed by means of XRD should enable to point the regions within granules structures where water molecules effectively interact with internal granules physical organisation on macromolecular level.

Research limitations/implications: The time length of m(t) record was limited to ~11000 s in case of humidification by the nature of the process. The whole range of measurements was limited to max ~23 % of water uptake in order to prevent the molecular structure irreversible changes.

Practical implications: The ε′ monitoring of humidification turned out to be much more selective than only gravitational measurement of mass change. The correlation of both is giving new possibilities of modelling approach. The XRD observed changes within physical structures of rice starch granules seems to be of great importance for modelling of water behaviour in starch.

Originality/value: For the first time humidification process was monitored in statu nascendi, without disturbing geometry of granules starch by means of ε’ evolution record. It was enabled by application of interdigit comb capacitor as sensing unit. The high quality of XRD records enables a new insight into details of reversible swelling process of rise starch granules.

Keywords: Bio-polymers; Micro–granular matter; Water uptake; Interdigit dielectrometry; Biological water

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PROPERTIES

1. Introduction

Bio-polymers of many types, bio-compatible materials [1-3] and starch among them [4-6] are subject of modern technological investigations. It is stimulated by their numerable pharmaceutical and nutritional applications.

Water molecules behaviour within micro-granular bio-polymeric matter which can be in the form of granular starch, plays key role in many processes in nature and in many technological processes [4-6]. Enzymatically driven, biochemical synthesis within plants [7] and also within mammalian's liver of main starch polymeric components amylose and amylopectin or glycogen [7] occurs. In plants, amylose and amylopectin are physically, precisely packed and form a physical structure called starch granules. This packing depends on the biological origin of the given starch but have also a collection of similarity features shared by starches of different origin. Physical structure of starch granules were very long a subject of many investigations [8-10]. Granules of many starches consist of many dense (crystalline) and amorphous (less dens) layers and forms multi-layer like structure. Within the scale of granule size one has to do with generally two cases: small starches granules like rise, have very narrow distribution of size, big ones like potato and rye or sago possess uni-modal or bi-modal wide distribution of granules sizes. Amylose and amylopectin polymers have a form of linear and branched polymers with glucose basic unit. Starch granules play a role of energy stores in plants seeds. Starch granules are also final product of food industry and water behaviour in the individual 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. Water molecules as guests on granules surfaces and within granules internal structures (internal surfaces) exert many kinds of locally specific influences. One should expect that probably holistic approach of fractal nature may open the new possibilities of biological water behaviour modelling.

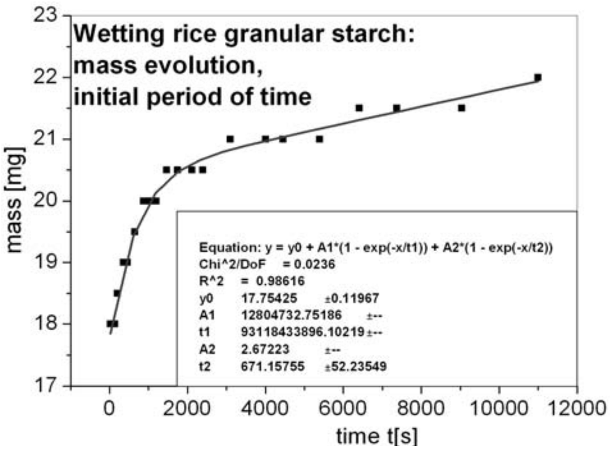

Fig. 1. Water vapour adsorption and absorption by dry rice granular starch: sample mass increase along the initial exposition time on saturated water vapour at 23 ^{0}C

2. Sample preparation and characterisation

Granular rise starch samples were kindly supplied by Prof. P. Tomasik from University of Agriculture in Krakow. Portion of rise granules were heated at 42 ^{0}C in technical vacuum in order to remove a adsorbed and capillary water and next it was inspected under optical microscope, photographed and its granules diameters distribution of investigated population was measured. The investigated population of rise granular starch turned out to have very narrow distribution of granules diameters. In practice it can be characterized as 4.65 ± 0.7 [μm]. As compared to other kinds of starches, rise starch can be treated as homogeneous as far as the granules size is concerned.

