Evaluation of Compatibility of Poly(vinyl chloride)/ Starch Acetate Blends Using Simple Techniques

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ABSTRACT: Solution blending of poly(vinyl chloride) (PVC) and starch acetate (d.s. 2.5) synthesized in our laboratory was carried out in 1,4-dioxane. The compatibility of these blends based on the heat of mixing and the free-energy concept was examined theoretically. Experimental evidence for the compatibility of these blends was derived from viscometric and ultrasonic studies and density measurements. Interaction parameters suggest that polymer–polymer interaction is greater than polymer–solvent interaction in the blends under study. All the experimental and theoretical evidence show that the blends are incompatible at the compositions studied. Morphological studies showed a uniform dispersion of starch acetate in PVC. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1851–1861, 1999

Key words: starch acetate; PVC; blends; viscosity; interaction parameter

INTRODUCTION

Polymeric blends are dominating various application areas because of their tailor-made properties. However, their performance depends on the compatibility of the blend components. Various techniques such as dynamic mechanical analysis,[1] thermal analysis,[2] and electron microscopy[3] are used for the prediction of compatibility. These sophisticated techniques are not freely accessible everywhere. Hence, a simple viscometric method is used for the estimation of blend compatibility. Polymer–polymer interaction or polymer–solvent interaction based on solubility parameters can be predicted using viscometric data. The technique has been reported to predict the compatibility of polystyrene/poly(vinyl acetate) (PS/PVAc)[4,5]

blends in three different solvents. Kulshreshtha et al.[6] observed a decrease in the compatibility with increasing molecular weight of poly(vinyl chloride) (PVC) in PVC/ABS (acrylonitrile-butadiene-styrene tocopolymer) blends through viscometric studies. They found that the plot of absolute viscosity versus composition deviates from linearity according to the degree of compatibility. Chee[7] also applied this method to predict the miscibility of PVC/poly(methyl methacrylate) (PMMA), PMMA/PiBMA, and PVC/PiBMA [poly-(isobutylmethacrylate)]. For a ternary system comprising a solvent and two polymers, he suggested a differential parameter ΔB, as a simple measure of intermolecular interaction. According to Chee, $\Delta B \geq 0$ indicates miscibility and $\Delta B < 0$ indicates phase separation. The compatibility of polycarbonate (PC) and poly(hexamethylene sebacate) (PHMS) blends having different molecular weights was examined through viscometry using the Krigbaum and Wall parameter, Δb, by Shih and Beaty.[8] The negative values of Δb for PC/PHMS blends were assigned to the thermo-

dynamic incompatibility under equilibrium conditions. Polymer blends of PMMA/PVAc, PVC/PVAc, and PMMA/PS were found to be compatible, semicompatible, and incompatible, respectively, by Singh and Singh.[9] Thomas and Lizymol[10] tried to correlate the compatibility of the PVC–EVA polyethylene-co-vinyl acetate, PVC–SAN, and EVA–SAN polystyrene-co-acrylonitrile blends in solution and in the solid state.

In this article, we attempted to examine the compatibility of PVC/starch acetate (STAc) blends in solution through viscometric studies, ultrasonic velocity, and density measurements. The compatibility of the blend components was also examined in solid states through scanning electron microscopy (SEM) and FTIR of solution-cast films of the respective blends. One of the components, STAc, of the blends under study is found to have a biodegradability comparable to starch. PVC, on the other hand, is a nonbiodegradable plastic of a common use. By blending STAc with PVC, some amount of biodegradability can be introduced. Hence, biodegradability of these blends has also been tested.

EXPERIMENTAL

Materials

PVC ($\overline{M_n}$ = 51,000) and potassium acetate were from National Chemicals Vadodara, India and potato starch was from S.D. Fine Chemicals Vavodara, India. The Mumbai potato starch contained 19% amylose and 81% amylopectin on a dry basis and had a moisture content of 9.19% by weight. PVC was purified by reprecipitating from THF using a methanol nonsolvent. Starch, acetyl chloride (Ranbaxy, Delhi, India), and potassium acetate were used without further purification.

