Miscibility studies of Starch and Poly(4-styrene sulfonic acid) blend system

Y. N. Sudhakar[1], D. Krishna Bhat[2], M. Selvakumar[1]*

[1]Department of Chemistry, Manipal Institute of Technology, Manipal University, Karnataka, India.
[2]Department of Chemistry, National Institute of Technology, Surathkal, Karnataka, India.

*Corres.author: chemselva@rediffmail.com Tel.: +91 820-2571060

Abstract: Polymeric solutions were prepared using blends of starch with poly(4-styrene sulfonic acid) (PSSA) in water and their miscibility was determined by viscosity studies at 30 °C, 40 °C and 50 °C. Using interaction parameters such as Krigbaum's (Δb), Hong's (Δk_{AB}), Chee's (μ), Sun's (α), polymer-polymer, blend-solvent and heat of mixing there was the existence of positive interactions in the blend polymer solutions only up to 80% PSSA content. A significant variation of miscibility was observed with increase in temperature in the sample containing 70% PSSA content. Polymer blend films obtained by solution casting showed hydrogen bonding in Fourier transform infrared (FTIR) studies. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) studies also supported the results. A uniform surface of the miscible blend films were observed in scanning electron microscopy images, whereas segregation was observed for the immiscible blends.
Keywords: Polymer blends, miscibility, interaction parameters, solution properties, thermal gravimetric analysis, scanning electron microscopy.

Introduction and Experimental

Synthesis and preparation of new polymeric materials with improved mechanical properties, biocompatibility, and conductivity has been increasing for the last three decades. Usually, a polymer which may, perhaps, crystallize has been considered miscible with those polymers which are miscible with its amorphous fraction. There are many techniques[1-4] which determines the miscibility, but in complicated cases in which several amorphous phases with different compositions are present, they may not be predicted as miscible using these techniques. In such cases viscosity studies, along with temperature variation, are useful to justify whether blends are actually miscible or simply compatible.[5-9] Viscometry has been used widely to investigate polymer–polymer interactions and miscibility. From the viscometric measurements, reduced viscosities of homopolymers and their blends can be determined.[10] Using these solution viscosity data, various interaction parameters can be obtained. The Krigbaum and Wall [11] interaction parameter, Δb, of the blends, for instance, is obtained from the difference between the experimental interaction parameter (b_{12}) and theoretical interaction parameter (b^{*}_{12}) values. Interaction parameter Δb can be calculated as follows:

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

where C_m is the total concentration of polymers, $C_1 + C_2$, $(\eta)_m$ is the intrinsic viscosity of the blend and b_m is the overall interaction between two polymeric species. The values of b_m and $(\eta)_m$ can be determined from the slope and intercept of the reduced viscosity versus concentration plots using linear fits. b_{12} can be obtained experimentally from Eq. (2)

$$b_m = w_1^2 b_{11} + 2w_1 w_2 b_{12} + w_2^2 b_{22} \tag{2}$$

where w_1 and w_2 are the mass fractions of the two components, respectively, and b_{11} and b_{22} are the respective individual interaction parameters which can be obtained from the slope of the plots of the reduced viscosity versus concentration. The theoretical interaction parameter b^*_{12} was calculated from Eq. (3)

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

The difference in the theoretical b^*_{12} from Eq. (3) and the experimental b_{12} with Eq. (2) gives the Δb interaction parameter, i.e., Eq. (4)

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

If $\Delta b \geq 0$, it signifies miscibility, and $\Delta b < 0$ indicates phase separation. If the intrinsic viscosity of the individual polymers, i.e., η_1 and η_2, are sufficiently apart, Chee's[5] interaction parameter μ can be more effectively used to predict miscibility. The relation is given in Eq. (5).

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

If $\mu \geq 0$, blend is miscible and when $\mu < 0$ it is immiscible.

Sun et al.[9] have recommended another formula [Eq (6)] for the determination of polymer miscibility for blends in which hydrodynamic interactions are present in the system. The blend miscibility is predicted based on the α value, i.e., when $\alpha \geq 0$ is miscible and immiscible when $\alpha < 0$:

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

where, K_1, K_2, and K_m are the Huggins's constants for individual components 1, 2 and the blend, respectively. Based on Hong's extension[12] of Huggin's mutual interaction parameter Δk_{AB}, we have further carried out calculations to identify the miscibility between the unlike polymers in the blends. The difference Δk_{AB} between the theoretical interaction parameter value $k_{AB,t}$ and the experimental interaction parameter k_{AB} value provides information about the interaction between two polymers. The experimental k_{AB} value is related to b_{12} as per Eq. (7); hence, the k_{AB} value can be calculated using Eq. (8).

$$b_{12} = k_{AB} [\eta]_1 [\eta]_2 \tag{7}$$

$$k_{AB} = \frac{b_m - (b_{11} w_1^2 + b_{22} w_2^2)}{2 [\eta]_1 [\eta]_2 w_1 w_2} \tag{8}$$

The theoretical value of the factor $k_{AB,t}$ is derived from the geometric means of K_1 and K_2 as

$$k_{AB,t} = (K_1 K_2)^{0.5} \tag{9}$$

Thus, the difference between theoretical $k_{AB,t}$ and experimental k_{AB} gives Δk_{AB} [Eq. (10)]

$$\Delta k_{AB} = k_{AB} - k_{AB,\ t}$$

(10)

The blend is miscible if $\Delta k_{AB} \geq 0$ and immiscible if $\Delta k_{AB} < 0$.

The chemical structures of the polymeric components play an important role in order to enhance interactions which can promote miscibility. Starch is an abundant and low cost natural polymer which is an attractive raw material for use as oxygen and grease barriers, either by coating or as an additive in packaging materials. Starch consists of micro-scale granulates that contain crystalline regions of amylopectin due to its helical structures and amorphous regions of amylose and amylopectin branch units. When a starch solution in water is heated, the granules swell and rupture, the semi-crystalline structure is lost and the smaller amylose molecules start leaching out of the granule, forming a network that holds water and increases the mixture's viscosity. At this stage, other polymers are usually blended to form intermolecular bonding. During cooling or prolonged storage, semi-crystalline regions partially recovers, while the interaction between other polymers is via hydrogen bonding formed by the hydroxyl groups on the granule surface.[13] The hydrophilic starch, however, is incompatible with hydrophobic synthetic polymers, and simple mixing of these tends to result in phase separation.

