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Probing the boundaries of miscibility in model carbohydrates consisting of chemically derivatized dextrans using DSC and FTIR spectroscopy

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Abstract

Miscibility of carbohydrate polymers consisting of mixtures of chemically derivatized dextrans with charged side chains were studied as model systems. The effect of total polymer concentration and added NaCl on miscibility was investigated using DSC and FTIR Spectroscopy. DSC results showed a single T_g for samples prepared at low, medium and high polymer concentrations in the absence of NaCl; and at high concentrations in the presence of NaCl, indicating miscible systems. Two separate T_gs were obtained for samples prepared at low and medium polymer concentrations in the presence of NaCl, indicating immiscible systems. FTIR spectroscopy showed significantly different behavior for 1 T_g and 2 T_gs systems. The systematic changes in the FTIR spectra of miscible blends were assigned to the change in hydrogen bond distribution of the pure components in the mixture resulting from inter-molecular interactions. No such significant systematic change was observed in the FTIR spectra of immiscible systems.

Keywords: Miscibility; Carbohydrate; DSC; FTIR; Dextran; NaCl

1. Introduction

Food materials are composed of multiple polymer molecules with different chemistry and properties, such as carbohydrates, proteins and lipids. Increasing demand for new food formulations, with reduced carbohydrate or fat content and added nutraceutical compounds to deliver healthier foods, require formulating food products to include or exclude various ingredients. Ingredient miscibility (or immiscibility) is critical to control the processability, texture, sensory quality and stability of the final food products. Fundamental understanding of the molecular origins of the miscibility and interactions between food polymers and thereby developing a priori rules for molecular miscibility would enhance the predictive capabilities on how a set of ingredients will result in the quality attributes and stability needed in food products.

Many carbohydrate–protein systems have been shown to be immiscible, because there are significant differences in their hydrophilicity/hydrophobicity resulting from very different macromolecular chemistry, molecular conformation and affinity for water (Grinberg & Tolstoguzov, 1997; Michon, Buvelier, Launay, Parker, & Takerkart, 1995; Moraru, Lee, Karwe, & Kokini, 2002; Tolstoguzov, 1991, 1998, 2000b, 2003). Incompatibility and phase separation in carbohydrate–carbohydrate systems has also been observed even though the components are chemically closer to each other (Ahmad & Williams, 2001; Closs, Conde-Petit, Roberts, Tolstoguzov, & Escher, 1999; Garnier, Schorsch, & Doublier, 1995; German, Blumenfeld, Guenin, Yuryev, & Tolstoguzov, 1992; Kalichevsky, Orford, & Ring, 1986; Kalichevsky & Ring, 1987; Zimeri & Kokini, 2003a, 2003b, 2003c). Still, it is important to point out that most of the existing studies refer to mixtures of carbohydrates with significant differences in their chemical structure and composition.

Miscibility/compatibility in polymer systems can be investigated by measuring their glass transition temperature in

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solid state as a marker. Every amorphous polymeric system have 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 determine glass transition temperature. Using DSC, miscibility/immiscibility in polymer blends is determined through measurement of T_g of the components versus that of blends. Perfectly miscible polymer mixtures exhibit a single T_g located between the T_gs of the individual components with a sharpness of transition similar to that of the components. On the other hand, immiscible blends show multiple T_gs, corresponding to the T_g of each component in the mixture. DSC has been successfully used to show molecular miscibility/immiscibility in biopolymer systems, such as in fructose–amylopectin blends (Kalichevsky & Blanshard, 1993); in 7S and 11S soy globulins (Morales-Diaz & Kokini, 1997); in starch-meat extrudates (Moraru et al., 2002); in inulin–amylopectin mixtures (Zimeri & Kokini, 2003a); as well as in synthetic polymers, such as in phenolic resin–poly(acetoxystyrene) blends (Kuo & Chang, 2002); polyamide 66 and phenol formaldehyde resin blends (Hartikainen et al., 2004).

Fourier transform infrared (FTIR) spectroscopy is one of the many techniques that have been applied to investigate specific molecular bonding interactions in polymer blends (Coleman & Painter, 1990; Coleman, Graf, & Painter, 1991; Coleman & Painter, 2006; Hartikainen et al., 2004; Kolhe & Kannan, 2003; Kuo & Chang, 2001, 2002). When two polymers are in separate and distinct phases (complete immiscible systems), it can be assumed that one polymer does not recognize the existence of the other in IR spectral terms and vice versa. In that case, the spectrum of the blend reflects the appropriate addition of the IR spectrum of the two individual components. In the case of miscible or partially miscible polymer blends, the IR spectrum would show formation of new bands as the results of miscibility; and disappearance of some component bands. Shifts in the specific bands would give information on the switches from component specific bonds to the bonds between components (Chalmers & Everall, 1993; Coleman & Painter, 1990; Dong & Ozaki, 1997). For example, the sensitivity of FTIR spectroscopy to inter-molecular interactions have been shown for poly(vinyl acetate) and its miscible blends with poly(4-vinylphenol) at different ratios of the components (Coleman & Painter, 1990). In the IR spectrum, the carbonyl-stretching region of poly(vinyl acetate) and miscible blends of poly(vinyl acetate) and poly(4-vinylphenol) showed that the band at 1739 cm^{-1} was attributed to free poly(vinyl acetate) carbonyl groups (non hydrogen-bonded). As the ratio of poly(4-vinylphenol) increased in the blend, a band at 1714 cm^{-1} started to appear and its intensity increased at higher poly(4-vinylphenol) ratios. The band at 1714 cm^{-1} was the representative of poly(vinyl acetate) carbonyl groups that were hydrogen-bonded to the phenolic hydroxyl group of poly(4-vinylphenol), resulting in miscibility at the molecular level (Coleman & Painter, 1990).

