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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.

Keywords: Dextran; Miscibility; Glass transition temperature; Molecular weight

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.

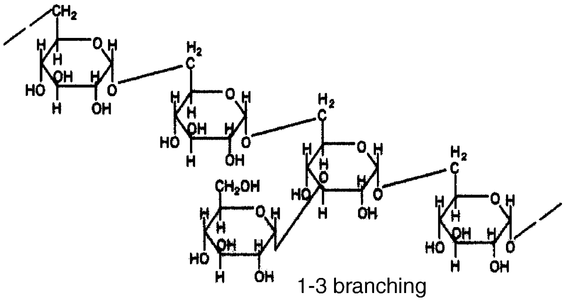

Fig. 1. Molecular structure of dextran.

Dextrans are high molecular weight polymers of glucose (Fig. 1) obtained by the fermentation of sucrose with the bacterium *Leuconostoc mesenteroides*, strain B512. About 95% of the linkages in dextran are α-D-(1–6), while the other 5% of linkages are α-D-(1–3), and account for branching (Ioan, Aberle & Burchard, 2000). Dextrans behave as flexible, slightly branched random coil polysaccharides rather than ideal random coils in dilute solutions (Nordmeier, 1993; Tvaroska, Perez & Marchessault, 1978) and are highly soluble in water at room temperature (Blondiaux, Jeney, Liley, Pugin, Sigrist, Heinzelmann & Spencer, 2001; Walsh, Arcelli, Ikoma, Tanaka & Mann, 2003). They are excellent model systems for food carbohydrate polymers as their molecular structures are similar and they are readily available in a wide range of molecular weights.

2.2. Moisture sorption isotherms of dextrans

Pure dextran samples were equilibrated at room temperature, at six water activity (a_w) values: 0.00; 0.12; 0.33; 0.52; 0.75; and 0.93, over P_2O_5 ($a_w=0.00$) and saturated solutions of the following salts: LiCl; $MgCl_2$; $Mg(NO_3)_2$; NaCl and KNO_3, respectively (Nyqvist, 1983). Moisture contents were measured using the AOAC method 950.46 (air-drying at 103 °C, 16–18 h), using a Thermolyne 9000 air-drying oven (Dubuque, IA). The water activity of each sample was measured using an Aqualab hygrometer (Decagon Devices Inc., Pullman, WA). Four replicate measurements were performed for each analysis. The moisture sorption isotherms were built by plotting moisture content vs. a_w. The experimental data was fitted to the Guggenheim–Anderson–DeBoer (GAB) model (Bell & Labuza, 2000; Singh & Heldman, 1993).

2.3. Sample preparation for thermal analysis

2.3.1. Pure dextrans

In order to understand the influence of molecular size on T_g, a systematic study of T_g vs. M_w at different a_w levels was carried out. All dextrans were used in pure powder form, as purchased from the manufacturer. The powders were equilibrated at the same water activities as in Section 2.2 at room temperature, in desiccators over P_2O_5 and super-saturated salt solutions.

Preparation of crucibles for thermal analysis. After equilibration, 20±2 mg of dextran was weighed into stainless steel, medium pressure DSC crucibles (Mettler Instrument Inc., Highstown, NJ). Then, the crucibles were sealed immediately.

2.3.2. Dextran mixtures

(a) *Mixtures formed by physical mixing of dextran powders*. After equilibration at $a_w=0.33$, pure dextran powders with $M_w=970$ and 2,000,000 were hand-mixed in equal amounts. Dextran mixture of 20±2 mg were weighed into DSC crucibles and the crucibles were sealed immediately. The same procedure was followed for obtaining mixtures of dextrans with $M_w=5{,}200$ and 2,000,000 at the same water activity ($a_w=0.33$).

(b) *Mixtures obtained by preliminary solubilization of dextrans*. 30% (w/w) (w.b.) polymer concentrated solutions of dextrans with $M_w=970$ and 2,000,000 were prepared and then mixed in w/w (d.b.) ratios of 50/50; 40/60; 30/70; 20/80 and 10/90, respectively, by hand-mixing at room temperature. All the solutions were freeze-dried for 36 h in a bench top freeze-dryer (The Virtis Company Inc., Gardiner, NY). The freeze-dried samples were ground at room temperature using a mortar and a pestle. The dry powders were then equilibrated at $a_w=0.33$. The same procedure was followed for preparing mixtures of dextrans with $M_w=5{,}200/M_w=2{,}000{,}000$ and $M_w=10{,}800/M_w=2{,}000{,}000$. From equilibrated mixtures, 20±2 mg was weighed into DSC crucibles and the crucibles were sealed immediately.

