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Water transport mechanisms in wheat gluten based (nano) composite materials

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ABSTRACT

An in depth investigation of water transport mechanisms has been undertaken on extruded wheat gluten (WG)/clay materials, which have been shown to display either a nanocomposite or a microcomposite structure depending on the nature of the nanoclay used (i.e. unmodified sodium montmorillonite (named HPS) or organically modified montmorillonite (Cloisite®30B), respectively). The interplay of two concomitant phenomena has been evidenced: first a plasticization of protein chains by water that favors water diffusivity and, second, a clusterization of water as revealed by the Zimm and Lundberg and Guggenheim–Anderson–de Boer theories leading to a slowdown and finally a decrease in water mobility within the polymer. Comparison between liquid and vapor water diffusivity showed a strong impact of the state of the water phase in contact, the water liquid diffusivity being three fold higher than water vapor diffusivity. This Schroeder's paradox could be related to the microporous structure of the extruded wheat gluten materials in which liquid water moves due to an additional capillary phenomenon resulting in a higher apparent diffusivity. As well predicted by the Bharadwaj's tortuosity-based mathematical model, the achievement of a well-exfoliated structure (as observed in the case of the WG-HPS system) has no effect on water diffusivity, whether the phase in contact is liquid or vapor. On the contrary, such a structure led to a significant reduction of the liquid water uptake that might be ascribed to water hydrogen bondings established between the hydrophilic sites of wheat gluten and the unmodified montmorillonite, in turn reducing their availability for water.

1. Introduction

In recent years, wheat gluten, a by-product of the starch industry had drawn great deal of attention for the development of agromaterials, due to its large availability at a reasonable price (around 1.3–1.4 €/kg), interesting functional properties, biodegradability and non-ecotoxicity [1]. Owing to good thermoplastic properties, wheat gluten can be processed by extrusion at temperature as low as 60 °C in the presence of hydrophilic plasticizers [2]. Wheat gluten-based materials are known to be water-sensitive due to the hydrophilic nature of many amino acids constituting their primary structure and to the substantial and necessary amount of hydrophilic plasticizer (glycerol, water) required to impart thermo-processability and film flexibility [3–5]. Such a water sensitivity is revealed by an important swelling when they are immersed in liquid water and by a high water adsorption and poor water barrier properties in high moisture conditions [6,7]. Thus, wheat gluten, as most of bio-sourced materials, required improvement of water resistance to offer sustainable applications.

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A recent work has shown that the water sensitivity and water transport properties could be slightly modulated by increasing the cross-linking of the wheat gluten protein network through a heat treatment [8]. One other route to enhance water resistance of bio-sourced materials that has received considerable attention in the last ten years is the introduction of layered silicates, such as montmorillonites (MMTs), within the polymer matrix to create a nanocomposite structure [9,10]. A barrier effect is usually expected from the introduction of nanoclays in a polymer matrix. This effect depends on clay content, clay nature (pristine or organoclays) as well as on clay dispersion state (size aspect ratio and orientation). Complete delamination and dispersion of nanoclays within the matrix, which are influenced by the nature of both the clay and the matrix, are generally considered to be at the origin of a tortuosity effect that is expected to result in an apparent diffusivity decrease. As previously highlighted by Chevillard et al. [11], the addition of nanoclays within an extruded wheat gluten (WG) matrix led to either a well-exfoliated nanocomposite structure or a microcomposite structure, depending on the chemical surface properties of the layered silicates used. A well-exfoliated nanocomposite structure was achieved in the case of unmodified MMT (HPS) due to the establishment of hydrogen bindings between the hydrophilic MMT and the protein chains of WG. On the contrary, a microcomposite structure was obtained for WG materials filled with organically modified MMT, as it is the case for Cloisite 30B (C30B), due to the predominant effect of the hydrophobic character of such nanoclays. These authors also demonstrated that the addition of nanoclays within an extruded WG matrix had little effect on liquid water diffusivity even when a well-exfoliated nanocomposite structure was obtained, while the maximal water uptake at equilibrium was significantly reduced. It appeared thus that water transport mechanisms in WG matrices are complex and require deeper investigations. In particular, it would be very interesting to validate the effect of the creation of a nanocomposite structure on both liquid and vapor water transport mechanisms (solubility and diffusivity) by identifying which parameter, between diffusivity (D) and solubility (S), is responsible for the decrease in water sensitivity of nanocomposite wheat gluten-based materials.