The combined use of DSC and FTIR spectroscopy has been shown to provide valuable information to demonstrate the miscibility and the mechanism of miscibility in synthetic polymer systems. For instance, Kuo and Chang (2002) and Hartikainen et al. (2004) have used carbonyl and hydroxyl stretching frequencies of the FTIR spectra in phenolic resin–poly(acetoxystyrene) blends and *N*-methylacetamide (NMA)-phenol blends, respectively, and have shown that the miscibility, determined with a single T_g behavior in blends by DSC, was due to the formation of inter-molecular hydrogen bonding between the components probed by FTIR spectroscopy.

In most mixture systems investigated in literature that use FTIR spectroscopy, only one of the components have a hydroxyl group in its monomeric unit that gives signature information in the hydroxyl stretching regions, whereas the other component in the mixture has a different group, such as a carbonyl group, that can make hydrogen bond with the hydroxyl group of the first component (Coleman & Painter, 1990; Coleman et al., 1991; Coleman & Painter, 2006; Hartikainen et al., 2004; Kuo & Chang, 2002). In these studies, carbonyl stretching regions together with hydroxyl stretching regions of the FTIR spectra of the components and the blends enable significant information about the specific bonding interactions in the systems. On the other hand, in a polymer mixture of two components where both components have multiple hydroxyl groups (as in the case of most carbohydrate polymers), the analysis would be more complex. In the current paper, we aim to extend the combined analysis of using DSC and FTIR spectroscopy to carbohydrate polymers to probe the miscibility and to understand the mechanism of miscibility in model systems consisting of mixtures of chemically derivatized dextrans. As the selected model carbohydrate system has charged side groups, the effect of ionic strength through addition of NaCl on miscibility of the systems was also investigated.

2. Materials and methods

2.1. Materials

Two chemically derivatized dextrans, dextran sulphate (DS500) and diethylaminoethyl dextran (DEAE) that are both produced from standard dextran with an average molecular weight of 500,000, were used (pK Chemicals A/S, Denmark). Dextrans are high molecular weight polymers of glucose. About 95% of the linkages in dextran are α-D-(1–6), while the other 5% of the linkages are α-D-(1–3), that 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 et al., 2001; Walsh, Arcelli, Ikoma, Tanaka, & Mann, 2003). They represent good

model systems for carbohydrate–carbohydrate interactions in foods since their molecular structure is similar to food carbohydrate polymers, such as amylopectin; they are commercially available in chemically derivatized forms; and they provide the precise and thorough characterization needed to conduct meaningful interpretable experiments compared to many other complex carbohydrate polymers.

Diethylaminoethyl dextran (DEAE) is a chemically derivatized dextran produced by reacting diethylaminoethyl chloride with standard dextran. It is a polycationic derivative and the degree of substitution corresponds to approximately 1 DEAE substituent per 3 glucose units (0.33 mol DEAE per 1 mol glucose) (Fig. 1).

Dextran sulphate (DS500) is another derivatized dextran that is produced by sulphating standard dextran. It is the polyanionic derivative in which each glucose unit has approximately two sulphate groups, located normally at C2 and C4 of the glucose units (2 mol sulphate per 1 mol glucose) (Fig. 2).

2.2. Sample preparation for DSC and FTIR spectroscopy measurements

The samples were prepared at different total polymer concentrations (30%, 50%, and 70% (w/w, w.b.)); and at various component ratios (0/100, 25/75, 50/50, 75/25, and 100/0 (w/w, d.b.)). The powders of the components were first mixed and then solubilized using deionized, distilled water at 45–50 °C to ensure complete solubilization of the powders in water, especially at high total polymer concentrations. The effect of salt addition on the miscibility was investigated using NaCl solutions with ionic strengths of 0, 1, and 2 M. The required amount of salt was added to the systems after solubilizing the dextran powders in water. By this way, "salting out effect" of NaCl, where salt competes for the available water resulting in insufficient solubilization of dextran, was eliminated. The prepared solutions were freeze-dried in a bench top freeze dryer (The Virtis Company Inc., Gardiner, NY). Dried samples were grinded using a mortar and a pestle. These ground samples were then equilibrated at a specific water activity to ensure that all samples analyzed were in similar conditions (at $a_w = 0.33$ over saturated $MgCl_2$ solution). After equilibration, the powder samples were directly used for analysis.

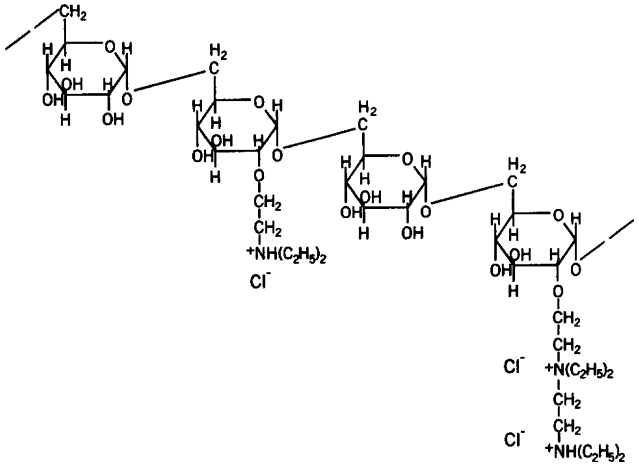

Fig. 1. Molecular structure of diethylaminoethyl dextran (DEAE).

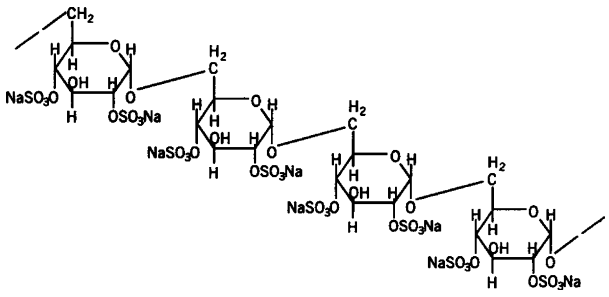

Fig. 2. Molecular structure of dextran sulphate (DS500).

2.3. Moisture content of samples

The 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 the samples were measured using an Aqualab hygrometer (Decagon Devices Inc., Pullman, WA). Two replicate measurements were performed for each analysis.