Synthesis of STAc

The starch was dried for 10 h in an oven at 100°C. The dried starch (100 g) was placed in a five-neck reaction kettle equipped with a condenser, dropping funnel, mechanical stirrer, and thermometer. About 250 mL of formamide and 10 g of potassium acetate were added and the solution was stirred for 1 h at 80°C. The reaction mass was cooled to 50°C and 110 mL of acetyl chloride was added dropwise over the period of 30 min. After complete addition, the reaction was allowed to proceed for 3 h at 80°C. The reaction mass was

poured into ice-cold water with constant stirring for the precipitation of STAc. Precipitates were washed with hot water to remove any unreacted starch. The dried product was then purified by dissolving in 1,4-dioxane and reprecipitating in water.

Preparation of the Blends

PVC and STAc was dissolved in 1,4-dioxane separately. A solution of STAc was added to that of PVC with constant stirring. The solution was stirred for 2 h at 40°C to ensure complete mixing. The total polymer concentration was kept at 1% w/v. Solution blends with 20/80, 30/70, 50/50, 70/30, and 80/20 w/v compositions of PVC/STAc were prepared.

Measurements

The viscosity measurements of dilute solutions of the polymer blends in 1,4-dioxane were carried out using a Schott Gerate AVS 350 Ubbelohde internal dilution viscometer. No kinetic energy correction was made because the efflux flow time of the solvents were around 100 s.[11] Since the intrinsic viscosities of the polymer blend solutions were below 2.0 dL/g, the effect of the shear rate was negligible. Ultrasonic velocity measurements were carried out on solutions using an ultrasonic interferometer (Mittal Enterprise, Model MX-3, India) technique[12] at a 1-MHz frequency at 30 ± 0.05°C.

The densities of the blend solutions were measured using a specific-gravity bottle and were correlated with the theoretically calculated values. The density of the STAc was determined by following the method described by Inczedy.[13] The solubility parameter of STAc was determined from the intrinsic viscosity data as per the procedure described elsewhere.[14] The solubility parameter of STAc was found to be 12.1 (cal/cm^3)$^{1/2}$ and that for PVC was taken as 9.6 (cal/cm^3)$^{1/2}$ as reported in the literature.

The surface morphology of the polymer films was studied by using a Leica Cambridge (stereoscan 440) scanning electron microscope (Cambridge, U.K.). The polymer film specimens were coated with gold (50 μm thick) in an automatic sputter coater (Polaron Equipment Ltd., USA). The accelerating potential of 10 kV was used for the analysis of the sample. The photographs of the representative areas of the sample were taken at different magnifications. FTIR spectra of pure

Figure 1 Effect of blend composition on heat of mixing: ($\bigcirc$) PVC as component 1; ($\bullet$) PVC as component 2; (- - -) upper compatibility limit.

PVC and STAc and the 70 : 30 PVC/STAc blend were recorded with a Perkin–Elmer FTIR (PE-1700) spectrophotometer using a KBr pallet for STAc and thin film for pure PVC and the blend.

RESULTS AND DISCUSSION

Characterization of STAc

The degree of substitution for starch derivatives is defined as the moles of substituents of hydroxyl groups per D-glucopyranosyl structural unit of the starch polymer. With three hydroxyl groups per unit, the maximum degree of substitution can be 3. The degree of substitution in the case of the STAc synthesized in our laboratory was observed to be 2.5.

The FTIR spectra of native and *esterified* starch confirms the esterification of the starch, as the strong ester carbonyl band appears at 1728 cm^{-1} in the final product. In the native starch spectrum, the characteristic broad band at 958–1190 cm^{-1} is attributed to C—O bond stretching.[15] Another strong broad band due to hydroxyl bond stretching appears at 3000–3600 cm^{-1}. The band intensity was observed to decrease after es-

terification of the starch with acetyl chloride in the quantitative analysis.

