

# Compatibility and Biodegradability of PMMA–Starch Cinnamate Blends in Various Solvents

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**ABSTRACT:** The compatibility of PMMA and starch cinnamate (STCN) blends prepared in tetrahydrofuran, 1,4-dioxane, and *N,N*-dimethylformamide has been examined through viscometry at 30°C. From the intrinsic viscosity, relative viscosity, reduced viscosity, and density measurements, the blends of the two polymers were observed to be compatible in all three solvents. The compatibility of the blends was also confirmed through FTIR and SEM studies. The blends were observed to be compatible on the basis of heat of mixing, but they were observed to be incompatible on the basis of polymer–polymer interaction parameters. Results obtained show that the compatibility predicted on the basis of viscometric and density measurements is not affected by the choice of solvents. Biodegradation studies showed 13% weight loss within 120 days in the case of the blend containing 30% STCN. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 488–496, 2001

**Key words:** miscibility; viscosity; blend; interaction parameter

## INTRODUCTION

Polymers represent the most abundant class of organic molecules in the biosphere.<sup>1</sup> The great demand for them has led to an extensive search for better waste-management strategies. Solid-waste management is becoming increasingly difficult as traditional landfills become scarce and ecologically undesirable. Therefore, scientists and industries are seriously looking for polymers that are biodegradable in their particular habitats. On the other hand, polymers that are biodegradable may have limited use for long-lived materials, since the latter should be resistant not only to chemical degradation and physical disintegration but also to biodegradation. Hence, the study of the biodegradability of blends containing syn-

thetic polymers and biopolymers is gaining in importance.

Polymer blends are intimate mixtures of two or more structurally similar or different polymers that interact through secondary forces.<sup>2</sup> The blends may be homogeneous or heterogeneous on a molecular level but should not exhibit visibly any obvious inhomogeneity. To be miscible, some attraction (at least no repulsion) between the two polymers must be present to overcome the intermolecular cohesive forces of the individual polymers. The miscibility of polymer blends is studied using optical microscopy, glass-transition temperatures and viscometric studies to discover the interaction parameter at molecular levels.<sup>3–8</sup>

According to Flory<sup>9</sup> the configuration of the polymer molecules depends on its environment. In a good solvent, because of the repulsive forces acting between segments of polymer chains, polymer solvent interaction results in expansion of the macromolecule.<sup>10</sup> As the interaction between the polymer and the solvent becomes weaker and

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weaker, the intermolecularly attractive interactions take over the repulsive interactions. Thus, as the solvent becomes poorer, there is shrinkage of the polymer coil. As a result, the nature of the solvent influences the viscosity of polymer solutions.

If the polymers are miscible in a ternary (two polymers and a solvent) system, in addition to polymer-solvent interaction and intrapolymer interactions, interpolymer interactions also influence the viscosity of the blends. Some authors have studied the importance of choice of solvent in viscosity.<sup>11-14</sup> Pingping et al.<sup>12</sup> have investigated the influence of solvents on the viscosity of dilute solutions of polycaprolactone-poly(vinyl chloride) blends. Raval and Devi<sup>13</sup> proposed that a polystyrene-poly(vinyl acetate) system had some compatibility in toluene, methyl ethyl ketone (MEK), and 1,4-dioxane, while Mamaza and Folaranmi<sup>14</sup> found the same system to be incompatible in toluene, MEK, and tetrahydrofuran (THF) at lower concentrations.

We have synthesized a series of starch esters with different side chains such as starch acetate,<sup>15</sup> starch phthalate,<sup>16</sup> and starch cinnamate in order to induce hydrophobicity in the starch. These ester-synthetic polymer blends were prepared in order to develop partially biodegradable polymers. In this article we evaluate the compatibility behavior of blends containing poly(methyl methacrylate) (PMMA), which is a common engineering plastic, with a modified starch, starch cinnamate (STCN), in solution. The influence of solvents on the viscosity of dilute solutions of the blends has been investigated. It has been proposed that the miscibility of two polymers is a result of the specific interaction between the carbonyl groups<sup>12</sup> of both PMMA and STCN. The solvents for the present work—*N,N*-dimethylformamide (DMF), tetrahydrofuran (THF), and 1,4-dioxane—have been selected on the basis of their ability to dissolve the two polymers and the difference in their solubility parameters. We attempt to interpret the experimental results through the polymer-polymer interaction parameters.

In order to verify the miscibility of the blends, a solid-state analysis through Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM) was done on films of the blends containing up to 30% STCN. The biodegradation of the blends was studied using the soil burial method.

## EXPERIMENTAL

### Materials

Poly(methyl methacrylate) (PMMA) with  $M_n = 180,000$  was supplied by Gujrat State Fertilizers and Chemicals Ltd., Vadodara, India, and was purified by reprecipitating from THF using methanol as a nonsolvent. Potato starch, cinnamic acid, thionyl chloride, and potassium acetate from s. d. fine Chemicals Ltd., India, were used without further purification. The starch contained 19% amylose and 81% amylopectin on a dry basis and had a moisture content of 9.2% by weight.

