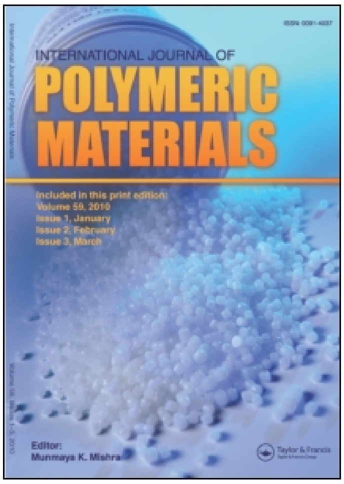

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Compatibility and biodegradability of blendsof starch cinnamate with various polymers

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COMPATIBILITY AND BIODEGRADABILITY OF BLENDS OF STARCH CINNAMATE WITH VARIOUS POLYMERS

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The compatibility of blends of starch cinnamate (StCn) with polyvinyl chloride (PVC), polystyrene (PS), and styrene acrylonitrile copolymer (SAN) has been examined through viscometry at 30°C. The results of the three systems are compared with the already reported PMMA/StCn system. From the intrinsic viscosity, relative viscosity, reduced viscosity, and density measurements the PVC/StCn and SAN/StCn blends were found to be compatible while PS/StCn blend was found to be incompatible. The compatibility of the blends was also confirmed by SEM analysis. The compatibility of these blends based on heat of mixing and polymer-polymer interaction parameter was also examined. Blends were observed to be compatible on the basis of heat of mixing theory but not on the basis of polymer - polymer interaction parameters. Biodegradation studies of compatible blends containing 30% StCn showed 13%, 15%, 18%, and 23% weight loss in case of PMMA, SAN, and PVC blends after 120 days.

Keywords: blend, miscibility, viscosity, interaction parameter, biodegradability

INTRODUCTION

Polymer–polymer miscibility, based on viscosity measurements of dilute polymer solutions, has been reported extensively [1–4]. Viscosity can also be used for the evaluation of interactions in polymer solutions [1–3,5] and determine the molecular weight and its

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distribution [6] as well as the degree of branching [7,8] in polymers. Because of its simplicity, viscometry became an attractive method to study the compatibility of polymers in solutions [9–14]. The basis for using viscosity of dilute solution as a parameter for the measurement of compatibility of polymer blends lies in the fact that, in solution, the repulsive interaction causes shrinkage of polymer coils leading to reduction in the viscosity of polymer mixture than the values calculated from the viscosities of the pure components using additivity law. On the other hand, attractive interaction increases the viscosity of the system.

In recent years, many workers [15–19] have reported the use of ultrasonic velocity measurements to reveal the extent of compatibility in highly viscous or solid-state polyblends. Ultrasonic attenuation was also used to predict the compatibility of polymers [20–22]. Sidkey et al. [23,24] studied the degree of compatibility of the blends of different types of rubbers in solution using ultrasonic methods. Singh et al. [15] have explained the compatible, semi-compatible, and incompatible nature of various polymer blend systems considering ultrasonic velocity and absolute density of the polymer blends in solutions. The ultrasonic velocity measurements have been extended to solid polyblends by Singh and Singh [25].

We have made use of these techniques to investigate the compatibility behavior of the blends of starch cinnamate with some commercial engineering plastics such as polystyrene (PS), poly (vinyl chloride) (PVC) and styrene acrylonitrile copolymer (SAN). They were chosen on the basis of difference in polarity to see its effect on compatibility. We have already investigated the compatibility of StAc/PVC and StCn/PMMA blends by the above-mentioned techniques [26,27].

EXPERIMENTAL

Materials

Poly (vinyl chloride) (PVC) with $\overline{M}n = 51{,}000$ from National Chemicals, Vadodara, India, styrene acrylonitrile copolymer (SAN) with $\overline{M}n = 10{,}000$ from ABS plastic, Vadodara, India, and polystyrene (PS) with $\overline{M}n = 170{,}000$, from Supreme Chemicals, Mumbai, India, were purified by reprecipitating them from THF using methanol as a non-solvent. Starch cinnamate was synthesized and purified by a procedure described earlier [26].

Preparation of the Blends

The synthetic polymers, PVC/SAN/PS and StCn were separately dissolved in 1,4-dioxane. Solution of StCn in 1,4-dioxane was added to that of the synthetic polymer 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, 40/60, 50/50, 60/40 and 80/20 w/v compositions of PVC/StCn, PS/StCn and SAN/StCn were prepared.

Measurements

Viscosity

The viscosity measurements of dilute solutions of the polymer blends were carried out using Schott Gerate AVS 350 Ubbelohde internal dilution viscometer at 30°C. No kinetic energy correction was made because the efflux flow time of solvents was around 100 seconds. Since intrinsic viscosities of the polymer blend solutions were below 2.0 dl/g the effect of shear rate was negligible.