The hydrophilic nature of starch was changed to hydrophobic on acetylation. The product was observed to be soluble in DMF, 1,4-dioxane, and dimethyl sulfoxide.

Theoretical Approach to Compatibility

Bohn[16] listed pairs of compatible and incompatible polymers in the molten states, whereas Schneier[17] used the heat of mixing for the prediction of the compatibility of polymeric components in blends. The heat of mixing is an approximate measure of the free energy of mixing[18,19] and indicates the degree of compatibility. Schneier[17] suggested the following equation for the calculation of the heat of mixing of two–component polymer blends:

$$\Delta H_m = \{x_1 M_1 \rho_1 (\delta_1 - \delta_2)^2 [x_2/(1 - x_2) M_2 \rho_2 + (1 - x_1) M_1 \rho_1]^2\}^{1/2} \quad (1)$$

where x, ρ, and M are the weight fraction of the polymer, the polymer density, and the monomer unit molecular weight, respectively. δ is the solu-

Figure 2 Δb versus composition plot for PVC/STAc blends.

bility parameter of a polymer. Subscripts 1 and 2 represent two polymeric components. The blends of two polymers are supposed to be compatible if the calculated heats of mixing of these polymers are found to be within the compatibility limit of 1×10^{-3} to 10×10^{-3} cal.

The heat-of-mixing concept was applied to the STAc/PVC blends and the results obtained are represented in Figure 1 as the heat of mixing versus the composition of the blends. The maximum heat of mixing was observed to be 58×10^{-3} cal at a blend composition of 20:80 PVC/STAc when PVC was considered as component 1 and 74.83×10^{-3} cal when STAc was considered as component 1 at a blend composition of 50:50 PVC/STAc, indicating the incompatibility of the blend components. Such a type of the dependence of the heat of mixing on the choice of the component as component 1 in eq. (1) was also observed by Hourston and Hughes[20] but was not observed by Schneier[17] and Singh and Singh.[9] Hence, the process needs a more detailed study of the blending of various polymer pairs.

The miscibility of polymers may also be predicted by the free-energy (ΔG) concept. For the mutual miscibility of two polymers, the following fundamental thermodynamic condition should be satisfied, where ΔG should be negative:

$$\Delta G = \Delta H - T\Delta S \qquad (2)$$

To fulfill this condition, ΔH has to be small. For this, $(\delta_1 - \delta_2)^2$ should, in turn, be relatively small. Therefore, the essential condition for the miscibility of two polymers is $\delta_1 \rightarrow \delta_2$, that is, $\delta_1 - \delta_2 \leq 0.5$. For PVC/STAc blends, $\delta_1 - \delta_2$ is 2.5. Hence, the blends are considered to be thermodynamically immiscible.

Viscometry of PVC/STAc Blends

Various approaches have been suggested for the viscometric studies of binary polymer systems to predict the compatibility. According to Krigbaum and Wall,[21] an ideally mixed polymer solution viscosity can be given by eq. (3):

$$\eta_{\text{sp(mix)}} = [\eta_1][C_1] + [\eta_2][C_2] + b_{11}C_1^2 \\ + b_{22}C_2^2 + (b_{11}b_{22})^{1/2}C_1C_2 \quad (3)$$

where $\eta_{\text{sp(mix)}}$ is the specific viscosity of the mixed polymer solution. $[\eta_1]$ and $[\eta_2]$ are the intrinsic viscosities of polymer components 1 and 2, respectively. C_1 and C_2 are the concentrations of components 1 and 2, respectively, in the mixed polymer systems, and b_{11} and b_{22} are specific interaction coefficients of the components in single-polymer solutions. Later, eq. (3) was modified by Catsiff and Hewett[22] as follows:

$$\eta_{\text{sp(mix)}} = [(\eta_{\text{sp(1)}})_c C_1 + (\eta_{\text{sp(2)}})_c C_2]/C \qquad (4)$$

Figure 3   Relative viscosity versus composition plot for PVC/STAc blends.

where $[\eta_{sp(1)}]_c$ and $[\eta_{sp(2)}]_c$ are the specific viscosities of polymer components 1 and 2, respectively, at concentration $C = C_1 + C_2$, where C_1 and C_2 are the concentrations of components 1 and 2, respectively, in the blend system.

