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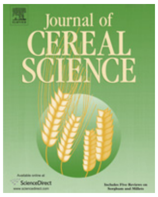

Dynamic water vapour sorption in gluten and starch films

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ABSTRACT

Water sorption of gluten and wheat starch films as a function of water activity was studied using gravimetric step-change sorption experiments. Films of different thicknesses were used with the aim to vary the characteristic diffusion time and to get insights in the contribution of the polymer-chain rearrangement in the sorption behaviour. It is shown that both starch and gluten are in the glassy state for a water activity a_w below 0.9. From comparison of the dynamical sorption curves with a Fickian diffusion model, it is shown that water diffusion in gluten films seems Fickian for $a_w < 0.7$, and non-Fickian for $a_w > 0.7$, while for starch films, non-Fickian sorption behaviour is observed for $a_w > 0.1$. The results show that polymer-chain rearrangement and the stress built up in the matrix play an important role in the sorption dynamics of these films. Even when the material is in the glassy state matrix relaxation phenomena play a role in the sorption behaviour of starch and gluten.

1. Introduction

Many important quality features of dry cellular solid foods, like e.g. crispness of cereals, snacks and bread crust, as well as stickiness, caking, and collapse of powders, are strongly affected by the water content and water transport during processing and storage. A good understanding of water uptake and migration is therefore of prime importance to control the quality of dry cellular solid foods. These foods are systems with a high level of complexity. The complexity involves their chemical composition (multicomponent), their morphology (different compartmented phases), their physical features (different aggregation states), and also their dynamical complexity (non-equilibrium systems). As a result, water sorption in cellular solid foods is not well understood yet. Knowledge about fundamental issues is needed in order to enable the increase in shelf life and to control the functional properties of these composite food products.

Water transport phenomena in complex food systems may be interpreted by understanding related phenomena in amorphous bio-polymers (Peppas and Brannon-Peppas, 1994). Cellular solid foods are composed of bio-polymers (carbohydrates and proteins) that are in an amorphous or partial amorphous state. Consequently, amorphous bio-polymers are relevant model systems to study water sorption and transport phenomena. Levine and Slade (1990) considered bio-polymers to behave similarly to synthetic polymers. Since a large amount of knowledge about diffusion processes in synthetic polymer–solvent systems has been acquired, this can be used as a starting point to increase our understanding of the diffusional behaviour in bio-polymers and hence in food systems.

Diffusion processes in polymer–solvent systems often deviate from the laws of the classical theory of molecular diffusion described by Fick's law (Vrentas et al., 1986). Solvent diffusion behaviour in polymers may be classified as Fickian, non-Fickian (anomalous, visco-elastic), Case II or super Case II (Peppas and Brannon-Peppas, 1994; Vrentas et al., 1986). Fickian diffusion (Case I) can be observed for polymer–solvent systems when the transport of the solvent is controlled by its concentration gradient. In this situation the dynamics can be described by a single diffusion coefficient. Another (extreme) situation is Case II, where the water transport is controlled by the relaxation of the polymer and described by a characteristic relaxation constant. Anomalous transport is the process with intermediate characteristics with polymeric chain rearrangements occurring on a time scale comparable to that of the diffusion process. This requires two or more parameters to describe

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Abbrevations: CK, Couchman–Karasz; DSC, differential scanning calorimetry; FH, Flory–Huggins; FV, free volume; FHFV, Flory–Huggins-free-volume; RH, relative humidity.

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the coupling of the diffusion and relaxation phenomena. Several theoretical models have succeeded in describing the diffusion process considering the physical properties of the polymer network and the interactions between the polymer and the solvent itself (for a review see e.g. Masaro and Zhu, 1999).

The physical mechanism of water transport in polymer systems can be determined by a variety of experimental techniques such as gravimetric sorption analysis, membrane permeation, fluorescence spectroscopy and dynamic light scattering (Masaro and Zhu, 1999). The simplest and most common method is the gravimetric sorption analysis. Differences in diffusional behaviour can be observed by performing gravimetric sorption experiments that traverse large ranges of temperature, water concentration, and polymer molecular weight or by varying the characteristic time of an experiment (Vrentas et al., 1986). The latter can be realized for step-change sorption experiments by varying the thickness of the sample and for oscillatory sorption experiments by varying the oscillation frequency (Vrentas et al., 1986).