Density

Densities of the blend solutions were measured by means of a specific gravity bottle and were correlated with the theoretically calculated values. Density of the blend components was determined by following the method described by Inczedy [28], while the solubility parameter of the polymer component was taken as the solubility parameter of the solvent in which the intrinsic viscosity was maximum [28,29].

Ultrasonic Velocity

Ultrasonic velocity measurements were carried out on solutions using an ultrasonic interferometer (Mittal enterprise, Model M X -3, India) at 1 MHz frequency at 30 ± 0.05°C.

Scanning Electron Microscopy

Surface morphology of solution cast films of blends containing up to 30% StCn was studied by using a Leica Cambridge (stereoscan 440) scanning electron microscope (SEM), Cambridge, U.K. 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 sample. The photographs of representative areas of the sample were taken at different magnifications.

For a better examination of dispersion of the two phases, films were etched for 24 h in 10% sodium hydroxide solution for the removal of dispersed starch cinnamate. The films were then washed thoroughly with distilled water and dried in a vacuum oven until constant weight. The etched films were further analyzed by SEM.

Degradation Study

Biodegradability of solution cast films of blends containing up to 30% StCn was studied as per the soil burial procedure reported by Potts et al. [30]. The blend films were photodegraded in air atmosphere at room temperature for 5 h using high-pressure mercury lamp (kpk 125 W, Philips, Holland). Intensity of incident light was 32 mW cm^{-2}. These UV-degraded samples were also examined by SEM.

RESULTS AND DISCUSSION

Solution Techniques

Viscosity

It is well known [1,13] that at a fixed concentration deviation from linearity for the relative viscosity vs. composition plots is a measure of the degree of incompatibility of polyblends. Incompatible blends give rise to S-shaped plots, indicating the existence of two phases with reversal of phases at intermediate composition. Figure 1 shows the relative viscosity vs. composition plots for the polyblends in 1,4-dioxane, at 1% w/v of total blend concentration. It was observed that the plots for PS/StCn blends were not linear, indicating incompatibility, while those for PVC/StCn, PMMA/StCn, and SAN/StCn

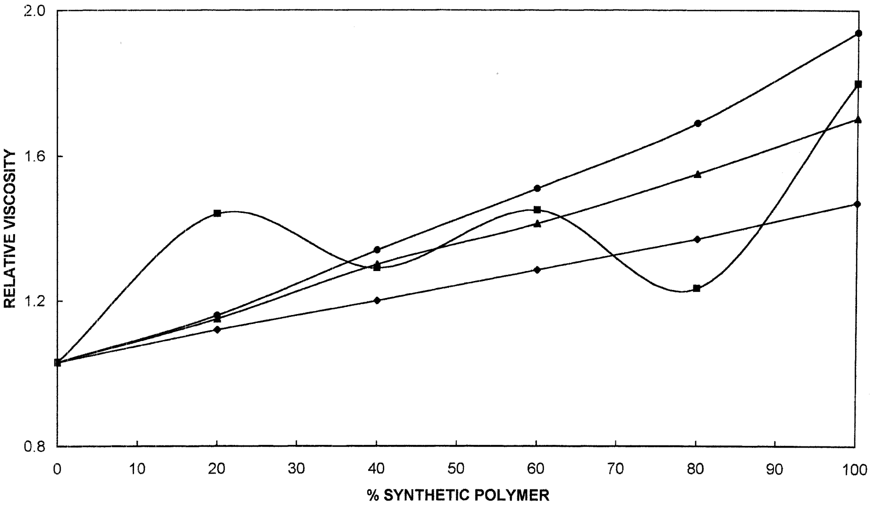


FIGURE 1 Relative viscosity vs composition plot for blends. ◆: PMMA/StCn, ■: PS/StCn, ▲: SAN/StCn, ●: PVC/StCn.

TABLE 1 Intrinsic Viscosity of StCn Blends

%	PMMA/STCN		SAN/STCN		PVC/STCN		PS/STCN	
StCn	CAL	EXP	CAL	EXP	CAL	EXP	CAL	EXP
00	–	0.401	–	0.581	–	0.767	–	0.666
20	0.330	0.336	0.472	0.482	0.621	0.633	0.536	0.513
40	0.255	0.267	0.363	0.371	0.474	0.482	0.411	0.400
60	0.181	0.200	0.253	0.263	0.328	0.333	0.285	0.268
80	0.108	0.120	0.144	0.150	0.181	0.195	0.160	0.157
100	–	0.035	–	0.035	–	0.035	–	0.035

blends were found to be linear, indicating compatibility of these blends. The compatibility of PMMA/StCn, PVC/StCn, and SAN/StCn systems may be a result of interactive forces between the components of polymers.