### Synthesis of Starch Cinnamate

Cinnamoyl chloride was synthesized by the conventional method and was purified by vacuum distillation. The starch was dried at 100°C for 10 h in an oven. The dried starch (100 g) was taken in a five-neck reaction kettle equipped with condenser, dropping funnel, mechanical stirrer, and thermometer. About 250 mL of formamide and 10 g of potassium acetate were added to it, and the solution was stirred for 1 h at 80°C. Reaction mass was cooled to 50°C, and 340 gm of cinnamoyl chloride was added drop-wise over a period of 30 min. After the complete addition of the cinnamoyl chloride, the reaction was allowed to proceed for 3 h at 110°C. The reaction mass was poured into ice-cold water, and there was constant stirring in order to precipitate starch cinnamate. The precipitates were then washed with hot water to remove any unreacted starch, and the dried product was purified by dissolving in acetone and reprecipitating in water.

### Preparation and Characterization of Blends

Solution blends of 1% w/v PMMA:STCN with percentage compositions of 100:0, 80:20, 60:40, 40:60, 20:80, and 0:100 were prepared in DMF, THF, and 1,4-dioxane. Viscosity measurements were made on a Schott Gerate (Germany) AVS 350 instrument using a suspended-level Ubbelohde internal dilution capillary viscometer. The temperature was maintained at 30°C ( $\pm 0.05^\circ\text{C}$ ) in a water bath with the help of a Schott Gerate CT 1650 heating system and a CK 160 cooling system. The ternary blend solutions were prepared<sup>12</sup> by thoroughly mixing measured volumes of two binary solutions of PMMA and STCN in the same solvent directly in the viscometer.

**Table I** Relative and Intrinsic Viscosities of PMMA–STCN Blends in Various Solvents

% PMMA	Relative Viscosity ( $\eta_r$ )			Intrinsic Viscosity ( $[\eta]$ mL/g)					
				Cal.	Obs.	Cal.	Obs.	Cal.	Obs.
	1,4-Dioxane	THF	DMF	1,4-Dioxane	THF	DMF			
100	1.47	1.41	1.38	40.1	40.1	34.9	34.9	34.3	34.3
80	1.37	1.33	1.30	33.0	33.6	28.6	29.4	28.1	28.6
60	1.28	1.24	1.23	25.5	26.7	22.3	24.1	22.0	22.5
40	1.20	1.17	1.16	18.1	20.0	16.0	16.6	15.8	16.2
20	1.12	1.10	1.09	10.8	12.0	9.7	10.0	9.7	10.0
00	1.03	1.04	1.02	03.5	03.5	03.5	03.5	03.5	03.5

The densities of the blend solutions were measured and were correlated with the theoretically calculated values, assuming it to be an additive property.<sup>14</sup> The density of STCN was determined by following the method described by Inczedy.<sup>17</sup> The solubility parameters of STCN and PMMA determined from intrinsic viscosity data, as per the procedure described elsewhere,<sup>18</sup> were found to be  $9.7 \text{ (cal/cm}^3)^{1/2}$  and  $10 \text{ (cal/cm}^3)^{1/2}$ , respectively.

The surface morphology of the films was examined using a stereoscan 440 (Leica Cambridge, U.K.) scanning electron microscope (SEM). Polymer specimens were coated with gold ( $50 \mu\text{m}$  thick) in an automatic sputter coater (Polaron Equipment Ltd., USA). The accelerating potential (10 kv) was used for analysis of the sample. Photographs of representative areas of the samples were taken at different magnifications.

FTIR spectra of pure PMMA and STCN and the 70:30 PMMA–STCN blends were recorded on a Perkin Elmer FTIR (PE-1700) spectrophotometer using KBr pallet for the STCN and thin film for the pure PMMA and the blend.

### Biodegradation

Biodegradation of all the blends was studied using the soil burial method according to the procedure used by Potts et al.<sup>19</sup> For this purpose a number of plastic containers of about 200 mL capacity were filled with compost soil obtained from a municipal yard waste compost site. Rectangular polymer samples (in triplicate) weighing about 0.2 g were placed in containers at a depth of about 5 cm. The compost was kept moist by sprinkling water at regular time intervals to maintain a moisture content of 40%–45%. The excess water was drained through the hole at the bottom of the

container. The containers were stored at about  $30^\circ\text{C}$ – $35^\circ\text{C}$ . The degradation of the samples was studied at regular time intervals (30 days) by removing the samples carefully from the soil and washing them gently with distilled water to remove the soil adhering on the surface. The samples were dried at  $60^\circ\text{C}$  under vacuum until there was a constant weight. The weight loss of the polymer in relation to time elapsed was recorded as a measure of degradation.

