Characterization and Miscibility Dynamics of Dextran-Poly(vinylpyrrolidone)-Water System

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Summary: The miscibility behavior and intermolecular interactions among Dextran (Dx) with different molecular weight and Polyvinylpyrrolidone (PVP) blends were studied as dilute aqueous solutions at 25 °C by viscosity method. The intrinsic viscosity and the interaction coefficient were experimentally measured for each polymer-water as well as for Dx-PVP-water systems. These results served for the prediction of miscibility of the Dx/PVP blends with various blend compositions by using$\Delta[\eta]_m$,Δb_m,Δk_{AB},ΔB,μ and α parameters. Except Dx4/PVP with its all compositions (Dx4 with nominal molecular weight of 110 000), other blend systems are found to be almost miscible. The density measurements of these polymer solutions and their blends were conducted in order to compare with the viscosity findings. Lastly, all Dx with different molecular weight, PVP and their blends were characterized by infrared spectroscopy (FT-IR), and differential scanning calorimetry (DSC).

Keywords: blends; dextran; miscibility; poly(vinylpyrrolidone); viscosity

Introduction

There is an increasing interest to blending in recent years both in research laboratories and in industry as it is being a new polymer production method.[1] Within the three basic types of blending, solution blending has two advantages over melt or dry blending. One of the advantages is that the equilibrium is attained between the different polymer components in solution. Other advantage is being able to measure the viscosity effectively.

The miscibility between the components of polymer blend (mixture) is an important factor in developing new materials based on polymer blends. Miscibility is defined as the ability to be mixed at a molecular level to produce one homogenous mixture. The miscible polymer blends are those, which satisfy the thermodynamic criteria for a single-phase system (i.e. free energy of mixing ΔG_m is negative). The majority of known polymeric mixtures are immiscible, however several miscible polymer blends have been found in last three decades.[1,2]

Two components in a polymer blend are in general not immiscible. In addition to dissimilarity in chemical structure, miscible blends may arise from specific interactions such as hydrogen-bonding, dipole-dipole forces, charge transfer complexes.[2]

Several techniques are extensively used in miscibility studies to prove polymer-polymer interactions. The studies in solid state are experimentally demanding and time consuming techniques. They require the expensive equipments like neutron scattering, electron microscopy, light scattering, spectroscopy etc. An alternative is viscosimetry which is simple, quicker and inexpensive. In literature, researchers proposed many criteria to determine polymer polymer miscibility by the viscosity method.[3–10] It is based on the assumption that interactions of polymers in solution have a great influence on the viscosity in the polymer A-polymer B-solvent system. While the two polymers are dissolved in the common solvent their hydrodynamic volume and conformation are

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affected by the solvent used, so polymer solvent interactions also play an important role in characterizing the viscosity behavior.[6,8,9]

Both of polymers used in this study have diverse applications in biomedical, pharmaceuticals and biotechnological fields because of their very low toxicty, biocompatible and biodegradable characteristics.[11] We focused on Dextran (Dx), which is only water soluble polysaccharide having three hydroxyl groups, one ring oxygen and one bridge oxygen prone to hydrogen bond acceptor, as one component of the blend. Polyvinylpyrrolidone (PVP) was chosen as the other component of the blend. It consists of polar imide group and nonpolar methylene and methine groups. The structures of studied polymers are given in Figure 1. Experimental studies show that Dx and PVP, can form hydrogen bond with water.[12,13] Therefore, a hydrogen bonding interaction is also expected to play a key role in estimating the miscibility of Dx/PVP blend.

