

A Study on Compatibility of Polymer Blends of Polystyrene/Poly(4-vinylpyridine)

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ABSTRACT: Blends of polystyrene/poly (4-vinylpyridine) have been prepared by casting from a common solvent. The compatibility of the blends was studied by using dilute solution viscometry (DSV), differential scanning calorimetry (DSC), Fourier transformation-infrared spectroscopy (FT-IR), and scanning electron microscopy (SEM). The relative viscosity versus composition plots for the blends are not perfect linear. The corresponding intrinsic viscosity values show negative deviation from ideal behavior when plotted against composition. Also, the modified Krigbaum and Wall interaction parameter, Δb , shows small and negative values for all compositions except for the blend PS/P4VP (25 : 75). The results indicate that the poly-

mers are incompatible but small interaction values predict physically miscible blends which eventually show phase separation, as is observed in the present studies. However, the blends as obtained show a single, composition-dependent, glass transition temperature that fits the Fox equation well, indicating the presence of homogeneous phase. The constant, k obtained from Gordon-Taylor equation suggests intermolecular attraction between these polymers. FT-IR and SEM support the results of DSV and DSC. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 1729–1735, 2011

Key words: polystyrene; poly (4-vinylpyridine); blends; compatibility; DSC; FTIR

INTRODUCTION

Blending of polymers is a route to enhance their material properties for better application. The advantage of this method lies in simplicity of preparation and control of the properties by varying the blend compositions. Compatibility of the two homopolymers is needed to an optimum extent for a blend to show superior properties. The compatibility signifies specific interaction such as dipole-dipole, ion-dipole, and hydrogen bonding. Various measurements like heat of mixing, viscometry, glass transition temperature, morphological studies by optical and electron microscopy, infrared spectroscopy, and dynamic mechanical analysis, are used to study polymer compatibility as mentioned extensively in literature.^{1–5}

The estimation of compatibility of different pairs of polymers based on viscosity data for ternary systems involving polymer/polymer/solvent has been attempted by several authors.^{6,7} Early work on using solution viscosity for probing the interacting polymer systems was reviewed by Oiabisi et al.¹ Dondos

et al.⁸ have observed a sharp crossover in the plots of reduced viscosity versus concentration for the immiscible blends of polymethylmethacrylate/polystyrene and PS/polyethylene glycol. Bouslah et al.⁹ has reported the compatibilization of an immiscible pair, PS and unmodified PMMA by incorporating cinnamic acid into the PS chains. Further, they⁶ modified PMMA by basic comonomers, 4-vinylpyridine and 2-vinylpyridine because these are known to be stronger hydrogen bond acceptor.^{10,11} Jiao et al.¹⁰ has shown formation of interpolymer complexes with P4VP, proton-accepting polymer with proton-donating polymers including poly(acrylic) acid and poly(*p*-vinyl phenol). Kosonen et al.¹² have bonded ethylene oxide oligomers to polystyrene-*block*-poly(4-vinylpyridine) with the interest of forming ion conducting medium. Torrens et al.⁷ has modified polystyrene by copolymerization with methacrylic acid to enhance polymer-polymer miscibility with poly (vinyl pyridine) and poly (vinyl pyrrolidone).

Pyridine-containing polymers have attracted interests in recent years because they can be used in various applications as water-soluble polymers and coordination reagents for transition metals, specially 4-vinylpyridine because of its more interesting properties resulting from higher accessibility of the nitrogen atom.¹¹ The electrical properties of silver particles deposited on softened poly(4-vinylpyridine)