In addition to 30% (w/w) (w.b.) polymer concentrated solution of dextrans with $M_w=970/M_w=2{,}000{,}000$; 50 and 70% (w/w) (w.b.) solutions of the same dextrans in w/w (d.b.) ratio of 50/50 were also prepared.

2.4. Measurement of T_g by Differential Scanning Calorimetry (DSC)

Thermal analysis was performed using a TA 4000 Thermal Analysis System with a DSC 30-S Cell/TC11 TA Processor (Mettler Instrument Inc., Highstown, NJ). Forty-microliter, medium pressure, stainless steel crucibles with O-ring were used for the analysis. An empty crucible was used as a reference. Calibration of the instrument was performed using indium as a standard. A heating rate of 10 °C/min was used throughout the study. Pure dextrans equilibrated at different water activities were scanned between −50 and 200 °C, depending on the a_w values of the samples. Mixtures obtained by preliminary solubilization and equilibrated at $a_w=0.33$ were scanned between 30 and 130 °C; mixtures formed by mixing dextran powders and equilibrated at $a_w=0.33$ were scanned between 0 and 150 °C. Rescans were performed immediately after each scan, in order to erase the thermal history of the samples and to confirm the location of the T_g, based on the reversibility of this second order transition. The glass transition temperature of dextran systems was determined from the DSC rescans, at the midpoint in the shift of the heat flow baseline, which corresponded to the temperature at which one-half of the change in the heat capacity, ΔC_P, occurred. The reported data are the averages of at least two replicate measurements.

2.5. Steady shear rheological measurements

Pure dextran solutions containing 20 and 40% dextrans with molecular weights of 970; 10,800; 43,000; 67,200 and 482,000 were prepared. Steady shear rheological measurements were conducted with shear rates ranging from 10^{-2} to 10^3 s^{-1}, at a frequency of 6.28 rad/s (1 Hz), using a strain-controlled rheometer, Advanced Rheometric Expansion System (ARES), in conjunction with the Orchestrator data collection and analysis software (Rheometric Scientific, Inc., Piscataway, NJ). Cone and plate geometry (interplaten gap = 0.05 mm) with 50 mm diameter was used. In order to avoid dehydration during measurements, the samples were thinly coated with mineral oil. Zero-shear viscosity for each sample was determined by extrapolating the apparent viscosity to low values of shear rate. The reported results are the average of at least two replicate measurements.

3. Results and discussion

3.1. Moisture sorption properties of dextrans

The moisture sorption isotherms of dextrans with M_w = 970; 10,800; 43,000 and 2,000,000 showed a sigmoidal shape (Fig. 2), which is typical of most food systems (Roos, 1995; Serris & Biliaderis, 2001), and fitted well to the Guggenheim–Anderson–de Boer (GAB) model (lines in Fig. 2).

At the same a_w, the moisture content increased with M_w, indicating higher moisture sorption capacity of the higher M_w dextrans, which was also reflected by the values of the 'monolayer moisture content' (M_o) calculated with the GAB model, which were: 5.13, 7.03, 7.73, and 8.73% for the dextrans with M_w = 970; 10,800; 43,000; and 2,000,000, respectively. This was likely caused by the larger number of available sites for water binding in the higher M_w dextrans.

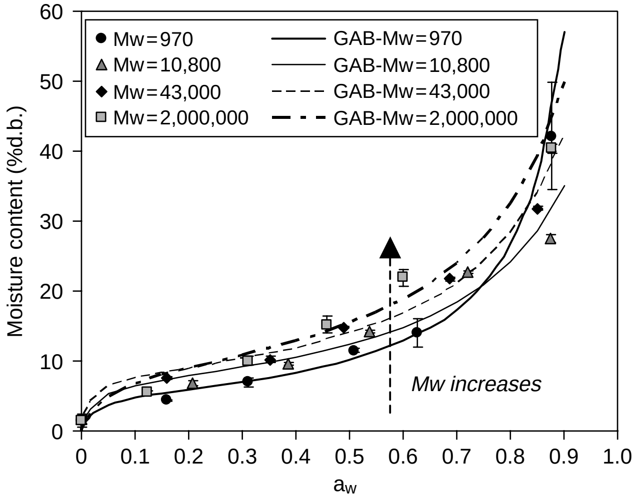

Fig. 2. Moisture sorption isotherms of dextrans.