Dilute solution viscosimetry (DSV) has been chosen as one of the method since it provides information on miscibility at the molecular level, and it is easy, fast and inexpensive when compared to other characterization methods in solid-state. Analysis of polymer miscibility in DSV is based on the Huggins equation [14] which expresses the reduced viscosity, $\frac{\eta_{sp}}{c}$, of a single polymer solution as a function of concentration, c,

$$\frac{\eta_{sp}}{c} = [\eta] + bc \tag{1}$$

where $[\eta]$ is the intrinsic viscosity which measures the effective hydrodynamic specific volume of an isolated polymer. Parameter b which reflects binary interactions between polymer segments, is related to the Huggins coefficient, k_H, given by $b = k_H[\eta]^2$. Krigbaum and Wall [15] adapted the Huggins equation to a mixture of two polymers in a common solvent as given below:

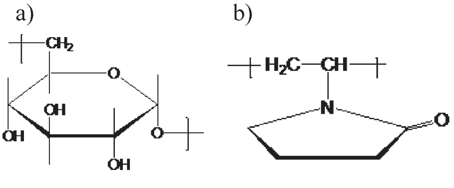

Figure 1.
The molecular structures of Dextran (Dx) and Polyvinylpyrrolidone (PVP) a) Dx and b) PVP.

$$\left(\frac{\eta_{sp}}{c}\right)_m = [\eta]_m + b_m c_m \tag{2}$$

$$b_m = b_{AA} w_A^2 + b_{BB} w_B^2 + 2 b_{AB} w_A w_B \tag{3}$$

$$[\eta]_m = [\eta]_A w_A + [\eta]_B w_B \tag{4}$$

where w is the weight fraction of respective components in the polymer blend solution, subscripts A, B, m, AB correspond to polymer A, polymer B, mixture(blend) and b_{AB} term, which is complex parameter including the thermodynamic interaction in the system,[16] is given by

$$b_{AB} = k_{AB}[\eta]_A[\eta]_B \tag{5}$$

In contrast, eq. 3 yields

$$b_{AB} = \frac{b_m - (b_{AA} w_A^2 + b_{BB} w_B^2)}{2 w_A w_B} \tag{6}$$

The experimental viscosity interaction coefficients, k_{AB}, have been determined from equations (5) and (6) in the following way:

$$k_{AB} = \frac{b_m - (b_{AA} w_A^2 + b_{BB} w_B^2)}{2[\eta]_A[\eta]_B w_A w_B} \tag{7}$$

k_{AB} (or b_{AB}) is a complex parameter including the thermodynamic and hydrodynamic interactions in the blend system, theoretical values of k_{AB} or b_{AB} are calculated as the geometric means of k_A and k_B or b_A and b_B

$$k_{AB,t} = \sqrt{k_A k_B} \tag{8}$$

$$b_{AB}^* = \sqrt{b_{AA} b_{BB}} \tag{9}$$

According to this criterion, comparison of the experimental values of k_{AB} with the theoretical values $k_{AB,t}$ could give information on interactions of the polymer pairs.

A positive difference between the experimental and the theoretical viscosity interaction coefficients is evidence of a miscible polymer pair; negative values of $\Delta k_{AB} = k_{AB} - k_{AB,t}$ refer to repulsive interaction and immiscibility.

The miscibility parameter,Δb_m, which is based on ideal solution behavior as the another version of interaction parameter (Δb_{AB}), is also used to predict miscibility of two polymers. It is simply evaluated as the difference the experimental b_m values of blends using the equation (2) from those of theoretically calculated b_m^{calc}values.

$$\Delta b_m = b_m - b_m^{calc} \tag{10}$$

where

$$b_m^{calc} = b_{AA} w_A^2 + b_{BB} w_B^2 + 2b_{AB}^* w_A w_B \tag{11}$$

To quantify the miscibility polymer blends, Chee[17] derived an interaction parameter ΔB which is directly proportional to the difference between observed b_m and average $\overline{b}$which is determined experimentally.

