Miscibility Studies of Chitosan and Starch Blends in Buffer Solution

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The miscibility of chitosan (CS) and starch in buffer solution (CH_3COOH and CH_3COONa) has been investigated by viscosity, density and refractive index methods at 303 K, 313 K, and 323 K. Various interaction parameters such as polymer-polymer and blend-solvent interaction parameters and heat of mixing have been calculated using viscosity and density data. The results indicated the existence of positive interactions in the blend polymer solutions and that they are miscible below 40% of starch compositions. The study also revealed that variation of temperature does have significant effect on the miscibility of chitosan and starch blends.

Keywords: Polymer blends, miscibility, polymer-solvent interaction, solubility interactions, hydrogen bonding

1 Introduction

In search of new materials with improved physicochemical and mechanical properties, the blending of polymers has received considerable attention of researchers in the past several decades; however polymer blends do not always have better properties. The final properties of the blends are determined by the miscibility of the polymers, which is greatly favored by formation of intermolecular hydrogen bonds between the component polymers. Chitosan [ß-(1, 4)-2-amino-2-deoxy-D-glucopyranose] is a natural polymer derived by deacetylation of chitin, which is the second most abundant biopolymer in nature next to cellulose (1). Compared with other polysaccharides, chitosan has several important advantages, including biocompatibility, biodegradability, no toxicity, good film-forming characteristics, excellent chemical-resistant and electrolytic properties. So, chitosan has been widely studied for use in clinics (2), drug delivery systems (3), solid polyelectrolytes (4), surfactants (5) and membranes on ultrafiltration, reverse osmosis and evaporation (6). However, its mechanical properties and other physical/chemical properties are not good enough to meet this wide range of applications. Incorporation with other natural or synthetic polymers is an effective approach for improving the physical/chemical properties of chitosan through the amino groups and hydroxyl groups on its backbone, including blending chitosan with other polymers (7–9), introducing cross-linking structure to the membrane (10, 11) and developing organic-inorganic hybrid membrane (12).

Starch is an abundant and low cost natural polymer. The hydrophilic starch is incompatible with hydrophobic synthetic polymers, and simple mixing blends tend to phase separation. Chitosan-starch blend films were prepared, and their structure and properties were studied by Pawlaket et al. (13). Using IR spectra and DSC analysis, they reported that two polysaccharides were compatible when the starch was less than 30% by weight. From X-ray diffraction patterns of blend films, it was observed that crystallization of starch was inhibited, and recrystallization of chitosan was also affected by starch. Thermogravimetric technique supported the same results.

Polymer blends are physical mixtures of structurally different polymers or copolymers, which interact through secondary forces with no covalent bonding, are miscible in molecular level. The basis of polymer-polymer miscibility may arise from any specific interaction, such as hydrogen bonding, dipole-dipole forces, and charge transfer, complexes for homopolymer mixtures (14–16). There have been various techniques of studying the miscibility of the polymer blends (17–23). Some of these techniques are complicated, costly and time consuming. Hence, it is desirable to identify simple, low cost and rapid techniques to study the miscibility of polymer blends.

Chee (21) and Sun et al. (24) have suggested a viscometric method for the study of polymer-polymer miscibility in solution. The subject of this study is to investigate the miscibility behavior of chitosan and starch blends using

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viscometric, density and refractive index methods at 303K, 313K, and 323 K. The effects on molecular interactions between poly-solvent and blend-solvent interaction parameters and heat of mixing were also determined. With amide and –CO- group in chitosan, which can function as a proton acceptor, and starch with its –OH groups functioning as weak proton donors, one may expect hydrogen bonding interaction leading to miscibility in CS/starch blends.

2 Experimental

2.1 Preparation of Polymer Solutions

1g of chitosan (Aldrich: medium molecular weight) was dissolved in buffer solution (0.1 M CH$_3$COOH and 0.2 M CH$_3$COONa) to give 1% (w/v) solution of pH 5.12. 1% (w/v) starch stock solution was prepared in distilled water and stirred at 353K. The different compositions of CS/starch blends were prepared by mixing appropriate amount of these stock polymer solutions in volume ratio (90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80, and 10/90).