2.4. Methods of analysis

2.4.1. Differential scanning calorimetry (DSC)

Thermal analysis is performed using a TA 4000 Thermal Analysis System with a DSC 30-S Cell/TC11 TA Processor (Mettler Instrument Inc., Highstown, NJ). 120 μl, 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 with scan ranges 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 T_g of dextran systems were 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.

2.4.2. Fourier transform infrared (FTIR) spectroscopy

A Bruker Equinox 55 FTIR-Attenuated Total Reflectance (ATR) (SensIR Durascope™) spectrometer (Bruker Optics Inc., Billerica, MA) was used for the analysis. Approximately 10 mg of powder samples was placed on the ATR crystal and the measurements were done by co-adding 100 scans with a resolution of 4 cm^{-1}.

3. Results and discussion

3.1. Glass transition temperature (T_g) of derivatized dextrans

According to Icoz, Moraru, and Kokini (2005), the T_g of the standard dextran with an average molecular weight (M_w) of 500,000 equilibrated at $a_w = 0.33$ was around 100 °C. In the current study, T_g of pure DEAE prepared from solutions at different polymer concentrations that were equilibrated at $a_w = 0.33$ were determined between 56 and 57 °C (Fig. 3). The difference of T_gs between the standard dextran of $M_w \sim 500{,}000$ and DEAE dextran produced from a similar molecular weight showed the effect of the added side chains on the mobility of the dextran. The addition of DEAE-subunits (0.33 mol DEAE/1 mol glucose) increased the mobility of dextran molecule significantly that resulted in decrease of T_g from around 100 to 56–57 °C. On the other hand, the T_g for DS500 at similar conditions was obtained around 106 °C (Fig. 3), which was slightly higher than the T_g of standard dextran with $M_w \sim 500{,}000$. Even though the substitution of sulphate groups in DS500 (2 mol sulphate/1 mol glucose) was significantly higher than the substitution in DEAE dextran, they did not contribute to the mobility of the system. The reason for obtaining slightly higher T_g than that of standard dextran would be due to having slightly higher molecular weight of DS500 compared to standard dextran because of the high number of added side chains. Long side chains even with lower degree of substitution (as in the case of DEAE dextran) promoted flexibility of the molecule and increased the mobility in the system, resulting in lower T_g as compared to the T_g of standard dextran with similar M_w; and as compared to another similar M_w derivatized dextran with short side chains even with higher degree of substitution (as in the case of DS500). The comparison between the T_g of derivatized dextrans and standard dextran at similar molecular weights shows that even small changes in the chemistry of a carbohydrate polymer change the thermal phase behavior of the system significantly.

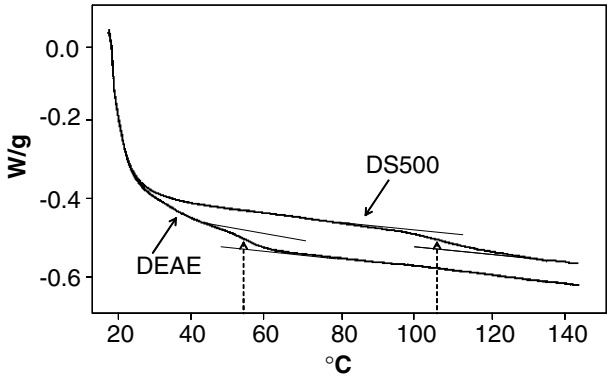

Fig. 3. DSC thermograms of DEAE and DS500 prepared from 30% polymer concentrated solutions in the absence of NaCl [IS(NaCl) = 0].

3.2. T_g as a marker of miscibility for mixtures prepared from different polymer concentrations and added NaCl

In the absence of NaCl [IS(NaCl) = 0], the T_g of DEAE prepared from 30%, 50%, and 70% polymer concentrated solutions were determined as 56.1 ± 0.28, 56.9 ± 0.14, and 56.3 ± 0.35 °C, respectively (Table 1). Similarly, T_g of DS500 prepared from different concentrated solutions were determined as 106.7 ± 0.28, 105.7 ± 0.64, and 105.4 ± 0.21 °C, respectively (Table 1). Samples prepared from different polymer concentrations in the absence of NaCl resulted in similar glass transition temperatures, as would be expected. The moisture contents of these samples [IS(NaCl) = 0] were also very comparable to each other (Table 2).

T_g values of mixtures prepared only at 50/50 ratio are reported, since sensitivity of DSC to monitor multiple T_g behavior in 25/75 and 75/25 ratios, if any, would be limited. Because as one of the component ratios gets smaller, as in the case of 25/75 or 75/25, the heat flow would also get smaller at a similar ratio, which would make T_g identification difficult. In the absence of NaCl [IS(NaCl) = 0], samples prepared from 30%, 50%, and 70% total polymer concentrated solutions showed a single T_g (Fig. 4) (82.9 ± 0.71, 82.1 ± 0.57, and 80 ± 0.71 °C, respectively) (Table 1), indicating miscible systems. Icoz et al. (2005) showed that the T_g of the mixed dextrans were controlled by their number-average molecular weight, rather than

Table 1
Glass transition temperature (T_g) of DS500 and DEAE systems prepared from 30%, 50%, and 70% polymer concentrations with added NaCl of IS = 0, IS = 1 M, and IS = 2 M

	T_g (°C)		
	IS(NaCl) = 0	IS(NaCl) = 1 M	IS(NaCl) = 2 M
DS500 – 30%	106.7 ± 0.28	100.8 ± 0.35	101.1 ± 0.21
DS500 + DEAE – 30% – 50/50	82.9 ± 0.71	$41.7 \pm 0.14/103.8 \pm 0.35$	$41.6 \pm 0.35/113.7 \pm 0.85$
DEAE – 30%	56.1 ± 0.28	47.0 ± 0.71	46.8 ± 1.06
DS500 – 50%	105.7 ± 0.64	100.1 ± 0.14	100.8 ± 0.35
DS500+DEAE – 50% – 50/50	82.1 ± 0.57		$40.7 \pm 0.21/111.9 \pm 0.28$
DEAE – 50%	56.9 ± 0.14	52.5 ± 0.71	50.1 ± 0.64
DS500 – 70%	105.4 ± 0.21	102.7 ± 1.20	102.4 ± 1.20
DS500 + DEAE – 70% – 50/50	80 ± 0.71	79.0 ± 1.41	78.6 ± 0.14
DEAE – 70%	56.3 ± 0.35	55.2 ± 0.07	51.3 ± 3.96