The intrinsic viscosity values for the homopolymers and their blends were obtained from the plots of η_{sp}/C vs. concentration. Theoretically, the intrinsic viscosity of mixture of two polymers is the result of weight average intrinsic viscosities of the two polymers taken separately.

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

In a ternary system, higher experimental values of intrinsic viscosities show evidence of attractive interaction between the polymer chains indicating compatibility. The experimental values of intrinsic viscosities of PVC/StCn, PMMA/StCn, and SAN/StCn blends (Table 1) were observed to be higher than those calculated from Equation (1), indicating blend compatibility, whereas observed lower experimental values for PS/StCn blends indicated tendency towards incompatibility.

Hence from relative viscosity and intrinsic viscosity studies, PMMA/StCn, PVC/StCn, and SAN/StCn blend systems were found to be compatible and the PS/StCn system was found to be incompatible.

Density and Compatibility

A comparison between the experimental and calculated densities shows that, for a compatible blend, experimental values are higher than values calculated assuming volume additivity of the constituents. This increase in the density is attributed to the greater chain packing resulting from increased molecular interaction and compatibility.

The densities of the blend solutions are given in Table 2. It was observed that the experimental values of densities are lower than the

TABLE 2 Density of StCn Blends in g/cm^3

% StCn	PMMA/STCN		SAN/STCN		PVC/STCN		PS/STCN	
	CAL	EXP	CAL	EXP	CAL	EXP	CAL	EXP
00	–	1.12646	–	1.04971	–	1.05502	–	1.17118
20	1.13617	1.17773	1.07477	1.09200	1.07902	1.08503	1.17195	1.17035
40	1.14589	1.17507	1.09984	1.13000	1.10302	1.12011	1.17272	1.17220
60	1.15560	1.17643	1.12490	1.14547	1.12703	1.14035	1.17349	1.17298
80	1.16532	1.17703	1.14997	1.16200	1.15103	1.16012	1.17426	1.17340
100	–	1.17503	–	1.17503	–	1.17503	–	1.17503

theoretically calculated ones for the PS/StCn blends, which may be attributed to the decreased chain packing due to weaker molecular interaction [31]. The PVC/StCn, PMMA/StCn, and SAN/StCn blends showed higher experimental values and hence compatibility, which supports the results obtained from viscometry.

Ultrasonic Velocity

Ultrasonic velocities vs. composition plots are expected to be linear in nature for compatible blends, whereas for incompatible blends non-linear plots with a sharp phase inversion at intermediate compositions are expected. Pronounced non-linearity was observed by Shaw and Singh [15] for the PMMA/PS blends at higher concentration and room temperature. Hourston and Hughes [14] also obtained non-linear plots for the poly (vinyl methyl ether)/PS, indicating incompatibility of the blends. The results obtained in our study are exhibited in Figure 2. The non-linear nature of the plot with a phase inversion indicates incompatibility of the PS/StCn blends. On the other hand, PVC/StCn, PMMA/StCn, and SAN/StCn blends showed more or less linear plots, indicating compatibility of these blends.

From this simple experimental technique it was observed that binary blends of StCn and synthetic polymers PMMA, SAN, and PVC are compatible whereas those with PS are incompatible.

Theoretical Parameters

Various theories predicted to examine the compatibility of polymers in solution blending have been discussed in detail elsewhere [26,27]. Hence, attempts were made to see whether the proposed theories can be applied to the systems under study.

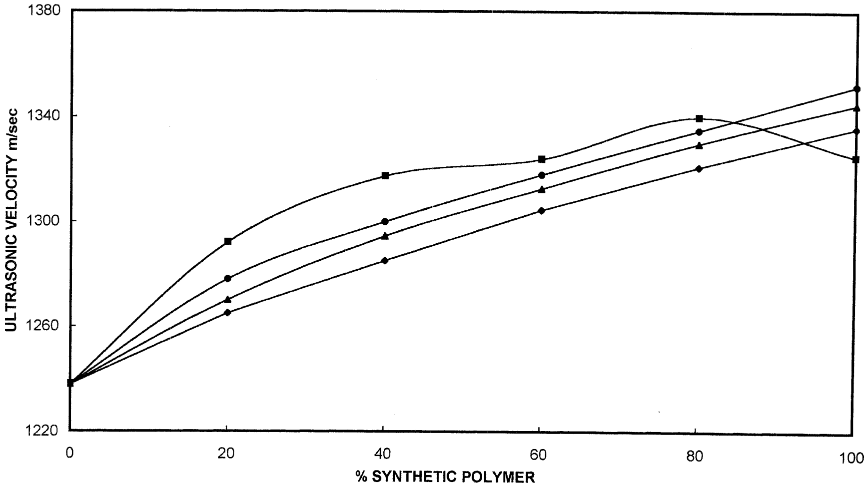


FIGURE 2 Ultrasonic velosity vs. composition plots for blends. ◆: PMMA/StCn, ■: PS/StCn, ▲: SAN/StCn, ●: PVC/StCn.