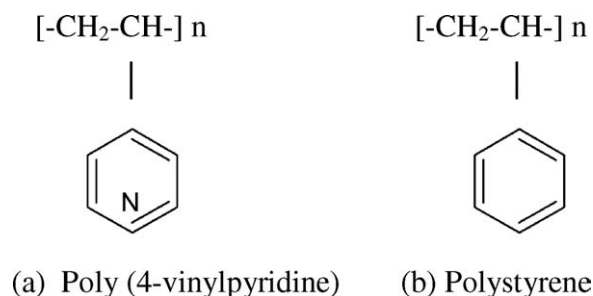
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(P4VP) indicate the formation of organized subsurface silver particulate film, i.e., organization of small silver clusters (approximately a few tens of nm) separated by smaller distance. Such structures showed electrical resistance in the range desirable for device applications. Whereas silver deposited on softened inert polymers like polystyrene (PS) substrates formed highly agglomerated structures with their room temperature resistances equaling that of the substrate, irrespective of the thickness deposited.¹³ PS, being inert is more stable against atmosphere compared with P4VP, which is hygroscopic in nature. Miscibility between the components polymers play a vital role in blending of polymers at the molecular levels. A compatible blend provides a firm basis for further application in devices. Earlier works^{6,7,9-11} have suggested the improvement of miscibility of PS with P4VP by incorporating proton donors like poly (acrylic) acid and poly (*p*-vinyl phenol) or methacrylic acid into the chains of PS with P4VP to utilize its proton acceptor nature. Further, reversible addition-fragmentation chain transfer polymerization was developed by Yuan et al.¹¹ for the controlled preparation of PS/P4VP triblock copolymers as PS-*b*-P4VP-*b*-PS and P4VP-*b*-PS-*b*-P4VP. To retain the properties of both the polymers PS and P4VP, blending is carried out through solution casting and it is expected that combination of PS and P4VP should give rise to organized subsurface silver particulate structures with the advantages of both the polymers.

The present study is carried out to assess the compatibility of PS/P4VP blends through viscometry, differential scanning calorimetry, Fourier transform-infrared spectroscopy, and scanning electron microscopy. Dilute solution viscometry is a simple and reliable method to investigate interactions of macromolecules in solution. It has been used as a complementary technique to prospect the effect of the position of nitrogen atom in the pyridine ring of P4VP on the interaction developed within PS/P4VP blends. The criterion of single composition dependent glass transition is used to investigate the miscibility of polymer blends by DSC. Specific interactions most often liberate a heat of mixing and contribute towards the free energy of mixing. Fourier transform-infrared spectroscopy is used to investigate specific interactions between the homopolymers in the blend compositions and compared to calorimetric results.

EXPERIMENTAL

Poly(4-vinyl pyridine) and polystyrene, used in this study, were procured from Sigma-Aldrich Chemicals Pvt. Ltd, Alfa-Aesar (A Johnson Mathley company), respectively. The molecular weights of P4VP and PS are 60,000 and 100,000, respectively. The structures of (a) P4VP and (b) PS are as follows:



Polymer blends were prepared through solution blending by mixing in a common solvent, dimethylformamide (DMF). Blends of PS/P4VP with different compositions {PS (w)/P4VP (w) = 0 : 100; 25 : 75; 50 : 50; 75 : 25; 100 : 0} were prepared. One gram of the total polymers at different ratios was dissolved in 20 mL of DMF at room temperature. The resulting solutions were stirred for 1 day to ensure thorough mixing. The stock solutions of PS, P4VP, and their different blend compositions were prepared in the common solvent DMF. Viscosity measurements were made using Ubbelohde Viscometer at 28°C with an accuracy of $\pm 0.2\%$. For DSC study, the solvent is allowed to evaporate in a thermostat for 24 h. The residuals of component polymers and their blends in powder form were then dried at 80°C for several days to ensure complete removal of any traces of residual solvent. DSC measurements were carried out using a Shimadzu DSC-50 in the temperature range 28–220°C. Small quantities of the samples, 8–10 mg were scanned at a heating rate of 10 K/min⁻¹ under N₂. FT-IR spectra of the blends were recorded using a Perkin-Elmer spectrometer (model 1000). Scanning electron microscopy (SEM) measurements were carried out on scanning electron microscope model JEOL JSM 5800 CV with image processing software. In our previous work, the silver particulate films were deposited on PS/P4VP, 50 : 50 by evaporation at 185°C in a vacuum better than 8×10^{-6} Torr. These films show the room temperature resistances in the desirable range as positive effect of blending PS with P4VP. Otherwise, the silver particulate films on softened PS gives rise to a very high room temperature resistance approaching that of the substrate resistance due to the formation of a highly agglomerated structure. On the other hand, films on softened P4VP gives rise to a room temperature resistance in the range of a few tens to a few hundred MΩ/□, which is desirable for device applications. The blend PS/P4VP, (50 : 50) seems to be incorporating the properties of P4VP as well as PS at higher temperature.