Table 2
Moisture content (% d.b.) of DS500 and DEAE systems prepared from 30%, 50%, and 70% polymer concentrations with added NaCl of IS = 0, IS = 1 M, and IS = 2 M

	% Moisture (d.b.)		
	IS(NaCl) = 0	IS(NaCl) = 1 M	IS(NaCl) = 2 M
DS500 – 30%	13.71 ± 0.52	12.54 ± 0.02	11.43 ± 0.08
DS500 + DEAE – 30% – 50/50	11.93 ± 0.72	11.36 ± 0.04	11.05 ± 0.00
DEAE – 30%	11.09 ± 0.74	11.79 ± 1.23	9.91 ± 0.03
DS500 – 50%	13.68 ± 0.90	13.48 ± 0.10	13.00 ± 0.20
DS500 + DEAE – 50% – 50/50	12.41 ± 0.93	12.48 ± 0.42	12.49 ± 0.01
DEAE – 50%	10.85 ± 0.02	11.59 ± 0.08	11.13 ± 0.11
DS500 – 70%	13.64 ± 0.45	13.58 ± 0.06	13.92 ± 0.27
DS500 + DEAE – 70% – 50/50	12.48 ± 0.31	12.06 ± 0.02	12.84 ± 0.85
DEAE – 70%	10.85 ± 0.21	11.26 ± 0.42	12.06 ± 1.88

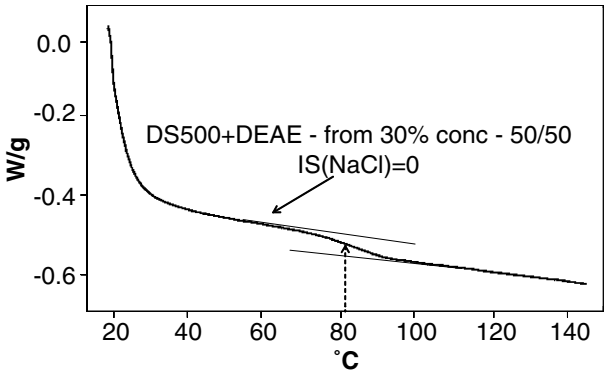

Fig. 4. Single T_g in 50/50 ratio of DS500 + DEAE prepared from 30% polymer concentrated solutions in the absence of NaCl [IS(NaCl) = 0].

weight-average molecular weights. When a small molecular weight dextran was mixed in equal weight proportions (50/50) with a high molecular weight dextran, the single T_g of the mixed system was closer to the T_g of the small molecular weight component. This was because when the two dextrans of different molecular weights were mixed in equal amounts, the mixture had higher number of small molecular weight dextran than high molecular weight dextran resulting in higher free volume in the system and causing the significant effect on the T_g of the mixture (Icoz et al., 2005). In the current study, since the two components in the blend (DS500 and DEAE) had similar molecular weights (around 500,000), the T_g of the 50/50 ratio mixtures were approximately at the midpoint of the T_gs of the individual components (Table 1).

T_g of both DS500 and DEAE samples prepared from 30% polymer concentration in the presence of NaCl [IS(NaCl) = 1 M or IS(NaCl) = 2 M] were lower than T_g of samples prepared from 30% concentrated samples in the absence of NaCl (100.8 ± 0.35 and 47.0 ± 0.71 °C at IS(NaCl) = 1 M; 101.1 ± 0.71 and 46.8 ± 1.06 °C at IS(NaCl) = 2 M compared to 106.7 ± 0.28 and 56.1 ± 0.28 °C at IS(NaCl) = 0) (Table 1). Both DEAE and DS500 are charged polymers (polyelectrolytes). There are strong repulsive forces between similarly charged monomers of a polyelectrolyte that result in highly swollen and stretched conformation of the molecule (Dobrynin, Rubinstein, & Obukhov, 1996; Jousset, Bellossent, & Galin, 1998; Lauten & Nystrom, 2000; Shinoda, 1978; Walstra, 2003). These strong repulsive interactions have shown to be screened by the addition of an electrolyte (such as salt) to the aqueous solution of charged polymer molecules (Basak, Nisha, Manorama, Maiti, & Jayachandran, 2003; Demetriades & McClements, 1998; Hellebust, Blokhus, & Nilsson, 2004; Lauten & Nystrom, 2000). A charged polymer can be assumed to behave as a soft sphere with an approximate effective radius (R_{eff}), which is the sum of hydrodynamic radius of gyration (R_g) and Debye screening length (κ^{-1}) (Tadros, 1996). Addition of an electrolyte increases the ionic strength and results in decrease of effective radius of the polyelectrolyte (Russel, 1991), because increase in ionic strength reduces κ^{-1}; and electrostatic screening reduces the repulsion of the charged groups along the polymer chain, resulting in decrease of R_g (Demetriades & McClements, 1998). Due to electrostatic screening effects in the presence of an electrolyte, flexibility of the polyelectrolyte increases favoring intra-molecular interactions, and leads to more compact and less expanded structure that occupies less volume (Basak et al., 2003). Hellebust, Nilsson, and Blokhus (2003) and Hellebust et al. (2004) has further shown that the addition of salt to a mixture of polyelectrolytes affects the phase behavior in the system, resulting in both associative and/or segregative phase separation depending on the ionic strength contributed by the addition of salt.