2.2 Viscosity

Viscosity measurements were done at 303K, 313K, and 323 K, using suspended level Ubbelohde viscometer with a flow time of 95s for distilled water. The prepared polymer solutions were further diluted [0.5, 0.4, 0.3, 0.2, and 0.1, (v/v)] using buffer solution, along with the pure polymer solutions and viscosity measurements were carried out. Solution viscosities at different temperatures were maintained in a thermostat bath, with thermal stability ±0.1°C.

2.3 Density and Refractive Index

The densities of 1% (w/v) solutions were measured at 303K, 313K, and 323 K, using specific gravity bottle. The refractive index of the blend solutions were measured using Abbe's refractometer with accuracy of measurements at ±0.05%.

3 Results and Discussion

3.1 Solution Property Studies

Chitosan has 2-acetamido-2-deoxy-β-D-glucopyranose and 2-amino-2-deoxy-β-D-glucopyranose (GlcN). The GlcN carry positive charge in the acid media and it exhibits an abnormal increase in the viscosity of the dilute solutions. This is because of charge repulsion between the positively charged free amino groups and thereby stretches out the molecule in absence of salt in the medium. When buffer solution was used as solvent, the repulsion due to
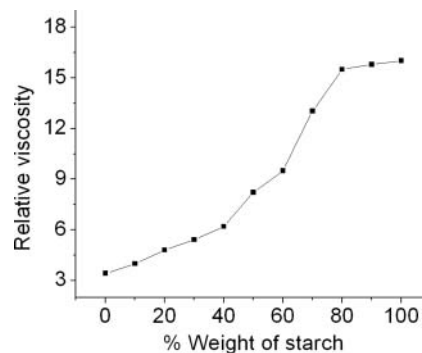
Fig. 1. Relative viscosity vs. composition of CS/starch blends at 303 K.

like charges was decreased and thus, viscosity behaved normally (25, 26).

From the viscosity data, relative and reduced viscosities of the polymer solutions have been calculated. The plot of relative viscosity vs. blend compositions (Fig. 1) was linear only below 40% starch composition in the blend for sample with 0.5 (v/v) total concentration. This behavior shows that the CS/Starch blend system is miscible only below 40% starch content (27). Huggin's plots of reduced viscosities of the component polymers and their blend compositions vs. concentrations at 303K, 313K, and 323 K temperatures are shown in Figures 2a–2c. Figures 2a–2c show a considerable higher slope for higher concentrations of CS fraction in polymer blend. This may be attributed to the hydrodynamic and/or thermodynamic interactions, like hydrogen bonding between OH group of starch and NH$_3^+$ of CS macromolecules in the blend solutions of higher CS fraction in polymer blend and phase separation in the blend solutions at lower CS fraction in polymer blend. Hence, the CS/starch is found to be miscible only when the starch content is less than 40% in the blend.

The interaction parameter of the component polymers and their blend compositions have been discovered from the plots of the reduced viscosity vs. concentration and are given in Tables 1 and 2. The slope of the curve gives the corresponding interaction parameter value, which has been evaluated on the basis of the classical Huggins equation (28). Krigbaumand Wall interaction parameter Δb of the blends (29) has been obtained from the difference between the experimental and theoretical values of the interaction parameters b_{12} and b^*_{12}. Polymer 1–polymer 2 interaction parameter Δb can be calculated as follows:

$$\frac{(\eta_{sp})_m}{C_m} = (\eta)_m + b_m C_m \quad (1)$$

where C_m is the total concentration of polymers $C_1 + C_2$, $(\eta_{sp})_m$ is the specific viscosity and b_m represents the global interaction between all polymeric species defined by the equation,