$$\Delta \mathrm{B} = \frac{b_m - \overline{b}}{2 w_A w_B} \tag{12}$$

where

$$\overline{b} = w_A b_{AA} + w_B b_{BB} \tag{13}$$

Accordingly, $\Delta B \geq 0$ signifies miscibility, whereas $\Delta B < 0$ indicates phase separation in the blend system. Garcia et al.[7] proposed a miscibility parameter,$\Delta[\eta]_m$, which is based on the differences between the experimental and calculated values of $[\eta]_m$treating the intrinsic viscosity as an excess property similar to those of real solutions. It states that miscibility exists if $[\eta]_m < [\eta]_m^{calc}$ and immiscibility if $[\eta]_m > [\eta]_m^{calc}$. Experimental and calculated intrinsic viscosities can be found from the equation (2) and equation (4) respectively

Chee suggested a more effective parameter,[18]μ, for blend solutions having sufficiently far apart $[\eta]_A$ and $[\eta]_B$ values

$$\mu = \frac{\dfrac{b_m - b_{AA}}{[\eta]_m - [\eta]_A} - \dfrac{b_{BB} - b_{AA}}{[\eta]_B - [\eta]_A}}{2\left([\eta]_B - [\eta]_m\right)} \tag{14}$$

$\mu > 0$ and $\mu < 0$ values represent miscibility and immiscibility, respectivelySun et al.,[19] suggested a new parameter, α in the absence of strong specific interaction forces between macromolecules

$$\alpha = k_m - k_{m1} \tag{15}$$

where

$$k_m = \frac{b_m}{[\eta]_m^2} \tag{16}$$

and

$$k_{m1} = \frac{k_A [\eta]_A^2 w_A^2 + k_B [\eta]_B^2 w_B^2 + 2\sqrt{k_A k_B}[\eta]_A [\eta]_B w_A w_B}{\left([\eta]_A w_A + [\eta]_B w_B\right)^2} \tag{17}$$

The α parameter calculated by using the equations (15)-(17) can be utilized to evaluate the presence of thermodynamic interactions. If α >0, attractive interactions occur between polymers indicating miscibility. If α<0, repulsive interactions generally take place and immiscibility is expected. If α = 0, there is no interaction.

Analysis of the viscosity data with all proposed criteria brings forth the fact that not all the proposed criteria may simultaneously satisfy the condition for the miscibility. Further, it has been reported that the parameters like molecular weight and molecular weight distribution of polymers, solvent used, and concentration of polymers play an important role in determining the miscibility of two polymers.[5,6]

Experimental Part

Dextrans with nominal molecular weights of 10 000 (T10), 40 000 (T40), 70 000 (T70), and 110 000 (T110) were obtained from Pharmacia (Uppsala, Sweeden). These samples were designated as Dx1, Dx2, Dx3, and Dx4 respectively. Polyvinylpyrrolidone (PVP) with a nominal molecular weight of 38 000 was obtained from BASF. All polymer samples were dried under vacuum prior to use. Triple distilled water was used as the solvent. All viscosity measurements for polymer solutions were performed at 25 °C by using an Ubbelohde type viscometer immersed in a constant temperature bath (Model DC 10 Haake thermostat) with temperature accuracy of ±0.1 °C. The flow times were recorded with an accuracy of ±0.01 s. The intrinsic viscosities and interaction coefficients were determined according to Huggins equation using solution of five concentrations. Plots of reduced viscosity values against concentration were linear for all systems with correlation coefficient of 0.98. Solutions with various proportions of Dx/PVP by weight (e.g. 0/100, 20/80, 40/60, 60/40, 80/20, and 100/0) were prepared with a total concentration of 0.5 $g.dL^{-1}$. For the density measurements an Anton Paar DMA 5000 oscillating tube densitometer with a precision of $5x10^{-6}$ $g.cm^{-3}$ was used. Gelman GHPP membrane (pore size $0.45\mu m$) was used to filter the solutions prior to measurements.

Fourier transform infrared (FTIR) spectra (KBr Pellets) of polymers and their blends were recorded with FTIR Shimadzu Spectrometer in the range of 400-4000 cm^{-1} wavelength, where 30 scans were taken at 4 cm^{-1} resolution.