The only exception to this trend was noted at $a_w > 0.7$ for the dextran with lowest molecular weight (M_w = 970), whose sorption isotherm exhibited a sharper slope at high a_w values (Fig. 2). The sharp increase in moisture content at high a_w values is characteristic of molecules with a crystalline behavior. It is, therefore, reasonable to believe that the low molecular weight dextrans could attain a crystal-like structure at high a_w, which would be possible given the 'rod-like' molecular organization reported by Gekko (1981) for dextrans with $M_w < 2,000$.

3.2. Effect of molecular weight on T_g of pure dextrans

Since at high water activities, T_gs were difficult to identify accurately due to the proximity of the ice melting transition, only the T_g values measured at $a_w < 0.5$ were used further in this analysis. As shown in Fig. 3, the T_g increased sharply with M_w up to a critical molecular weight, which was very close for all four data sets (Fig. 3 and Table 1). Above this critical molecular weight, T_g was relatively independent of molecular weight, as demonstrated by the very small slopes of the T_g vs. M_w plots, which confirms the earlier findings of Gropper et al. (2002). Given the fact that in this a_w range the lower molecular weight dextrans had lower moisture contents than the higher ones, as discussed in Section 3.1, the trend in T_g vs. M_w could not be attributed to the differences in moisture contents between dextrans with different molecular weights. If anything, the differences in moisture sorption properties have only decreased the differences in T_g between the high and low molecular weight dextrans.

The results were also consistent with the findings of Cowie (1975), who reported that the T_g dependence on molecular size for polystyrene, polybutadiene, polyisoprene and poly(α-methlystyrene) exhibited three different regions: a region of pronounced increase in T_g with molecular size, defined as the region where oligomers reached sufficiently long chain lengths to assume polymeric properties, followed by a region characterized by a lower, but steady increase in

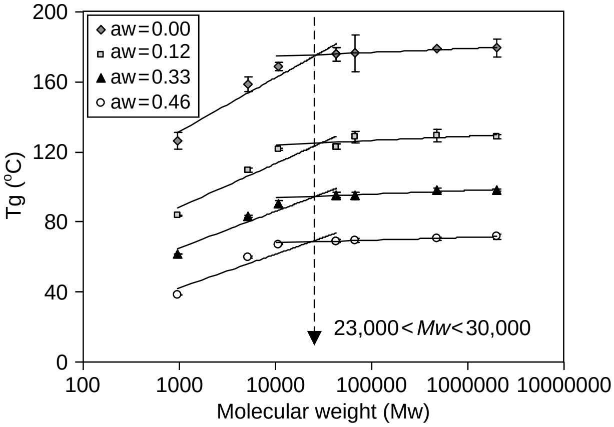

Fig. 3. Effect of molecular weight on the T_g of pure dextrans.

Table 1
Quantitative T_g vs. M_w correlations for dextrans at various a_w levels

a_w	$M_w \leq 43{,}000$		$M_w \geq 43{,}000$		Intersection	
	T_g vs. M_w	R^2	T_g vs. M_w	R^2	M_w	No. glucose residues
0.00	$y=13.30\ \mathrm{Ln}(x)+39.82$	0.92	$y=0.98\ \mathrm{Ln}(x)+165.58$	0.97	27,013	150
0.12	$y=10.77\ \mathrm{Ln}(x)+14.08$	0.88	$y=1.06\mathrm{Ln}(x)+114.29$	0.40[a]	30,368[a]	169[a]
0.33	$y=9.07\ \mathrm{Ln}(x)+2.49$	0.93	$y=0.89\mathrm{Ln}(x)+85.71$	0.87	26,256	146
0.46	$y=8.37\ \mathrm{Ln}(x)-15.51$	0.88	$y=0.68\mathrm{Ln}(x)+61.80$	0.99	23,269	129

[a] Weak correlation.