$$b_m = w_1^2 b_{11} + 2w_1 w_2 b_{12} + w_2^2 b_{22} \quad (2)$$
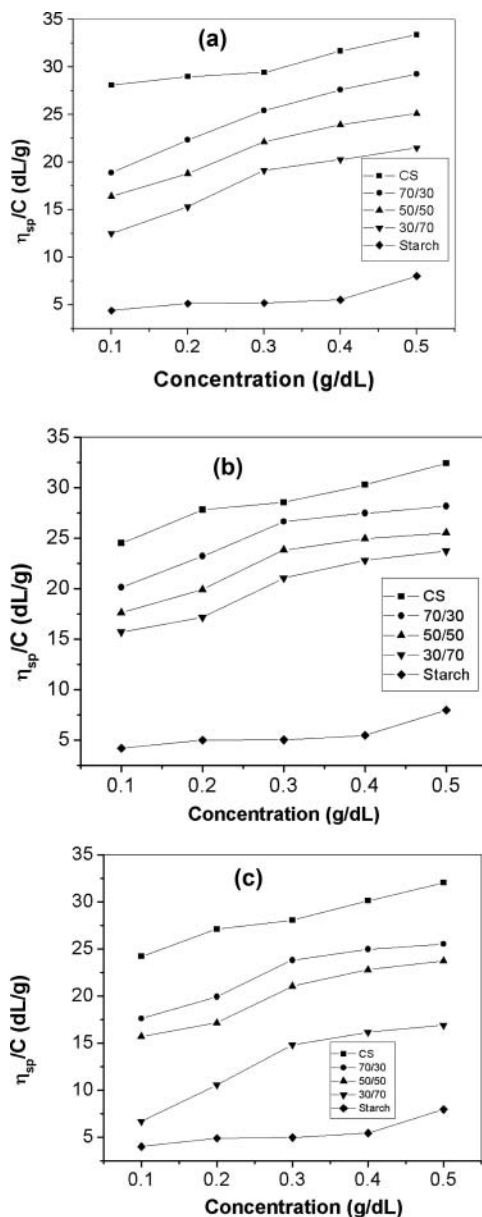
Fig. 2. Reduced viscosity vs. concentration of CS/starch blends at various temperatures (a) 30°C, (b) 40°C, (c) 50°C.

where w_1 and w_2 are weight fractions of polymer 1 and polymer 2, respectively, b_{12} is the interaction parameter of the blend system that can be calculated from Equation 2 and b_{11} and b_{22} are respective individual interaction parame-

ters. The interaction parameters b_{11}, b_{22}, and b_m have been calculated from the slopes of the plot of reduced viscosity vs. concentration (28). The interaction parameter b^*_{12} was then calculated theoretically by using equation,

$$b^*_{12} = (b_{11}b_{22})^{1/2} \qquad (3)$$

The difference (Δb) calculated from the theoretical b^*_{12} from Equation 3 and the experimental b_{12} with Equation 2 is given as:

$$\Delta b = (b_{12} - b^*_{12}) \qquad (4)$$

If Δb 0, blends are miscible; and if $\Delta b < 0$ phase separation occurs. It has been found that Δb values are positive (Table 1) for CS/starch blend ratios: 90/10, 80/20, 70/30 and 60/40 blend compositions in buffer solution. Increase in temperature shows that 70/30 and 60/40 blends are immiscible at 323 K. This suggests that the blends are miscible only in the 90/10 and 80/20 range for temperature at 323 K. The positive values of Δb explain the existence of intermolecular interactions due to hydrogen bond between the different chains.

If η_1 and η_2 are sufficiently apart, a more effective parameter μ, defined by Chee (21), can be used to predict the compatibility. The relation is given by,

$$\mu = \frac{\Delta b}{(\eta_2 - \eta_1)^2} \qquad (5)$$

Where, η_1 and η_2 are intrinsic viscosities of pure component solutions. The blend is miscible when $\mu \geq 0$ and immiscible if $\mu < 0$. The values of μ, calculated with aforementioned expression at different temperatures for the present system have been presented in Table 2.

