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Polymer–polymer interactions in dextran systems using thermal analysis

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Abstract

Miscibility of carbohydrate polymers with similar chemistry at low water activity (a_w) was studied using dextran mixtures as model systems. Dextrans with weight-average molecular weights (M_w) ranging from 970 to 2,000,000 were used. Mixtures were prepared both by blending in powder form, and by dissolving in water and mixing, followed by freeze-drying. All mixture samples were equilibrated at $a_w = 0.33$, and their glass transition temperatures (T_g) were determined by thermal analysis.

For pure dextrans, T_g increased with M_w up to a critical M_w approximately between 23,000 and 30,000; reaching a plateau at higher M_w. The physical blend of dextrans in powder form resulted in dual T_g even after melting of the blends, indicating immiscibility; whereas for dextrans that were dissolved in water and mixed, only one T_g was observed, indicating miscibility. T_g of miscible systems was better related to the number-average molecular weight than weight-average molecular weight.
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1. Introduction

Food materials are composed of multiple polymer molecules with different chemistry and properties. Increasing demand for new food formulations, which have reduced carbohydrate or fat content and added nutraceutical compounds to deliver healthier foods to the consumer, require including or excluding various ingredients. The processability, texture, palatability and stability of these food products are greatly influenced by the compatibility/incompatibility between their polymeric components.

Thermodynamic incompatibility is the result of enthalpy and entropy barriers caused by the size and incompatible chemistry of different biopolymers and is a frequent phenomenon observed for many biopolymer mixtures. The incompatibility does not allow the formation of mutually miscible biopolymer mixtures, and results in phase separation (Antonov & Zubova, 2001). Incompatibility and phase separation are common in carbohydrate–protein systems, due to their molecular size and differences in hydrophilicity/hydrophobicity resulting from very different macromolecular chemistry, conformation and affinity for water (Grinberg & Tolstoguzov, 1997; Michon, Buvelier, Launay, Parker & Takerkart, 1995; Moraru, Lee, Karwe & Kokini, 2002; Tolstoguzov, 1991, 1998, 2000b, 2003).

Phase separation in carbohydrate–carbohydrate systems has also been observed in many cases, despite closer and more compatible chemical composition and structure of the components. Zimeri and Kokini (2003a–c) have shown that immiscibility occurs even in chemically similar systems, such as mixtures of inulin and amylopectin, which exhibited phase separation in limited moisture environments.

Amylose and amylopectin were found to be immiscible even in moderately concentrated (6%) aqueous solutions as the result of large differences in molecular weight (Kalichevsky & Ring, 1987). Immiscibility in the same system was confirmed by German, Blumenfeld, Guenin, Yuryev & Tolstoguzov (1992), who concluded that phase separation occurred due to precipitation of amylopectin, which reduced the quality of the solvent and thus facilitated the aggregation of amylose.

Dextran and locust bean gum (LBG) were found to be partially immiscible in aqueous solutions at 20 °C, forming a LBG-rich gel in the upper phase and a liquid lower phase that contained only dextran (Garnier, Schorsch & Doublier,

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1995). Phase separation was observed in LBG/starch and guar gum/starch mixtures of different concentrations, where separation increased at higher molecular weight of LBG (Ahmad & Williams, 2001). Concentrated solutions of dextran ($M_w = 472,000$) and amylose were immiscible as well (Kalichevsky, Orford & Ring, 1986).

Phase separation was also reported for mixtures of guar–amylopectin (Closs, Conde-Petit, Roberts, Tolstoguzov & Escher, 1999), dextran–agarose (Medin & Janson, 1993), gelatin–iota carrageenan (Michon et al., 1995), starch–glycerol (Forssell, Mikkila, Moates & Parker, 1997), sucrose–globular proteins (Antipova & Semenova, 1995), and starch–sorbitol (Gaudin, Lourdin, Le Botlan, Ilari & Colonna, 1999).