T_g with molecular size, and a plateau region, at very high chain length. Slade and Levine (1991b) have attributed the independence of T_g on M_w at large molecular weights to entanglement coupling that occurs in high molecular weight polymers, essentially leading to an infinite molecular weight bound network. It appears that dextran molecules attained their entanglement coupling molecular weight in the range of $10{,}800 < M_w < 43{,}000$. The value of M_w that marked the change in behavior was estimated from the intersection of the regression lines in Fig. 3 to be ranging between 23,000 and 30,000 (Table 1). These values should not be considered as the absolute M_w, where intermolecular entanglements occurred, but rather as an indicator of the M_w range, where these phenomena took place. This M_w range was also confirmed by steady shear rheological measurements, in which the shear rate dependence of apparent viscosity was determined for different molecular weights at two different concentrations. Zero-shear viscosity (η_0) vs. M_w of dextrans at 20 and 40% concentrations (Fig. 4) showed an increase in η_0 with M_w. The dependency became stronger (i.e. a steeper slope of the regression line) at a molecular weight of around 22,000, very close to the critical molecular weight estimated from the T_g vs. M_w plots in Fig. 3. This confirmed that the onset of intermolecular entanglements of dextran molecules would have chains of approximately 120–165 glucose units.

Fig. 3 shows that the glass transition temperature of pure dextrans decreased with increased water activity, as expected. T_g of bone-dry ($a_w=0.00$) dextrans with $M_w=970$ and 2,000,000 were 126.4 and 179.5 °C, respectively. The T_g of the highest M_w dextran was close to, but slightly smaller, when compared to the T_g of amylopectin from waxy maize starch ($M_w=400{,}000{,}000$ (Gluck-Hirsch, 1998)), which was reported to be at 185.6 °C by Zimeri and Kokini (2003a). Amylopectin is a glucose polymer as dextran, with α-D-(1–4) linkages together with some α-D-(1–6) linked branches (Jacobs & Delcour, 1998; Parker & Ring, 2001). When the T_g vs. M_w relationship for dextrans at $a_w=0.00$ (Table 1) was applied for amylopectin, a T_g value of 185 °C was obtained, which is very close to 185.6 °C, the experimental T_g value determined by Zimeri and Kokini (2003a). This could be interpreted as a validation of the T_g vs. M_w relationship for glucose polymers, including starch, which emphasizes the practical value of the findings of this paper.

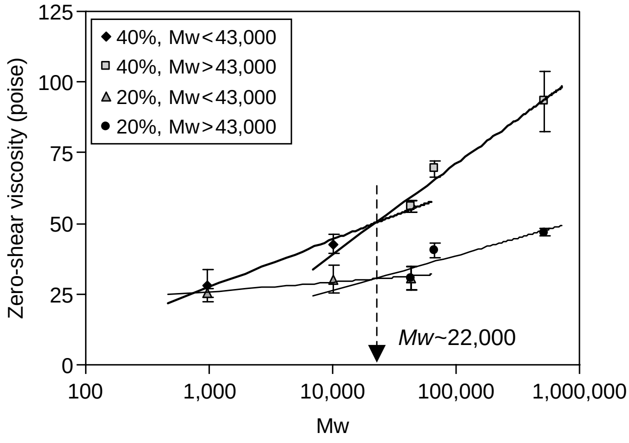

Fig. 4. Zero-shear viscosity behavior for 20 and 40% dextran solutions with different molecular weights.

3.3. Influence of mixture preparation method on miscibility of dextran systems

The miscibility study was conducted using dextran systems equilibrated at $a_w=0.33$. When dextrans with $M_w=970$ and 2,000,000 were physically blended in equal amounts in powder form, two separate T_gs, very close to the T_gs of the two individual components in the blend, were obtained (Fig. 5A). The lower T_g of the blend was 63.7 °C, which is very close to the T_g of pure $M_w=970$ ($T_g=61.7$ °C), and the higher T_g of the blend was 101.7 °C, which is close to the T_g of the pure $M_w=2{,}000{,}000$ ($T_g=98.2$ °C). To ensure that intimate mixing occurred between the two dextrans, the blends were subjected to successive heating and cooling cycles by rescanning them in the DSC multiple times. Even after this treatment, two separate T_gs were still observed in the DSC thermograms (Fig. 6).

