

Miscibility Studies of Polysaccharide Xanthan Gum/PVP Blend

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Abstract Miscibility characteristics of Xanthan gum and Poly (vinyl pyrrolidone) (PVP) in common solvent water were studied by viscometry, ultrasonic velocity and density techniques at 30 and 50 °C. Blend films of Xanthan gum/PVP were prepared by solution casting method and characterized by scanning electron microscopic (SEM) and differential scanning calorimeter (DSC) techniques. Using the viscosity data, interaction parameters of Chee's (μ) and Sun's (α) were computed to determine their miscibility. The values obtained revealed that blends were miscible when PVP content is up to 70% in blend at 30 °C. Xanthan gum/poly (vinyl pyrrolidone) blends showed miscibility in all composition at 50 °C. The results were then confirmed by ultrasonic velocity, density, and DSC techniques. Compatibility in the above compositions may be due to the formation of hydrogen bonding between the carbonyl group in PVP and hydroxyl group in Xanthan gum. Further, the results revealed that change in temperature had significant effect on the miscibility of Xanthan gum/Poly (vinyl pyrrolidone) blends.

Keywords Xanthan gum · PVP · Blends · Ultrasonic · SEM

Introduction

Blending of polymers is one of the simplest means to obtain a variety of physical and chemical properties from the constituent polymers [1]. The gain in newer properties depends on the degree of compatibility or miscibility of the polymers at a molecular level. Generally, the polymer–polymer miscibility is due to some specific interactions like dipole–dipole forces, hydrogen bonding and charge transfer complexes between the polymer segments [2–4].

Literature survey reveals various techniques of studying the miscibility of polymer blends [5]. Viscometric [6, 7] ultrasonic and density [8, 9], scanning electron microscopy (SEM) [10] and differential scanning calorimeter (DSC) [11] techniques have suggested studying the miscibility of polymer blends.

As a part of research programme, we have studied the miscibility of Xanthan gum/PVP blends by using viscometry, ultrasonic velocity, density, SEM and DSC techniques. We have selected these polymers because they have many pharmaceutical and food industrial applications. Xanthan gum is a high molecular weight, water-soluble, anionic polysaccharide produced by the bacterium *Xanthanomas Campestris*. The properties of Xanthan gum have made it appealing product for use in a variety of industries including the food, cosmetics, agricultural, and petroleum industries [12, 13]. The Xanthan molecule consists of a backbone of four glucose units with charged side chains located at alternating units [14]. As a polyelectrolyte polymer, its molecular structure depends primarily on the ionic strength of the side-chains and the free ions in the solvent [15]. In an aqueous solution with no added ions, the Xanthan molecule is extended due to the electrostatic repulsion of the negatively charged side-chains. When salt is added to semi-dilute solutions, charge screening causes the side chains to

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collapse down to the back bone, driving a transition in the structure which gives the Xanthan molecule a rigid rod like shape [13, 16]. Poly (vinyl pyrrolidone) is an amorphous polymer; it has several pharmaceutical applications [17]. In addition, PVP is able to form complexes with a wide range of compounds through hydrogen-bond formation between its carbonyl group and the hydroxyl groups of water, alcohols, and hydroxyl-containing polymers like poly (vinyl alcohol) [18, 19].

Viscometric analysis of polymer–polymer miscibility in dilute solution is based on the Huggins equation, which reflects the relationship between specific viscosity and polymer concentration. In this study, the polysaccharide Xanthan gum is blended with Poly (vinyl pyrrolidone) in different compositions and at different temperatures in 0.1 M NaCl solution. Since Xanthan gum is anionic in nature, we could not apply Huggins equation to the Xanthan gum in water solution, so the Xanthan gum solution was made in 0.1 M NaCl for viscosity studies [20].