On the other hand, the viscometric behavior of polymers was described by Huggins [23] as

$$\eta_{sp}/C = [\eta] + k[\eta]^2 C \qquad (5)$$

By substituting $k[\eta]^2$ as b, a term which arises from polymer interaction at a finite concentration, eq. (4) can be written as

$$\eta_{sp(mix)} = [\eta_1][C_1] + [\eta_2][C_2] + b_{11}C_1^2$$
$$+ b_{22}C_2^2 + [(b_{11} + b_{22})/2]C_1C_2 \qquad (6)$$

Equations (3) and (6) are identical except for the coefficient of the C_1C_2 term, which is a polymer–polymer interaction. According to Krigbaum and Wall,[21] the interaction coefficient for ideal mixing of polymer solutions is given as

$$b_{12} = (b_{11}b_{22})^{1/2} \qquad (7)$$

whereas from eq. (6) the interaction coefficient can be written as

$$b_{12} = (b_{11} + b_{22})/2 \qquad (8)$$

Sometimes, when the value of b_{11} or b_{22} is negative, the value of b_{12} according to eq. (7) becomes imaginary. Thus, Krigbaum's definition of b_{12} is unrealistic under this condition. Therefore, we

Figure 4 A plot of reduced viscosity versus concentration of PVC/STAc blends in 1,4-dioxane: (●) 100% PVC; (■) 80% PVC; (▲) 70% PVC; (○) 50% PVC; (□) 30% PVC; (△) 20% PVC; (◆) 100% STAc.

used eq. (8) for the calculation of the interaction coefficient.

The compatibility of a polymer mixture is predicted by the parameter Δb (ref. 21):

$$\Delta b = b_{12} - b_{12}^{*} \qquad (9)$$

where b_{12} is the experimental value for every composition of the blend and b_{12}^{*} is referred to the coefficient of interaction between polymers 1 and 2, calculated from eq. (8).

Negative values of Δb indicate blends containing incompatible polymers, while positive values of Δb show the compatibility of polymers due to the attraction interaction. The Δb versus composition plot for PVC/STAc blends are illustrated in Figure 2. Negative values of Δb were observed for

almost all compositions of PVC/STAc, indicating incompatibility of the blends.

Another approach to the compatibility of the blends is through viscosity measurements. Figure 3 shows representative plots of relative viscosity versus composition plots for PVC/STAc polyblends at 0.8% w/v of the total blend concentration. It is well known that[6,24] deviation from linearity for the relative viscosity versus concentration plots measures the degree of incompatibility of polyblends. Plots for incompatible blends give rise to an S-type of curve, indicating two-phase formation with a reversal of phases at an intermediate composition. It was observed that the relative viscosity versus concentration plots for PVC/STAc blends are not linear, indicating that the two polymers are incompatible. This may be

Table I Observed and Calculated Intrinsic Viscosities of PVC/STAc Blend Systems at 30°C

PVC/STAc (%)	$[\eta]$ (dL/g)	
	Observed	Calculated
80 : 20	0.60	0.63
70 : 30	0.52	0.56
50 : 50	0.39	0.42
30 : 70	0.23	0.27
20 : 80	0.17	0.20

$$[\eta_{sp(mix)}/C]_{C \to 0} = [\eta_1][C_1/C]_{C \to 0}$$
$$+ [\eta_2][C_2/C]_{C \to 0} \quad (10)$$

Table I shows the observed and calculated values of the intrinsic viscosities for the PVC/STAc blend systems. It was observed that the calculated intrinsic viscosities for the blends are higher than the experimentally observed ones. For compatible blends, the observed values are higher than the ideal ones. Hence, the blends under study show a tendency toward incompatibility.

due to repulsive forces between the two polymers involving the chloride of PVC and the carboxyl oxygen of STAc.