Heat of Mixing

Figure 3 shows the variation in the heats of mixing [32] for the blends of various compositions. The calculated values of PS/StCn blends are above the compatibility limit and those of PVC/StCn,

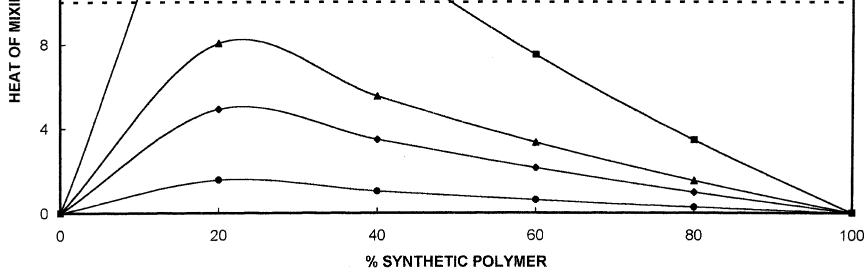


FIGURE 3 Effect of blend composition on heat of mixing. ◆: PMMA/StCn, ■: PS/StCn, ▲: SAN/StCn, ●: PVC/StCn- - -: upper compatibility limit.

PMMA/StCn, and SAN/StCn blends are within the limit proposed by Schneier [32] for the compatible blends. These observations also confirm the experimental results obtained through viscosity, density, and ultrasonic velocity measurements.

Interaction Parameters

ΔB Parameter. The values of interaction parameter ΔB calculated as per Chee's equation [2,26] is plotted in Figure 4 for different blend compositions, in terms of weight percentage of synthetic polymer in the blend. It is observed that values of Chee's interaction parameter for all the blends are lower than zero, indicating incompatibility of blends at all compositions. PVC/StCn blends showed maximum deviation from zero.

Δb Parameter. The interaction parameters Δb calculated as per Pingping's equation [33] are given in Figure 5. The nature of the plots is similar to that observed in Figure 4. However, the values of interaction parameter Δb were relatively larger than ΔB. These results are quite contradictory to the results obtained from viscometric and density data. Thus in the present systems, the use of these interaction parameters failed to confirm experimentally observed compatibility of the blends under study. We have already reported the failure of Chee's method to predict the observed experimental miscibility in the case of

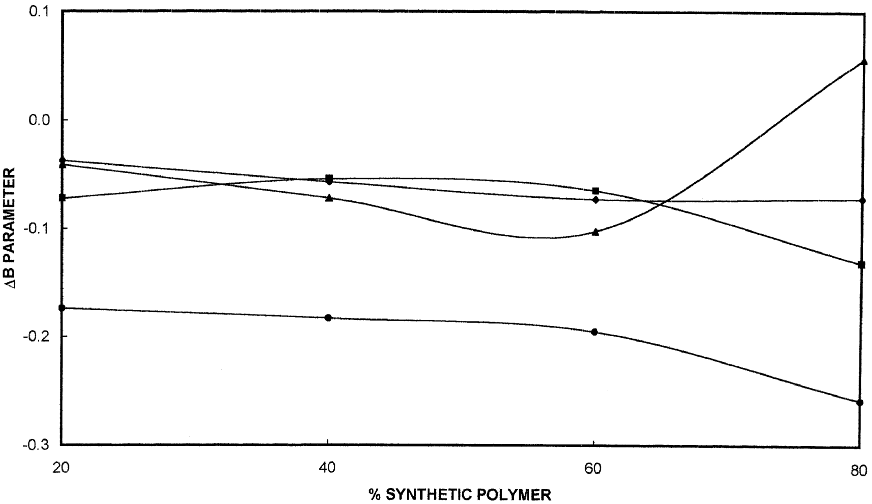


FIGURE 4 ΔB vs composition plot for blends ◆: PMMA/StCn, ■: PS/StCn, ▲: SAN/StCn, ●: PVC/StCn.