## RESULTS AND DISCUSSION

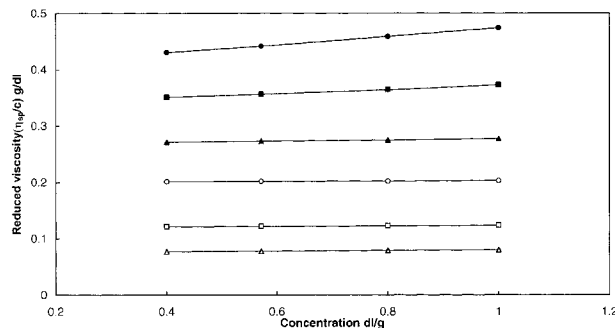
### Characterization of Starch Cinnamate

The degree of substitution, determined from the yield and elemental analysis ( $C = 67.27$ ,  $H = 5.25$ , and  $O = 27.47$ ) of the synthesized STCN was observed to be 1.8. Comparison of the FTIR spectra obtained for native and esterified starch confirms the esterification of starch. A sharp band for a carbonyl group appeared at  $1690 \text{ cm}^{-1}$  in the starch ester. In addition to this, bands were also observed for the aromatic ring at  $1628 \text{ cm}^{-1}$ ,  $1415 \text{ cm}^{-1}$ , and  $3062 \text{ cm}^{-1}$ . The hydrophilic nature of starch was observed to change to hydrophobic on esterification. The product was observed to be soluble in DMF, 1,4-dioxane, acetone, and THF.

### Solution Techniques

#### Viscometry

The results obtained in viscometric studies of solution blending of PMMA and STCN in the three solvents at 1% total concentration are given in Table I. It is well known that deviation from linearity in the plots of relative viscosity versus composition depends on the degree of compatibility of



**Figure 1** Effect of concentration on reduced viscosity of blends in 1,4-dioxane. ● : 100% PMMA ; ■: 80% PMMA; ▲: 60% PMMA; ○: 40% PMMA; □: 20% PMMA; △: 100% STCN.

the blends.<sup>7,11</sup> Plots for compatible systems are linear, while S-type plots indicate phase separation with reversal of phases at intermediate composition. The plots obtained for the PMMA-STCN blends using the data in Table I gave straight lines with a correlation coefficient 0.9990, 0.9986, and 0.9986 in, respectively, 1,4-dioxane, THF, and DMF. This indicates compatibility of the two polymers in all three solvents, which may be a result of interactive forces between the two polymers.

Figure 1 shows the variation in reduced viscosity ( $\eta_{sp}/C$ ) with the concentration of the blend solution in 1,4-dioxane. Similar results were obtained in DMF and THF. Dondos et al.<sup>20</sup> and Schultz and Stockmayer<sup>21</sup> have reported the crossing over of the systems, which are completely incompatible. This crossover, at which there is a change of slope, occurs at a concentration related<sup>20</sup> to the molecular weight of the constituent homopolymers, and its sharpness has been attributed<sup>20</sup> to the lack of compatibility between the polymers. The crossover defines a critical concentration above which there are strong repulsive or attractive interactions between the combining macromolecules of different chemical structures. Since no such crossover is observed for the system under study in any of the three solvents, this can be used as evidence of compatibility between PMMA and STCN at the concentration under study.

The intrinsic viscosity values for PMMA, STCN, and their blends were obtained from the plots of  $\eta_{sp}/C$  versus concentration. The abscissa gives the intrinsic viscosity, and the slope gives the polymer-polymer interaction parameter,  $b$ , of the corresponding polymer and blends. Theoretically,

the intrinsic viscosity of a mixture of two polymers is the weight average of the intrinsic viscosity of each individual polymer in that mixture.

$$[\eta_{sp(\text{mix})}/C]_{C \rightarrow 0} = [\eta]_2[C_2/C]_{C \rightarrow 0} + [\eta]_3[C_3/C]_{C \rightarrow 0} \quad (1)$$

The experimental values of intrinsic viscosities of the blends were higher than those calculated from eq. (1) for all solvents (Table I), indicating compatibility of the polymers in the solvents under study. In a ternary system higher experimental values of intrinsic viscosities provide evidence of the interaction between the polymer chains. The observed order of interaction in different solvents was 1,4-dioxane > THF > DMF.

The above order can be explained by the difference in the polymer-solvent interaction  $\Delta\chi$

$$\Delta\chi = |\chi_{12} - \chi_{13}| \quad (2)$$

where  $\chi$  is the interaction parameter and subscripts 1, 2, and 3 refer to solvent and polymers, respectively. According to Robert et al.,<sup>22</sup> the incompatibility of polymers in solution increases as the difference in the polymer-solvent interaction— $\Delta\chi$ —increases, and it plays a considerably larger role than a polymer-polymer interaction in controlling the compatibility.

In the present study the polymer-solvent interaction parameters were calculated from this equation

$$\chi = (\delta_1 - \delta_2)^2 V/RT \quad (3)$$

where  $V$  is the molar volume of the solvent,  $R$  is the universal gas constant,  $T$  is the absolute temperature,  $\delta_1$  is the solubility parameter of the solvent, and  $\delta_2$  is the solubility parameter of either polymer. For PMMA-STCN blends in 1,4-dioxane, the value  $\Delta\chi$  is very small (0.01), indicating a stable compatible system. For THF and DMF the values 0.06 and 0.17 of  $\Delta\chi$  are higher relative to that in 1,4-dioxane. This explains the order observed in intrinsic viscosities.