The use of functionalized polymers represents a good way to obtain interacting polymers which can produce a single-phase material with enhanced properties, including their film forming properties. Poly(styrene sulfonic acid) (PSSA) is an often used model compound in polyelectrolyte chemistry and can be prepared from well defined, commercially available polystyrene samples.[14] Due to low product cost, applications of PSSA as proton conducting membranes in various electrochemical devices are also interesting.[15,16] However, the application of PSSA is problematic, due to poor mechanical properties. Similar to this work, Atanu et al.[17] have reported that the two component system of starch and poly (acrylic acid) (PAA) in a 5% aqueous solution formed a synergistic mixture at 60:40 ratio and showed interaction between the acid groups of the PAA and the OH groups of starch. With the $SO_3^-H^+$ group in PSSA, which can function as a proton donor, and starch with its –OH groups functioning as a weak proton acceptor, one would expect hydrogen bonding interactions leading to miscibility in PSSA/starch blends.

In the present work, as a part of our ongoing research on biodegradable polymers,[8,18] we have studied the miscibility behavior of the PSSA and starch using viscometry studies and further polymer blend films were characterized using scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and thermal gravimetric analysis (TGA) techniques. The effects of molecular interactions of the relationship between polymer-polymer and blend-solvent interaction parameters and heat of mixing were also determined at various temperatures.

Preparation of polymer solutions

1% (v/v) of PSSA based on 18% solution from Sigma-Aldrich, USA, was prepared in water. 1% (w/v) potato starch (Merck, India) stock solution was prepared in distilled water and stirred at 353K until dissolution of the granules. PSSA/starch blend compositions, namely, 100/0, 90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80, 10/90 and 0/100 were prepared by mixing appropriate amounts of the 1% individual polymer stock solutions. The solutions were used for viscosity studies.

Preparation of blend films

PSSA/starch blend compositions, namely, 80/20, 50/50 and 20/80, were prepared by mixing appropriate amounts of the 1% individual polymer stock solutions. 20 ml of the prepared blend solutions and pure polymer solutions were taken in five petri dishes having a diameter 6 cm and kept in a hot air oven at 60 °C for 24 hours until non-sticky and pale yellow films (colorless for starch film) were obtained. The films were dried under vacuum at 50 °C for 5 hours. The thickness of the obtained films ranged between ~0.8 mm and ~0.9 mm.

Viscosity studies

Viscosity measurements were done at 30, 40, and 50 °C, using a suspended level Ubbelohde viscometer with flow time of 95 s for distilled water. The prepared polymer solutions were further diluted [0.5, 0.4, 0.3, 0.2, and 0.1, (v/v)] using distilled water, along with the pure polymer solutions, and viscosity measurements were carried out. Solution viscosities at different temperatures were determined in a thermostated bath, with thermal stability of ±0.1 °C.

FTIR, DTA-TGA and SEM studies

FTIR measurements of the polymer films were carried out using 20 scans at 1 scan/s and 4 cm^{-1} resolution at room temperature using a Shimadzu FTIR-8400S spectrophotometer (Japan). The DTA and TGA, measurements were done on a Shimadzu TGA-60 (Japan). Thermal studies were performed over a temperature range 25-400 °C at a heating rate of 10 °C/min under nitrogen atmosphere. Surfaces of the pure and blend polymer films were sputtered with gold and SEM studies were carried out in a JEOL JSM-6380LA SEM (Japan).

Results and Discussion

Solution property studies
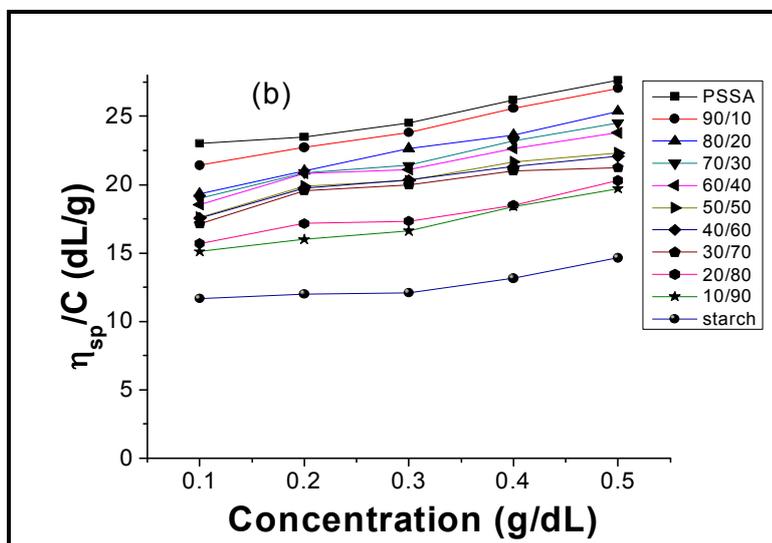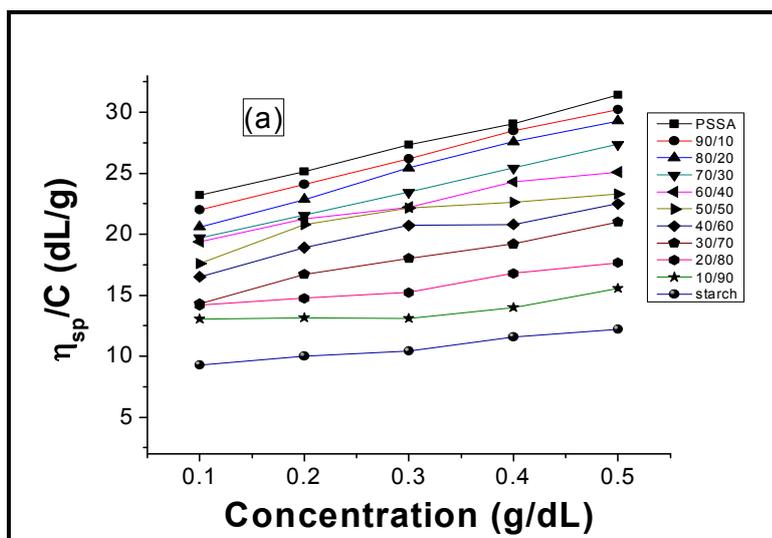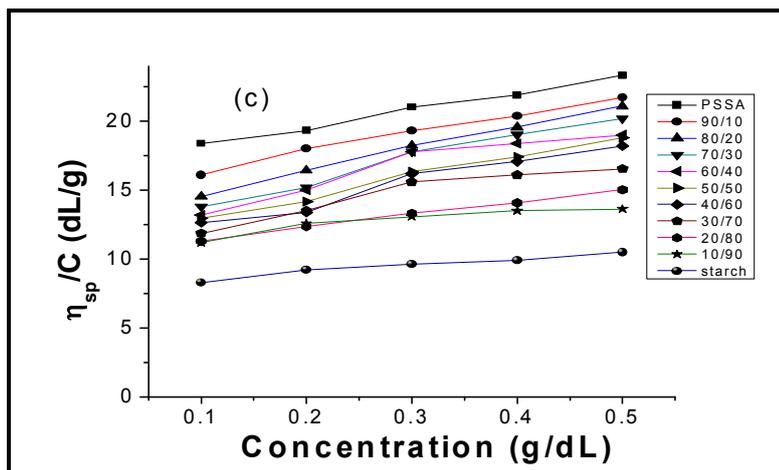
Figure 1. Reduced viscosity versus concentration of PSSA/starch blends at (a) 30 $^{\circ}$C (b) 40 $^{\circ}$C (c) 50 $^{\circ}$C