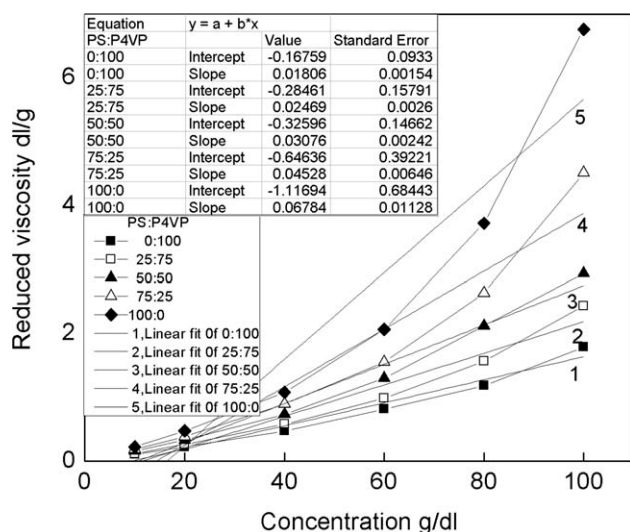


Figure 1 Reduced viscosity versus concentration of PS/P4VP blends.

RESULTS AND DISCUSSION

Viscosity measurements

The effectiveness of dilute-solution viscometry is based on the assumption that mutual interactions of macromolecules in solution have a great influence on the viscosity in TPS (two polymers in a solvent).⁷ Therefore, compatibility among the polymers depends on the fact that the repulsive interactions among polymer molecules cause their shrinkage, leading to a lowering of solution viscosity, while attractive interaction increases the viscosity.

The relative and reduced viscosities of homopolymer and their blends are found from viscometric measurements. The intrinsic viscosity values of homopolymers and their blends were determined at 27°C in DMF by extrapolation to zero concentration of the plots of reduced viscosity (η_{sp}/C) versus concentration as shown in Figure 1. The plots are not perfect linear, but no crossover is seen. A sharp crossover in the plots of reduced viscosity versus concentration indicates incompatibility of blends.⁸ Therefore, some order of compatibility is expected in the blends.

Figure 2 shows a plot of relative viscosity versus blend composition at the original total concentration of 0.05 g/mL. It is not found to be perfect linear for entire range. This indicates that the PS/P4VP blends are not hundred percent incompatible blend system.^{6,14,15} The concentration value is much lower than the critical concentration C'' estimated by $C'' = 1/[\eta]$.⁶ In the absence of specific interactions within the blend, polymer coils are independent if the solution concentration is below the critical concentration.⁶ The mixed solutions in DMF of PS and P4VP were clear indicating that no strong interactions are taking place between the blend components chains.

As proposed by Krigbaum and Wall,¹⁶ the specific viscosity, η_{sp} of a solution polymer blends can be expressed as:

$$(\eta_{sp})_m = [\eta_1]C_1 + [\eta_2]C_2 + b_{11}C_1^2 + b_{22}C_2^2 + 2b_{12}C_1C_2 \quad (1)$$

where $[\eta_1]$ and $[\eta_2]$ are the intrinsic viscosities of component polymers 1 and 2, C_1 and C_2 are the concentrations of polymers 1 and 2 in solution of polymer blend, b_{11} and b_{22} are specific interaction coefficients of polymers 1 and 2 in single polymer solutions and b_{12} is the interaction coefficient for the polymer blend of component polymers 1 and 2. The coefficient b_{11} is related to the constant k in the Huggins equation, when component polymer 1 is alone in the solution. This also applies to b_{22} .

$$\eta_{sp}/C = [\eta] + k[\eta]^2C \quad (2)$$

The relationship between b_{11} and k can be written as

$$b_{11} = k_1[\eta]^2 \quad (3)$$

where k_1 is the Huggins constant for component polymer 1 in solution. The theoretical interaction coefficient between the two polymers, b_{12}^* can be expressed as:

$$b_{12}^* = (b_{11}b_{22})^{1/2} \quad (4)$$

According to Krigbaum and Wall,¹⁶ information on the intermolecular interaction between polymer 1 and polymer 2 can be obtained by comparison of