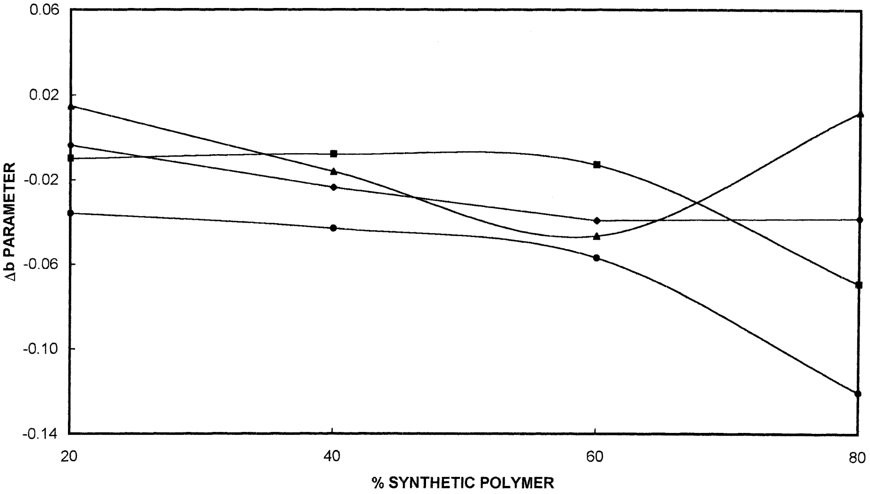


FIGURE 5 Δb vs composition plot for blends ◆: PMMA/StCn, ■: PS/StCn, ▲: SAN/StCn, ●: PVC/StCn.

blends of StCn with PMMA. Danait and Deshpande [4] have also reported the failure of Chee's method for PVC/poly(n-butyl methacrylate). Hence Chee's model needs reorientation or needs to state more specifically its limitations for the prediction of blend compatibility. For all our blend systems Pingpin's method was also found to be inadequate to predict the compatibility.

μ Parameter. From Table 1 it can be seen that the intrinsic viscosities of the commercial polymer and StCn differ widely. Therefore, Chee's parameter [2] (μ parameter) proposed for the systems differing considerably in their intrinsic viscosities was used for the prediction of compatibility. Figure 6 shows μ versus composition plots for our blends. All the blends showed negative deviation. However, the observed trend was not different than one observed in Δb and ΔB studies. Hence consideration of μ parameter also could not explain experimental results.

The failure of the theories based on the interaction parameters for our systems is for the reasons already reported [26] for PMMA/StCn system. Sun et al. [3] proposed that in the Huggin's equation [7] the Huggin's coefficient K_H, which is related to "b," originates from a superposition of several types of interactions. Therefore the term b_{23} in the field shear force is not a simple measure of intermolecular thermodynamic interaction in the bulk state. Since the parameters Δb, ΔB and μ are related to the term b_{23}, they fail for our system, Hence,

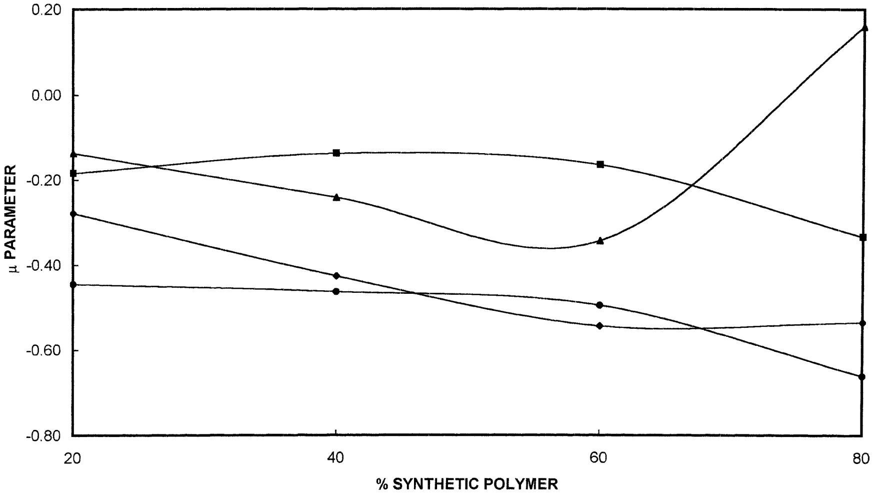


FIGURE 6 μ parameter vs composition plot for blends. ◆: PMMA/StCn, ■: PS/StCn, ▲: SAN/StCn, ●: PVC/StCn.

the new criterion α suggested by Sun et al. [3] was applied to the system under study.

α Parameter. The plots of α parameter (Figure 7) for almost all the blends lie within the compatibility limit except PMMA/StCn system.