For determination of the interaction parameters of the PSSA/starch blend system, reduced viscosities of the pure components and blends were characterized at 30 °C, 40 °C, and 50 °C, and are shown as Huggin's plots in Figs. 1a-c. The plots were linear for higher concentrations of PSSA in the blends showing that the blends were miscible. As the PSSA concentration was decreased various cross-overs in the plots were observed indicating immiscibility of the blends.[19] Based on the experimentally observed $(\eta)_m$ for the ternary (water/polymer 1/polymer 2) systems, the parameters of the miscibility criteria proposed by Krigbaum et al. (Δb) and Huggin's mutual interaction, Δk_{AB} were calculated using Eqs. (1-4 and 7-10) and are listed in Table 1. The miscibility interaction parameters, μ, and α proposed by Chee and Sun et al. were derived from Eqs (5 and 6) and are tabulated in Table 2. Based on the sign convention, and the values in Tables 1 and 2, PSSA/starch blends were miscible for 90/10 and 80/20 compositions at the studied temperatures. A further decrease in relative PSSA content led to higher interactions between solvent and polymers. The positive values suggest the existence of sufficient hydrogen bonding sites present in the structure of these polymer systems. Interestingly, for the 70/30 ratio, although the α value of the blend indicated immiscibility at 30 and 40 °C, it was predicted to be miscible at 50 °C. The reason for this behavior at higher temperature is due to amylopectin chain disentanglement at higher temperature leading to exposure of functional groups and the formation of interaction between neighboring polymer chains.

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

PSSA/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}
PSSA	27.33	-	-	25.11	-	-	20.33	-	-
90/10	28.37	0.143	0.159	25.28	0.132	0.1876	20.45	0.124	0.1005
80/20	28.23	0.152	0.1237	24.25	0.126	0.1928	20.66	0.178	0.1022
70/30	21.20	0.001	-0.0245	20.30	-0.022	-0.1268	18.74	-0.003	-0.0117
60/40	20.65	-0.033	-0.1004	20.11	-0.074	-0.1433	18.81	-0.249	-0.1457
50/50	19.23	-0.054	-0.1042	18.66	-0.112	-0.2316	17.59	-1.236	-0.2412
40/60	17.60	-0.128	-0.1834	18.32	-0.179	-0.2243	16.63	-1.461	-0.5655
30/70	17.31	-0.122	-0.1459	17.1	-0.218	-0.2175	15.40	-1.249	-0.4376
20/80	15.25	-0.173	-0.1255	16.78	-0.256	-0.3611	15.22	-1.334	-0.4213
10/90	8.966	-0.453	-0.653	10.24	-0.592	-0.8743	9.21	-1.732	-0.9366
starch	5.86	-	-	6.8	-	-	5.92	-	-

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

PSSA/starch (v/v)	At 30 °C		At 40 °C		At 50 °C	
	μ	α	μ	α	μ	α
90/10	0.0423	0.0124	0.0401	0.0248	0.0371	0.0220
80/20	0.0319	0.0160	0.0276	0.0158	0.0201	0.0165
70/30	-0.0068	-0.0008	-0.0211	-0.0004	0.0121	0.0001
60/40	-0.0101	-0.0088	-0.0045	-0.0023	-0.0132	-0.0058
50/50	-0.0280	-0.0102	-0.0152	-0.0104	-0.0142	-0.0181
40/60	-0.0273	-0.0168	-0.0127	-0.0054	-0.0172	-0.0287
30/70	-0.0372	-0.0185	-0.0180	-0.0027	-0.0193	-0.0365
20/80	-0.0538	-0.0222	-0.0224	-0.0266	-0.0227	-0.0418
10/90	-0.0877	-0.0236	-0.0245	-0.0125	-0.0254	-0.0495

Analysis of the viscosity data with all the corresponding proposed interaction parameters brings forth the fact that not all the criteria may simultaneously satisfy the condition for the miscibility. Schneier[20] suggested using the heat of mixing (ΔH_m) as a factor [21-22] for studying the miscibility of blends using the solubility parameters, δ, of the sample polymers and Eq. 11. The values of δ are PSSA [~18 $(J/cm^3)^{1/2}$] and starch [~34.0 $(J/cm^3)^{1/2}$].[23]

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

where (δ_1, δ_2), (w_1, w_2), (M_1, M_2) and (ρ_1, ρ_2) are the solubility parameters, mass fractions, the monomer molecular weights, and the densities of individual polymer components 1, 2, respectively. The values of ΔH_m are plotted in Figure 2 versus blend compositions. It is clear that the values were almost zero, indicating the heat liberation by mixing the two polymers was low. Schneier in his studies noted that, for the miscible polymer pairs 10 mcal mol^{-1} marked the upper limit of miscibility. The heat of mixing of PSSA/starch blends at almost all compositions except those with PSSA content higher than 80%, were found to be between 25.5 to 12.6 mcal mol^{-1}, i.e., above the value considered to be the upper limit of miscibility. This behavior might also be due to the large molecular weight difference between PSSA and starch.
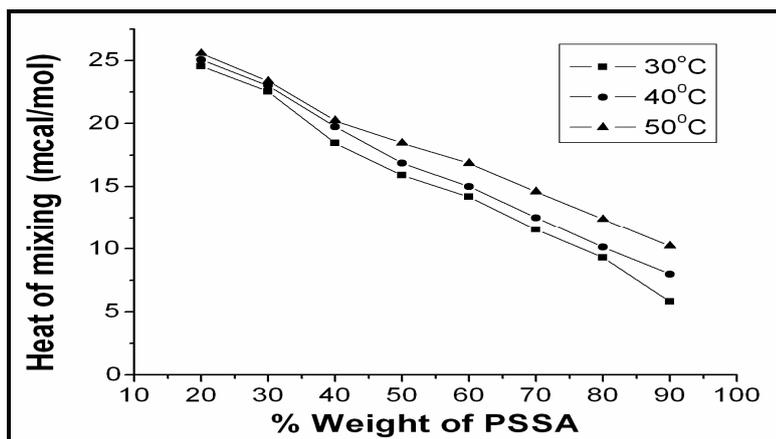
Figure 2. Heat of mixing of PSSA/starch blends at different temperatures.