Differential scanning calorimetry (DSC) analyses of samples were performed in the range of on a DSC (TA instruments Q10 series) under nitrogen atmosphere. An empty aluminum pan used as a reference and heating rate 10 °C/min was applied throughout the study with scan ranges between 0 and 160 °C.

Results and Discussion

Viscosity Measurements

The viscosity data are tabulated in Table 1. From this table, it is clear that intrinsic values of the different compositions reflect

Table 1.
Viscosity data for Dx /PVP blend system under different blend composition at 25 °C.[a]

System	$[\eta]_m$ (dL.g^{1})	b_m (dL.g^{-1})^2	$[\eta]_m^{calc}$ (dL.g^{1})	b_m^{calc} (dL.g^{-1})^2	Δb_m	$\Delta[\eta]_m$
Dx 1/PVP						
0/100	0.133	0.151				
20/80	0.110	0.150	0.115	0.118	0.032	−0.005
40/60	0.089	0.146	0.096	0.089	0.057	−0.007
60/40	0.075	0.122	0.078	0.064	0.058	−0.003
80/20	0.058	0.083	0.059	0.043	0.040	−0.001
100/0	0.041	0.026				
Dx 2/PVP						
20/80	0.128	0.158	0.148	0.125	0.033	−0.020
40/60	0.135	0.149	0.162	0.102	0.047	−0.027
60/40	0.149	0.111	0.176	0.082	0.029	−0.025
80/20	0.179	0.085	0.191	0.063	0.022	−0.012
100/0	0.205	0.047				
Dx 3/PVP						
20/80	0.180	0.187	0.157	0.113	0.074	0.023
40/60	0.182	0.115	0.181	0.081	0.034	0.001
60/40	0.208	0.064	0.206	0.054	0.010	0.002
80/20	0.223	0.038	0.229	0.033	0.005	−0.006
100/0	0.254	0.016				
Dx 4/PVP						
20/80	0.220	0.099	0.171	0.120	-0.021	0.049
40/60	0.228	0.062	0.205	0.095	-0.033	0.023
60/40	0.244	0.066	0.241	0.072	-0.006	0.003
80/20	0.282	0.041	0.275	0.053	-0.012	0.007
100/0	0.313	0.035				

[a] In the table $[\eta]_m^{calc}$:calculated from Equation (4), b_m^{calc}: calculated from Equation (13).

the change in molecular dimensions of Dx and PVP as a result of interaction between unlike chains. Moreover, the interaction parameter values are also presented to study the interaction between both polymers in the blends to give useful insight about the attractive and repulsive interactions. One can see that the intrinsic viscosity for Dx2, Dx3 or Dx4 is always higher than for Dx1 or PVP which is in accordance with their molecular weights. With respect to the values of interaction parameter, those for Dx1, Dx2, Dx3 or Dx4 are lower than that of PVP. Besides observed, calculated viscosity data are presented in this table in order to make comparison between them. For Dx1/PVP blend, observed intrinsic viscosities are very slightly lower (can be negligible with 5%) than the calculated values by the additivity rule shown as equation (4). For Dx2/PVP blend, a minor negative deviation is seen indicating that observed intrinsic viscosities are lower than calculated ones. Moreover, other two blends show higher observed intrinsic viscosities.