Miscibility/compatibility in polymer systems can be investigated by studying their phase transitions. Every amorphous polymeric system has a glass transition temperature (T_g), where segment motions of molecules, such as long range rotational and translational motions, are thermally activated (Ferry, 1980; Sperling, 2001; Tolstoguzov, 2000a). Differential Scanning Calorimetry (DSC) is one of the most commonly used thermal methods to establish miscibility/immiscibility in polymer blends through measurement of the glass transition temperature of components versus that of the blend. Perfectly miscible polymer mixtures have a single T_g located between the T_gs of the individual components, while immiscible blends show multiple T_gs, corresponding to the T_gs of each component in the mixture (Cocero & Kokini, 1991; Cascone, Polacco, Lazzeri & Barbani, 1997; Hartikainen, Lehtonen, Harmia, Lindner, Valkama, Ruokolainen & Friedrich, 2004; Shamblin, Taylor & Zografi, 1998; Sperling, 2001; Tolstoguzov, 2000a). DSC has been successfully used to show molecular miscibility/immiscibility of protein systems (Morales & Kokini, 1997, for 7S and 11S soy globulins); carbohydrate systems (Zimeri & Kokini, 2003a, for inulin–amylopectin mixtures); or carbohydrate–protein systems (Moraru et al., 2002, for starch–meat extrudates).

Understanding the molecular weight–glass transition relationship is important in characterizing and predicting the properties of biopolymers. The molecular weight of polymers can be characterized by the number-average molecular weight (M_n) and by the weight-average molecular weight (M_w)

$$M_n = \frac{\sum_i N_i M_i}{\sum_i N_i} = \frac{\sum_i w_i}{\sum_i \frac{w_i}{M_i}} \tag{1}$$

$$M_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i} = \frac{\sum_i w_i M_i}{\sum_i w_i} \tag{2}$$

where N_i is the number of specie i; M_i is the molecular weight of specie i; and w_i is the weight fraction of specie i (Sperling, 2001). The increase in glass transition temperature with molecular weight is reported by many authors

(Aklonis & MacKnight, 1983; Gropper, Moraru & Kokini, 2002; Ruan, Long, Chen, Huang, Almaer, Taub & Pulse, 1999; Slade & Levine, 1991a; Sperling, 2001), which is a consequence of the decrease in free volume with increasing molecular weight, caused by increased number of connected monomeric units in the system and decreased number of end groups (Aklonis & MacKnight, 1983; Sperling, 2001). The decrease in free volume and limited chain mobility lead to increase in the glass transition temperature. At very high molecular weights, the concentration of chain ends is negligible which results in the glass transition temperature to be independent of molecular weight at high molecular weights (Aklonis & MacKnight, 1983). There is also extensive indication in the literature that most thermodynamic properties of polymers depend on their number-average molecular weight (Aklonis & MacKnight, 1983; Billmeyer, 1984; Furuya, Iwai, Tanaka, Uchida, Yamada & Arai, 1995; Gabarra & Hartel, 1998; Van Krevelen & Hoftyzer, 1976).

Although it is, generally, agreed that incompatibility and immiscibility can occur in carbohydrate–carbohydrate mixtures, the molecular mechanisms that cause these phenomena are still poorly understood and are the subject of scientific debate. It is also important to point out that most of the existing studies refer to mixtures of carbohydrates with significant differences in their chemical structure and composition. The molecular and the thermodynamic basis of immiscibility in biological polymers of food origin are yet to be well established. The current research aims to further the fundamental understanding of molecular miscibility/immiscibility in carbohydrate mixtures using dextrans mixed in different modes, as a model for structurally compatible systems with different molecular weights.

2. Materials and methods

2.1. Materials

Seven dextrans with weight-average molecular weights of 970 (lot no: 289350); 5,200 (lot no: 288649); 10,800 (lot no: 291111); 43,000 (lot no: 285740); 67,200 (lot no: 279504); 482,000 (lot no: 286753) and 2,000,000 (lot no: 285645) (Amersham Biosciences, Piscataway, NJ) were used.
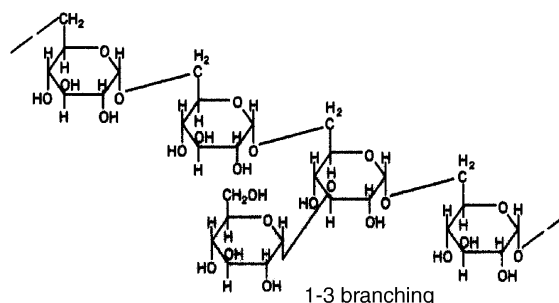

Fig. 1. Molecular structure of dextran.