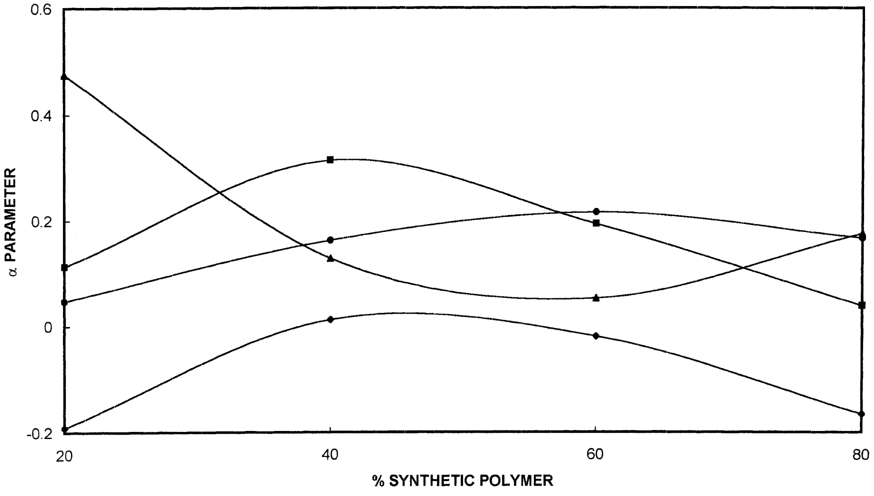


FIGURE 7 α parameter vs composition plot for blends. ◆: PMMA/StCn, ■: PS/StCn, ▲: SAN/StCn, ●: PVC/StCn.

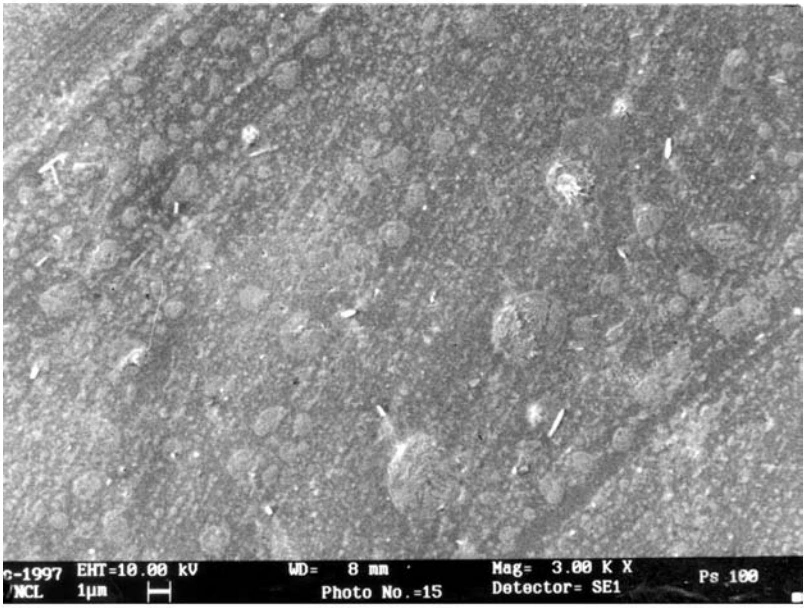
Thus, α parameter shows results contradictory to experimental results for the blends of PS and PMMA. Hence, this theory is inapplicable to the blends under study. Zhu Pingping [33], too, observed the failure of this theory, in his investigation on miscibility of PS-PMMA blends.

Thus, it can be concluded that starch cinnamate is compatible with the synthetic polymers, which are polar in nature (PVC, PMMA and SAN), but incompatible with PS, which is a non-polar polymer.

Morphological Study

The uniformity of dispersion was examined by scanning electron microscopy of solution cast films of the blends containing up to 30% StCn.

In the case of PS/StCn system (Figures 8a–8g), it was observed that with increasing concentration of StCn the size of the dispersed phase increases (Figures 8b, 8c) and the StCn particles are uniformly distributed. The morphology of the etched films (Figures 8d, 8e) showed



(a)

FIGURE 8 Scanning electron micrograph of Ps/StCn blends. (a) 100/0, (b) 80/20, (c) 70/30, (d) 100/0, etched with 10% NaOH solution, (e) 70/30, etched with 10% NaOH solution, (f) 100/0, UV degraded, (g) 70/30, UV degraded.