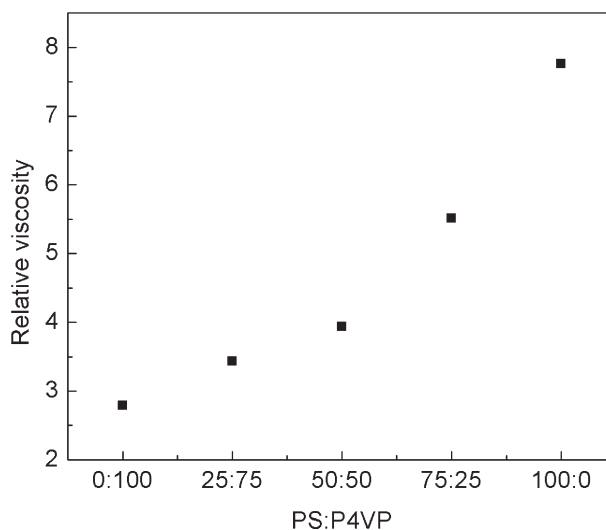


Figure 2 Relative viscosity versus composition of homopolymers in the blend for the original total concentration of 0.05 g/mL.

TABLE I
Intrinsic Viscosity and Interaction Parameter of PS/P4VP Blends

Blend comp of PS/P4VP	Intrinsic viscosity		Slope of red viscosity vs. concentration curve	Experimental value, b_{12}	Theoretical value, b_{12}^*	Δb	μ
	Experimental (dL/g)	Theoretical (dL/g)					
0 : 100	0.167	0.167	0.018	–	–	–	–
25 : 75	0.284	0.402	0.024	0.053	0.034	0.019	0.021
50 : 50	0.325	0.638	0.03	0.017	0.034	–0.017	–0.019
75 : 25	0.64	0.874	0.045	0.018	0.034	–0.016	–0.017
100 : 0	1.11	1.11	0.067	–	–	–	–

experimental b_{12} and theoretical b_{12}^* values. Hence, the miscibility of binary polymer blends can be characterized by the interaction parameter, Δb :

$$\Delta b = b_{12} - b_{12}^* \quad (5)$$

Negative values of Δb are found for solutions of incompatible polymer system, while positive values of Δb refer to attractive interaction in compatible systems. We can reduce the eq. (1) to the following form when total concentration of the mixture (C) approaches zero.

$$(\eta_{\text{spm}}/C)_{c \rightarrow 0} = [\eta_1](C_1/C)_{c \rightarrow 0} + [\eta_2](C_2/C)_{c \rightarrow 0} \quad (6)$$

Polymer 1-polymer 2 interaction, Δb , and theoretically $(\eta_{\text{sp}})_m$ can be calculated¹⁴ as follows:

$$(\eta_{\text{sp}})_m/C_m = [\eta]_m + b_m C_m \quad (7)$$

where C_m is the total concentration of polymers, $C_1 + C_2$, and $[\eta]_m$ is the intrinsic viscosity of blend. It can be theoretically defined as;

$$[\eta]_m = [\eta]_1 X_1 + [\eta]_2 X_2 \quad (8)$$

where X_1 and X_2 are weight fractions of polymer 1 and polymer 2, respectively. Interaction parameter, b_{12} , can be defined by the equation

$$b_m = X_1^2 b_{11} + X_1 X_2 b_{12} + 2 X_2^2 b_{22} \quad (9)$$

where b_m defines the global interaction between all polymeric species. b_{12} may be obtained experimentally by eq. (7).

All the calculated and experimental values are summed up in Table I. The experimental intrinsic viscosity values are compared with their weighed average values and are found to be lower than the theoretical values. Shih and Beatty¹⁵ have studied immiscible systems by this method and found that the intrinsic viscosity always shows a negative deviation due to the repulsive interaction between

the polymers. Hence, these blends were not thermodynamically compatible under equilibrium conditions.

The repulsive deviation causes a reduction in the hydrodynamic volume of the polymer molecules, and hence, the viscosity of the solution is reduced. It is found that Δb values are very much less than unity and negative for all the blends except for the blend 25 : 75, for which slightly positive value of Δb predicting some order of compatibility. Also, positive deviation in 25 : 75 can be attributed to increase in the proportion of the polar group, P4VP in the blend.⁷ The difference between η_1 and η_2 are found to be large and therefore, a more effective parameter μ can be defined to predict about the compatibility.¹⁴

$$\mu = \Delta b / (\eta_2 - \eta_1)^2 \quad (10)$$

Low values of μ observed in Table I may be due to weaker interaction between the polymers. The lower values of interaction parameters indicate that the PS and P4VP are not fully compatible, but physically miscible up to a certain extent.

