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Interfacial rheological and wetting properties of deamidated barley proteins

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ABSTRACT

The goal of the present study is to provide a detailed description of rheological and wetting properties of barley protein and establish a linkage between these properties and the protein structure. In order to achieve this goal, we first measure the interfacial properties, including interfacial tension and interfacial rheology (viscous modulus and elastic modulus). Secondly, we investigate the secondary structural changes of the deamidated barley protein and hydrolysates through FTIR. Thirdly, we measure molecular weight by using HPLC. Finally, we determine the wetting properties with dynamic contact angle measurements. The solubility of barley protein can be greatly enhanced by applying deamidation process. After deamidation, more flexible secondary structures are detected through FTIR analysis. These changes in secondary structure are reflected in interfacial properties. The interfacial protein concentration and rheological properties of protein samples are determined by interfacial tension measurement. The equilibrium interfacial tension and contact angle for protein solution decrease as the concentration of protein increases. The deamidated protein with large molecular weight parts shows the highest elastic modulus, while hydrolysates with low molecular weight shows the highest viscous modulus. The results also indicate that deamidated protein forms more stable film at interface compared to the low molecular hydrolysates.

1. Introduction

Seeping a nice cold beer in hot summer day to applying cosmetics on skins – all these modern day consumer products contain barley as one of the key ingredients. Followed by wheat, rice and corn, barley is ranked as the fourth most widely cultivated cereal in the world. Barley was the first food grain consumed by human race before wheat and rice became more popular. Recently, due to the growing attentions on health benefit of β-glucan, barley is regaining more and more interest as a food ingredient. Moreover, barley protein demonstrated good emulsifying property because of its unique structure with balanced hydrophobic and hydrophilic amino acid residues (Wang et al., 2010). It is also demonstrated that barley protein, with high molecular weight polypeptides, could aggregate to build a strong film at oil-water interface. The high molecular weight polypeptides absorb and unfold at the interface. They greatly increase the stability of emulsion system by inhibiting close contact between each oil droplets, thus diminishing the chance of flocculation and coalescence (Wang et al., 2010). A limited knowledge is available about the wetting and interfacial rheology properties of these barley proteins. The goal of the present work is to provide detailed description of such properties and establish a linkage between these properties and its structure.

With prolamin and glutelin as the major fractions, barley protein has very poor solubility, hence it is quite difficult to quantify the surface rheology and wetting properties of such proteins. We have successfully demonstrated in our recent studies that the solubility can be enhanced by more than 60% by the deamidation process (Zhao, Tian, & Chen, 2011). By investigating the surface rheology and wetting properties, we will reveal more insight into the interfacial dynamics. Surface tension decides the magnitude of the surface forces whereas the contact angle dictates the direction of the surface forces. Surface forces are one of the major forces for manipulating fluid at micro-scale, particularly in micro-fluidic

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devices. Hence, it is important to have the complete information about the surface forces. On the other hand, the information related to the interfacial rheology, including the interfacial elasticity and viscosity, is very much needed for the food industry (Bilgi & Çelik, 2004; Brugger, Vermant, & Richtering, 2010; Maldonado-Valderrama & Patino, 2010; Romero et al., 2012; Tadros, 1994; Wilde, Mackie, Husband, Gunning, & Morris, 2004). Structural and mechanical properties of the interface affect the stability, production, and texture of the final product (Maldonado-Valderrama & Patino, 2010). The surface rheology is connected to the stability of the emulsion, and elasticity of the interface, which may play an important role in deciding such properties. In recent years, interfacial rheology is a widely studied topic for different colloidal solutions (Bos & van Vliet, 2001; Chen, Prokop, Susnar, & Numann, 1998; Kihm & Deignan, 1995; Kim, Koczo, & Wasan, 1997; Liggieri, Ferrari, Mondelli, & Ravera, 2005; Maldonado-Valderrama & Patino, 2010; Waghmare & Mitra, 2013) but very little attention has been given to characterize such properties for barley proteins.

Traditionally, the major thrust in the research communities has been in the detailed understanding of the selective nutrients of barley such as starch and β-glucan. In recent years, deamidation and hydrolysis have been applied to barley proteins to improve its solubility (Yalcin & Celik, 2007; Zhao, Tian, & Chen, 2010, 2011). Deamidation refers to a chemical reaction in which an amide functional group is removed, whereas hydrolysis refers to a chemical reaction in a molecule of water are added to the protein molecule chain. The solubility of barley protein hydrolysates have been increased by 10%–60% based on different parameters (Yalcin & Celik, 2007), while the solubility of deamidated barley proteins have been improved by more than 60% with a 10% deamidation degree. The increase in solubility improves barley protein functionalities, such as foaming and emulsifying capacity, which has been studied quite extensively (Yalcin, Celik, & Ibanoglu, 2008; Zhao et al., 2010, 2011). It was reported that the foaming properties of both barley protein isolates (BPI) and barley protein hydrolysates were greatly influenced by the pH of the solution. It was found that the hydrolysis did not improve the foaming ability (Yalcin et al., 2008). Zhao et al. demonstrated that deamidated barley can effectively improve the emulsifying properties of barley protein (Zhao et al., 2010, 2011).