In the studied blend systems, the observed interaction parameter (b_m) values are higher than those of calculated ones for Dx1, Dx2, and Dx3 with PVP. However, in Dx4/PVP blend system, their observed $b_m$values are lower. These results show tendency to increase as the composition PVP increases, the affinity of Dx1, Dx2 and Dx3 towards PVP increases. Nevertheless, in Dx4/PVP blend system, its affinity

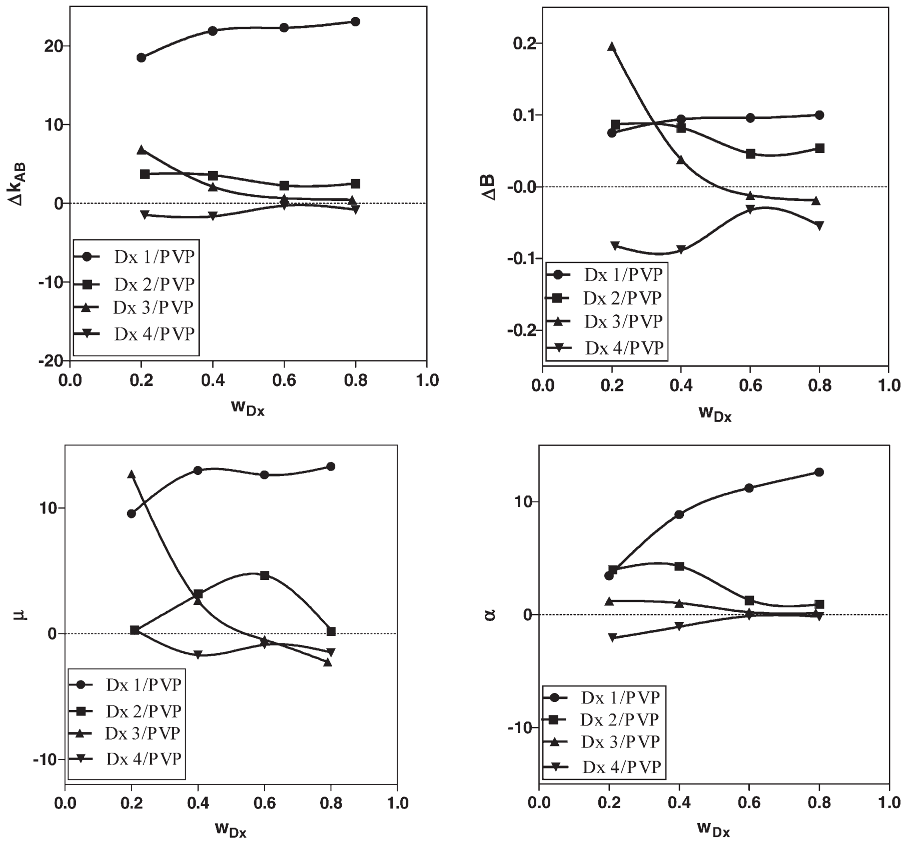

Figure 2.
Plots of Δk_{AB},ΔB,$\mu$and α as a function of weight fraction of Dx, w_{Dx} for Dx1/PVP/H_2O, Dx2/PVP/H_2O, Dx3/PVP/H_2O, and Dx4/PVP/H_2O blend systems.

decreases. In these blend systems with the different compositions, it was reported that the intrinsic viscosity of blend, $[\eta]_m$, is lower than the calculated $[\eta]$ of the pure polymers. They indicate miscibility on the basis of real solution behavior in Dx1, Dx2 and some composition of Dx3. On the other hand, these negative values of $\Delta[\eta]_m$ can be considered as the evidence of the existence of specific interactions in the polymer blends.

Based on the experimental viscosity results, for the each polymer-water and polymer-polymer-water systems, the miscibility parameters proposed by Krigbaum and Wall, Chee and Sun et al., were computed using the related equations. The plots of miscibility parameters Δk_{AB}, ΔB, μ and α versus weight fraction of Dx are illustrated in Figure 2. According to Figure 2, Δk_{AB} criterion except Dx4/PVP blend, all blends have positive values implying attractive interactions between the components of the blend. It is obvious that the results from α criterion are the same. While ΔB or μ criterion proposed by Chee, both have positive values for most of the compositions. However, some compositions for Dx3/PVP and all composition for Dx4/PVP blends, these values are negative suggesting that they may exhibit phase separation and hence immiscibility. The effect of increasing molecular weight of one of the components is to decrease all the miscibility parameter values of mixtures and thus decrease the miscibility of the blends.