Experiment

Polymers used for the present study were Xanthan gum and Poly (vinyl pyrrolidone) (Molecular weight 3,60,000). The total weight of the two components in solution always maintained at 0.1 g/dL. Stock solutions of homo-polymers Xanthan gum, PVP and their blends of different compositions (90/10, 70/30, 50/50, 30/70 and 10/90) were prepared in water. Viscosity measurements were done at 30 and 50 °C using Ubbelohde Suspended Level Viscometer (USLV). Different temperatures were maintained in a thermostat bath with a thermal stability of ± 0.05 °C. Ultrasonic velocity measurements were performed by an ultrasonic interferometer technique [8]. During the experiment, different temperatures 30 and 50 °C were maintained by circulating water from thermostat with a thermal stability of ± 0.05 °C, through the double walled jacket of the ultrasonic experimental cell. The experimental frequency was 2 MHz. Densities of the solutions were measured at 30 and 50 °C using specific gravity bottle. For SEM and DSC studies, thin film of Xanthan gum, PVP and their blends were prepared by solution casting method. Films were dried using IR Lamp. Scanning Electron Microscopic (SEM) analysis were recorded using a JOEL (JSM 6380LA) analyzer. DSC measurements were performed in TA Q200 Differential Scanning Calorimeter, under nitrogen atmosphere. In DSC measurements, heating/cooling/heating technique was used. In first cycle of measurements, sample was heated to 90 °C and equilibrated to remove remaining water content in the blend films, then cooled to -10 °C and reheated to 250 °C. The heating/cooling/heating rate was set at 10 °C.

Results and Discussion

From viscometric measurements, reduced viscosities of homo-polymers Xanthan gum, PVP and their blend compositions (90/10, 70/30, 50/50, 30/70 and 10/90) were measured at 30 and 50 °C. Reduced viscosities of the pure polymers and their blend compositions are plotted against concentrations and are shown in Figs. 1 and 2 respectively. From the Fig. 1 it is clear that the Huggin's plots are composed of two regions with varying slopes for Xanthan gum/PVP blends. In the present work Fig. 1 indicates little higher slopes for 90/10, 70/30, 50/50 and 30/70 blend at 30 °C respectively. This is may be attributed to the mutual attraction of macromolecules in solution which leads to increase of hydrodynamic volume. Similar observations were also made by Haiyang et al. [21] and Raviprakash and Rai [22] in case of PVC/Poly caprolactone and sodium alginate/polyethyleneglycol, respectively and reported that both the systems having miscibility windows. And at 50 °C Huggin's plots are composed of higher slopes for Xanthan gum/PVP blends indicates the miscibility.

In order to quantify the miscibility of polymer blends, Chee [6] suggested the general expression for interaction parameter when the polymers are mixed in weight fractions w_1 and w_2 as

$$\Delta B = \frac{b - \bar{b}}{2w_1w_2} \quad (1)$$

where $\bar{b} = w_1b_{11} + w_2b_{22}$ where b_{11} and b_{22} are the slopes of the viscosity curves for the components and b is related to Huggins coefficient K_H as,