3. Mass evolution during humidification of granular rise sample

The portion of freely stacked granules of initial mass of 18 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 11000 s. The resulting m(t) curve is shown in the Fig.1. Above this time, the changes of sample mass exceeded balance resolution and were very slow.

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.1. Final water uptake of about 4.2 mg was observed after 11000 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.

4. Monitoring of effective dielectric properties evolution during humidification of rise starch population sample

The method of effective dielectric permittivity measurement 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]. Dried sample of rise granules population was placed on the surface of measuring flat sensor inside of measuring chamber with constant temperature and humidity, relative humidity was raised up to about 99 % at 23 ^{0}C. Monitoring measurements were carried out during 40000 s (about 11.1 h). Dielectric measurements were performed at each time point for 12 values of frequency and 1 V amplitude of measuring electric field.

The collected set of effective dielectric quantities involves: dielectric permittivity (ε'), dielectric loss tangent (tanδ) and phase angle (Φ) between measuring ac voltage applied to the sample and current response for each frequency.

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

Effective dielectric permittivity (EDP) of granular rise sample as function of time of its exposition on saturated water vapour at room temperature is presented in the Fig.2.

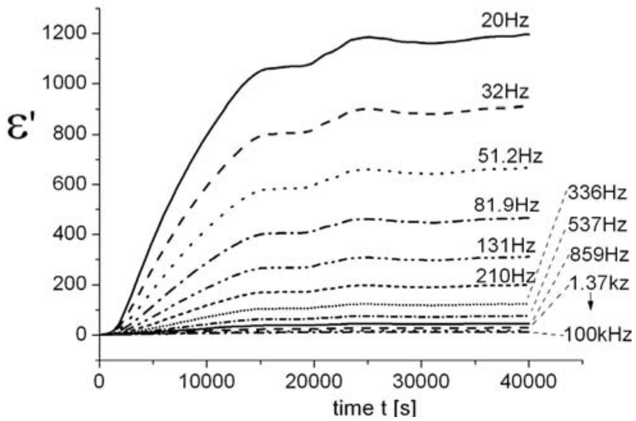

Fig. 2. Effective dielectric permittivity of granular rise sample as function of its exposition time on saturated water vapour at room temperature for selected frequencies

Independently on measuring frequency, one can infer minimum four stages of ε'(t) dependence assigned as A (~0 to ~15000 s), B (~15000 to ~20000 s), C (~20000 to ~25000 s) and D (for time>~25000 s) in the Fig.2. 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 centres 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.1. Up to $2\cdot10^4$ s one can postulate the correlation by means of fit equation for m(t) written in the frame on the Fig.1. Stage B (Fig.2) ranges from about $1.5\cdot10^4$ s to $2\cdot10^4$ s. It represents slower ε'(t) increase 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 $2\cdot10^4$ s begins the stage assigned as C in the Fig.2. It involves a saturation 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 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 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 ~$2.5\cdot10^4$ 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.

The EDP, evolves during water vapour uptake from ~1.5 to ~1100 value. This evolution was lasting up to ~30000 [s]. One should keep in mind that measured values of EDP represent not only rise starch granules system but they also characterize the dynamic system of rise starch granules and saturated water vapour between granules together with slowed down adsorption-desorption processes taking place in partially open confinements regions of inter-granular contacts. One should take into consideration that water vapour behaviour 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. The form of frequency dependence of EDP will be a matter of separate publication.