To know whether interaction between polymer-polymer was greater or blend-solvent was greater, by using Flory–Huggins theory[21] based on the values obtained from Eq. (12) can be resolved. Using the solubility parameters of the component polymers, the polymer-polymer interaction (χ_i) can be calculated.

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

where V_i, R, and T are the molar volume of the water, universal gas constant, and temperature (K), respectively.[24,25] The blend-solvent interaction parameters were calculated according to the method adopted by Singh and Singh.[26] The solubility parameters of the blend (δ) were calculated from the additive relationship:

$$\delta = w_1 \delta_1 + w_2 \delta_2 \tag{13}$$

Tables 3 and 4 list the interaction parameters of the polymer–polymer blend systems and blend–solvent interaction parameters, respectively. From these data, we observed that the net polymer–polymer interactions were lower than those observed for blend-solvent interactions for the studied blend compositions (50/50 and 20/80 blend ratio) at three different temperatures. Based on the similar miscibility observation found in the literatures[27-29], the lower values indicate that the blends were miscible when the PSSA content was above 80% in the blend.

Table 3. Polymer-polymer interaction parameters for the PSSA/starch in the blend.

Temperature (°C)	Polymer	χ_i calculated from Eq. (12)
30	starch	0.0252
	PSSA	0.6532
40	starch	0.0233
	PSSA	0.6604
50	starch	0.0210
	PSSA	0.6872

Table 4. Blend-solvent interaction parameters at different temperatures.

Temperature (°C)	PSSA/starch (v/v)	δ calculated from Eq. (13)	χ_i calculated from Eq. (12)
30	80/20	9.545	0.0218
	50/50	9.452	0.5610
	20/80	9.325	0.6452
40	80/20	9.545	0.0220
	50/50	9.452	0.5625
	20/80	9.325	0.6235
50	80/20	9.545	0.0225
	50/50	9.452	0.5623
	20/80	9.325	0.6985

So, the present study indicates the existence of miscibility when the PSSA content was more than 80% in the blend and below this composition, there was no interaction between the polymer segments, which led to immiscibility of the polymer blends. The interactions range from the strong, chemical type interactions such as hydrogen bonding between PSSA and starch, to merely physical entanglements between them. Starch is preferably high molecular weight, substantially linear chain molecules. The highly branched structure of the amylopectin molecule favors the branches to interact intramolecularly, due to the proximity of the branches within a single molecule. The existence of PSSA/starch miscibility leads to poor or ineffective amylopectin molecule entanglements/interactions with other starch molecules, particularly other amylopectin molecules. Figure 3 represents the most probable schematic interactions between the two polymers with hydrogen bonding. The disentanglement of the starch molecules at lower concentration enables the PSSA to be chemically interacting and/or physically entangle with the branched amylopectin molecules such that the OH groups associate with one another via the sulphonate groups of the PSSA polymer chain.
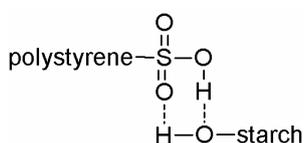
Figure 3. Schematic interactions between PSSA/starch polymers with hydrogen bonding.

FTIR spectroscopic studies
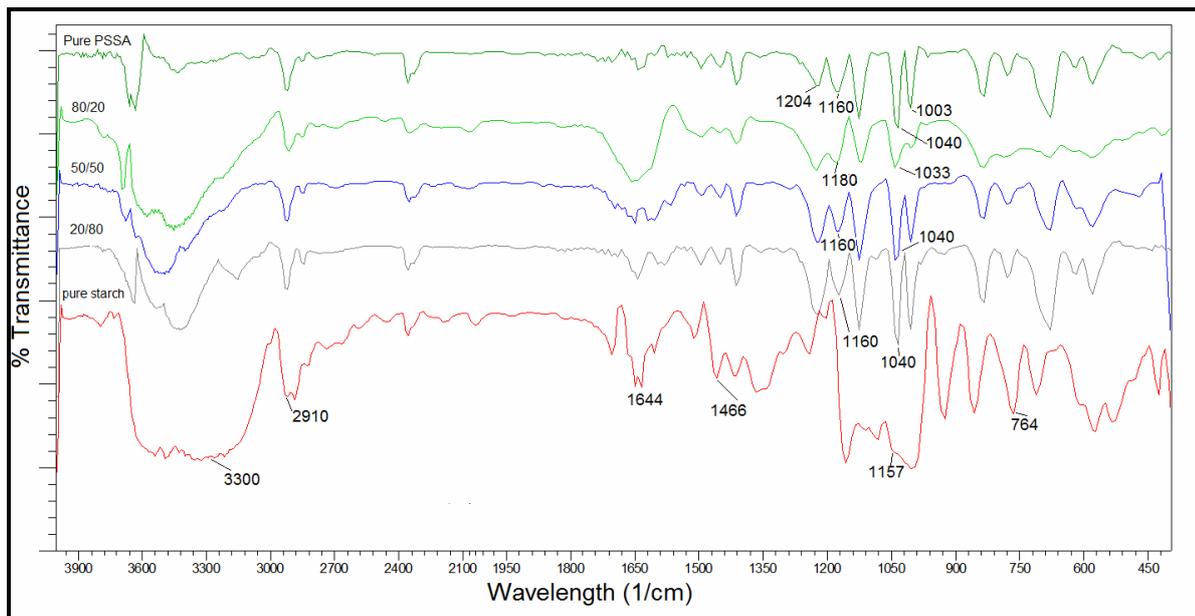
Figure 4. FTIR spectra of films consisting of pure components and different PSSA/starch blend ratios.