Despite extensive physical mixing and thermal melting of the two dextrans, miscibility at macromolecular level was not achieved in the blends. This was most likely due to the limited free volume in the highly concentrated amorphous mixtures which did not allow the re-arrangement and interpenetration of the long dextran molecules. Branching of the large molecular weight dextran might have also prevented molecular interpenetration, through steric hindrance. Thus, the two molecular species retained their

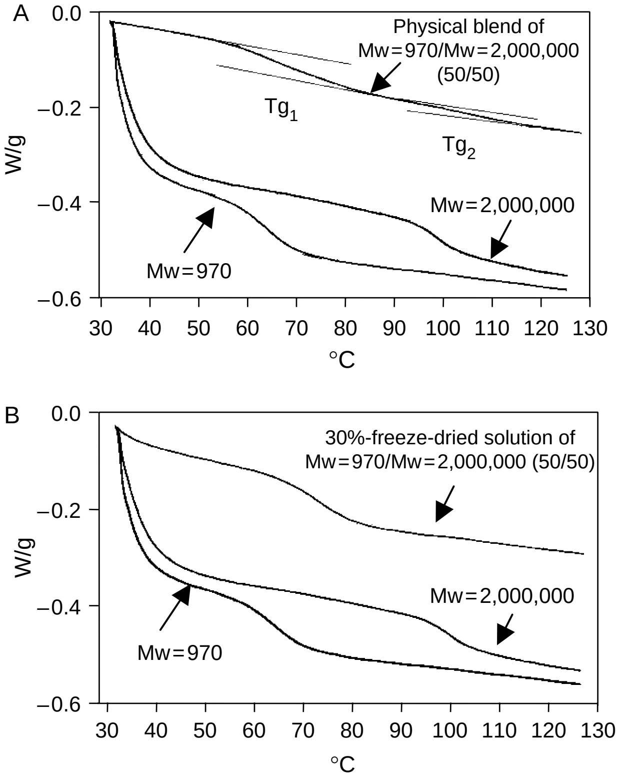

Fig. 5. Influence of mixture preparation method for $M_w=970/M_w=2{,}000{,}000$ (50/50): (A) physical blend of dextrans; (B) 30% concentrated, freeze-dried solution of dextrans.

individuality and phase behavior within the time of the experiment.

The results were different when mixtures were obtained after a preliminary solubilization step. The samples prepared by mixing equal amounts of 30% dextran solutions of $M_w=970$ and 2,000,000, followed by freeze-drying, exhibited a single T_g, located between the T_g of the two individual components at around 68.2 °C (Fig. 5B). This demonstrated the presence of a single phase and molecular miscibility of the two dextrans. In solution, due to the high free volume and entropy of the system, it became possible for the small dextrans to come close to the backbone and side branches of the larger dextran molecules and intimately interdisperse with them. Upon removal of the solvent (water) by freeze-drying, the dextrans remained interwoven as a single phase and as a result exhibited a single T_g. Fig. 7 shows a conceptual model of the two types of mixed dextran systems. The same mixing behavior was observed for mixtures obtained by mixing 50 and 70% dextran solutions

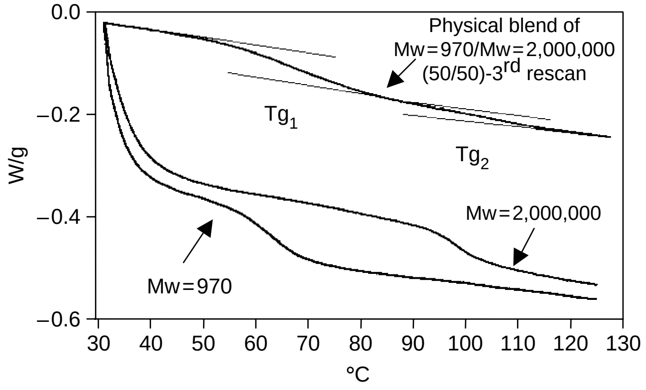

Fig. 6. Third DSC rescan of physical blend of dextran mixture with $M_w=970/M_w=2{,}000{,}000$ (50/50).