Sun et al. (24) have suggested a new formula for the determination of polymer miscibility as follows:

$$\alpha = K_m - \frac{K_1[\eta]_1^2 w_1^2 + K_2[\eta]_2^2 w_2^2 + 2\sqrt{K_1 K_2}[\eta]_1[\eta]_2 w_1 w_2}{\{[\eta]_1 w_1 + [\eta]_2 w_2\}^2} \qquad (6)$$

Where, K_1, K_2, and K_m are the Huggins's constants for individual components 1, 2 and the blend, respectively. The long-range hydrodynamic interactions are considered while deriving this equation. They have also suggested that a blend will be miscible when $\alpha \geq 0$ and immiscible when $\alpha < 0$. The α values for the present system at various

Table 1. Δb, Δk_{AB} and slope of reduced viscosity vs. concentration plot values for the CS/starch blends at different temperatures

| CS/starch (v/v) | Slope b_m | At 30°C | | Slope b_m | At 40°C | | Slope b_m | At 50°C | |
		Δb	Δk_{AB}		Δb	Δk_{AB}		Δb	Δk_{AB}
70/30	26.01	0.264	0.1337	20.33	0.826	0.1928	20.66	0.169	0.2250
50/50	22.59	0.166	0.1061	17.65	1.312	−0.2316	18.59	−1.506	−0.2692
30/70	18.25	−0.084	−0.2344	12.88	−1.274	−0.3668	9.22	−1.542	−0.5350

Table 2. μ, and α values for the CS/starch blends at different temperatures

CS/starch (v/v)	At 30°C		At 40°C		At 50°C	
	μ	α	μ	α	μ	α
90/10	0.0533	0.0104	0.0501	0.0248	0.0484	0.0210
80/20	0.0439	0.0170	0.0398	0.0458	0.0312	0.0450
70/30	0.0378	0.0195	0.0341	0.0084	0.0289	0.0227
60/40	0.0320	0.0206	−0.0245	0.0823	−0.0254	−0.0158
50/50	−0.0300	−0.0228	−0.0411	−0.0104	−0.0441	−0.0381
40/60	−0.0253	−0.0459	−0.0342	−0.0054	−0.0757	−0.1427
30/70	−0.0612	−0.0145	−0.0640	−0.0027	−0.0901	−0.8085
20/80	−0.0868	−0.0258	−0.0874	−0.0266	−0.1253	−0.3488
10/90	−0.1021	−0.0849	−0.1125	−0.0125	−0.1442	−0.1255

temperatures have been listed in Table 2. The computed values show that both μ and α values for the system under study are positive for 90/10, 80/20, 70/30, and 60/20 ratios at temperatures 303 K and 313 K. The positive values for 90/10, 80/20, 70/30 blends at 323 K indicate that only these composition is miscible. Further, calculations to identify the miscibility of blends based on Huggins constant. The Huggins constant is a parameter that could also be used to express the interaction between like and unlike polymers (29). Hong et al. (30) used Huggins constant parameter k_{AB} value concerned with b_{AB} as shown in the below equations for different polymers.

$$b_{AB} = k_{AB}[\eta]_A[\eta]_B \qquad (7)$$

and

$$k_{AB} = \frac{b_m - \left(b_A w_A^2 + b_B w_B^2\right)}{2[\eta]_A[\eta]_B w_A w_B} \qquad (8)$$

The factor k_{AB}, is a theoretical value derived from the geometric means of k_A and k_B as:

$$k_{AB,t} = (k_A k_B)^{0.5} \qquad (9)$$

The deviation from the theoretical value also provides information about the interaction between unlike polymers as shown in:

$$\Delta k_{AB} = k_{AB} - k_{AB,t} \qquad (10)$$

The positive Δk_{AB} value indicates that the polymer mixture in solution-state is miscible. Table 1 shows the Δk_{AB} values for our system, which are positive for up to 50/50 compositions indicating the miscibility of the blends at 303K and313K, but at 323 K the negative values for the 50/50 to 30/70 blends, show that the blends are not miscible at these temperatures. This may be due to the loss of specific interactions between the polymer and solvents at such relatively high starch content and temperature.