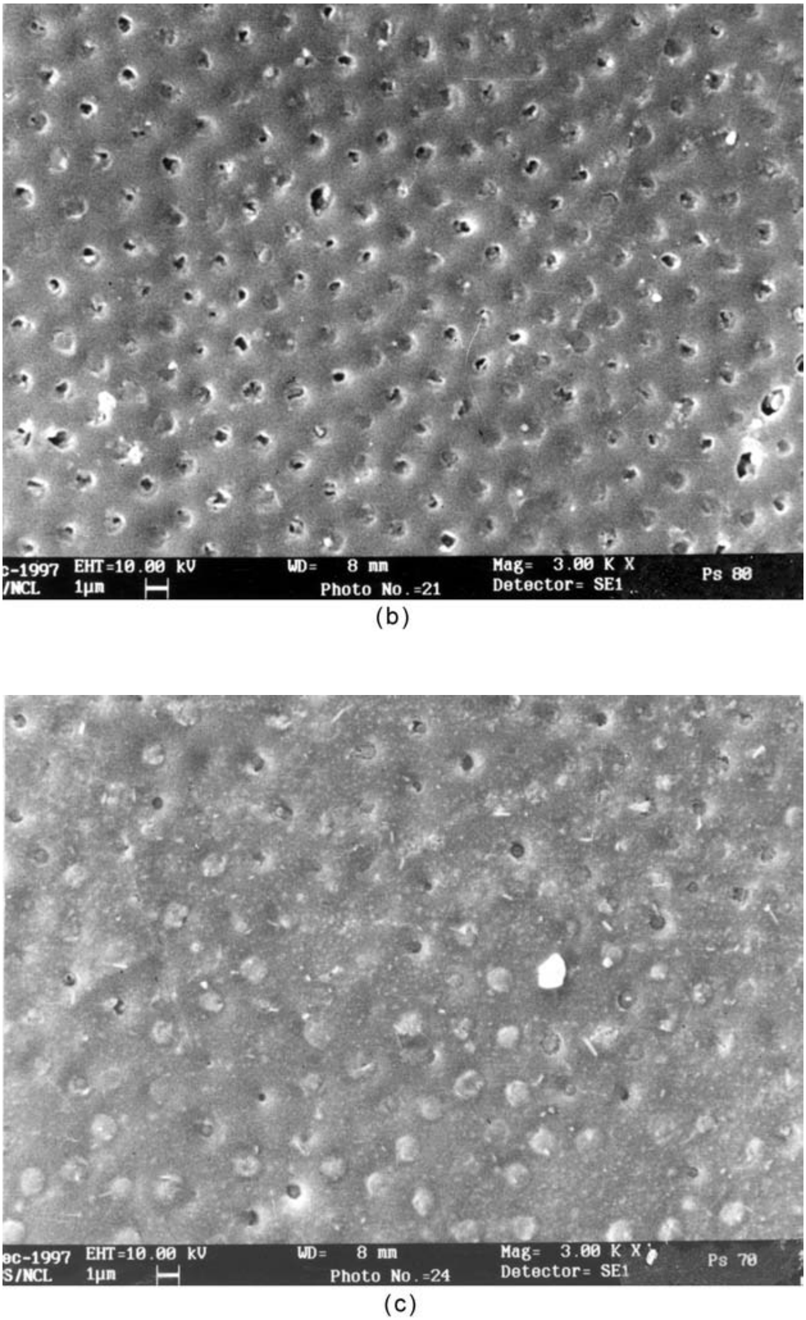
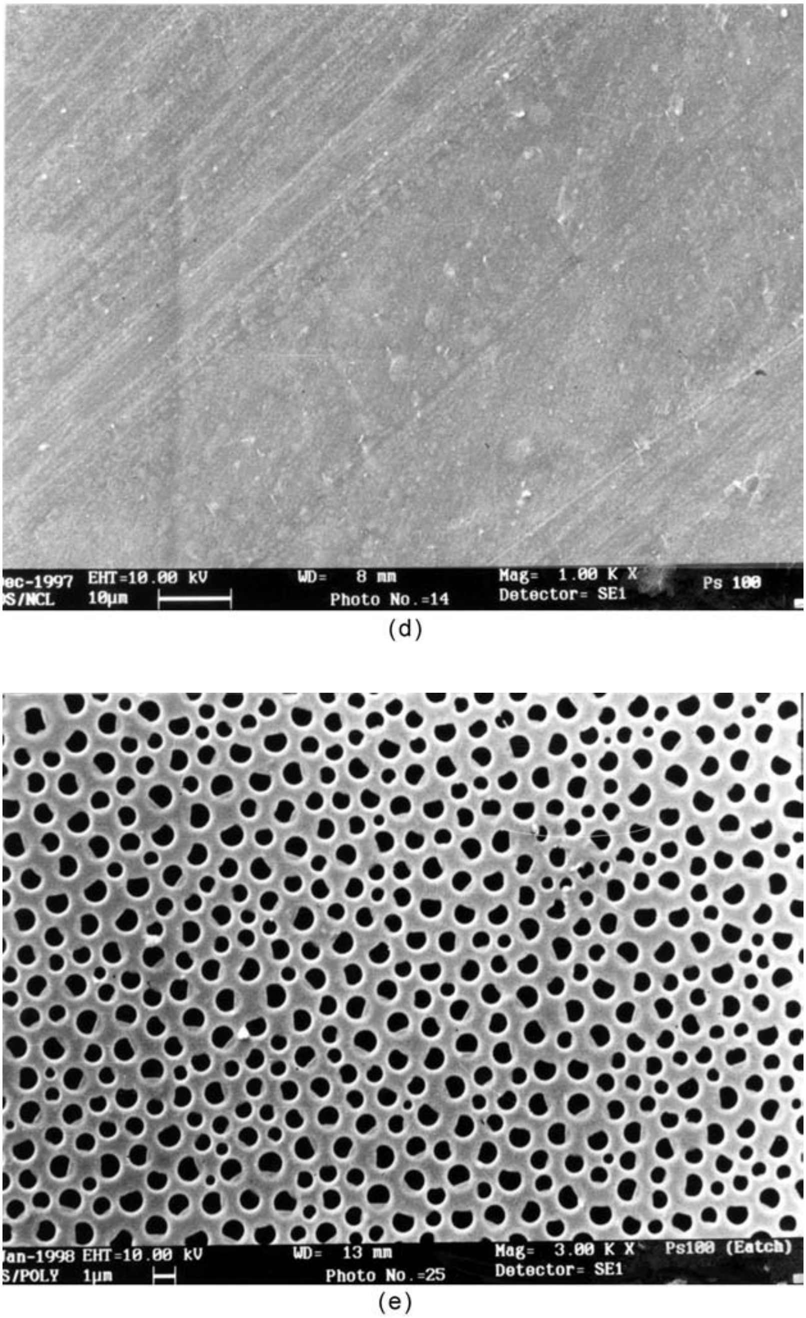