In the current study, both DEAE and DS500 became more flexible upon addition of NaCl; and as the T_g data showed, the mobility in the polymers increased, resulting in lower T_g values in the presence of added NaCl compared to systems without NaCl (Table 1). Moisture contents of these samples were slightly different from each other; for example, moisture content of DS500 prepared from 30% solutions at IS(NaCl) = 0, 1, and 2 M were 13.71%, 12.54%, and 11.43% (d.b.), respectively (Table 2). Lower moisture content at IS(NaCl) = 2 M than IS(NaCl) = 1 M resulted in slightly similar T_g value of the two samples. If these two samples have closer moisture contents, then T_g of sample with IS(NaCl) = 2 M would be slightly lower than the reported value due to plasticization effect of water, which

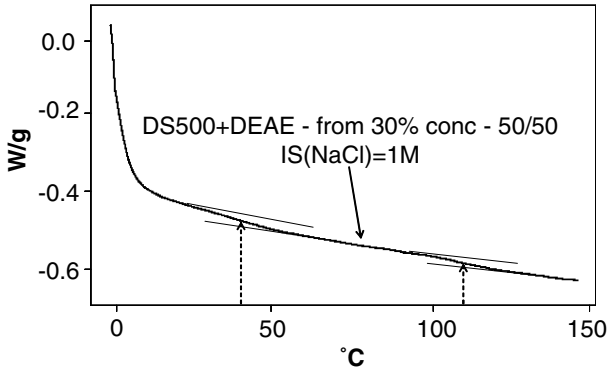

Fig. 5. Two T_gs in 50/50 ratio of DS500 + DEAE prepared from 30% polymer concentrated solutions with IS(NaCl) = 1 M.

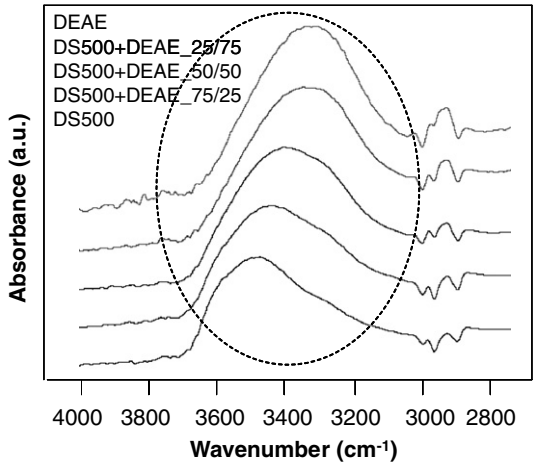

Fig. 6. Hydroxyl stretching regions of FTIR spectra for DS500 + DEAE blends prepared from 30% polymer concentration in the absence of NaCl [IS(NaCl) = 0].

would more clearly show the effect of more addition of NaCl (1 M vs. 2 M) on the T_g behavior of the samples.

In the 50/50 mixture of the same system, there were 2 T_g values (Table 1) (41.7 ± 0.14 and 103.8 ± 0.35 °C at IS(NaCl) = 1 M (Fig. 5); 41.6 ± 0.35 and 113.7 ± 0.85 °C at IS(NaCl) = 2 M), representing the T_g of the individual components in the blend, indicating immiscibility between the components. The explanation of immiscibility of two polyelectrolytes in the presence of added salt would be due to "preferable" intra-molecular interactions in the components rather than inter-molecular interactions between the components. At IS(NaCl) = 0, both polyelectrolytes had intra-molecular repulsive forces so when these polyelectrolytes came together, they got involved in inter-molecular interactions, resulting in miscible systems with 1 T_g. However, in the presence of NaCl, the repulsive forces were screened and the intra-molecular interactions were enabled, decreasing the possible inter-molecular interactions and resulting in 2 T_gs.

Similar behavior was observed for samples prepared from 50% total polymer concentrated solutions and their blends. On the other hand, for samples prepared at 70% polymer concentration, the effect of added NaCl (1 and 2 M) on reducing the T_g of pure components were less compared to samples prepared at lower polymer concentrations (Table 1). The T_g of the individual components prepared at 70% concentration in the presence of NaCl were closer to the T_gs in the absence of NaCl. There was also a single T_g in the mixed systems. Because at high polymer concentrations, the concentration of the counter-ions in the polyelectrolyte was also high, so the presence of NaCl did not significantly affect the mobility and miscibility in the systems. Therefore, the polyelectrolyte at high polymer concentration, even in the presence of added NaCl, behaved closer to the system in the absence of salt.

3.3. FTIR spectroscopy for miscible/immiscible systems to investigate specific bonding interactions

Hydroxyl stretching regions of FTIR spectra (~4000–2700 cm^{-1}) for DS500 + DEAE blends prepared from 30% polymer concentration in the absence of NaCl is given in Fig. 6. Molecules containing hydroxyl groups can self-associate and can form intra-molecular interactions through formation of hydrogen bonds between their hydroxyl groups, forming dimers and higher multimers. Hydrogen bonds are dynamic in nature, so they continuously break and reform by the thermal motion. At any instant of time, there exists a number of free (non-hydrogen bonded) monomers, hydrogen bonded dimers and multimers; and the changes in concentration and temperature affect their distribution (Coleman et al., 1991; Coleman & Painter, 1995). Coleman and Painter (1995) have shown the infrared spectra of the hydroxyl stretching region of 2-propanol, a small molecule with a hydroxyl group that can form hydrogen bonds, in cyclohexane (an inert solvent that can not make any hydrogen bonds with 2-propoanol) at different temperatures and concentrations. Bands at 3630, 3530, and 3350 cm^{-1} are assigned to non-hydrogen bonded hydroxyl groups, hydrogen bonded dimers and hydrogen bonded multimers, respectively (Coleman & Painter, 1995). These assigned bands would form the basis for the observed bands in hydroxyl stretching regions of dextran systems in the current study. Moreover, Kuo and Chang (2002) investigated the specific interactions in phenolic resin and poly(acetoxystyrene) (PAS) blends using FTIR spectroscopy. Hydroxyl stretching frequencies have shown that pure phenolic resin had a broad band at 3350 cm^{-1}, which was due to large number of hydrogen-bonded hydroxyl groups, and a narrow band at 3525 cm^{-1}, which was assigned to the free hydroxyl groups. The band at 3525 cm^{-1} decreased with PAS content and the band at 3350 cm^{-1} shifted to 3384 cm^{-1} with increasing PAS content, indicating the switch from hydroxyl–hydroxyl bond to hydroxyl–carbonyl bond. Their result have shown that inter-molecular hydrogen bonding occurred between the hydroxyl group of the phenolic resin and the carbonyl group of PAS (Kuo & Chang, 2002).