### Density

Table II shows calculated and experimental densities of the polyblends. The experimental density values were higher than those calculated using Mamza's equation<sup>14</sup>—and more pronounced with



**Table II** Density of PMMA–STCN Blend in Various Solvents (g/mL)

% PMMA	1,4-Dioxane		THF		DMF	
	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.
100	1.12646	1.12646	1.08126	1.08126	1.00719	1.00719
80	1.13617	1.17727	1.08104	1.08147	1.00723	1.00839
60	1.14589	1.17507	1.08082	1.08107	1.00727	1.00799
40	1.15560	1.17643	1.08060	1.08241	1.00731	1.00749
20	1.16532	1.17703	1.08038	1.08056	1.00735	1.00744
00	1.17503	1.17503	1.08016	1.08016	1.00739	1.00739

1,4-dioxane—possibly because of close packing of the polymer chains, suggesting molecular interaction and compatibility of PMMA–STCN blend systems in all the solvents.

### Theoretical Considerations

Various theories have made predictions about the compatibility of polymers in solution blending. Attempts were made to find out whether these proposed theories could be applied to the system under study.

### Heat of Mixing

Schneier<sup>23</sup> examined blend compatibility based on heat of mixing. The heat of mixing, which may be an approximate measure of polymer–polymer compatibility,<sup>9,24</sup> was calculated using the equation developed by Schneier.

$$\Delta H_m = \{x_1 M_1 \rho_1 (\delta_1 - \delta_2)^2 [x_2 / (1 - x_2) M_2 \rho_2 + (1 - x_1) M_1 \rho_1]^{1/2}\} \quad (4)$$

where  $x$ ,  $\rho$ , and  $M$  are the weight fraction of polymer, polymer density, and monomer-unit molecular weight, respectively,  $\delta$  is the solubility parameter of a polymer, and subscripts 1 and 2 represent two polymeric components. The blends of two polymers are supposed to be compatible if their calculated heats of mixing are within the compatibility limit of  $1 \times 10^{-3}$  to  $10 \times 10^{-3}$  cal.<sup>23</sup>

Figure 2 shows the variation in the heats of mixing calculated from eq. (4) for PMMA–STCN blends of various compositions. The values obtained were  $1 \times 10^{-3}$  to  $6.92 \times 10^{-3}$  cal, which are within the limits proposed by Schneier for compatible blends. According to Schneier<sup>23</sup> and Singh and Singh,<sup>6</sup> which polymer is chosen as the first component does not have a significant effect on the maxima of the curve. However, in the present

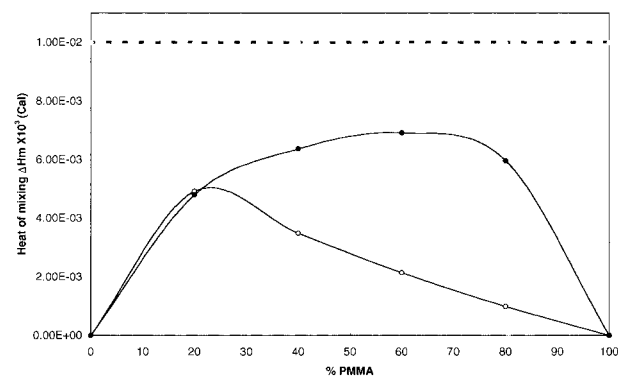
system whether a polymer was chosen as component 1 or component 2 had an effect on the maxima of curve, as observed earlier by Hourston and Hughes<sup>8</sup> for poly(vinyl methyl ether)–polystyrene and by Thakore et al.<sup>15</sup> for poly(vinyl chloride) (PVC)/starch acetate systems.

### Polymer–polymer Interaction Parameters

$\Delta b$  Parameter. Chee<sup>25</sup> proposed an interaction parameter,  $\Delta B$ , to determine polymer–polymer miscibility, which can be calculated as

$$\Delta B = b_{23} - (b_{22} + b_{33})/2 \quad (5)$$

where  $b_{22}$  and  $b_{33}$  are specific interaction coefficients of polymers 2 and 3 determined from the individual polymer solution and  $b_{23}$  represents the interaction between polymers 2 and 3 in a mixed-polymer solution. According to Chee,<sup>25</sup>  $\Delta B \geq 0$  signifies miscibility whereas  $\Delta B < 0$  indicates phase separation. However, Walsh and Cheng<sup>26</sup> and Bosma et al.<sup>27</sup> observed that this parameter wasn't useful in the case of PVC–PMMA blends,



**Figure 2** Effect of blend composition on heat of mixing. ○: PMMA as component 1; ●: PMMA as component 2; ---: upper compatibility limit.

instead citing dynamic mechanical measurements and enthalpy relaxation techniques as the bases for determining the compatibility of the two polymers in blends.