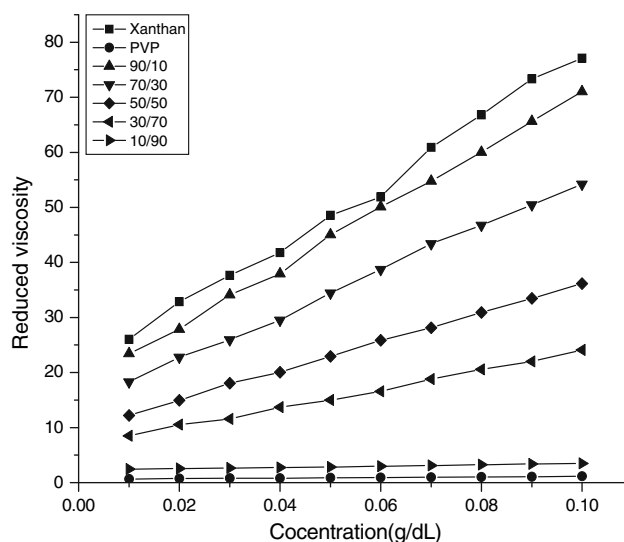


Fig. 1 Huggin's plot for 0.1% w/v Xanthan Gum/PVP blend in solution at 30 °C

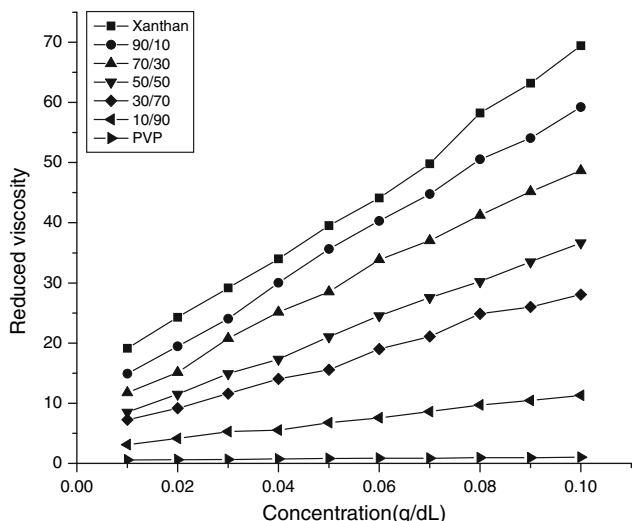


Fig. 2 Huggin’s plot for 0.1% w/v Xanthan Gum/PVP blend in solution at 50 °C

$$b = K_H[\eta]^2 \tag{2}$$

For ternary system, it is also given by

$$b = w_1^2b_{11} + w_2^2b_{22} + 2w_1w_2b_{12} \tag{3}$$

where w_1 and w_2 are the weight fractions of Xanthan gum and PVP respectively and b_{12} is slope for the blend solution.

However, Chee’s theory fails to account for the experimental data when intrinsic viscosities of pure components are far apart. In such cases he defined a more efficient parameter to predict compatibility,

$$\mu = \frac{\Delta B}{\{[\eta]_2 - [\eta]_1\}^2} \tag{4}$$

where $[\eta]_1$ and $[\eta]_2$ are intrinsic viscosities of pure component solutions. The polymer blend is miscible if $\mu \geq 0$ and immiscible when $\mu < 0$.

Later Sun et al. [7] have suggested a most satisfactory new equation for the determination of polymer miscibility as

$$\alpha = K_m - \frac{K_1[\eta]_1^2w_1^2 + K_2[\eta]_2^2w_2^2 + 2\sqrt{K_1K_2}[\eta]_1[\eta]_2w_1w_2}{\{[\eta]_1w_1 + [\eta]_2w_2\}^2} \tag{5}$$

where K_1 , K_2 and K_m are the Huggins constants for individual components 1, 2 and blend respectively. The long-range hydrodynamic interactions are considered while deriving the Eq. 5. The polymer blend is miscible if $\alpha \geq 0$ and immiscible when $\alpha < 0$. Hence, it can be defined as Xanthan gum/PVP blends are found to be miscible when PVP content is up to 70% in the blend compositions at 30 °C and Xanthan gum/PVP blends are miscible in entire compositions at 50 °C. The interaction parameters Chee’s

Table 1 Interaction parameters μ and α of Xanthan Gum/PVP blends at 30 and 50 °C

Xanthan gum/PVP compositions	At 30 °C		At 50 °C	
	μ -values	α -values	μ -values	α -values
90/10	+0.639	+0.237	+0.558	+1.410
70/30	+0.303	+0.476	+0.641	+1.909
50/50	-0.204	+1.178	+0.928	+1.091
30/70	-0.132	+1.191	+1.329	+1.537
10/90	-0.738	-0.944	+1.388	+1.795

(μ) and Sun’s (α) of the blend compositions at 30 and 50 °C are presented in the Table 1. Similar observations are also made by Basvaraju et al. [20] in case of Xanthan gum/PEO, and reported that, blend is semi compatible at 30 and 40 °C.

To confirm this further, we have measured ultrasonic velocity (v) and density (ρ) of the blends under consideration at different compositions at 30 and 50 °C. The variations in ultrasonic velocity and density with the blend compositions are shown in Figs. 3 and 4 respectively. The Adiabatic compressibility β_{ad} of different blend composition evaluated by using following equation:

$$\beta_{ad} = 1/(v^2\rho)$$

where (v) is the ultrasonic velocity and (ρ) is the density. The graphs show both linear and non linear regions (Fig. 5). It has been already established that the variation is linear for miscible blend and non linear for immiscible blend [23]. In the present case, the variation was found to be linear when the PVP content is up to 70% in blend compositions at 30 °C and linearity was observed in all