Specific interactions like hydrogen bonding should be responsible for the miscibility observed between Dx and PVP. Considering polar functional groups of blend component of the polymers in this work (as is seen Figure 3), it can be interpreted by the favorable interactions occur between carbonyl oxygen of pyrrolidone ring of PVP and hydroxyls of Dx under the condition where miscibility is exhibited between PVP and Dx, hydrogen bonding interaction between the two polymers should be strong enough to overcome the intra- and intermolecular hydrogen bonding among Dx chains themselves as it is shown in Figure 3. As the molecular weight of Dx in the blend increases, the probability for a Dx chain to establish hydrogen bonding interaction with a chain of its own kind increases, since PVP chains become less available in the medium. Consequently, immiscibility of the two polymers is obtained. This possible interaction in Dx4/PVP blend is supported by their negative values of all studied miscibility parameters.

Density Measurements

The concept of miscibility predicted by viscosity was correlated to the findings of

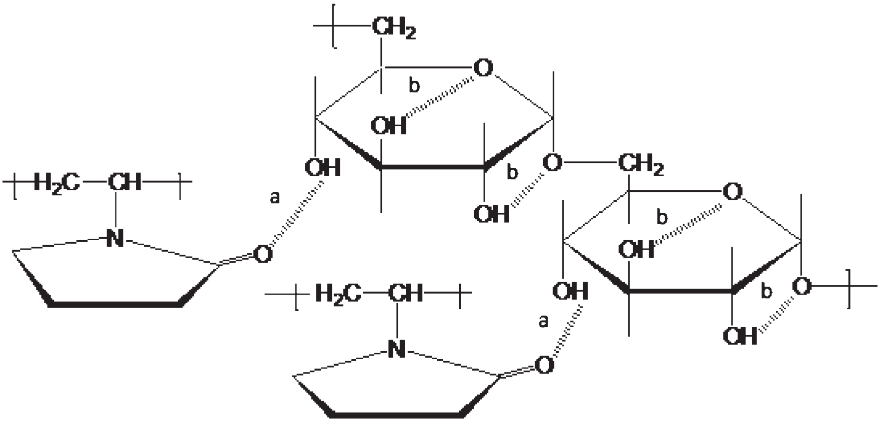

Figure 3.
The scheme of possible structure of Dx/PVP blend (a): intermolecular hydrogen bond (b): intramolecular hydrogen bond.

solution density measurements of polymer blends. If a system is miscible, an attractive interaction between the components of the system will cause an increase in the density of the resulting blend.[20] However, our intention was to look for a correlation with our viscosity results. Hence, the concentrations of the polymer blend solutions used for density measurements and viscosity measurements were the same. The density of the polymer blends was calculated from the density values of component polymers assuming an additive contribution, according to their weight fractions

$$d_m = w_A d_A + w_B d_B \qquad (18)$$

where *d* and *w* represent density and weight fraction of polymer components respectively.

The observed and calculated densities of the polymer blend solutions are given in Table 2. In all blends, the observed densities are good agreement with calculated densities obtained from equation (18). It is also found that the observed density of blend solutions increases as the weight fraction and molecular weight of Dx increases. Since all Dx/PVP blends have almost identical density values, it seems quite natural that the deviation observed in density may not be very large for this concentration (0.5 g.dL^{-1}). These density results are consistent with results published in the literature.[21,22] In the first report,[21] density measurements for dextran-poly(ethylene glycol)-water system were examined and it was found to be only marginally higher than the calculated values of single polymer solutions within a concentration range from 2.5 to 3.7% w/w. In the second report,[22] the density of aqueous solutions of five different Dx samples (molecular weight ranging from 10,000 to 500,000) was measured using an oscillating tube densitometer at 20° and 30 °C within polymer concentrations up to 0.35 g.mL^{-1}. It was reported that, there were no differences in the density of the aqueous solutions of Dx samples except the highest molecular weight one. In our blend systems, since there is no significant difference between the experimental and calculated our density results, we did not make any correlations with those of viscosity.