The heat of mixing (ΔH_m) was also used as a measure to study (31–33) the blend compatibility. According to Schneier (32) ΔH_m of the polymer blends is given by:

$$\Delta H_m = \left\{ w_1 M_1 \rho_1 (\delta_1 - \delta_2)^2 \right.$$
$$\left. \times \left[\frac{w_2}{(1 - w_2)M_2\rho_2 + (1 - w_1)M_1\rho_1} \right]^2 \right\}^{1/2} \quad (11)$$

Where W, M, and ρ are the weight fractions of the polymer, the monomer molecular weight, and the polymer density respectively, and δ represents the solubility parameters of the polymers. The δ values of CS [$\sim$41 $(J/cm^3)^{1/2}$] and starch [$\sim$34.0 $(J/cm^3)^{1/2}$] were taken from the literature, (34, 35) and these values were used to calculate ΔH_m with Equation 12. Figure 3 shows the variation of ΔH_m vs. blend composition. It is evident (Fig. 3) that the variation follows almost a linear pattern, without any reversal (increase followed by decrease or vice versa) in the trend for CS/starch blend range of 90/10, 80/20, 70/30 and 60/40. This behavior further confirms that the blend solutions are miscible in these CS/starch blend range as the values are almost near to zero, since heat liberated is very small for these blends. For lower CS fraction in the polymer blend compositions,
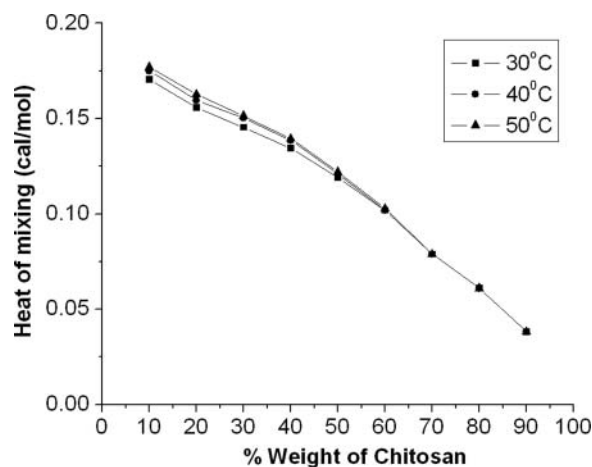
Fig. 3. Heat of mixing of CS/starch blends at different temperatures.

Table 3. Polymer-Polymer interaction parameters for the CS and starch in the blend

Temperature (K)	Polymer	χ_i calculated from Equation 12
298	Chitosan	0.0515
	Starch	0.3822
313	Chitosan	0.0500
	Starch	0.3401
323	Chitosan	0.0492
	Starch	0.3034

Fig. 4. Variation of density of CS/starch blend solutions with chitosan blend composition at different temperatures.

slight deviation of the plot from linearity may be due to the large difference in the molecular weights of CS and starch samples used, causing initial increase in heat of mixing. Further, the heat of mixing calculated at different temperatures varied slightly with temperature, the ΔH_m values for 323 K at lower CS fraction in the blend deviates away from other temperature values indicating phase separation. This behavior shows that the effect of temperature on miscibility of the blends is significant and that the specific interactions that make the blends miscible are also moderately strong.