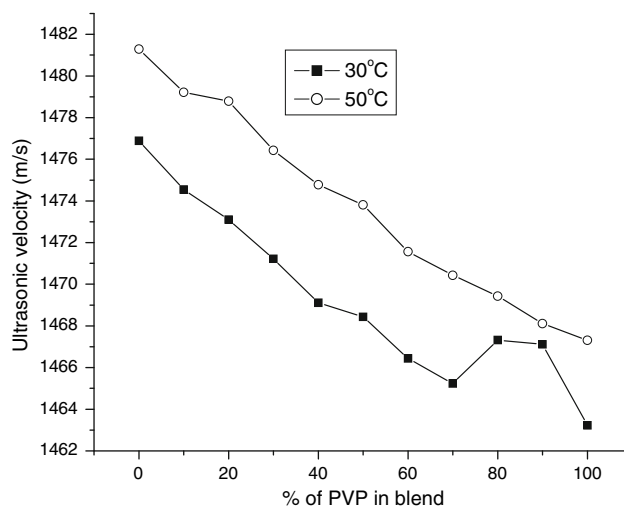


Fig. 3 Effect of temperature on the variation of Ultrasonic velocity with the Composition of 1% w/v of Xanthan Gum/PVP blend at 30 and 50 °C

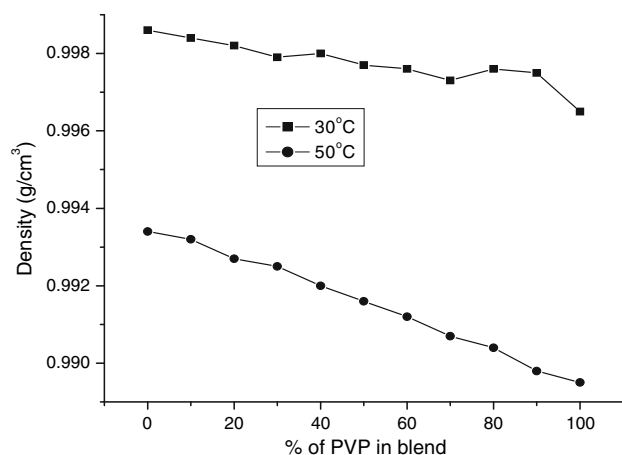


Fig. 4 Effect of temperature on the variation of density with the composition of 1% w/v of Xanthan Gum/PVP blend at 30 and 50 °C

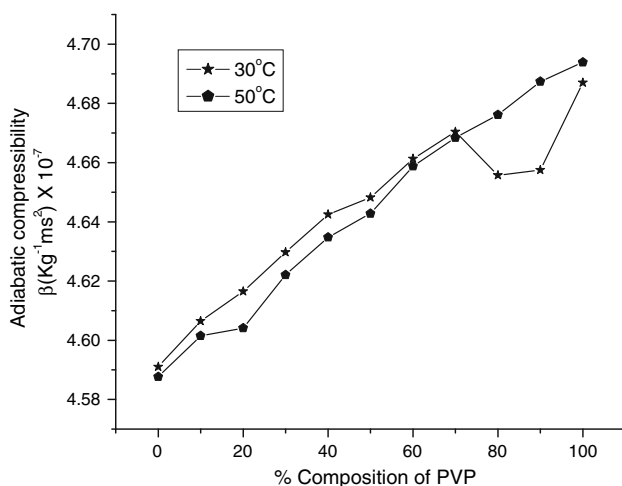


Fig. 5 Effect of temperature on the variation of Adiabatic Compressibility with the composition of 1% w/v of Xanthan Gum/PVP blend at 30 and 50 °C

compositions at 50 °C. This observation is in confirmation with μ and α value. So the present study indicates the existence of semi-compatibility at 30 °C and compatibility at 50 °C. Miscibility in the above blend compositions may due to the hydrogen-bond formation between its carbonyl group of PVP and hydroxyl groups of Xanthan gum.