Based on the band assignments mentioned by Coleman and Painter (1995) and Kuo and Chang (2002), Fig. 6 was interpreted as follows: individual DEAE showed a broad

band at 3286 cm^{-1} due to high number of hydrogen bonded OH groups (in the form of multimers). Individual DS500 had a shoulder in the similar region (at 3250 cm^{-1}) due to a number of hydrogen bonded OH groups (in the form of multimers). DS500 (Fig. 2) has one hydroxyl group per glucose molecule that can make intra-molecular hydrogen bonds and these groups are much less than those in DEAE (Fig. 1), which was confirmed in the spectra as a shoulder rather than a broad band at 3250 cm^{-1}. DS500 also showed a broad band at 3450 cm^{-1} due to hydrogen bonded OH (in the form of dimers); and a shoulder around 3600 cm^{-1} due to free OH groups. The shoulder of DS500 around 3600 cm^{-1} disappeared as DEAE was introduced into the system, showing that those free OH groups participated in hydrogen bonding with DEAE. The shoulder of DS500 at 3250 cm^{-1} was still present in the blends although its magnitude was getting smaller. The broad band of DS500 at 3450 cm^{-1} and the broad band of DEAE at 3286 cm^{-1} shifted towards each other in mixtures, indicating that the components were forming inter-molecular hydrogen bonds with each other. This was shown by the broad bands at 3420, 3381, and 3323 cm^{-1} for 75/25, 50/50, and 25/75 blends, respectively (Fig. 6).

Another significant region that can be analyzed in terms of interactions in dextran systems was the C–OH stretching region of FTIR spectra (~990–1060 cm^{-1}). Because when a hydroxyl group next to a carbon atom is involved in hydrogen bond formation, the bond between C and OH would also be affected. C–OH stretching vibrations of DS500 + DEAE blends prepared at 30% polymer concentration in the absence of NaCl is shown in Fig. 7. DEAE had a single peak around 1003 cm^{-1}. DS500 had two peaks at 1010 and 976 cm^{-1}, respectively. In the blends, as DS500 was introduced into DEAE, the following shifts in the bands occurred: A peak around 1005 cm^{-1} and a shoulder around 990 cm^{-1} in DS500 + DEAE(25/75) blend; two peaks around 1007 and 985 cm^{-1} in DS500 + DEAE(50/50) blend; two peaks around 1009 and 978 cm^{-1} in

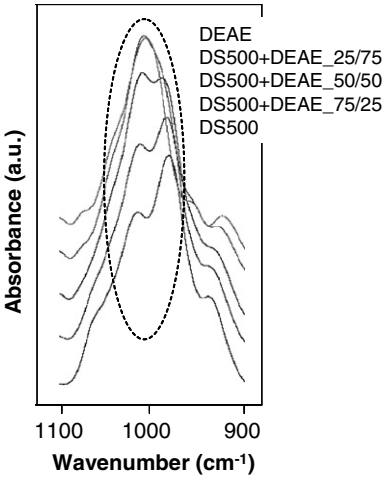

Fig. 7. C–OH stretching region of FTIR spectra for DS500 + DEAE blends prepared from 30% polymer concentration in the absence of NaCl [IS(NaCl) = 0].

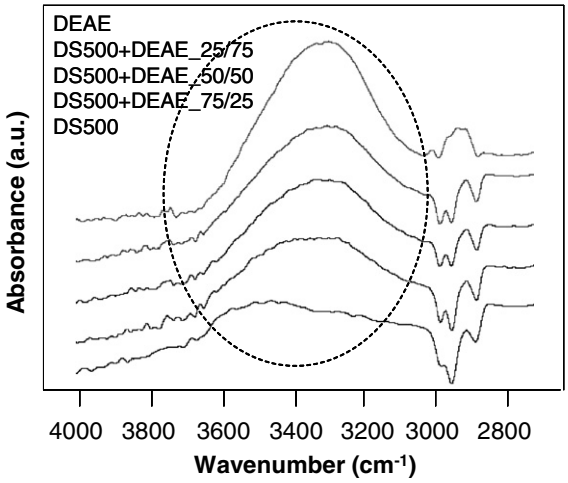

Fig. 8. Hydroxyl stretching regions of FTIR spectra for DS500 + DEAE blends prepared from 30% polymer concentration with IS(NaCl) = 1 M.

DS500 + DEAE(75/25) blend. The systematic shift/change in the bands of mixtures indicated the switches from intra-molecular hydrogen bonds to inter-molecular hydrogen bonds between the components that affected the C–OH vibrations. These blends have shown a single T_g behavior determined by DSC (Table 1). Therefore, the formation of hydrogen bonds between the two components in the blend is concluded to be the mechanism for the formation of miscibility observed by thermal analysis. Other blends that showed a single T_g behavior have shown similar FTIR spectra.