Figure 4 shows the FTIR spectra of the pure polymers and their blends. In the spectrum of the pure starch film, a broad band at 3300 cm^{-1} was observed due to the hydrogen-bonded hydroxyl groups that contribute to the complex vibrational stretches associated with free inter- and intra-molecular bound hydroxyl groups. A sharp band at 2910 cm^{-1}, which is characteristic of C-H stretches associated with the ring methane hydrogen atoms, was observed. The bands at 1644 cm^{-1} and 1466 cm^{-1} were assigned to the O-H bending of water and CH_2, respectively. The bands from 764 to 1157 cm^{-1} were attributed to the C-O bond stretching.[31] A strong absorption band centered at 1204 cm^{-1} was the asymmetric stretching vibration of the O=S=O unit of PSSA. The peak at 1003 cm^{-1} results from the vibrations of the phenyl ring substituted with a sulfonic group.[32] The broadening of this peak and overlapping with the phenyl ring attached to the sulfonic anion peak located at 1126 cm^{-1} indicates the deprotonation of the sulfonic acid peak in 80/20 PSSA/starch blend ratio. In the same way, the region of 1160 and 1040 cm^{-1} of the IR spectra that corresponds to the vibration of the sulphonate groups, showed displacements to 1180 cm^{-1} and 1033 cm^{-1} when compared with pure PSSA. This would be attributed to the interactions between the sulphonate group of the PSSA and –OH group of starch. As the starch content was increased, the spectra of 50/50 and 20/80 PSSA/starch blend ratios show no characteristic shift in the peaks. The –OH groups of starch strongly interacting, by hydrogen bonds, with -SO_3^- in the blend. This could be the reason of the displacements of the peaks observed in the IR spectra and allows us to assume miscibility in 80/20 PSSA/starch blend ratio.

Thermal studies
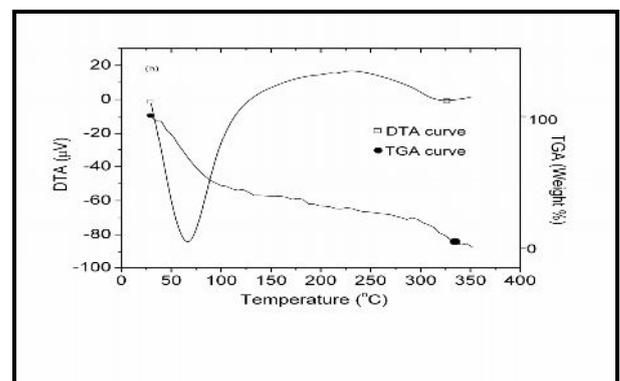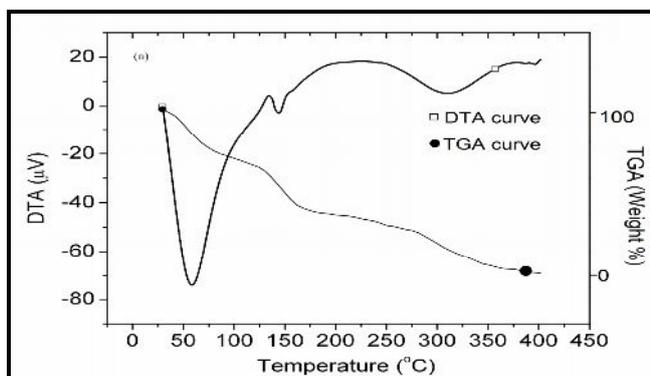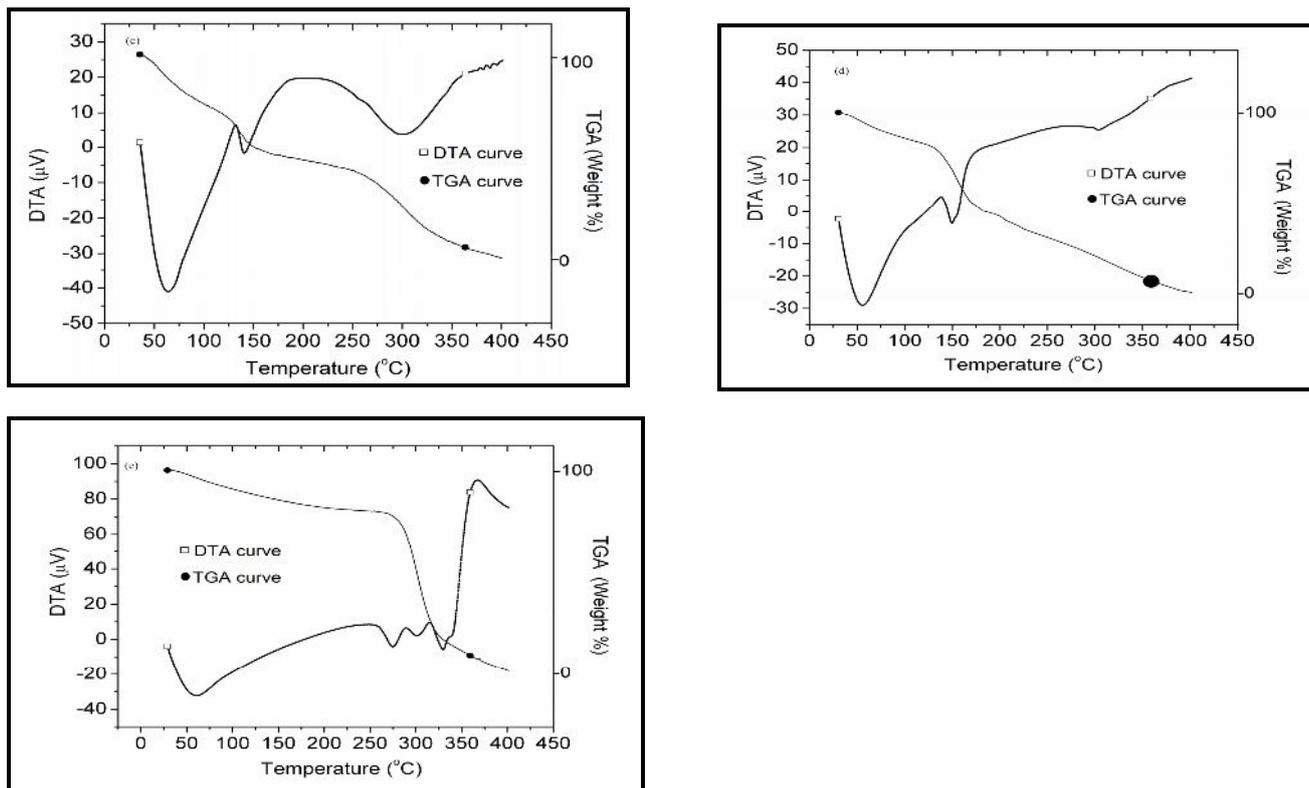
Figure 5a-5e. TGA and DTA traces obtained by heating samples from 25 °C to 400 °C at a heating rate of 10 °C/min under nitrogen atmosphere for (a) pure PSSA, (b) 80/20, (c) 50/50, (d) 20/80 and (e) pure starch.