Figure 4 shows the effect of the concentration on the reduced viscosity ($\eta_{sp/c}$) for the blends in 1,4-dioxane. In the earlier studies, many authors observed a sharp crossover for two polymers which are completely incompatible.[5] Such a crossover has not been observed with the blends under study. Hence, the blends may have a tendency to be compatible at some extreme composition as suggested by Mamza and Folaranmi.[5] The behavior of an ideal system can be predicted by using the following equation derived from eq. (4):

Ultrasonic Velocity

Ultrasonic velocity versus composition plots are expected to be linear in nature for compatible blends, whereas for incompatible blends, nonlinear plots with a sharp phase inversion at intermediate compositions are expected. Pronounced nonlinearity was observed by Singh and Singh[9] for the PMMA/PS blends at a higher concentration and room temperature. Similar results were observed by Hourston and Hughes[20] for the poly(vinyl methyl ether)/PS solid incompatible blends.

The results obtained in our study of PVC/STAc blends are exhibited in Figure 5. The nonlinear nature of the plot with a phase inversion indicates the incompatibility of the blends.

Figure 5 Ultrasonic velocity versus composition plot for PVC/STAc blends.

Table II   Observed and Calculated Densities of Solutions of PVC/STAc Blends at 27°C in 1,4-Dioxane

PVC/STAc (%)	Densities (g/mL)	
	Observed	Calculated
80 : 20	1.054	1.057
70 : 30	1.056	1.058
50 : 50	1.055	1.060
30 : 70	1.056	1.062
20 : 80	1.054	1.063

The densities of the blend solutions are given in Table II. The observed values for the densities are lower than the theoretically calculated ones, which is the result of decreased chain packing due to lesser molecular interaction[25] due to lesser compatibility.

Interaction Parameters

A polymer-blend solution is a ternary system composed of two different polymers and a solvent.

Hence, there are three types of interactions in the solution of a polymeric blend:

1. Polymer–solvent interaction.
2. Polymer–polymer interaction.
3. Blend–solvent interaction.

The interaction parameter (χ_{12}) is related to the solubility parameters by the equation[26,27]

$$\chi_{12} = (\delta_1 - \delta_2)^2 V_m/RT \tag{11}$$

where V_m is the molar volume of the smaller repeat unit; R, the universal gas constant; T, the absolute temperature; δ_1, the solubility parameter of polymer 1 or a blend of a particular composition; and δ_2, the solubility parameter of polymer 2 or the solvent, as the case may be.

Polymer–Solvent Interaction

The polymer–solvent interaction difference is given by

Figure 6   Scanning electron micrograph of PVC/STAc blends: (a) 100/0; (b) 90/10; (c) 80/10; (d) 70/30. (a′,b′) respective blends etched with 10% NaOH solution.

(a)

(b)

Figure 6 (*Continued from the previous page*)

$$\Delta\chi = \chi_{SA} - \chi_{SB} \qquad (12)$$

where χ_{SA} is the interaction parameter for the solvent and polymer A and χ_{SB} is the interaction parameter for the solvent and polymer B. According to Delmas et al.,[28] the smaller the $\Delta\chi$ the more the compatibility of the polymer in that solvent. The difference between the polymer–solvent interaction parameters $\Delta \chi$, calculated from eq. (12), was observed to be 0.15.

Polymer–Polymer Interaction

The interaction parameter between the polymers in the blends was calculated using eq. (11) for the PVC/STAc system where PVC was taken as components 1 and 2 and was observed to be 4.68 $\times 10^{-1}$ and 20.5 $\times 10^{-1}$, respectively.