In an attempt to solve these issues, the influence of clay nature (pristine or organoclays) on the water vapor sensitivity of WG-based materials was investigated by measuring the water vapor sorption kinetics using a Cahn microbalance. Three types of formulations have been tested, an unfilled WG material and WG materials filled with either an unmodified sodium MMT or an organically modified MMT. Wheat gluten/clay (nano)composites were prepared via bi-vis extrusion, which is the process the most largely used at the industrial scale. Water vapor transport properties (sorption and diffusivity) evaluated from sorption kinetics were compared with liquid water transport properties, and then discussed in relation to the structure and thermodynamic characterization of the materials. To understand water transport mechanisms, water sorption isotherms were modeled using the Guggenheim–Anderson–de Boer equation and the water clustering phenomenon was evaluated owing to the Zimm and Lundberg's theory.

2. Experimental section

2.1. Materials

Commercial vital wheat gluten was kindly supplied by Syral (Belgium) under the reference AMYGLUTEN 110. Its moisture and protein content was approximately 10% and 80%, respectively. Two types of nanoclays were used as received in this study: an unmodified sodium montmorillonite provided by Laviosa (Italy) under the reference HPS and an organically modified montmorillonite carrying a methyl, tallow, bis-2-hydroxyethyl quaternary alkylammonium salt, supplied by Southern Clay (Rockwood Clay Additives GmbH, France) under the reference Cloisite®30B (C30B). Cation exchange capacity values are 129 meq.100 g^{-1} for HPS and around 93 meq.100 g^{-1} for C30B. Further information (interlayer distance, organic content, interlayer cation organic cation saturation 3D models organic cations present in C30B) on nanoclays are given in Chevillard et al. [12]. Chemicals, unless specified separately, were purchased from Sigma Aldrich in pure analytical quality.

2.2. Preparation of wheat gluten-based materials

The preparation of wheat gluten-based materials was extensively detailed in a previous work [11]. Briefly, wheat gluten-based materials were prepared via bi-vis extrusion using a co-rotating twin screw extruder (Coperion, ZSK25, Stuttgart, Germany). The total length of the screw was 42D and the screw speed was set at 150 rpm. The first and second heating zones were constantly set at 40 °C and the 10 other heating zones at 60 °C. The ratio nanoclays/wheat gluten was adjusted to have a final inorganic filler content corresponding to 5 wt.%. Water, used as plasticizer, was fed with a weight pump with a ratio water/powders of 2/405 (w/w). After extrusion, extrudates were cooled and air-dried before being cut using a pelletizer and then allowed to dry in ambient room conditions until constant weight. Water content of final granulates was 9 wt.% (measured after drying 24 h at 105 °C). They were characterized by a height of 2.3 ± 0.2 mm, a diameter of 5.1 ± 0.4 mm, and a weight of 53 ± 2 mg. Samples were packed in polyethylene hermetic bags and stored in dark room at 4 °C until experiments.

Prior to measurement of water vapor sorption kinetics, granulates were cut into thin discs of about 400 μm of thickness to allow further diffusivity identification (see Section 2.4). To do this, granulates were saturated at 100% relative humidity (RH) and then cut using a vibration microtome (Microm HM650V, Microm Microtech, France). Then thin discs were stored at 0% RH on silicagel for at least 48 h before being used. Thickness of these thin discs was measured using a micrometer (Braive Instruments, Chécy, France). Prior to DSC measurement, granulates were ground using a Dangoumeau ball mill (Dangoumeau, Prolabo, France) to obtain a final particle size of about