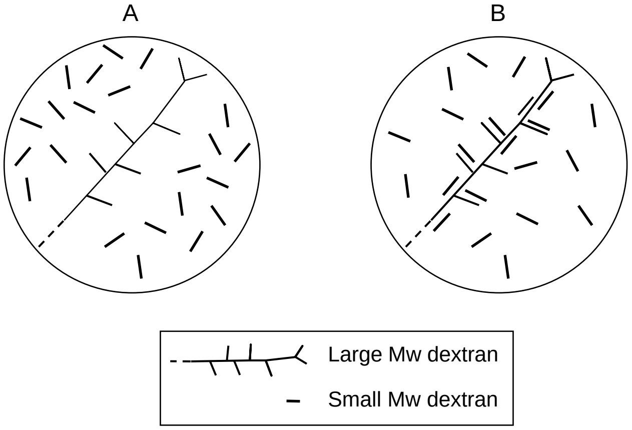

Fig. 7. Conceptual model of the mixed dextran systems: (A) without prior solubilization; (B) with prior solubilization.

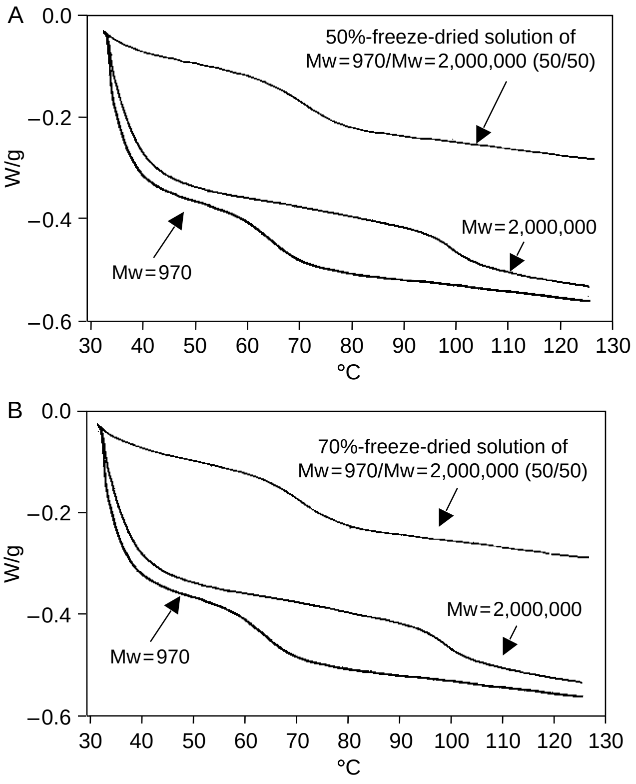

Fig. 8. Thermal behavior of freeze-dried dextran solutions of $M_w=970/M_w=2{,}000{,}000$ (50/50): (A) 50% concentrated solutions; (B) 70% concentrated solutions.

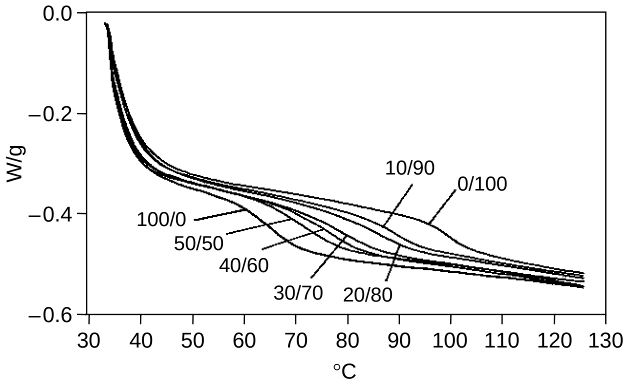

Fig. 9. Effect of $M_w=970$ on T_g of 30% concentrated, freeze-dried solutions of dextrans (the numbers indicate the $M_w=970/M_w=2{,}000{,}000$ ratio (w/w, d.b.)).

and T_g values of 69 °C were obtained for both concentrations (Fig. 8), indicating miscibility even in higher total polymer concentrations.

An interesting observation in the miscible dextran systems under investigation was that when dextran with $M_w=970$ was mixed in equal weight proportions with dextran of $M_w=2{,}000{,}000$, the T_g of the equal-mixture was closer to the T_g of the low M_w component (Fig. 5B). Since the two dextrans were mixed in equal amounts, the mixtures contained a much larger number of small dextran molecules; roughly 2,000 molecules of $M_w=970$ per 1 molecule of $M_w=2{,}000{,}000$. As shown in Fig. 9, even in the presence of a small amount of low M_w dextran (10/90), the T_g of the mixture was still far from T_g of high M_w component. Even small amounts of low M_w dextrans introduced a significant increase in free volume in the system, which led to a significant increase in molecular mobility and thus a significance effect on the T_g of the mixtures. This indicated that the T_g of the mixed dextran systems were controlled by their number-average molecular weight (M_n), rather than their weight-average molecular weight (M_w). The calculated values of the blends' M_n are shown in Table 2.

