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Relationship between the glass transition temperature and the melt flow behavior for gluten, casein and soya

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Abstract

The effects of moisture content (25–45% wwb) and temperature (75–120 °C) on the viscosity of gluten, soya and rennet casein systems was studied using a capillary rheometer. An attempt was made to relate the viscosities to the glass transition temperature measured by differential scanning calorimetry, dynamic mechanical thermal analysis and the phase transition analyzer. The temperature where the material flowed was also determined by the latter technique. All three-protein systems showed shear and extension thinning. Over the shear rate range investigated ($\sim$1–10^3 s^{-1}), gluten had a substantially lower viscosity than the other two proteins, although the difference was less pronounced at the highest temperature studied. This low viscosity is reflected by lower values of the glass transition temperature, the melt flow temperature and the dynamic moduli E' and E'' in the rubbery state. The results are discussed in terms of the structure and heat induced changes for the three proteins and their relevance to food processing considered.

Keywords: Glass transition; Viscosity; Rheology; Extrusion; Differential scanning calorimetry; Dynamic mechanical thermal analysis; Phase transition analyzer; Plasticization; Protein

1. Introduction

The rheological behavior of protein ''melts'' at relatively low water contents ($\sim$15–50% wwb) is important for extrusion processing to produce food products such as texturised vegetable proteins (TVP). In addition, rheological behavior of gluten at low water contents is one factor influencing baking performance. There have been extensive studies on the viscosity of biopolymer melts using both pressure capillary rheometry and on-line extrusion rheometers (Bhattacharya, 1993; Breuillet et al., 2002; Fujio et al., 1991; Singh and Smith, 1999; Zhang et al., 1998). The variables generally studied are temperature, shear rate and water content (Colonna et al., 1989; Harper, 1981) although time dependent changes such as protein associations have sometimes been taken into account (Morgan et al., 1989; Remsen and Clark, 1978).

More recently there has been an increasing interest in the glassy state in foods (Blanshard and Lillford, 1993). The glass transition temperature (T_g) has been measured extensively for both carbohydrate and protein dominated systems, generally using differential scanning calorimetry (DSC) or dynamic rheological methods. Of particular interest for food applications has been the plasticizing role of water, sugars, polyols and other low molecular weight additives (Kalichevsky et al., 1992a, b, 1993; Morales and Kokini, 1997; Pommet et al., 2003; Roos, 1995; Zhang et al., 2005).

A technique that has been recently developed to provide information both about the glass transition temperature

Abbreviations: C–K, Couchman–Karasz; DMTA, dynamic mechanical thermal analysis; DSC, differential scanning calorimetry; G–T, Gordon–Taylor; PTA, phase transition analyzer; SPI, soya protein isolate; TVP, texturised vegetable protein

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and the melt rheology of biopolymer systems, particularly within the context of extrusion processing, is the phase transition analyser (PTA) (Plattner et al., 2001). In the PTA a piston applies pressure to material initially in a closed chamber and the temperature is increased. The glass transition temperature is associated with the point where the material softens, giving rise to increased movement of the piston. A flow temperature, T_f, can also be determined by replacing the closed die at the base of the chamber by one containing a small hole. T_f is taken as the temperature where the material flows as evidenced by a continuous movement of the piston at a constant temperature. For maize these two temperatures have been shown to differ for crops grown in different locations and have been related to extrusion behavior (Plattner et al., 2001).

In this study, three protein systems were examined: gluten, soya and casein. All three are used in extrusion processes, and gluten and soya are also important in baked products. Large amounts of information can be found in the literature about their structure and their properties in extrusion (Bhattacharya and Hanna, 1986; Chen et al., 1978; Damodaran and Paraf, 1997; Jao et al., 1978; Kitabatake and Doi, 1992). Gluten is an amorphous mixture of polypeptides that can be divided according to their functionality into monomeric and polymeric polypeptides. Monomeric polypeptides consist mainly of storage proteins called gliadins. They can aggregate by non-covalent interactions and contribute to the viscosity and extensibility of gluten. The vast majority of polymeric polypeptides are found in the glutenin fraction. Their amino acid compositions are similar to the gliadins. They are additionally stabilized by disulfide bonds, and tend to contribute to the elasticity and strain hardening behavior of gluten (MacRitchie and Lafiandra, 1997; Weegels et al., 1996). Soya consists of mainly 7S and 11S globulins. The 7S globulin is a trimer with a molecular weight around 150–200 kD (Fukushima, 1991). The 11S globulin is composed by six subunits and has a reported molecular weight of 300–400 kD (Fukushima, 1991; Pearson, 1982). Soya is used to produce TVP (Zhang et al., 2001) and is functionally involved in gelation and emulsification (Utsumi et al., 1997). Casein is the principal protein in bovine milk and consists of four components, α_{s1}- (38%), α_{s2}- (10%), β- (36%) and κ-casein (13%), which have molecular weights in the range of 19–26 kD and vary in hydrophobicity (Dalgleish, 1997). In milk, they are arranged in a micelle. In rennet-coagulated casein, micellar aggregation by hydrophobic bonding is thought to precede coagulation. Rennet casein performs well in dry spinning processes where it is extruded at temperatures of 70 °C and above (Visser, 1988).

One objective of the work described in this paper is to determine if more conventional methods for determining a glass transition temperature, DSC, dynamic mechanical thermal analysis (DMTA) and melt rheology (pressure capillary rheometry) are consistent with the information obtained from the PTA. A second objective was to obtain further information about the relationship between protein type, the glass transition temperature and the melt rheology.

2. Materials and methods

2.1. Materials

Rennet casein was obtained from Kerry Foods Ltd (High Protein Milk Extract, UK), gluten from RIBA S.A. (Glutenflor Supervital, Barcelona, Spain), and soya protein isolate (SPI) from Protein Technologies International (SUPRO 500E, Leper, Belgium).

2.2. Methods

2.2.1. Sample preparation

2.2.1.1. Capillary rheometry. Samples were prepared by adding the required amount of water to the powder and mixing with a Kenwood mixer (KenWood Mixer KMC 500, KenWood) to ensure homogeneity. Gluten forms a viscoelastic dough when mixed with water; so to prepare a homogenous powder it was necessary to freeze the hydrated material in liquid nitrogen, prior to milling it to a powder using a Knifeter 1095 Sample Mill (Foss Tecator, Hoganas, Sweden). For all three proteins water content was measured after each experiment performed with the capillary rheometer and was found to match the predicted water content.

2.2.1.2. DSC and PTA. Samples were equilibrated over P_2O_5 or saturated salt solutions of $MgCl_2$, $Mg(NO_3)_2$, KI, NaCl or KNO_3 or distilled water, which produced equilibrium relative humidities (RH) of 0%, 32.8%, 52.8%, 68.9%, 75.3%, 93.7% and 100%, respectively. Samples were equilibrated at room temperature for at least seven days.

2.2.1.3. DMTA. Samples were prepared by hydrating to ~17% water at 100% RH overnight and then pressing to a thickness of 0.5–1 mm in a mold under pressure $\sim 3.1 \times 10^3$ kPa at a temperature between 70 and 90 °C. Samples were then cut into $20 \times 8 \times 1$ mm strips and stored over salt solutions of various relative humidities (as for DSC and PTA: Section 2.2.1.2) to obtain a variety of water contents. Samples were stored for at least a week before measurements were made. Following equilibration, the water content was checked for agreement with predicted values and the measured values were used in the interpretation of the results. Before the measurement, the sample was coated with silicone oil (Dow Corning, USA) to avoid water loss.

2.3. Water content

Water contents were obtained by drying to constant weight at 105 °C.