Table 2.
Density Data for studied blend systems under different blend compositions.

at 25 °C.System	Observed density (g.cm^{-3})	Calculated density (g.cm^{-3})
Dx1/PVP		
0/100	0.998108	
20/80	0.998203	0.998264
40/60	0.998366	0.998419
60/40	0.998530	0.998575
80/20	0.998727	0.998730
100/0	0.998886	
Dx2/PVP		
20/80	0.998293	0.998267
40/60	0.998449	0.998427
60/40	0.998614	0.998586
80/20	0.998732	0.998746
100/0	0.998906	
Dx3/PVP		
20/80	0.998286	0.998278
40/60	0.998469	0.998448
60/40	0.998635	0.998619
80/20	0.998774	0.998789
100/0	0.998959	
Dx4/PVP		
20/80	0.998293	0.998273
40/60	0.998416	0.998438
60/40	0.998580	0.998602
80/20	0.998756	0.998767
100/0	0.998932	

Glass Transition Temperature (Tg)

The DSC thermogram of(a) Dx1 (b) Dx1/PVP blend (60/40) and (c) PVP are shown in Figure 4. The Tg values for the dextran-pvp blend against pure polymer are summarized in Table 3. Increasing Molecular weight of Dx was shown to increase the T_g of the polymer which would theoretically be expected result. The immiscibility of two polymers is demonstrated by the retention of the Tg values of both individual components. If two components are partially miscible, their Tg would shift toward each other.[23] In Table 3. shows that there is increase in Tg of the pure Dx1 and Dx2 after blending with polyvinylpyrolidone. This increase in Tg may be attributed to the presence o intermolecular hydrogen bonding between the component polymers. In Figure 4, It was observed small peaks in

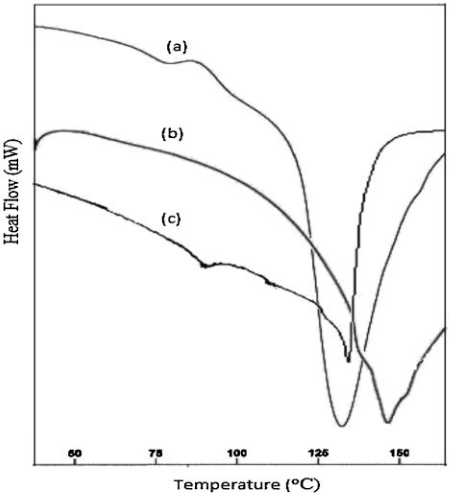

Figure 4.
DSC thermograms of (a) Dx1 (b) Dx1/PVP blend (60/40) and (c) PVP.

Table 3.
Glass transition temperatures of different molecular weight Dextran, PVP and their blends.

Sample	Tg (sample)
Dx4	102
Dx4/PVP[a]	90
Dx3	94
Dx3/PVP[a]	75
Dx2	87
Dx2/PVP[a]	114
Dx1	76
Dx1/PVP[a]	130
PVP	80

[a] Dx/PVP weight fraction: 60/40.

Dx1 and PVP thermograms due to endothermic transition. However, there was no peak corresponding to Dx1 or PVP, indicating that the blend is miscible.