Figures 5a-e shows the results of TGA and DTA analysis of PSSA/starch blend ratios and pure components. The TGA and DTA curves of pure PSSA film (Figure 5a) showed three stages in which first weight loss was up to 17% with maximum rate at 58.56 °C and a broad peak in DTA curve in this temperature region can be related to the evaporation of unbound water from the polymer blend matrix. The second weight loss starts at 125 °C and ends at 152 °C with 12% weight loss, wherein the glass transition temperature of the PSSA was observed[33] and this transition led to the evaporation of the bound water molecules in the PSSA matrix. This was supported by sharp peak in the DTA curve. Third weight loss starts at 275 °C with maximum rate of 316 °C and it can be related to depolymerisation of PSSA chains. The pure starch (Figure 5e) showed two weight loss events centered at 49 °C, which can be related to unbound water. The second thermal event was observed at about 274 °C with a maximum rate of 329 °C and was related to the degradation of starch, which includes the parallel process of dehydration and demethoxylation[33] as also supported in the corresponding DTA curve.

The thermograms of the blends containing 50% and 20% of the PSSA (Figure 5c and 5d) showed weight loss events similar to the pristine PSSA and starch indicating their immiscibility in the blend system. Nevertheless, the weight loss pattern of the blend containing 80% of PSSA showed (Figure 5b) only events characteristic for pure starch as there is an absence of the thermal event distinctive of pure PSSA at 136-151 °C and moreover the shift in the degradation thermal event starting at 274 °C with maximum rate at 355 °C. This provides some evidence of interactions between the polymers.[35] Comparatively, this study is supporting the FTIR analysis.

Scanning electron microscopic studies
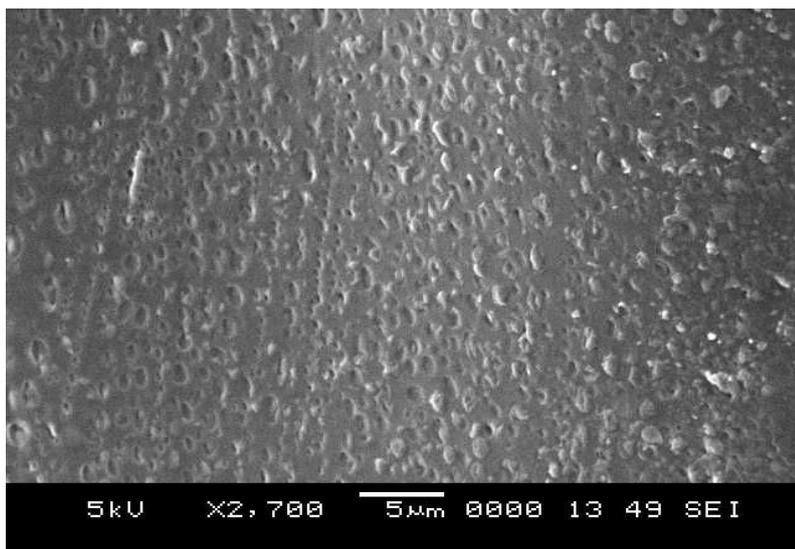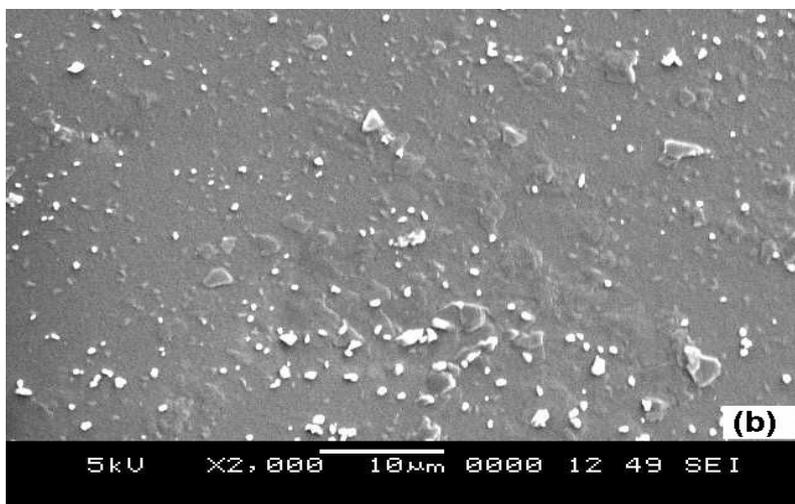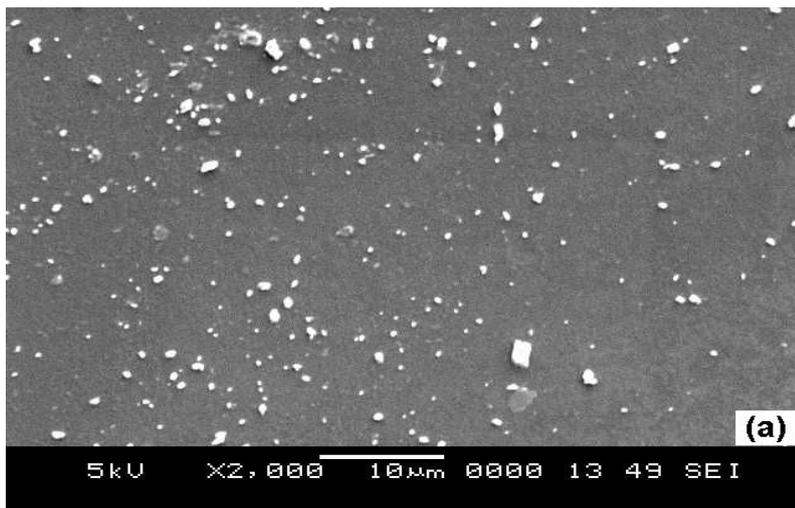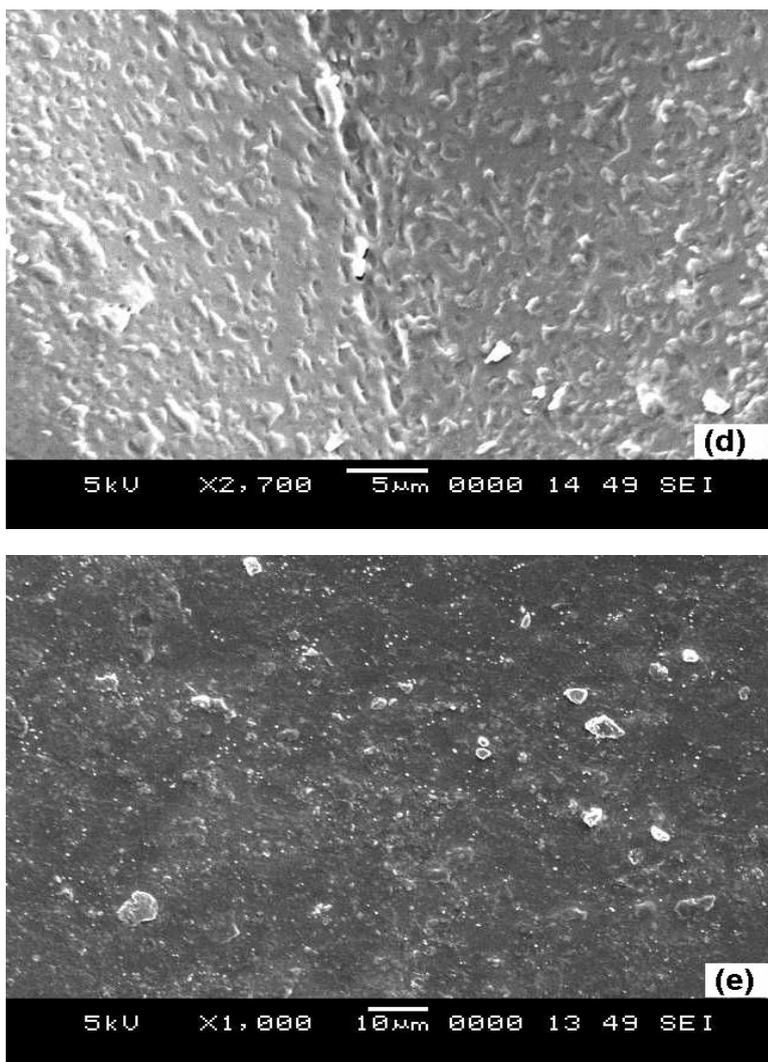
Figure 6a-6e. SEM images of films consisting of (a) pure PSSA, (b) 80/20, (c) 50/50, (d) 20/80 and (e) pure