Several gravimetric studies on sorption behaviour of biopolymer systems have been published. Step-change sorption experiments were carried out in dry biscuit (Guillard et al., 2004), wheat gluten based films (Guillard et al., 2003), and potato starch based films (Masclaux et al., 2010). In all cases, water sorption kinetics was described by Fickian diffusion including a water concentration dependent diffusion coefficient. Del Nobile and co-workers developed a model where Fickian diffusion, including a concentration dependent diffusivity, and polymer relaxation were combined to describe the sorption relaxation kinetics in chitosan films (Del Nobile et al., 2004). Meinders and co-workers published oscillatory and step-change sorption experiments in bread crusts. The sorption dynamics at low a_w during step-change experiments were described by the Fickian diffusion model. Nevertheless, it was shown that relaxation phenomena play a role in water sorption dynamics for large a_w (van Nieuwenhuijzen et al., 2008, Meinders and van Vliet, in press). Furthermore it was shown that the water sorption behaviour of small bread particles could be reasonably well described by the free-volume theory (Meinders and van Vliet, 2009). The water sorption behaviour in these small bread crust particles is dominated by the sorption behaviour of the components, while on a larger scale, when the water activity of the solid material is can be considered in equilibrium with that of the air phase and the water migration distance is large compared to the cell wall thickness of the solid matrix, the overall water flux through the system is dominated by the flux through the air phase and thus by the morphology of the porous cellular material (Esveld et al., in press-a, b, Voogt et al., 2011). For the outer crust of bread, which is important for the crispness sensation, the water migration distance is small compared to the cell wall thickness so that the water transport in the solid material becomes important.

The objective of the current work is to get a better understanding of the water vapour sorption of the main components of wheat flour. Therefore films of gluten and starch were made in order to reduce the complexity of the systems and study their water sorption behaviour without the interference of another component. Gravimetrical step-change sorption experiments were performed and compared with a Fickian diffusion model in order to locate water activity regions that show different diffusional behaviour. Films of different thicknesses were used with the aim of varying the characteristic diffusion time and getting insights into the contribution of polymer matrix relaxation in the sorption behaviour. The glass–rubber transition of the studied systems was taken into account as a first approach to discriminate possible physical mechanisms involved in water transport.

2. Materials and methods

2.1. Preparation of films

2.1.1. Gluten films

Gluten (Protimax 137) was purchased from Avebe Latenstein (Nijmegen, the Netherlands). Gluten films were prepared, adapting the method presented by Gontard et al. (1992). Wheat gluten (7.5 g) was dispersed in 100 ml of 70% w/w solution of water/ethanol through a sieve at 313 K. The pH of the solution was adjusted to pH = 4 with acetic acid. The film-forming solution was then immediately poured on a levelled polypropylene dish (97 mm in diameter). Different quantities of solution were poured onto the dishes in order to obtain different film thicknesses. The film-forming solution was dried in a climate chamber at 303 K and 80% RH for 48 h to evaporate volatile solvents (ethanol, acetic acid, and water). These conditions were chosen in order to obtain a non-brittle film, and therefore the film could be handled. The result was a yellowish translucent self-supporting film. This film was cut in the desired shape for further use.

2.1.2. Starch films

Native wheat starch (Excelsior) was purchased from Avebe (Veendam, the Netherlands). Starch films were prepared from a starch/water solution by casting. Starch (5% w/w) was dispersed in distilled water and heated up until 368 K for 10 min to allow complete gelatinization. The solution was instantaneously poured onto the levelled polypropylene dish (97 mm diameter). Different quantities of solution were poured onto the dishes in order to obtain different film thicknesses. The film-forming solution was dried in a climate chamber at 296 K and 80% RH for 48 h to evaporate the volatile solvent (water). The result was a translucent self-supporting film which could be easily removed from the dish in which it was formed. This film was cut in the desired shape for further use. In order to melt the crystals that might have been formed during film formation, the films were heated in a stove at 348 K for 1 h. Thermo modulated differential scanning calorimetry (DSC Q200, TA Instruments, New Castle, USA) was used to investigate the recrystallization of the starch. The starch films were weighed and distilled water was added at a 3:1 (v/w) water to sample ratio in stainless steel pans (TA Instruments Inc., New Castle, USA). The samples were heated from 283 K to 403 K at a rate of 10 K/min. The DSC thermograms did not exhibit an endotherm for melting of the recrystallized starch.

2.2. Film thickness

The thickness of the films used in the step-change sorption experiments was measured before this experiment with a hand micrometre (accuracy 1 μm) at five random positions on the film and an average value was calculated. The thickness standard deviation for both films is around 5%.

2.3. Moisture content

The moisture content of the samples was determined gravimetrically by drying the samples in an oven at 378 K for at least 48 h in order to obtain constant weight.

2.4. Dynamic water vapour sorption experiments

Dynamic water vapour sorption experiments were performed using an automatic multi-sample moisture sorption analyzer SPSx-11μ (Projekt Messtechnik, Ulm, Germany).