



Modulating state transition and mechanical properties of viscoelastic resins from maize zein through interactions with plasticizers and co-proteins



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ARTICLE INFO

Article history:

Received 19 April 2014

Received in revised form

11 August 2014

Accepted 19 August 2014

Available online 6 September 2014

Keywords:

Zein

Viscoelasticity

Glass transition

Secondary structure

ABSTRACT

Viscoelastic properties have been observed in maize zein above its glass transition temperature; however, current understanding of how these viscoelastic polymers can be further manipulated for optimal performance is limited. Using resins formed via precipitation from aqueous ethanolic environments, this study presents a framework for understanding how state transition and viscoelastic properties of zein can be controlled through interactions with plasticizers and co-proteins. Resins plasticized with oleic acid exhibited reduced water absorption and glass transition temperatures and formed low elasticity/high extensibility resins. Incorporation of casein increased water absorption and glass transition temperatures and imparted a four-fold increase in material strength/elasticity, as compared to zein alone. Plasticizers and co-proteins influenced zein secondary structure in the resin systems by decreasing and increasing low-frequency β -sheet structures (1640–1615 cm^{-1}), respectively. This work demonstrates that specific protein/plasticizer and protein/co-protein interactions are capable of promoting fundamental differences to zein's behavior in viscoelastic systems and could serve as a basis for improving the functional properties of this underutilized material in various food and biomaterial applications.

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1. Introduction

The zein protein fraction is a complex mixture of alcohol-soluble proteins present in the maize endosperm, which are classified into four subgroups differing in molecular weights and abundance: α -zein ($M_r = 19$ and 22 kDa, 75–85% of total protein), β -zein (14 and 16 kDa, 10–15%), γ -zein (28 kDa, 5–10%), and δ -zein (10 kDa, trace amounts) (Shewry and Tatham, 1990). Zein has been at the center of a continuing research effort for over a century; however, interest in its properties has intensified in recent years due to the protein's availability as a byproduct of the corn wet milling industry. Much of this research has looked to capitalize on the protein's versatility as a structurant in a variety of systems. Such efforts include using zein as a possible wheat substitute in gluten-free dough systems (Lawton, 1992), as biocompatible scaffolds to aid in hard tissue repair and regeneration (Gong et al., 2006), and in various film and

coating applications for food and biomaterial systems (reviewed in detail by Taylor et al., 2013).

Several structure–function relationships have been established regarding zein's ability to function as a viscoelastic material. Viscoelastic properties were first demonstrated in zein-starch dough systems, provided the protein was hydrated and mixed above its glass transition temperature (Lawton, 1992). Secondary structural transformations have also been observed in zein's viscoelastic state, with notable increases in β -sheet structures at the expense of α -helical domains (Mejia et al., 2007).

Two approaches have demonstrated the ability to influence zein's viscoelastic properties: (i) plasticizers and (ii) co-protein interactions. Plasticizers are commonly employed to enhance polymer flexibility by means of reducing its glass transition temperature such that the polymer exists in its rubbery state at lower temperatures and/or moisture contents. Oleic acid in particular has been the subject of several investigations on zein plasticization, due to its demonstrated strong ability to influence the microstructural and tensile properties of zein film and resin systems (Lai and Padua, 1997; Budi Santosa and Padua, 1999). To explain the oleic acid's plasticizing effect on zein, Lai et al. (1999) proposed that oleic acid

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forms intermittent, liquid-like phases, which surround stacked zein platelets and improves material flexibility by forming a three-dimensional sponge-like network (Wang et al., 2008). More recent work on zein film systems alludes to a somewhat more complicated mechanism of action. Xu et al. (2012) suggested that the amphiphilic nature of oleic acid changes the supermolecular structure of zein and allows the fatty acid to serve as an internal (i.e. molecular) plasticizer for the protein.

Co-protein interactions have been defined as the addition of a secondary protein source intended to fundamentally change the structural and rheological characteristics of a protein-based viscoelastic material (Erickson et al., 2012). In zein-starch dough systems, co-protein implementation was demonstrated as successfully imparting gluten-like viscoelastic behavior to improve the protein's potential for bread making applications (Mejia et al., 2012; Fevzioglu et al., 2012). Rombouts et al. (2012) found the extractability, kinetics of polymerization, and denaturation temperatures of BSA/gluten mixtures to be similar to those of isolated gluten systems. This finding could suggest a dominating role of gluten proteins over co-protein interactions with regards to the properties of the system. With the exception of some initial experiments addressing casein addition on the secondary structure of zein-starch doughs (Mejia et al., 2012), co-protein studies to date have yet to deviate from non-gluten systems. Detailed investigations of co-proteins from other sources could provide additional mechanistic insight necessary to expand the concept of co-protein interactions towards the more general area of exploring synergistic relationships in multi-protein systems and their capabilities to influence the micro- and macro-scale properties of viscoelastic materials.