Figures 6a-e shows SEM images of the blend polymers at different blending ratios (film). Figure 6a and Figure 6e shows images of the pure PSSA and pure starch films, respectively. In Figure 6a, it was observed to be containing uniform surface, while segregated granules in Figure 6e. After adding the starch, the interaction between the PSSA and starch was quiet appreciable and granules were visible on the surface for 80/20 blend ratio (Figure 6b). The dual compatibility of starch towards PSSA tends to lessen the driving force for the separation of the PSSA phase and led to better development of the film. The interaction produced a more relaxed network in the 50/50 blend matrix (Figure 6c). However, the structure becomes increasingly heterogeneous (Figure 6d) with an increase in the starch content due to the aggregation of the ester group of starch forming new crystalline domains. These domains would cover some polar domains of the PSSA and hence, reduces the interaction between the electrolyte ions and polar section of the polymer matrix. The pores in the micrographs indicate the occurrence of phase-separation in the polymer electrolytes. The several pores or craters, which have formed on the surface, were due to the rapid evaporation of the solvent (water). The difference in the pore size was related to the difference in the driving force for phase separation.[36]

Conclusions

In summary, the miscibility behavior of PSSA/starch blends has been studied in the temperature range of 30, 40 and 50 °C using solution viscosity measurement. The μ, α, Δb and Δk_{AB} interaction parameters indicated that the PSSA/starch blend ratios (90/10 and 80/20) are miscible in all studied temperatures. As the temperature was increased to 50 °C, positive interactions were obtained for 70/30 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. Furthermore, FTIR, TGA and SEM studies supported the miscibility of two polymers

at 80/20 PSSA/starch blend ratio, whilst, another blend samples maintained their individual characteristic features in the blend system.