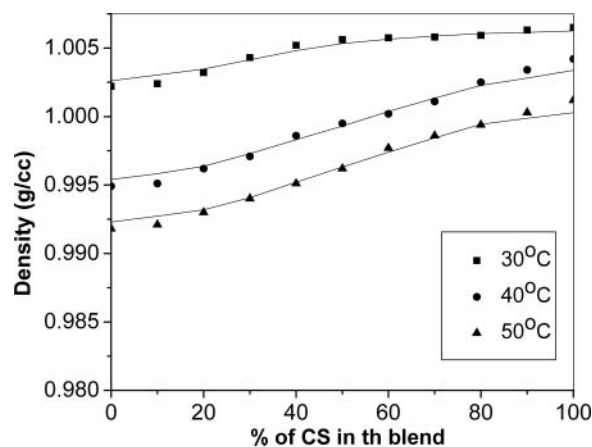### 3.2 Polymer-polymer and Polymer Blend-solvent Interactions

The interaction parameters between polymer-polymer and polymer blend-solvent are a measure of miscibility. The polymer–polymer interaction parameters (χ_i) have been computed from Flory–Huggins theory (31) with:

$$\chi_i = \left(\frac{V_i}{RT} \right)(\delta_2 - \delta_1)^2 \tag{12}$$

where δ_1 and δ_2 are the solubility parameter of component polymers. In this equation, V_i is an appropriately chosen 'reference volume' of the solvent (buffer), 70.9 cm^3/mol, R is the gas constant and T is temperature (K). The blend/solvent interaction parameters have also been calculated according to the method adopted by Singh and

Singh (38). The solubility parameters of the blend (δ) was calculated from the additively relationship,

$$\delta = X_1\delta_1 + X_2\delta_2 \tag{13}$$

where X_1 and X_2 are the mass fractions and δ_1 and δ_2 are the solubility parameters of the component polymers in the blend system. The interaction parameters of the polymer–polymer blend systems have been presented in Table 3, whereas the blend–solvent interaction parameters are given in Table 4. From these data, we observed that the net polymer–polymer interactions were lower than those observed for blend–solvent interactions for studied blend compositions (50/50 and 30/70 blend ratio) at three different temperatures. Such a difference between polymer–polymer interactions and blend–solvent interactions suggested the compatible nature of the blends only below 40% starch content in the blend and below 30% at 323 K.

Table 4. Blend-Solvent interaction parameters at different temperatures

Temperature (K)	CS/starch (v/v)	δ calculated from Equation 13	χ_i calculated from Equation 12
303	70/30	9.294	0.0331
	50/50	9.210	0.2029
	30/70	9.126	0.3005
313	70/30	9.294	0.0419
	50/50	9.210	0.4320
	30/70	9.126	0.4480
323	70/30	9.294	0.0527
	50/50	9.210	0.4399
	30/70	9.126	0.4965
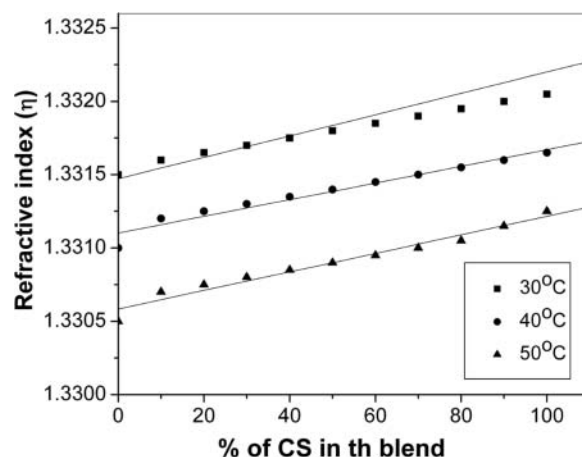
Fig. 5. Variation of refractive index values of CS/starch blend solutions with chitosan blend composition at different temperatures.
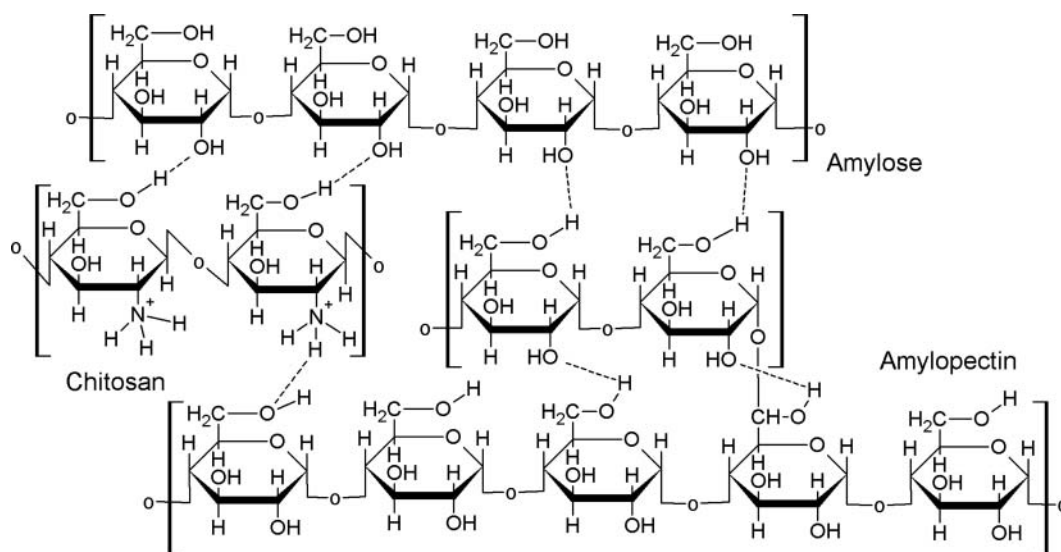
Fig. 6. Molecular structures and hydrogen bonding in chitosan/starch blends.