6. Dielectric loss tangent evolution during humidification of rise granules population for selected frequencies

The effective dielectric loss tangent (EDLT) time and frequency characteristics for selected frequencies were measured for the same time period and frequency values as for EDP case. The measurements outcomes are demonstrated in the Fig.3. EDLT dimensionless value for a given frequency represents total energy losses occurring inside the sample during one cycle of external electric field. Thus, it involves losses originating from dielectric relaxation, ac conduction and possibly contribution of electric field in slowed down dynamic adsorption-desorption processes. They are taking place in inter-granular spaces/contacts, on granules surfaces and inside granules structures. Time and frequency dependence of EDLT shown in the Fig.3 can be characterized as follows: as compared to EDP frequency dependence is reversed. The whole time evolution takes place within ~23000 s. The initial fast increase with characteristic transient maximum is strongly frequency dependent and next up to ~15000 s is followed by partial decline. At ~23000 s relatively small local minimum occurs, followed by stabilization of EDLT values for all frequencies applied in experiment. Transient initial energy losses can be described by local maximum dependence on frequency. Transient character of initial EDLT in time may originate from the heat of wetting absorption and following excess energy dissipation. The relatively rapid step down visible at ~23000 s for highest frequencies, above 500 Hz will be a subject of separate study.

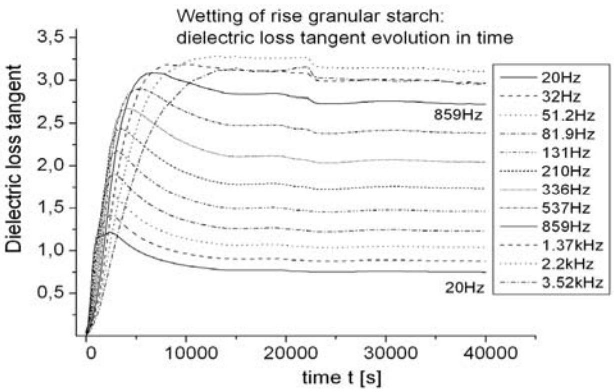

Fig. 3. Dielectric loss tangent evolution along time of dry rise granular starch exposition to saturate water vapour at room temperature together with its frequency dependence

7. Phase angle evolution during humidification of rise granules population for selected frequencies

The phase angle (Φ) dependence on time and selected frequencies for rise granular starch population is shown in the Fig.4. Time scale was presented in the log form in order to enable readability of details of experimental outcomes. The main features of Φ evolution in time can be specified as follows: in the initial stage (~0 to ~200 s) Φ values are of weak frequency dependent and located within the range 84 to 87 deg which is characteristic for weekly conducting dielectric state of dry rise starch. The higher frequency, the bigger Φ value (Fig.4). The frequency dependence of Φ is weak but monotonic one. Within this range of time values of Φ maintain almost constant. This can be interpreted as a time needed for the deeper penetration of water vapour from the surface of the granules stacked up to penetration depth region of measuring electric field. The next stage ranges from ~200 s to 10000 s. Within this range, the fast increase is taking place and for each frequency after local maximum frequency dependent declination occurs. As result of this process the final frequency dependence of Φ become reversed.

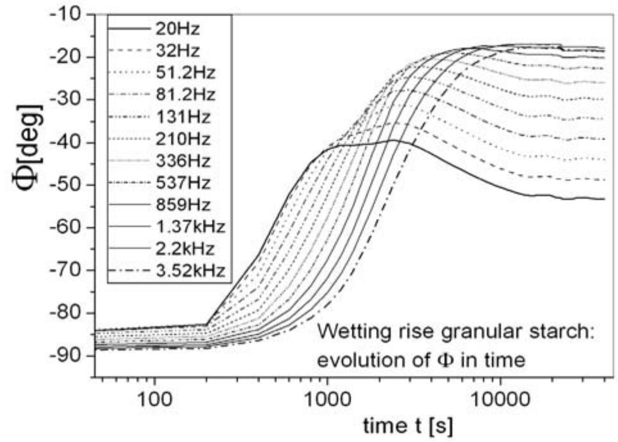

Fig. 4. Phase angle between measuring voltage and current response: evolution in time of dry rise granular starch sample exposition on saturated water vapour at room temperature for selected frequencies