Differential scanning calorimetry

DSC endothermograms for the homopolymers and their blends are shown in Figure 3. All the blends exhibit a single T_g , intermediate between those of the parent polymers, PS and P4VP indicating the miscibility of these blends. The theoretical values of these can be predicted using Fox equation¹⁷ and Gordon-Taylor equation.¹⁸

$$1/T_g = X_1/T_{g1} + X_2/T_{g2} \quad (11)$$

$$T_g = (X_1 T_{g1} + k X_2 T_{g2}) / (X_1 + k X_2) \quad (12)$$

where, X_1 , X_2 , T_{g1} , and T_{g2} are the weight fractions and glass transition temperatures corresponding to polymer 1 and polymer 2, respectively. k is a constant which gives a semiquantitative measure of degree of the interaction between the two polymers. All the experimental and calculated values of T_g are shown in

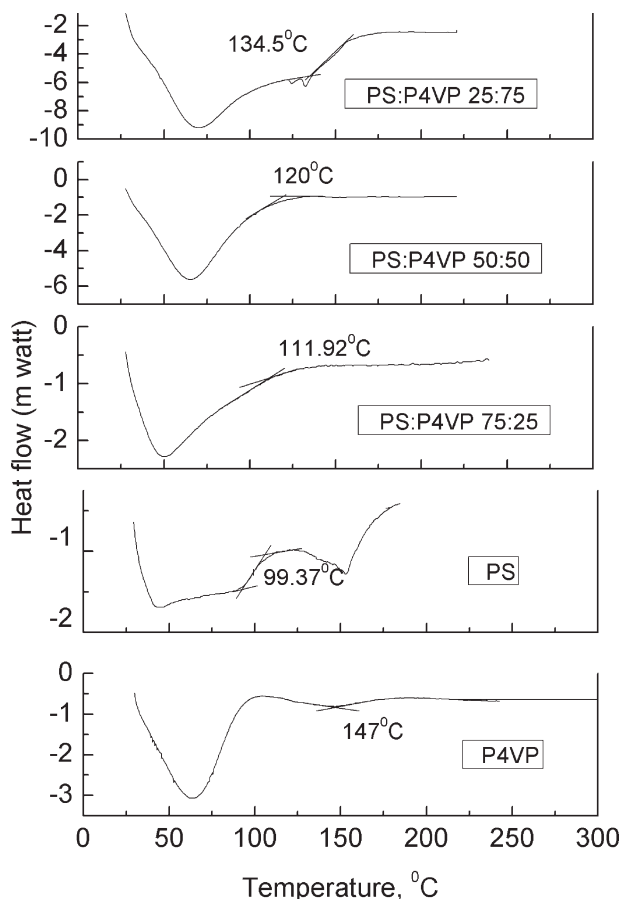


Figure 3 DSC thermograms of PS/P4VP blends.

Table II. Positive deviation observed from Fox equation is attributed to intermolecular interaction between the polymers. Figure 4 shows the plot of T_g with blend composition. It is well established that when interactions between blend components are strong, such as those affected by Hydrogen bonding, the experimentally determined T_g of the blends are higher than those calculated from the additivity rule as a result of the reduction of polymer chains mobility in the blend.⁶ To estimate the strength of the intermolecular interactions within the PS/P4VP blends, we used the Gordon-Taylor equation to verify through the linear fit in Figure 5. Slope (k) of the

TABLE II
Experimental and Theoretical Glass Transition Temperatures of PS/P4VP Blend

Blend comp of PS/P4VP	Experimental T_g value (°C)	Theoretical T_g value (°C)
	DSC	Fox equation
0 : 100	147	-
25 : 75	134.5	133.33
50 : 50	120	118.6
75 : 25	111.92	108
100 : 0	99.37	-