To confirm the miscibility behavior of the blends further, density, and refractive index values of the blend solutions have been measured at three different temperatures. The variation of the density and refractive index with the blend composition is shown in Figures 4 and 5, respectively. It was already established (21, 39) that the variation is linear for miscible blend and nonlinear for immiscible blend. In the present case, the variation is found to be linear when the starch content is less than 40% at 303K, 313K, and 323 K, respectively and as the starch content in the blend increases, non-linear region is exhibited (Fig. 4), while in refractive index (Fig. 5) no much variation is observed. This outcome is in confirmation with μ and α values. So the present study indicates the existence of miscibility windows when the starch content is less than 40% in the blend. And below this composition, there will not be much interaction between the polymer segments, which leads to immiscibility of the polymer blend. CS and starch polymers suitable for use herein preferably interact with the starch molecules on the molecular level in order to form a substantially compatible mixture. The interactions range from the strong, chemical type interactions such as hydrogen bonding between chitosan and starch, to merely physical entanglements between them. Chitosan is preferably high molecular weight, substantially linear chain molecules. The highly branched structure of a amylopectin molecule favours the branches to interact intramolecularly, due to the proximity of the branches within a single molecule. Thus, the amylopectin molecule has poor or ineffective entanglements/interactions with other starch molecules, particularly other amylopectin molecules. Figure 6 represents schematic interactions between two polymers with hydrogen bonding. The compatibility with starch enables chitosan to be chemically interacting and/or physically entangle with the branched amylopectin molecules such that the amylopectin molecules associate with one another via the chitosan polymer chain. The high molecular weight of the chitosan enables it to simultaneously interact/entangle with several starch molecules. The linking function of the high polymers is particularly important for starches high in amylopectin content. Here, the miscibility of blend may be due to some specific interaction like H-bonding between CS and starch.

4 Conclusions

The miscibility behavior of CS and starch blends has been studied in the temperature range of 303K, 313K, and 323 K. The miscibility has been analysed by solution viscosity, density, and refractive index measurement of the blend solutions and calculating various interaction parameters based on these data. The μ and α interaction parameters indicated the presence of positive interactions in the system, when the starch content is less than 40% in the blend and 50% for Δb and Δk_{AB} at 303K and 313K. As the temperature 323 K immiscibility was seen in 60/40 blend ratio, the heat of mixing estimations of the blends indicated that the effect of temperature has some significant effect on the miscibility of the blends.

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