Blend–Solvent Interactions

The compatibility of blends, particularly in solution blending, is also influenced by the blend–solvent interaction and the difference in polymer–solvent interaction.[4] The solubility of a polymer

blend in any solvent is determined from the solubility parameters of the constituents. Hence, eq. (11) can also be used for the calculation of the blend–solvent interaction parameter.[4,29] For blend–solvent interaction, the solubility parameters of the blends of different compositions were calculated using the following equation[9]

$$\delta = x_1\delta_1 + x_2\delta_2 \qquad (13)$$

where x_1 and x_2 are weight fractions of the components of blends and δ_1 and δ_2 are their solubility parameters. Table III gives the interaction parameters χ_{bs} and δ for PVC/STAc blends in 1,4-dioxane. It is observed that in most cases the polymer–polymer interaction exceeds the blend–solvent interaction irrespective of PVC being component 1 or 2 . Hence, solution studies carried out in 1,4-dioxane reflect mainly on the compatibility behavior of the polymer blends.[9]

Solid-state Analysis

Morphological Study of PVC–STAc Blends

The uniformity of the dispersion was examined through SEM of solution-cast films of the 100/0, 90/10, 80/20, and 70/30 PVC/STAc blends. From the results illustrated in Figure 6(a– d), it is observed that with increasing concentration of STAc the size of the dispersed phase continues increasing. Figure 6(b) exhibits wrinkling of the surface for 90/10 PVC/STAc blends. Wrinkle formation may be due to the strain developed between the two immiscible phases or the formation of weak van der Waal's forces between polymer chains. It can be observed that the wrinkles disappear with increase in the concentration of STAc [Fig. 6(c,d)]. However, for a better examination of the dispersion of the two phases, films were etched for 24 h with a 10% NaOH solution for the removal of the

Table III Blend–Solvent Interaction Parameters of PVC/STAc System

PVC/STAc (%)	Solubility Parameter δ (cal/cm^3)$^{1/2}$	Interaction Parameter χ_{bs}
80 : 20	9.68	3.640 $\times 10^{-1}$
70 : 30	9.72	2.560 $\times 10^{-1}$
50 : 50	9.80	1.030 $\times 10^{-1}$
30 : 70	9.88	0.174 $\times 10^{-1}$
20 : 80	9.92	0.014 $\times 10^{-1}$

Figure 7 FTIR spectra of (1) PVC ———, (2) 70 : 30 PVC/STAc blend – · – · –, (3) STAc - - - - .

dispersed STAc. From the micrography of the etched films [Fig.6(a′,b′)], it is observed that no etching takes place for pure PVC. But the films containing STAc clearly show etching of the dispersed phase. The uniformity of the holes created supports uniform distribution of STAc without any interaction with PVC. The size of the dispersed particles in the 90/10, 80/20, and 70/30 blends was observed to be 1.18 μm (average of 12 particles), 3.83 μm (average of 18 particles), and 7.84 μm (average of 24 particles), respectively.

FTIR Spectra

The FTIR spectra of pure PVC, STAc, and the blend (70:30 PVC/STAc) are given in Figure 7. The characteristic absorption frequencies for PVC (650 cm^{-1}) and the carbonyl frequency for STAc (1730 cm^{-1}) are not found to be affected in the blends showing the absence of interaction between the two components of the blend.

Biodegradation Studies

PVC/STAc blends were examined for their biodegradability by 2% inoculation of *Bacillus* culture at 30 ± 1°C for 1 month at a shaking condition (160 ± 10 rpm). The pH of the buffer medium (Bushell Hass, Himedia Laboratories Pvt. Ltd., Mumbai) was 7.2. Controlled experiments were also carried out without a culture. It was observed that both sets gave an approximately 10% weight loss. From the results, it can be suggested that due to the poor interaction between PVC and STAc leaching of STAc takes place from the samples even in controlled experiments.

CONCLUSIONS

The blends of PVC/STAc were predicted to be incompatible theoretically. The viscometric, ultrasonic velocity, density measurements, solid-state analysis, and biodegradation studies also led to the same conclusion. Morphological studies also showed that the distribution of the particles of STAc in the PVC matrix is uniform.

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