Pingping<sup>28</sup> proposed another parameter ( $\Delta B$ ), based on the Krigbaum and Wall equation,<sup>29</sup> claiming it is more reasonable and more suitable to determining polymer-polymer miscibility. This parameter is given by

$$\Delta b = b_{23} - (b_{22}b_{33})^{1/2} \quad (6)$$

where  $\Delta B \geq 0$  signifies miscibility, while  $\Delta B < 0$  indicates immiscibility. In eqs. (5) and (6),  $b_{23}$  represents the interaction between different polymer molecules in a mixed-polymer solution, which can be obtained from polymer-solution behavior, as described by Huggin's equation<sup>30</sup>

$$\eta_{sp}/C = [\eta] + bC \quad (7)$$

where  $[\eta]$  is the intrinsic viscosity and  $b$  is the polymer-polymer interaction term at finite concentrations related to Huggin's coefficient,  $k_H$ , and is given as

$$b = k_H[\eta]^2 \quad (8)$$

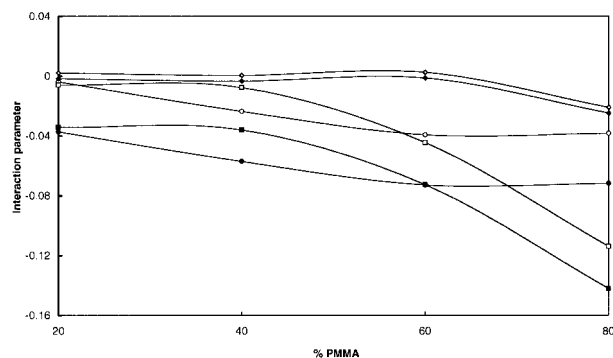
Eq. (7) can be readily adopted to a ternary system containing a solvent (component 1) and two polymers (components 2 and 3). In a ternary system the total polymer-polymer interaction ( $bC^2$ ) depends on the concentration and intrapolymer and interpolymer interactions, which is given as  $C_2(C_2b_{22} + C_3b_{23})$  for component 2 and  $C_3(C_2b_{23} + C_3b_{33})$  for component 3. Thus

$$bC^2 = b_{22}C_2^2 + b_{33}C_3^2 + 2b_{23}C_2C_3 \quad (9)$$

where  $C_2$  and  $C_3$  are the concentrations of components 2 and 3, respectively, in a mixed-polymer solution;  $C$  is the concentration of a mixed-polymer solution; and  $b$  is obtained from the slope of the plots of  $\eta_{sp}/C$  versus  $C$  of the respective polymer blends. Therefore

$$b_{23} = bc^2 - b_{22}C_2^2 - b_{33}C_3^2/2C_2C_3 \quad (10)$$

The values of  $\Delta B$  and  $\Delta b$  calculated from eqs. (5) and (6) have been plotted in Figure 3 for different compositions in terms of the weight percentage of PMMA in the blend. It is clear from this figure that the interaction parameter plot in DMF lies close to zero, while those in THF and 1,4-dioxane



**Figure 3** Interaction parameter versus composition plot for PMMA-STCN blends.  $\Delta B$ —●: 1,4-dioxane; ■: THF; ◆: DMF.  $\Delta b$ —○: 1,4-dioxane; □: THF; : DMF.

lie in the negative region. A similar trend was observed for both interaction parameters ( $\Delta B$  and  $\Delta b$ ). However, the values of  $\delta b$  obtained from Pingping's equation were found to be higher than those of  $\Delta B$  obtained from Chee's equation, although the two plots were parallel to each other. The trend shown in Figure 3 indicates the absence of any interaction in DMF and the existence of repulsive interactions between the polymer components of the blends in THF and 1,4-dioxane, which suggests an incompatible blend system. These results contradict the results obtained from viscometric and density data. Failure of Chee's method to predict the observed miscibility of PVC-poly(*n*-butyl methacrylate) through viscosity measurements was also reported by Danait and Deshpande.<sup>31</sup> Pingping's method was also found to be inadequate to predict the compatibility of the present blend system.

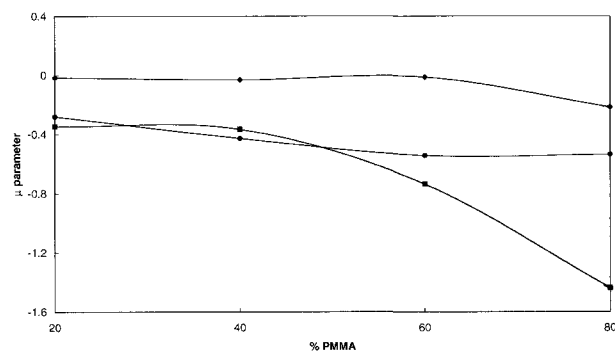
$\mu$  Parameter. Chee<sup>25</sup> has also proposed another interaction parameter,  $\mu$ , for a polymer system having intrinsic viscosities far apart, which can be calculated as

$$\mu = \{(b - b_{22}/[\eta] - [\eta]_2) - (b_{33} - b_{22}/[\eta]_3 - [\eta]_2)\}/2([\eta]_3 - [\eta]) \quad (11)$$

where  $b$  is calculated using eq. (9) and  $[\eta]$  is the mean viscosity, calculated as

$$[\eta] = [\eta]_2W_2 + [\eta]_3W_3 \quad (12)$$

For miscible blends  $\mu \geq 0$ , while for immiscible blends it is negative. It can be seen in Table I that the intrinsic viscosities of PMMA and STCN differ widely. Therefore, eq. (11), proposed by



**Figure 4**  $\mu$  parameter versus composition plot for PMMA–STCN blends. ●: 1,4-dioxane; ■: THF; ◆: DMF.

Chee,<sup>21</sup> was used to predict compatibility. Blends of PMMA–STCN showed negative deviation in all three solvents, as presented in Figure 4. DMF values were close to zero, indicating neither attraction nor repulsion, while in THF and dioxane the values showed a large deviation, which again indicates incompatibility.