The results are consistent with the reports of Gabarra and Hartel (1998); Lourdin et al. (1997); Wang and Jane (1994), who observed strong effect of small amounts of low molecular weight components on the properties of large molecular weight molecular species. Kalichevsky & Blanshard (1993) investigated the effect of different ratios of fructose and amylopectin on the mechanical properties of the mixtures and concluded that at fructose concentrations above 20%, the mechanical properties of the mixture started to be dominated by fructose. The explanation could reside in the fact that the small molecular weight component acts as a plasticizer for the large polymeric molecule. However, these authors did not mention the significance of the number of low molecular weight species quantitatively.

Table 2
Molecular size characteristics of the dextran blends obtained after solubilization

Blend composition (%M_w1/%M_w2)	Equivalent M_n of blend	Polydispersity index (M_w/M_n) of blend
A. $M_w=970/M_w=2{,}000{,}000$		
50/50	1,939	516
40/60	2,423	495
30/70	3,230	434
20/80	4,841	331
10/90	9,658	186
B. $M_w=5{,}200/M_w=2{,}000{,}000$		
50/50	10,373	97
40/60	12,949	93
30/70	17,229	81
20/80	25,732	62
10/90	50,811	35
C. $M_w=10{,}800/M_w=2{,}000{,}000$		
50/50	21,484	47
40/60	26,783	45
30/70	35,552	39
20/80	52,858	30
10/90	102,994	17

The change in T_g with M_n for miscible dextran blends is shown in Fig. 10. A logarithmic relationship between T_g and M_n for all mixtures under investigation was found.

For the dextran mixtures of $M_w=970$ and 2,000,000:

$$T_g = (10.91)\mathrm{Ln}(M_n) - 12.90 \tag{3}$$

For the mixtures of $M_w=5{,}200$ and 2,000,000:

$$T_g = (2.55)\mathrm{Ln}(M_n) + 61.14 \tag{4}$$

For the mixtures of $M_w=10{,}800$ and 2,000,000:

$$T_g = (1.41)\mathrm{Ln}(M_n) + 74.84 \tag{5}$$

At $M_n > 10{,}000$, the sharp increase of T_g with increasing M_n started to level off and for mixtures of 10,800/2,000,000, the T_g values of mixtures with different component ratios were not significantly different from one another. According

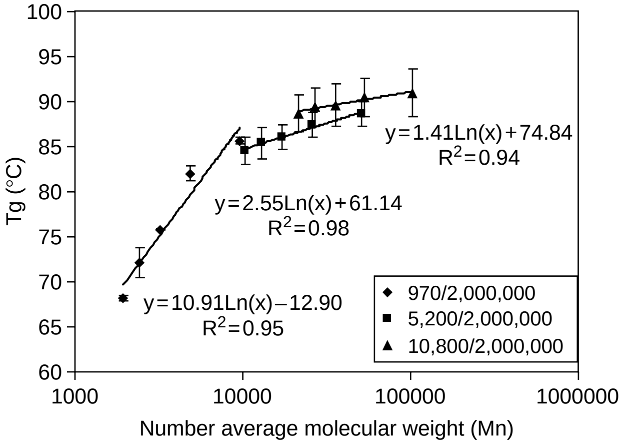

Fig. 10. Effect of M_n on T_g of the 30% concentrated, freeze-dried solutions of dextran mixtures.

to Billmeyer (1984), T_g of glass-forming polymers increases with increasing M_n up to a certain limit, where a plateau occurs due to entanglement coupling of the high molecular weight polymers leading to an entangled network of infinite molecular weight. In case of the dextran mixtures investigated in this work, the leveling off could also be due to the fact that, as the M_n increased, the homogeneity of the system also increased, as demonstrated by the polydispersity index values shown in Table 2, and the T_g values tended asymptotically to the T_g of the largest dextran.

The same dependency of the phase behavior on the method of sample preparation was obtained for the equal-mixture of dextrans with $M_w = 5{,}200$ and 2,000,000 (thermograms not shown). These findings prove that even when molecular species that have a similar chemical structure with different molecular weights are mixed, miscibility is not always the case, despite thermodynamic compatibility. Physical factors, such as the method of mixing, can influence miscibility and phase behavior drastically. This is extremely important in food systems, where combining various ingredients in different ways (i.e. with or without prior solubilization) can lead to food matrices with different, distinct properties.