Glass Transition Temperature Measurements

The glass transition temperature (T_g) of individual polymers Xanthan gum, PVP and their different blend compositions (90/10, 70/30, 50/50 and 30/70) are recorded from the DSC, T_g thermograms and are shown in Fig. 6. (a, b, c, d). Blends exhibited a single T_g , intermediate to those of Xanthan gum and PVP. The glass transition temperature was taken as the mid point of the change of slope in DSC curves [24]. The T_g of miscible blends can be predicted

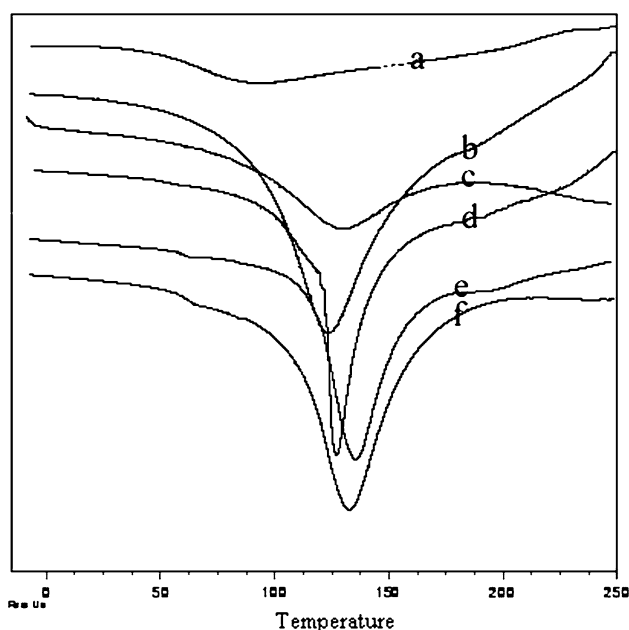


Fig. 6 DSC thermograms of a Pure PVP b Pure Xanthan Gum c 90/10 Xanthan Gum/PVP blend

theoretically by using the Fox equation a [25] and Woods equation b [26]

$$1/T_g = X_1/T_{g1} + X_2/T_{g2} \quad (a)$$

$$T_g = W_1 T_{g1} + W_2 T_{g2} \quad (b)$$

where X_1 , X_2 , T_{g1} and T_{g2} are the weight fractions and glass transition temperature of the corresponding to polymer 1 and polymer 2 respectively.

The experimental T_g value for 90/10, 70/30, 50/50 and 30/70 Xanthan gum/PVP blends compared with theoretical T_g values are summarized in Table 2. The experimental T_g value for 90/10, 70/30, 50/50 and 30/70 of Xanthan gum/PVP blends were found to be slightly higher than that of theoretically calculated T_g values implying an intermolecular interaction between the polymers [27].

Table 2 Experimental and Theoretical T_g values of Xanthan Gum, PVP and their blends

Xanthan/PVP blend compositions	Experimental T_g values (°C)	Theoretical T_g values (°C)	
		Fox equation	Wood's equation
Xanthan	46.5	–	–
90/10	48.9	47.7	48.1
70/30	52.1	50.3	51.3
50/50	55.1	53.3	54.5
30/70	58.4	56.7	57.7
PVP	62.5	–	–