The failure of the above theories, which are based on the interaction parameters for the PMMA–STCN system, can be explained as follows. Sun et al.<sup>32</sup> proposed that in Huggin's equation the Huggin's coefficient  $k_H$ , which is related to  $b$ , originates from a superposition of several types of interactions, that is, the hydrodynamic and thermodynamic contributions. Therefore, the term  $b_{23}$  in the field shear force is not a simple measure of intermolecular thermodynamic interaction in the bulk state. Thus, according to Sun et al.<sup>32</sup> eqs. (5) and (6) are not suitable for the prediction of the miscibility of polymer blends. Since  $\mu$  is also related to  $b$ , it was also observed to have failed for our system. Hence, the new criterion,  $\alpha$ , suggested by Sun et al.,<sup>32</sup> was applied to the system under study.

**$\alpha$  Parameter.** According to Cragg and Bigelow,<sup>33</sup> for a ternary blend system, three types of interactions contribute to the value of Huggin's coefficient,  $k_H$ ,

1. Long range hydrodynamic interaction of pairs of single molecules,  $k_{H1}$

$$k_{H1} = \{k_2[\eta]_2^2W_2^2 + k_3[\eta]_3^2W_3^2 + 2(k_2k_3)^{1/2}[\eta]_2[\eta]_3W_2W_3\} / [\eta]_2W_2 + [\eta]_3W_3)^2$$

2. The formation of double molecules,  $k_{H2}$

$$k_{H2} = K'([\eta]_2 - [\eta]_1)/[\eta]^2$$

3. Intermolecular attraction or repulsion,  $k_{H3}$

$$k_{H3} = \alpha$$

$\alpha > 0$  for attraction,  $\alpha < 0$  for repulsion

Therefore,

$$k_H = k_{H1} + k_{H2} + k_{H3} \quad (13)$$

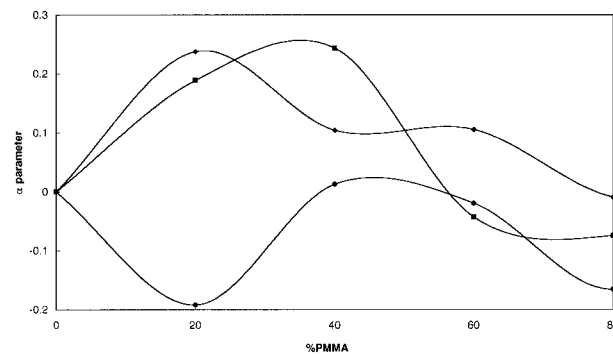
At sufficiently low concentrations and in the absence of strong specific forces of attraction between molecules, the term  $k_{H2}$  can be neglected. So  $k_H$  is given by

$$k_H = \{k_2[\eta]_2^2W_2^2 + k_3[\eta]_3^2W_3^2 + 2(k_2k_3)^{1/2}[\eta]_2[\eta]_3W_2W_3\} / [\eta]_2W_2 + [\eta]_3W_3)^2 + \alpha \quad (14)$$

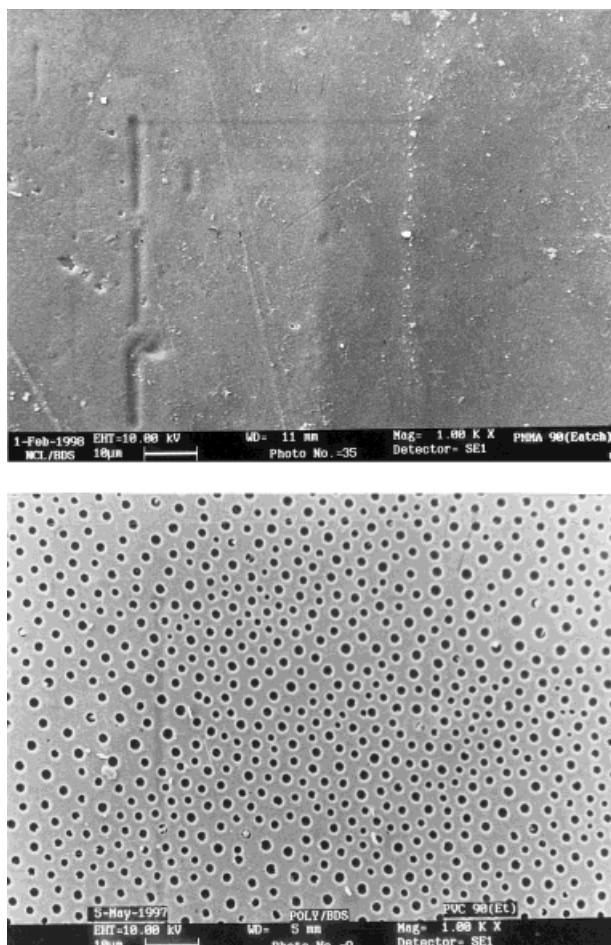
Sun et al.<sup>32</sup> proposed that the value of  $\alpha$  can be used to determine the miscibility of blends for a ternary system ( $\alpha = 0$  for no interaction,  $\alpha > 0$  for attraction, and  $\alpha < 0$  for repulsion). Therefore,