8. Micro-structure evolution during humidification of rise granules population

Water influence on organic macro-molecular systems was a subject of many investigations. In the case of granular starches it is believed that generally action of water molecules within granules internal structure is complex and among others its action can be as plasticizer [16]. In reversible range of granules swelling, the subtle differences caused by small amount of water molecules can be observed only by method of collecting a substantial amount of diffracted gamma rays. We applied diffractometer system XPERT-PRO, Cu-Kα, 1.540598 Å and 1.544426 Å, scan range 2.000 - 50.000 deg, step size 0.050 deg. Diffractograms were collected continuously 12 h each. Results for dry and wet rise granules population are presented in the Fig.5. The preliminary data presented above are probably the first ones involving comparison of granules microstructure evolution caused by water molecules in reversible swelling. One can follow changes in amorphous and crystalline components of granules organization. Generally, percentage of crystalline structure calculated by standard method equals ~22 % for dry rise starch and ~18 % for wet one. Some peaks undergoes elevation, others are shifted down. For angles less than ~25 deg (Fig.5) the whole structure elements with d_{hkl} values smaller than ~3.7 Å water induces more amorphous structure. For the rest part of XRD graph, (d_{hkl}>3.7 Å, up to ~18 Å) the amorphous component is damped down. For explanation of peaks behavior the preparation of spatial method will be necessary. The investigated rise starch granular structure has advantage when compared to other types of starches: it consists of almost mono-sized granules and complications originating from granules sizes distributions can be omitted.

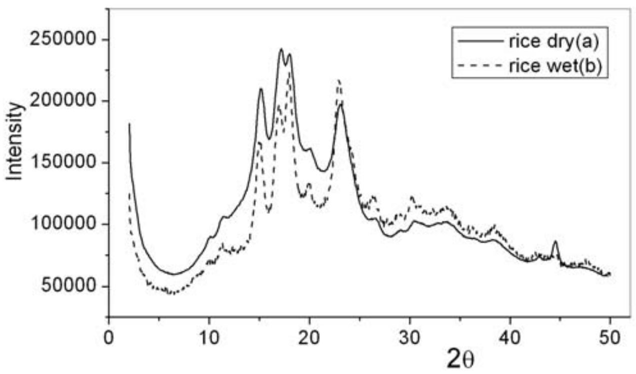

Fig. 5. XRD diffractograms for rice granular starch: a- dried at 42 ^{0}C in technical vacuum, and b-wetted in saturated water vapor atmosphere at room temperature

9. Conclusions

Population of about 2000 micro-granules of rye starch, with diameter about 4.7 μm, initially dried 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. They reflect generally adsorption and absorption of water molecules in the initial stadium of wetting process of rise granular starch population.

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 to both processes, than only mass recording. In the case of humidification of rise starch granules population it was possible to infer about 5 stages of water molecules uptake and rearrangement within the time scale up to $4{\cdot}10^4$ s and ~4 mg mass increase. The effective permittivity rises up from ~1.5 value to 1000 and more in case of 20 Hz measuring frequency. These values are prescribed not to granular population only but to the system of starch granules together with the saturated water vapor filing inter-granular spaces as well as inter-granular contacts. The dynamic of water dipoles in those regions is slowed down. This is the origin of very high EDP values of the system. Humidification process seen via EDP values is frequency sensitive and it can be used for modeling of will be a subject of further quantitative analysis. Transient state of EDLT consists of three periods of time: first rapid growth with frequency dependent maximum, the second decaying down (to about 15000 s) and third, slow relaxation terminating at about 23000 s, which is of unknown origin and will be a subject of further investigation. Details of this transient state are seen in the phase angle evolution characterized by reversing of frequency dependence.

XRD diffraction data, for dry and wet rise granular starch seemed to be of great importance and can be a base for identification of internal starch granules regions where during reversible swelling water molecules exerts its specific influence called in the literature as biological water. Correlation of EDP 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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