The overarching goal of this collective work is to manipulate zein's properties to drive particular behaviors for desirable protein performance for many food and non-food applications. In this regard, we systematically investigated relationships between secondary structure, state transitions, and resulting mechanical properties of zein-based systems modified using the above mentioned plasticizer and co-protein approaches. The specific objective of this study was to explore the influence of each approach on the functional (i.e. rheological behavior at small and large deformations), material (i.e. moisture sorption and glass–rubber transitions), and structural properties (protein secondary structural features) of viscoelastic zein systems. Moreover, these effects were evaluated for the first time across multiple scales, to assess how viscoelasticity can be enhanced and manipulated in non-wheat cereal protein systems.

2. Materials and methods

2.1. Materials and resin preparation

Commercial zein (Z3625), oleic acid (364525), and casein (C7078) were purchased from Sigma–Aldrich (St. Louis, USA) and used as received without further purification. Viscoelastic resins were selected to model zein's array of potential applications (e.g. gluten-free dough systems, bioplastics, film/coating applications) and were prepared using a procedure adapted from Lai and Padua (1997). Zein (16%, w/v) was solubilized in aqueous-ethanol mixtures (75% EtOH, by volume) and heated to 75 °C using a temperature controlled magnetic stirrer (IKA RCT Basic, Staufen, Germany). Samples were mixed for 30 min, cooled to room temperature, and precipitated through a sevenfold addition of cold (4 °C) water. The resulting slurries were separated via centrifugation, decanted, and the insoluble material was collected as a soft solid. Resins were initially developed by hand until a cohesive mass was formed, then subsequently mixed by repeated passes through

a pasta press. Mixing through the pasta press was standardized to ensure resins had consistent mechanical histories by passing each resin through the press eight times (rotating the resin 90° clockwise following each pass) and then performing the same procedure on the opposite side. After mixing, samples were immediately analyzed for secondary structural and small and large deformation rheological changes. Samples for sorption experiments and thermal analysis were dried at 30 °C overnight, cryo-milled into fine powders (Retsch Grindomix GM200, Haan, Germany), and lyophilized for 24 h.

To assess the effects of plasticizers and co-proteins on resin properties, samples were prepared at 20% and 30% (w/w) oleic acid and 15% and 20% (w/w) casein addition levels, respectively. Plasticizers and co-proteins were added to zein solutions during mixing once samples reached 75 °C. Zein/oleic acid systems were mixed for 30 min, as previously described for isolated zein systems; however, zein/casein blends were allowed to mix for 3 h to avoid micro-heterogeneity between protein phases that was observed to be due to insufficient mixing times. Sample preparation for zein/casein systems was adjusted by pre-dissolving casein in the aqueous phase.

2.2. Dynamic water vapor sorption experiments

Dynamic water vapor sorption experiments were performed using an automatic multi-sample moisture sorption analyzer SPSx-111 (Projekt Messtechnik, Ulm, Germany). This instrument allows analyzing up to 23 samples simultaneously in a climatic chamber. In this instrument, the relative humidity (RH) inside the climatic chamber is conditioned by mixing a dry nitrogen gas flow with a gas flow saturated with water. The instrument is equipped with a dew point analyzer and a microbalance (WXS206SDU Mettler-Toledo, Greifensee, Switzerland) for accurate measurements of RH and weight, respectively. Water sorption is measured by measuring the variation in weight of a sample caused by changes in environmental RH. Weight changes were measured at time intervals of at least of 7 min. Samples were dried above P₂O₅ for at least three days before the start of the dynamic water vapor sorption experiments. The sorption measurement procedure involved an initial drying at 30 °C for 500 min followed by increases from 0% up to 90% RH at 10% RH increments and from 90% to 95% RH at 25 °C, with 50 h equilibration times at each stage. The mass at the maximum residence time was assumed to correspond to that of the moisture sorption isotherms. All analyses were performed in duplicate. Following data collection, moisture sorption isotherms for each sample were constructed, and the resulting profiles were modeled using the Guggenheim-Anderson-De Boer (GAB) equation (Anderson, 1946). Differences in sorption behavior between zein/plasticizer, zein/co-protein and isolated protein systems (e.g., zein and casein) were evaluated using one-way ANOVA with post-hoc Tukey tests used to form statistical groupings ($\alpha = 0.05$).

2.3. Modulated differential scanning calorimetry (MDSC)

MDSC was used to measure the glass transition temperature (T_g) of the zein resins. The materials were stored at 25 °C in hermetic sealed containers over different saturated salt solutions: KNO₃ ($a_w = 0.93$), KCl ($a_w = 0.84$), NaCl ($a_w = 0.75$), Ca(NO₃)₂ ($a_w = 0.51$), K₂CO₃ ($a_w = 0.432$), MgCl₂ ($a_w = 0.33$), CH₃CO₂K ($a_w = 0.22$) and LiCl ($a_w = 0.12$). Around 15 mg of powder were placed in open aluminum pans (Tzero pan, TA Instruments, New Castle, USA) and equilibrated to the desired water activity (a_w). In order to ensure that equilibrium was reached, the material was in parallel placed in AquaLab sample cups (Decagon Devices, Pullman, USA) and measured using a water activity meter (Decagon Devices, Pullman,

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