$$\alpha = k_H - k_{H1} \quad (15)$$

Hence, Sun et al.,<sup>32</sup> based on Cragg and Bigelow's considerations,<sup>33</sup> proposed that eq. (15) can be used to determine the miscibility of polymer blends. The plot of  $\alpha$  calculated from eq. (15) versus the PMMA concentration (Fig. 5) shows the positive  $\alpha$  values in DMF and the negative values in 1,4-dioxane. In THF with up to 50 wt % of PMMA the  $\alpha$  values remained positive. But



**Figure 5**  $\alpha$  parameter versus composition plot for PMMA–STCN blends. ●: 1,4-dioxane; ■: THF; ◆: DMF.



**Figure 6** Scanning electron micrograph of 90:10 blends etched with 10% NaOH solution: (a) PMMA-STCN, (b) PVC-STAc.

when the PMMA concentration increased further, the values shifted to the negative region. Hence, this theory was also partially applicable to the system under study. A similar observation was made by Pingping<sup>28</sup> in his investigation on the miscibility of PS-PMMA blends.

All this evidence leads to the conclusion that in the present blend system polymer-polymer interaction is more dominant than polymer-solvent interaction.

### Solid-State Analysis

#### Morphological Study

The solution-cast films of the blends were etched for 24 h with 10% sodium hydroxide solution for the removal of dispersed STCN. A representative micrograph of 80:20 PMMA-STCN blend [Fig. 6(a)] indicates no etching of STCN because of the

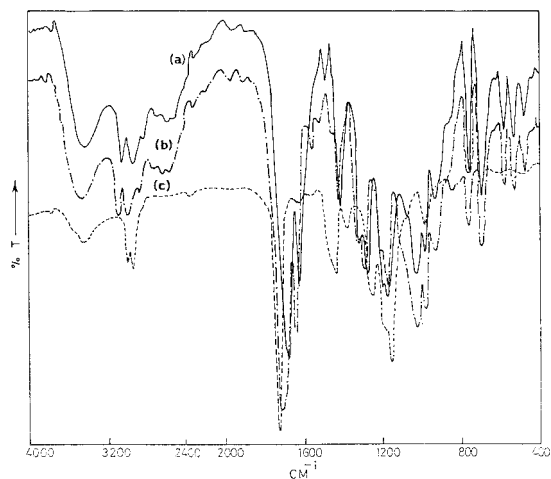
interactive forces between the two phases and therefore their compatibility. In our earlier studies on PVC-starch acetate blends,<sup>15</sup> the etching of blend film exhibited holes created from the selective etching of starch acetate in a sodium hydroxide solution [Fig. 6(b)].

#### FTIR Spectra

The FTIR spectra of pure PMMA, STCN, and the 70:30 PMMA-STCN blend are given in Figure 7. Characteristic carbonyl frequencies for PMMA and STCN were observed at 1732 and 1688  $\text{cm}^{-1}$ . Lizymol and Thomas<sup>34</sup> have observed a broadening of the carbonyl absorption frequency in cases of compatible blends of PVC-EVA [poly(ethylene-co-vinyl acetate)]. A similar broadening of the carbonyl band was also observed in the present case, indicating compatibility.

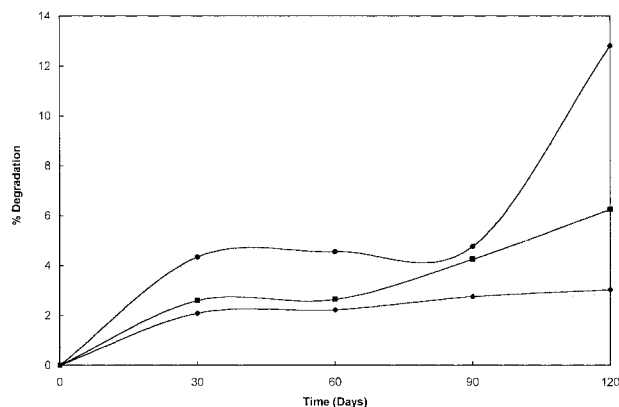
#### Biodegradation

The results of the soil degradation of PMMA-STCN blends containing up to 30% STCN are given in Figure 8. It can be observed that the percent of degradation increases with an increase in the weight percentage of STCN in the blend. At the end of 4 months the 70:30, 80:20, and 90:10 blends showed about 13%, 6%, and 3% weight loss, respectively, while pure PMMA showed no loss. Rapid and substantial weight loss in films containing 30% STCN may be the result of greater accessibility of starch to microorganisms in these films, as Peansky et al.<sup>35</sup> have shown that 30% starch by volume is required to assure inter-



**Figure 7** FTIR spectra of pure components and blend: (a) STCN, (b) PMMA-STCN (70:30), (c) PMMA.





**Figure 8** % degradation versus time for PMMA–STCN blends. ●: 70:30, ■: 80:20, ◆: 90:10.

connectivity, while at lower concentrations only surface starch would be accessible to microorganisms. This indicates that starch ester has been preferentially removed, leaving the PMMA matrix.