Acknowledgment

References

1. Sarasam, A.R., Krishnaswamy, R.K. and Madihally, S.V., Blending chitosan with polycaprolactone: effects on physicochemical and antibacterial properties, Biomacromolecules, 2006, 7, 1131-1138.
2. Wan, Y., Wu, H., Yu, A.X. and Wen, D.J., Biodegradable polylactide/chitosan blend membranes, Biomacromolecules, 2006, 7, 1362-1372.
3. Liu, Y. and Messmer, M.C., Surface Structures and Segregation of Polystyrene/Poly(methyl methacrylate) Blends Studied by Sum-Frequency (SF) Spectroscopy, Journal of Physics and Chemistry B, 2003, 107, 9774-9779.
4. Zhang, X., Kale, D.M. and Jenekhe, S.A., Electroluminescence of Multicomponent Conjugated Polymers. 2. Photophysics and Enhancement of Electroluminescence from Blends of Polyquinolines, Macromolecules, 2002, 35, 382-393.
5. Chee, K.K., Determination of polymer-polymer miscibility by viscometry, European Polymer Material, 1990, 26, 423-426.
6. Palladhi, R. and Singh, R.P., Ultrasonic and rheological investigations on Interacting blend solutions of poly (acrylicacid) with poly (vinylpyrrolidone) or poly(vinylalcohol), European Polymer Journal, 1994, 30, 251-257.
7. Toti, U.S. and Aminabhavi, T.M., Different viscosity grade sodium alginate and modified sodium alginate membranes in pervaporation separation of water + acetic acid and water + isopropanol mixtures, Journal Membrane Science, 2004, 228, 199-208.
8. Kumar, M.S., Bhat, D.K. and Renganathan, N.G., Miscibility of polymethylmethacrylate and polyethyleneglycol blends in tetrahydrofuran, Journal of Applied Polymer Science, 2009, 111, 452–460.
9. Sun, Z., Wang, W. and Fung, Z., Criterion of polymer-polymer miscibility determined by viscometry, European Polymer Material, 1992, 28, 1259-1261
10. Huggins, M.L., The viscosity of dilute solutions of long-chain molecules. IV. Dependence on concentration, Journal of American Chemical Society, 1942, 64, 2716-2718.
11. Krigbaum, W. and Wall, F.J., Viscosities of binary polymeric mixtures, Journal of Polymer Science, 1950, 5, 505-514
12. Hong, P.D., Huang, H.T. and Chou, C.M., Study of the solvent effect on miscibility between poly(vinyl chloride) and poly(methyl methacrylate) in the solution state – viscometric measurements, Polymer International, 2000, 49, 407-411.
13. Shanks, R.A. and Gunaratne, L.M.W.K., Gelatinization and retrogradation of thermoplastic starch characterized using modulated temperature differential scanning calorimetry, Journal of Thermal Analysis and Calorimetry, 2011, 106, 93-99.
14. Vink, H., A new convenient method for the synthesis of poly(styrenesulfonic acid), Macromolecular Chemistry, 1981, 182, 279-281.
15. Sun, J., Jordan, L.R., Forsyth, M. and MacFarlane, D.R., Acid–Organic base swollen polymer membranes, Electrochimica Acta, 2001, 46, 1703-1708.
16. Yu, J., Yi, B., Xing, D., Liu, F., Shao, Z., Fu, Y. and Zhang, H., Degradation mechanism of polystyrene sulfonic acid membrane and application of its composite membranes in fuel cells, Chemical Physics, 2003, 5, 611-615.
17. Atanu, B., Willet, J.L., Gordon ,H.S., Finkenstadt, V.L. and Cheng, H.N., Complexation and blending of starch, poly(acrylic acid), and poly(N-vinyl pyrrolidone), Carbohydrate Polymer, 2006, 65, 397–403.
18. Sudhakar, Y.N., Sowmya, Selvakumar, M. and Krishna Bhat D., Miscibility studies of chitosan and starch blends in buffer solution, Journal of Macromolecular Science, Part A. Pure Applied Chemistry, 2012, 49:12, 1099-1105.

19. Dondos, A., Skondras, P., Pierri, E. and Benoit, H., Hydrodynamic crossover in two-polymer mixtures from viscosity measurements, Macromolecular. Chemistry, 1983, 184, 2153-2158.
20. Schneier, B.O., Polymer compatibility, Journal of Applied Polymer Science, 1973, 17, 3175-3185.
21. Flory, P.J., Principles of Polymer Chemistry, Cornell University Press, New York, 1953.
22. Krause, S., Crystal structures and morphology of thin-film, melt-crystallized, and polymerized poly (ethylene naphthalene), Journal of Macromolecular Science Part C, 1972, 7, 251-255.
23. Brandrup, J., Immergut, E. H. and Grurlke, E.A. Polymer hand book, Wiley Interscience: New York, 1999.
24. Kern, R.J., Component effects in phase separation of polymer-polymer-solvent systems, Journal of Polymer Science, 1956, 21, 19-25
25. Hildebrand, J.H., Scott, R.L, The Solubility of Non-electrolytes, 3rd ed.; Princeton, NJ:Van Nostrand Reinhold, 1950.
26. Singh, Y.P. and Singh, R.P., Compatibility studies on solutions of polymer blends by viscometric and ultrasonic techniques, European Polymer Material, 1983, 19, 535-541.
27. Varada, R.A., Siddaramaiah and Reddy, R.L., Ultrasonic, refractometric, and viscosity studies of some polymer blends in solution, Journal of Applied Polymer Science, 1998, 70, 1823-1827.
28. Jayaraju, J., Raviprakash, S.D., Keshavayya, J. and Rai, S.K., Miscibility studies on chitosan/hydroxypropylmethyl cellulose blend in solution by viscosity, ultrasonic velocity, density, and refractive index methods, Journal of Applied Polymer Science, 2006, 102, 2738-2742.
29. Kumar, M.S. and Bhat, D.K., Miscibility of poly(methylmethacrelate) and cellulose acetate butyrate blends in dimethyl formamide, Indian Journal of Chemical Technology, 2008, 15, 547-554.
30. Kolhe, P. and Kannan, R.M., Improvement in Ductility of Chitosan through Blending and Copolymerization with PEG: FTIR Investigation of Molecular Interactions, Biomacromolecules, 2003, 4, 173-180.
31. Mano, J.F., Koniarova, D. and Reis, R.L., Thermal properties of thermoplastic starch/synthetic polymer blends with potential biomedical applicability, Journal of Material Science: Materials in Medicine, 2003, 14, 127-135.
32. Mokrini, A. and Acosta, J.L., New ion conducting systems based on star branched block copolymer, Polymer, 2001, 42, 8817-8824.
33. Bozkurt, A., Anhydrous proton conductive polystyrene sulfonic acid membranes, Turkish Journal of Chemistry, 2005, 29, 117-123.
34. Ling-hao, H., Rui, X., De-bin, Y., Ying, L. and Rui, S., Effects of blending chitosan with peg on surface morphology, crystallization and thermal properties, Chinese Journal of Polymer Science, 2009, 27, 501−510.
35. Jingbo Y., Kun L., Xuesi C. and Vitaliy V.K., Miscibility studies of the blends of chitosan with some cellulose ethers, Carbohydrate Polymer, 2006, 63, 238–244.
36. Rhoo, H.J., Kim, H.T., Park, J.K. and Hwang, T.S., Ionic conduction in plasticized PVCPMMA blend polymer electrolytes, Electrochimica Acta, 1997, 42, 1571-1579.

*****

International Journal of ChemTech Research

(Oldest & Original) [www.sphinxsai.com]

CODEN (USA): IJCRGG, ISSN: 0974-4290 [www.sphinxsai.com]

Subject areas: Chemistry, Chemical Technology.

International Journal of ChemTech Research is selected by -

CABI, CAS(USA), SCOPUS, MAPA (India), ISA(India),DOAJ(USA),Index Copernicus, Embase database, **EVISA, DATA BASE(Europe),** Birmingham Public Library, Birmingham, Alabama, RGATE Databases/organizations for Indexing and Abstracting.

[www.sphinxsai.com]

*****