3.4. Relationship between T_g and composition of dextran systems

The dextran mixtures prepared from 30% dextran solutions displayed a single T_g, located between the T_gs of the individual components (Fig. 5B). The relationship between the glass transition temperature and the composition of a compatible polymer blend is typically described by the Couchman–Karasz equation (Couchman & Karasz, 1978). Yet, in practice many deviations from this additivity based equation have been observed; in numerous situations, the experimental T_g values being either smaller or larger than the predicted ones (Schneider, 1997). In case of the miscible dextran blends analyzed in this study, the experimental T_g values were lower than the T_g values predicted by the Couchman–Karasz equation using T_g and ΔC_P of the individual components at $a_w = 0.33$ (Fig. 11). According to Schneider (1997), this is typical of polymer blends characterized by weak interaction energies. Such blends show less or no local ordering due to hetero-contact formation, which leads to enhanced conformational mobility and higher free volume as compared to the additivity based predictions. For the dextran blends, it is expected that two factors were responsible for the above-mentioned behavior: the weakness of dextran–dextran interactions, consisting mostly of non-polar, hydrogen bonds, and steric hindrance caused by conformational differences. It was also observed that the departure from the predicted values was higher for the $M_w = 970/M_w = 2{,}000{,}000$ mixtures ($\Delta T_g = 6.7$–8.7 °C) as compared to the $M_w = 5{,}200/M_w = 2{,}000{,}000$ mixtures ($\Delta T_g = 4.3$–7.2 °C) and the $M_w = 10{,}800/M_w = 2{,}000{,}000$ mixtures ($\Delta T_g = 4.4$–6.0 °C). This trend is contrary to the reports of Schneider (1997), who observed increased deviation with increased molecular weight of PVME/PS blends' components. In the case of the dextran blends, the similarity of the molecular structure and conformation increased as the molecular weight of the low M_w component increased, diminishing the departure from the additive theory.

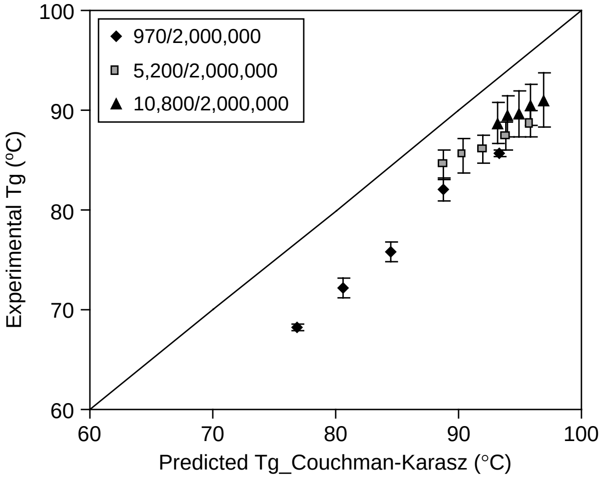

Fig. 11. Comparison of T_g predictions by Couchman–Karasz equation with experimental T_g values for 30% concentrated, freeze-dried solutions of dextran mixtures.

4. Conclusions

This study has demonstrated that miscibility of biopolymers is affected by a multitude of factors, and that under certain circumstances even polymers with same chemistry/molecular structure and with different molecular weights can exhibit immiscibility at molecular level. In dextran systems, molecular miscibility was only attained when pre-solubilization in a common solvent was allowed. For the compatible/miscible systems, the lower molecular weight component resulted in a significant increase of the molecular mobility in the system, affected the T_g of the mixtures and to a great extent dictated the phase behavior of the polymeric blend.

Through thermal analysis, the dependence of glass transition temperature on molecular size was determined for both the individual dextrans and their mixtures. Glass transition temperature of pure dextrans increased with M_w and reached a plateau at higher M_w. For miscible blends, glass transition temperature was better related to the number-average molecular weight, which is related to the number of the polymeric chains, than weight-average molecular weight, which is related to the weight of the chains. The knowledge on compatibility/miscibility of carbohydrate mixtures acquired in this work can be used as a tool to design food and biomaterials of desired or improved properties.

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