Hydroxyl stretching regions of FTIR spectra for DS500 + DEAE blends prepared from 30% polymer concentration and at NaCl added [IS(NaCl) = 1 M] is given in Fig. 8. FTIR spectra of these blends, which showed 2 T_gs with DSC, did not show such systematic change in the bands compared to those with a single T_g. IR spectrum of the pure

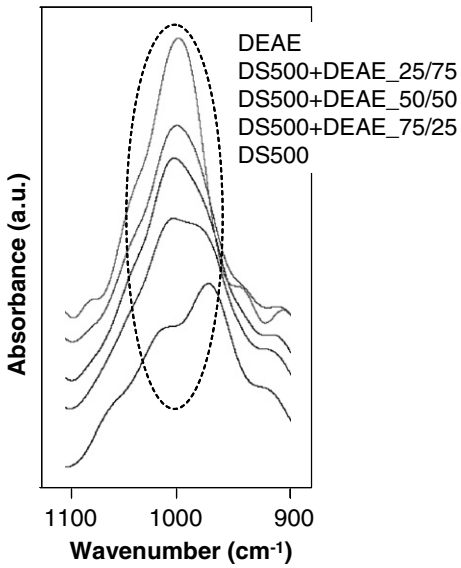

Fig. 9. C–OH stretching region of FTIR spectra for DS500 + DEAE blends prepared from 30% polymer concentration with IS(NaCl) = 1 M.

components, DEAE and DS500, showed similar bands as those in Fig. 6. The bands of the mixtures got broader rather than any kind of shifts or changes in the bands. Similarly, C–OH vibrations for this system did not show the systematic change in the bands of the mixtures (Fig. 9). For example, DEAE showed a peak around 1002 cm^{-1}; DS500 + DEAE(25/75) blend had a single peak around 1004 cm^{-1}; DS500 + DEAE(50/50) blend also had a single peak around 1005 cm^{-1}; DS500 shows two peaks around 1010 and 977 cm^{-1}; and DS500 + DEAE(75/25) blend has two peaks similar to pure DS500, around 1007 and 995 cm^{-1}. These results can be interpreted as the "appropriate addition" of IR spectra of pure components (Chalmers & Everall, 1993; Dong & Ozaki, 1997). Other blends that showed 2 T_gs with thermal analysis had similar FTIR spectra.

4. Conclusions

Thermal analysis of systems consisting of DS500 and DEAE has shown miscible and immiscible systems with 1 T_g or 2 T_gs, depending on the polymer concentrations and the addition of salt (NaCl): 1 T_g for samples prepared from low, medium and high polymer concentrations in the absence of salt, and for samples prepared from high concentrations in the presence of salt; and 2 T_gs for samples prepared from low and medium polymer concentrations in the presence of salt. FTIR spectroscopy provided analysis on the possible bonding interactions that was combined with thermal analysis to explain the mechanism of miscibility in the carbohydrate systems through formation of hydrogen bonding interactions between the components in the blend. Systems that showed 2 T_gs with thermal analysis did not have sufficient inter-molecular hydrogen bonding to form miscible systems.

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References

Ahmad, F. B., & Williams, P. A. (2001). Effect of galactomannans on the thermal and rheological properties of sago starch. *Journal of Agricultural and Food Chemistry, 49*, 1578–1586.

Basak, P., Nisha, C. K., Manorama, S. V., Maiti, S., & Jayachandran, K. N. (2003). Probing the association behavior of poly(ethylene glycol)-based amphiphilic comb-like polymer in NaCl solution. *Journal of Colloid and Interface Science, 262*, 560–565.

Blondiaux, N., Jeney, S., Liley, M., Pugin, R., Sigrist, H., Heinzelmann, H., et al. (2001). Structured peg-dextran surfaces for bio-applications. *European Cells and Materials, 6*(1), 62.

Chalmers, J. M., & Everall, N. J. (1993). Vibrational spectroscopy. In B. J. Hunt & M. I. James (Eds.), *Polymer characterization* (pp. 69–114). London: Chapman & Hall.

Closs, C. B., Conde-Petit, B., Roberts, I. D., Tolstoguzov, V. B., & Escher, F. (1999). Phase separation and rheology of aqueous starch/galactomannan systems. *Carbohydrate Polymers, 39*, 67–77.

Coleman, M. M., Graf, J. F., & Painter, P. C. (1991). *Specific interactions and the miscibility of polymer blends*. Lanchaster, PA: Technomic Publishing, Co.

Coleman, M. M., & Painter, P. C. (1990). Infrared-absorption spectroscopy. In J. I. Kroschwitz (Ed.), *Polymers: Polymer characterization and analysis* (pp. 371–403). New York: Wiley & Sons, Inc.

Coleman, M. M., & Painter, P. C. (1995). Hydrogen bonded polymer blends. *Progress in Polymer Science, 20*, 1–59.

Coleman, M. M., & Painter, P. C. (2006). *Miscible polymer blends: Background and guide for calculations and design*. Lancaster, PA: DEStech Publications, Inc..

Demetriades, K., & McClements, D. J. (1998). Influence of dextran sulfate and NaCl on the flocculation of oil-in-water emulsions stabilized by a nonionic surfactant. *Journal of Agricultural and Food Chemistry, 46*(10), 3929–3935.

Dobrynin, A. V., Rubinstein, M., & Obukhov, S. P. (1996). Cascade of transitions of polyelectrolytes in poor solvents. *Macromolecules, 29*(8), 2974–2979.

Dong, J., & Ozaki, Y. (1997). FTIR and FT-Raman studies of partially miscible poly(methylmethacrylate)/poly(4-vinylphenol) blends in solid states. *Macromolecules, 30*(2), 286–292.

Ferry, J. D. (1980). *Viscoelastic properties of polymers* (3rd ed.). New York: Wiley & Sons, Inc.

Garnier, C., Schorsch, C., & Doublier, J. L. (1995). Phase separation in dextran/locust bean gum mixtures. *Carbohydrate Polymers, 28*, 313–317.

German, M. L., Blumenfeld, A. L., Guenin, Y. V., Yuryev, V. P., & Tolstoguzov, V. B. (1992). Structure formation in systems containing amylose, amylopectin, and their mixtures. *Carbohydrate Polymers, 18*, 27–34.

Grinberg, V. Y., & Tolstoguzov, V. B. (1997). Thermodynamic incompatibility of proteins and polysaccharides in solutions. *Food Hydrocolloids, 11*(2), 145–158.

Hartikainen, J., Lehtonen, O., Harmia, T., Lindner, M., Valkama, S., Ruokolainen, J., et al. (2004). Structure and morphology of polyamide 66 and oligomeric phenolic resin blends: Molecular modeling and experimental investigations. *Chemistry of Materials, 16*(16), 3032–3039.