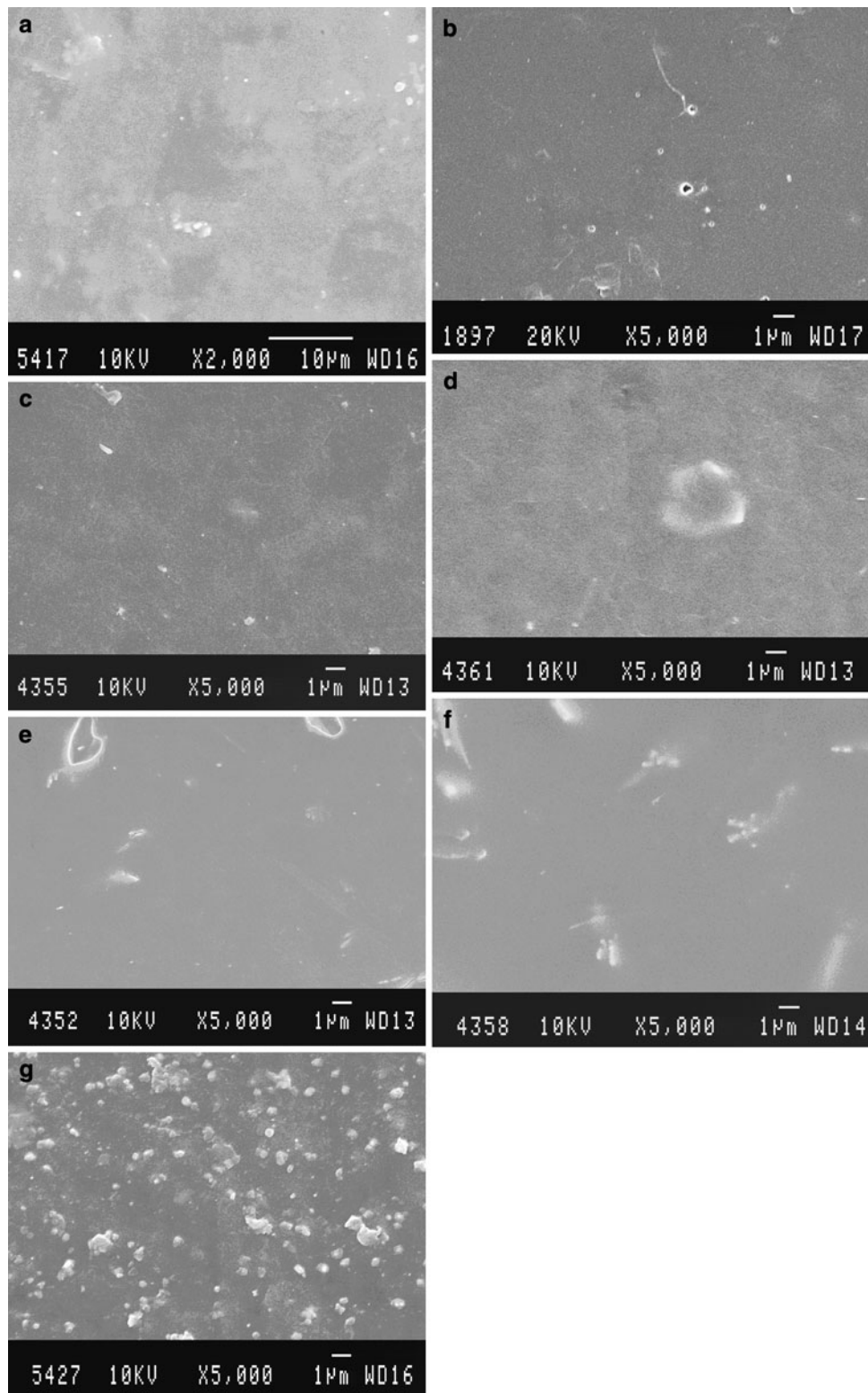


Fig. 7 Scanning electron micrographs for **a** Xanthan Gum, **b** PVP **c** 90/10 Xanthan Gum/PVP Blend, **d** 70/30 Xanthan Gum/PVP Blend, **e** 50/50 Xanthan Gum/PVP Blend and **f** 30/70 Xanthan Gum/PVP Blend, and **g** 10/90 Xanthan Gum/PVP Blend

Morphology Study of Xanthan Gum/PVP Blends

Scanning electron microscopy is a powerful technique to determine miscibility of polymer blend. The uniformity of the dispersion was examined through SEM of the solution casted films of neat polymers Xanthan gum, PVP and their blends 90/10, 70/30, 50/50 30/70 and 90/10 and are shown in Fig. 7 (a, b, c, d, e, f, g). Homogeneity was observed when PVP content is up to 70% in blend compositions indicates miscibility. Above this critical composition non-homogeneity was observed indicates immiscibility. The morphology study of Xanthan gum/PVP blends were also confirmed the semi-compatible nature of the blend.

Conclusions

Based on viscosity, ultrasonic velocity, and density measurements, it is concluded that Xanthan gum/PVP blends were found to be semi-compatible at 30 and compatible at 50 °C. It was observed that a raise in temperature of 20 °C had significant effect on the miscibility of Xanthan gum/PVP blend. Compatibility in the above compositions may be due to the formation of hydrogen bond formation. The semi-compatible nature of the blend was also confirmed by SEM and DSC studies.

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