## CONCLUSIONS

PMMA–STCN blends were found to be compatible from the experimental results of viscometric and density measurements in all three solvents under study. This observation was supported by the heat of mixing data and by solid-state analysis through FTIR and SEM. However, on the basis of polymer–polymer interaction parameters such as  $\Delta B$ ,  $\Delta b$ ,  $\mu$ , and  $\alpha$ , the blends were found to be incompatible in all three solvents. Among the three solvents compatibility was found to be highest in 1,4-dioxane, followed by THF and DMF. Apart from that, the solvents did not have a significant effect on compatibility behavior. The blends under study also show potential as biodegradable polymers.

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## REFERENCES

1. Eggersdor, M.; Warwel, S.; Wulff, N. R. *Perspektiven für die Chemie*; VCH Verlagsgesellschaft, Weinheim, 1993.
2. Sher, M.; Kawi, H. *Chem Eng J* 1978, 1, 24.

3. Hugelin, P. C.; Dondos, A. *Die Makromol Chem* 1969, 126, 206.
4. Gul, V. E.; Penskaya, E. A.; Kuleznev, V. N. *Kolloidzh* 1965, 27, 341; *Colloid J* 1965, 27, 283.
5. Kundu, A. K.; Ray, S. S.; Adhikari, B.; Maiti, S. *Eur Polym J* 1986, 22, 369.
6. Singh, Y. P.; Singh, R. P. *Eur Polym J* 1983, 19, 535; *Eur Polym J* 1984, 20, 201.
7. Kuleznev, V. N.; Melinkova, O. L.; Klykova, V. D. *Eur Polym J* 1978, 14, 455.
8. Hourston, D. I.; Hughes, I. D. *Polymer* 1978, 19, 1181.
9. Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: New York 1978; p 507.
10. Renyuan, Q. *The Molecular Weight Measurement of Polymer*; Science Press: Beijing, 1958.
11. Kulshreshtha, A. K.; Singh, B. P.; Sharma, Y. N. *Eur Polym J* 1988, 24, 191.
12. Pingping, Z.; Haiyang, Y.; Shiqiang, W. *Eur Polym J* 1998, 34, 91.
13. Raval, H.; Devi, S. *Die Angew Makromolek Chem* 1995, 27, 227.
14. Mamza, P. A. A. P.; Folaranmi, F. M. *Eur Polym J* 1996, 32, 909.
15. Thakore, I. M.; Desai, S.; Sarwade, B. D.; Devi, S. *J Appl Polym Sci* 1999, 71, 1851.
16. Thakore, I. M.; Desai, S.; Sarwade, B. D.; Devi, S. *Eur Polym J*, to appear.
17. Inczedy, J. *Analytical Application of Ion exchange*; Pergamon Press: U.K 1966, p.116.
18. Sperling, L. H. *Introduction to Physical Polymer Science*; Wiley: New York, 1992; p 68.
19. Potts J.E.; Clendinning R.A.; Ackart, W.B. USEPA Contract No. CPE. 70-124,1972 pp.22.
20. Dondos, A.; Skondras, P.; Pierri, E.; Benoit, H. *Makromolek Chem* 1983, 184, 2153.
21. Schultz, G. V.; Stockmayer, W. H. *Makromolek Chem* 1986, 87, 2235.
22. Robert, A.; Patterson, D.; Delmas, G. *Macromolecules* 1977, 10, 704.
23. Schneier, B. O. *J Appl Polym Sci* 1973, 17, 3175.
24. Krause, S. *J Macromol Sci* 1972, C7, 251.
25. Chee, K. K. *Eur Polym J* 1990, 20, 423.
26. Walsh, D. J.; Cheng, G. L. *Polymer* 1984, 25, 459.
27. Bosma, M.; Ten Brinke, G.; Ellis, T. S. *Macromolecules* 1988, 21, 1465.
28. Pingping, Z. *Eur Polym J* 1997, 33, 411.
29. Krigbaum, W. R.; Wall, F. T. *J Polym Sci* 1950, 5, 505.
30. Huggins, M. L. *J Am Chem Soc* 1942, 64, 277.
31. Danait, A.; Deshpande, D. D. *Eur Polym J* 1995, 31, 1221.
32. Sun, Z.; Wang, W.; Feng, Z. *Eur Polym J* 1992, 28, 1259.
33. Cragg, L. H.; Bigelow, C. *J Polym Sci* 1955, 16, 177.
34. Lizymol, P. P.; Thomas S. *Eur Polym J* 1995, 31, 1221.
35. Peansky J. S.; Long, J. M.; Wool, R. P. *J Polym Sci B: Polym Physics* 1991,29, 565.