FT-IR Characterization

The FTIR spectra of Dx1 and PVP and their blends are shown in Figure 5. In the FT-IR spectrum of dextran (f) the presence of -OH groups could be confirmed by the appearance of band at 3450 cm^{-1} range, C–H stretching at 2935 cm^{-1}, C–H bending and rocking vibrations at 1450cm^{-1} and 950 cm^{-1}. A broad band from 1200 to 1050 cm^{-1}characterizing asymmetrical –C–O–C– stretching of the ring. The Infrared spectrum of polyvinylpyrolidone (PVP) is given in Figure 4e, strong C=O absorption peak from the amide group of PVP at 1680 cm^{-1}, C–N group appeared at 1286 cm^{-1}, C–H stretching and bending vibration frequencies were observed 2800-3000 and 1430-1495 cm^{-1}, respectively In the spectra of the blends, all the absorption bands related to both components were present. The intensity of band 1680cm^{-1} characterizing the C=O–bonds of amide

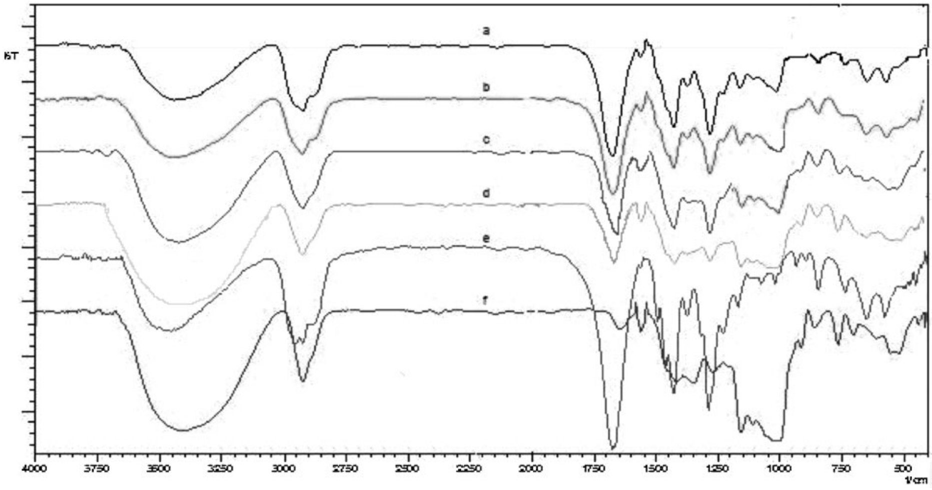

Figure 5.
FTIR spectra of samples a) Dx1/PVP (20/80) b) Dx1/PVP (40/60) c) Dx1/NVP (60/40) d) Dx1/NVP (80/20) e) PVP f) Dx1.

increases PVP content of blend is increased. Characteristic absorption peaks for Dx2/PVP, Dx3/PVP and Dx4/PVP blends were observed at the same shift values.

Conclusion

In this study, the miscibility dynamics and intermolecular interactions were examined by viscosity and density data of dilute solution of Dx/PVP blends at various compositions. Miscibility of two polymers are estimated by using$\Delta[\eta]_m$,Δb_m,Δk_{AB},ΔB, $\mu$and α parameters. Based on sign convention, it is clear that Dx1/PVP and Dx2/PVP blends are miscible, Dx3/PVP blend is almost miscible, and Dx4/PVP blend is immiscible.

The degree of miscibility follows as Dx1/PVP $>$ Dx2/PVP$\geq$Dx3/PVP $>$ Dx4/PVP in water, at least in the studied composition and concentration ranges. This miscibility trend is dependent on molecular weight of a component Dx polymer.

The miscibility of Dx and PVP blend systems are attributed to the existence of intermolecular hydrogen bonds between the component polymers. However, immiscible Dx/PVP blends are due to the existence of intramolecular hydrogen bonds.

The experimental and calculated density values agree with each other. So, in terms of density, Dx-PVP-water systems show additive effect from the two polymers. For this reason, no correlations were done on density findings with those of viscosity.

The homopolymer and their blends were evaluated by FT-IR spectroscopy. Characteristic absorption peaks of homopolymers were observed in Dx1/PVP, Dx2/PVP, Dx3/PVP and Dx4/PVP blends. It was noted that Tg value of Dx, PVP and their blends by using DSC.

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