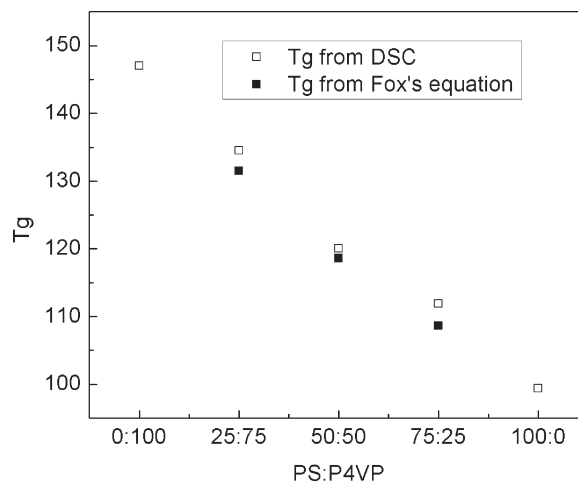


Figure 4 Glass transition temperature versus composition of PS/P4VP.

straight line obtained is found to be 0.85, indicating interaction between the polymers.¹⁸ The intercept is about 100.47°C which corresponds to T_g of pure PS.

Fourier transform-infrared spectroscopy

The proton donor PS copolymer, PSMAA (PS-methacrylic acid) with P4VP in solvent chloroform observed the specific interactions with the formation of hydrogen bonds, at a frequency $\nu = 1607 \text{ cm}^{-1}$ corresponding to the $-\text{COOH} \dots \text{N} \leq$ hydrogen bond.⁷ Therefore, the incorporation of MAA into PS results in an augmentation in miscibility with P4VP, in comparison with the PS/P4VP system, which is highly in compatible.⁷ The present solution cast PS/P4VP blends, needs to be applied in thin film form at higher temperature around 200°C. Therefore, we need to ascertain about their compatibility at higher

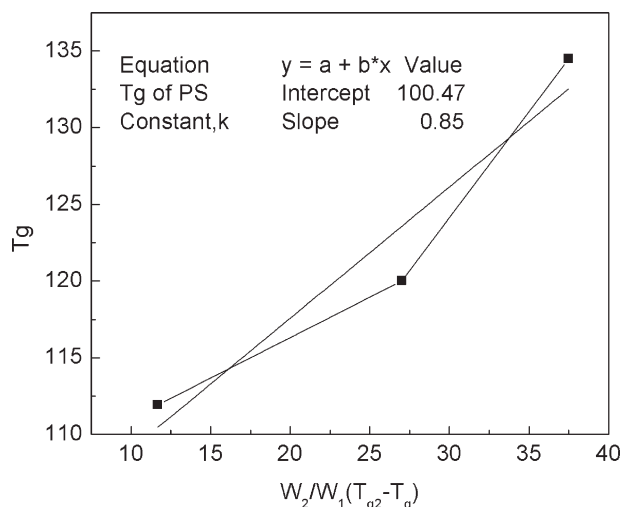


Figure 5 Verification of Gordon-Taylor equation for PS/P4VP blends.

temperature. Figure 6 is the FT-IR of the sample of the polymer blend PS/P4VP, 50 : 50 before and after DSC being carried out. This shows the absorption bands at 1598 and 1414 cm^{-1} corresponding to the pyridine ring of P4VP and at 822 cm^{-1} to the single substituted pyridine appeared in the spectra of PS/P4VP blend. Similarly, for PS, the absorption peaks at 1493 and 1448 cm^{-1} , which were characteristic of the phenyl ring and the peak at 697 cm^{-1} , corresponding to the signals of the single substituted phenyl ring, appeared for the blend as well. Similar trends were observed by the triblockpolymers PS-P4VP-PS and P4VP-Ps-P4VP, which were synthesized by chain transfer agent.¹¹ In case PS-*block*-P4VP, the stretching bands overlap.¹² The silver particulate film deposited on PS/P4VP (50 : 50) resulted in desired structure underlying the property of PS and P4VP.¹⁹ Figure 6 shows no shift in the frequency leads to the absence of hydrogen bond. Thus, the possibility of protonation of nitrogen of P4VP²⁰ is ruled out but some intermolecular interaction at higher temperature leads to single T_g composition.