From the existing literature, it suggests that even though significant progress has been made in addressing properties like solubility, emulsifying and foaming capacity for barley proteins, however, a lack of information still exists in characterizing the interfacial characteristics and rheological properties of these proteins and eventually connecting these properties to the protein structure and protein molecular weight. In this present study, we have characterized the wetting properties, the interfacial tension and the interfacial rheology by using Krüss DSA 100; and the protein secondary structure by using FTIR (Fourier Transform Infrared Spectroscopy); and the weight-average molecular weight of each sample by using HPLC (high-performance liquid chromatography).

2. Material and methods

2.1. Materials

Barley grains (Metcalfe) were kindly provided by Alberta Agricultural and Rural Development, Lacombe, Alberta. Barley Protein Isolates were extracted from barley grains based on our previous work (Zhao et al., 2010, 2011). The commercial canola oil was purchased from a local supermarket (Edmonton, AB, Canada). The viscosity of canola oil is 78.2 m Pa at 20 °C and its density is around 0.914–0.917 g/cm^3 at room temperature (Przy-bylski et al., 2005). It has been reported that the impurities in vegetable-oil may lead to significant changes in the interfacial properties (Gaonkar, 1989; Gunstone, 2009) and purified oil needs to be used for such experiments. One of the major concerns with selected commercial canola oil is the lack of information about its synthesis-process, impurities and degradation. Therefore, we cannot standardize the purification process for the selected oil and to develop such process is beyond the scope of this present study. Hence, for the present study, we have neglected the effect of such impurities. Additionally, the available commercial oils has lots of variations in its properties due to their various sources and particular batch-processing condition hence, the development of standard purification process is beyond the scope of this study. Moreover, the impurity part in all kinds of barley protein isolates can be left over carbohydrates, fibre, and minerals present in barley grain or salts produced by neutralization during protein extraction. These contaminants do not have surface activities. So we have neglected their influence on interfacial properties measurement. The deionized (DI) water was obtained from Millipore system, and the corresponding equilibrium surface tension of pure water in air was 67.2 ± 1.8 mN/m at room temperature (22 °C). All other chemicals were of reagent grade. Contact angle measurements are performed on the polydimethylsiloxane (PDMS) substrates that are prepared with the Sylgard 184 Silicone Elastomer kit.

2.2. Methods

2.2.1. Barley protein preparation

Barley protein isolates were extracted from barley grains using alkaline extraction, based on methods reported by Wang et al. (2010). Pearled barley flour was dispersed in alkaline solution for 1.5 h. After extraction, the supernatant was separated by centrifuge, followed by adjusting the pH to around 5 to precipitate the barley protein. All precipitated barley proteins were then freeze-dried into powder and stored at 4 °C for further utilization. The barley protein isolates were prepared by one time production process. These isolates were further used for preparing the deamidated and hydrolysate samples. Additional details on the protein sample preparation can be found elsewhere (Wang et al., 2010).

2.2.2. Deamidation

The deamidated barley protein, obtained from barley protein isolates (around 1000 g in total) described above, was prepared by alkaline methods, the details of which are already reported in the literature (Zhao et al., 2010, 2011). The deamidation process was conducted in triplicates, and the average deamidation degree of the protein samples (measured by Ammonia Assay Kit) was recorded as 13% (named as deamidated protein) and 33% (named as highly deamidated protein), respectively. Such two samples of deamidated proteins were used for further analysis. Deamidated barley protein was dispersed in DI water and pH was maintained at 7.0 using 0.5 M NaOH or 0.5 M HCl solution. The dispersion was constantly stirred overnight using magnetic stirrer at room temperature, followed by centrifugation at 1200 × g for 10 min. The clear supernatant was separated from the top of centrifuged protein suspension, and its protein concentration was determined by dye assay with bovine serum as the standard. The concentration of protein solution was expressed as a percentage of protein content divided by the total volume of supernatant serum. In order to obtain the protein solution with different concentrations, initially a protein solution of 7% in concentration was prepared and subsequent dilution process was performed to achieve different protein concentrations (such as 1%, 2%, 3%, 4%, 5%).