Hellebust, S., Blokhus, A. M., & Nilsson, S. (2004). Associative and segregative phase behavior of a mixed aqueous cationic surfactant and anionic hydrophilic polymer system. *Colloids and Surfaces A, 243*, 133–138.

Hellebust, S., Nilsson, S., & Blokhus, A. M. (2003). Phase behavior of anionic polyelectrolyte mixtures in aqueous solution: effects of molecular weights, polymer charge density, and ionic strength of solution. *Macromolecules, 36*(14), 5372–5382.

Icoz, D. Z., Moraru, C. I., & Kokini, J. L. (2005). Polymer–polymer interactions in dextran systems using thermal analysis. *Carbohydrate Polymers, 62*(2), 120–129.

Ioan, C. E., Aberle, T., & Burchard, W. (2000). Structure properties of dextran: 2. Dilute solution. *Macromolecules, 33*, 5730–5739.

Jousset, S., Bellossent, H., & Galin, J. C. (1998). Polyelectrolytes of high charge density in organic solvents: synthesis and viscosimetric behavior. *Macromolecules, 31*(14), 4520–4530.

Kalichevsky, M. T., & Blanshard, J. M. V. (1993). The effect of fructose and water on the glass transition of amylopectin. *Carbohydrate Polymers, 20*, 107–113.

Kalichevsky, M. T., Orford, P. D., & Ring, S. G. (1986). The incompatibility of concentrated aqueous solutions of dextran and amylose and its effect on amylose gelation. *Carbohydrate Polymers, 6*, 145–154.

Kalichevsky, M. T., & Ring, S. G. (1987). Incompatibility of amylose and amylopectin in aqueous solution. *Carbohydrate Research, 162*, 323–328.

Kolhe, P., & Kannan, R. M. (2003). Improvement in ductility of chitosan through blending and copolymerization with PEG: FTIR investigation of molecular interactions. *Biomacromolecules, 4*(1), 173–180.

Kuo, S. W., & Chang, F. C. (2001). Effects of copolymer composition and free volume change on the miscibility of poly(styrene-co-vinylphenol) with poly(ε-caprolactone). *Macromolecules, 34*, 7737–7743.

Kuo, S. W., & Chang, F. C. (2002). Miscibility behavior and specific interaction of phenolic resin with poly(acetoxystyrene). *Macromolecular Chemistry and Physics, 203*, 868–878.

Lauten, R. A., & Nystrom, B. (2000). Linear and nonlinear viscoelastic properties of aqueous solutions of cationic polyacrylamides. *Macromolecular Chemistry and Physics, 201*, 677–684.

Michon, C., Buvelier, G., Launay, B., Parker, A., & Takerkart, G. (1995). Study of the compatibility/incompatibility of gelatin/iota-carrageenan/water mixtures. *Carbohydrate Polymers, 28*, 333–336.

Morales-Diaz, A., & Kokini, J. L. (1997). Glass transition of soy globulins using differential scanning calorimetry and mechanical spectrometry. *Biotechnology Progress, 13*, 624–629.

Moraru, C. I., Lee, T-C., Karwe, M. V., & Kokini, J. L. (2002). Phase behavior of a meat-starch extrudate illustrated on a state diagram. *Journal of Food Science, 67*(8), 3026–3032.

Nordmeier, E. (1993). Static and dynamic light-scattering solution behavior of pullulan and dextran in comparison. *The Journal of Physical Chemistry, 97*(21), 5770–5785.

Russel, W. B. (1991). Concentrated colloidal dispersions. *MRS Bulletin: Materials Research Society, 16*(8), 27–31.

Shinoda, K. (1978). *Principles of solution and solubility*. New York: Marcel Dekker, Inc.

Sperling, L. H. (2001). *Introduction to physical polymer science* (3rd ed.). New York: Wiley & Sons, Inc.

Tadros, T. F. (1996). Correlation of viscoelastic properties of stable and flocculated suspensions with their interparticle interactions. *Advances in Colloid and Interface Science, 68*, 97–200.

Tolstoguzov, V. B. (1991). Functional properties of food proteins and role of protein–polysaccharide interaction. *Food Hydrocolloids, 4*(6), 429–468.

Tolstoguzov, V. B. (1998). Functional properties of protein–polysaccharide mixtures. In S. E. Hill, D. A. Ledward, & J. R. Mitchell (Eds.), *Functional properties of food macromolecules* (pp. 252–277). Maryland: Aspen Publisher.

Tolstoguzov, V. B. (2000a). Foods as dispersed systems: Thermodynamic aspects of composition-property relationships in formulated food. *Journal of Thermal Analysis and Calorimetry, 61*, 397–409.

Tolstoguzov, V. B. (2000b). Compositions and phase diagrams for aqueous systems based on proteins and polysaccharides. *International Review of Cytology, 192*, 3–31.

Tolstoguzov, V. B. (2003). Some thermodynamic considerations in food formulation. *Food Hydrocolloids, 17*(1), 1–23.

Tvaroska, I., Perez, S., & Marchessault, R. H. (1978). Conformational analysis of (1–6)-α-D-glucan. *Carbohydrate Research, 61*, 97–106.

Walsh, D., Arcelli, L., Ikoma, T., Tanaka, J., & Mann, S. (2003). Dextran templating for the synthesis of metallic and metal oxide sponges. *Nature Materials, 2*, 386–390.

Walstra, P. (2003). *Physical chemistry of foods*. New York: Marcel Dekker, Inc. pp. 137–202.

Zimeri, J. E., & Kokini, J. L. (2003a). Phase transitions of inulin–amioca systems in limited moisture environments. *Carbohydrate Polymers, 51*, 183–190.

Zimeri, J. E., & Kokini, J. L. (2003b). Rheological properties of inulin-waxy maize starch systems. *Carbohydrate Polymers, 52*, 67–85.

Zimeri, J. E., & Kokini, J. L. (2003c). Morphological characterization of the phase behavior of inulin-waxy maize starch systems in high moisture environments. *Carbohydrate Polymers, 52*, 225–236.