Scanning electron microscopy

Figure 7(a,b) show the SEM of PS: P4VP (50 : 50) samples after and before the DSC have been carried out. It is clear that after DSC the blend mixed better than the blend as obtained at room temperature by solution cast which eventually show phase separation after few days of preparation. Figure 7(b) clearly shows the dispersed phase of polymers whereas Figure 7(a) indicates better compatibility of polymers. This can be attributed to mixing of homopolymers around 200°C during the process of DSC. This is an

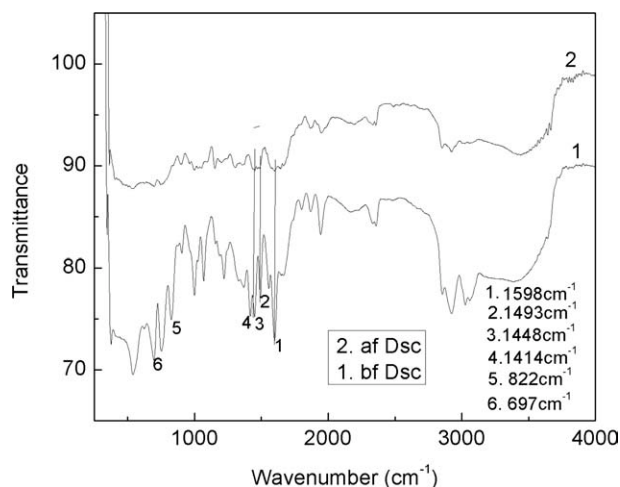


Figure 6 FT-IR for PS/P4VP (50 : 50) before and after DSC.

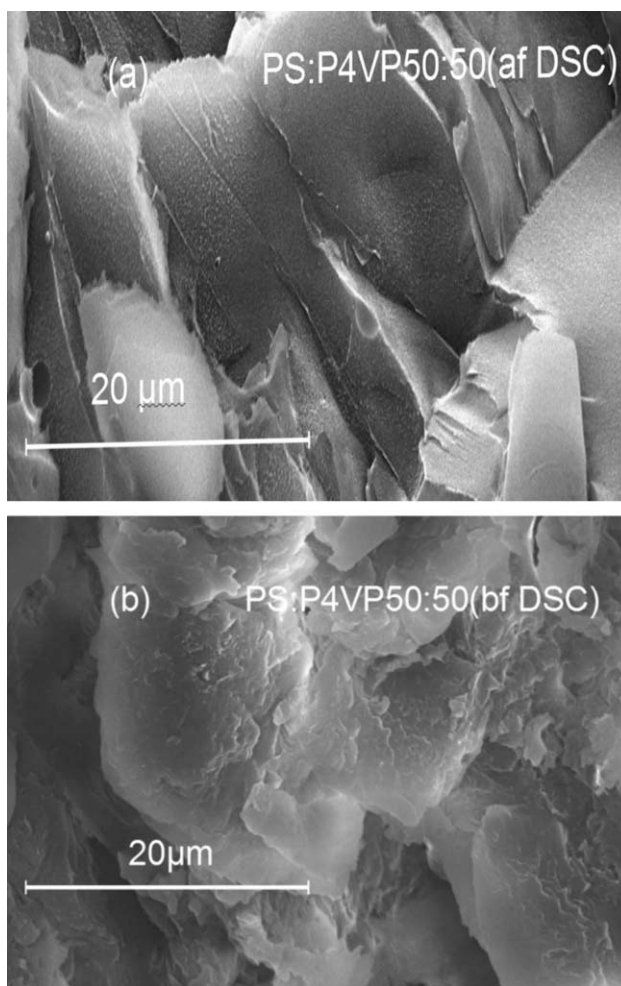


Figure 7 SEM photographs of PS/P4VP (50 : 50) (a) after DSC and (b) before DSC.

indication of suitable compatibility of these blends at higher temperature.

CONCLUSIONS

The following conclusions may be drawn from the studies on the compatibility of PS/P4VP blends.

1. Viscometry studies indicate a very small interaction parameter resulting in physically miscible blends.
2. DSC studies indicate a single T_g in all the cases indicating the formation of compatible blends. This may be due to some intermolecular interaction at higher temperature. Hence, the blends found some order of compatibility at higher temperatures.
3. FT-IR and SEM support the results of miscibility as well as DSC.

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