FIGURE 8 (*Continued*.)



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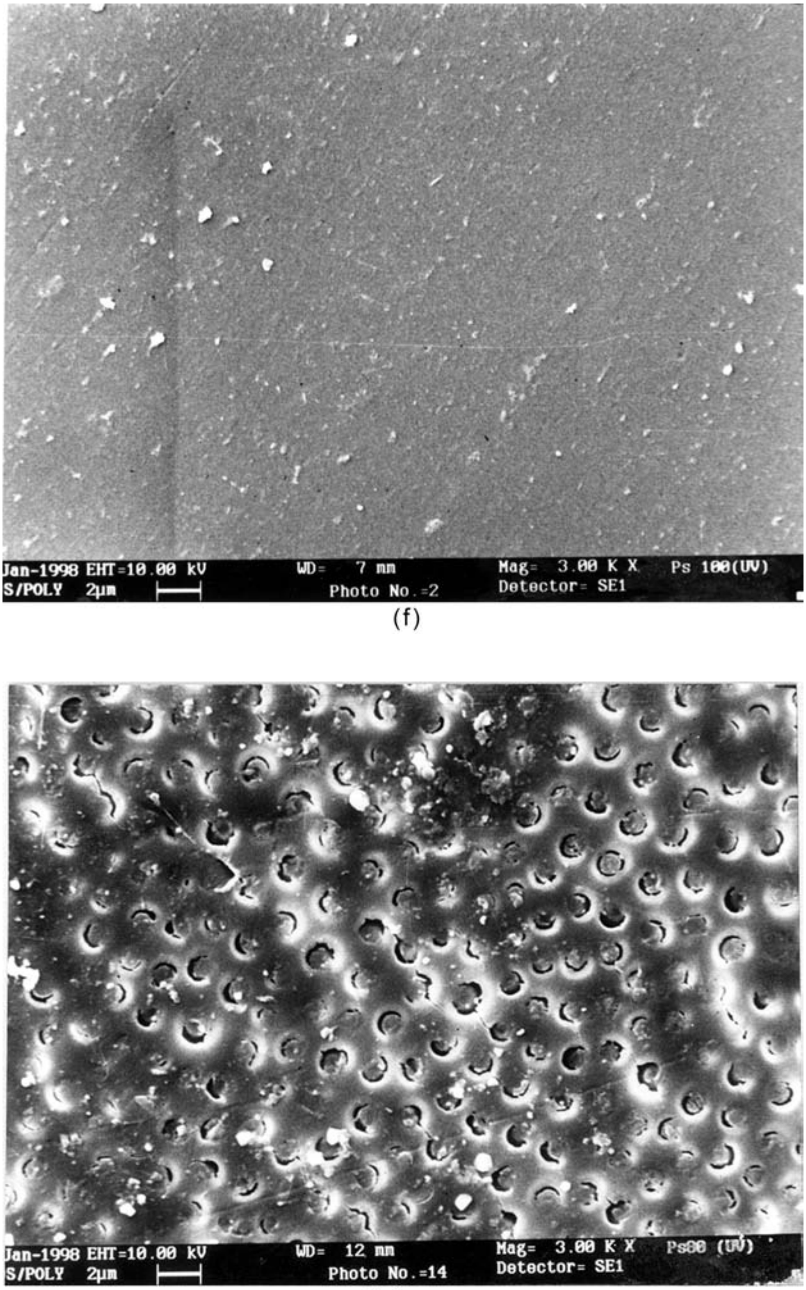


(f)

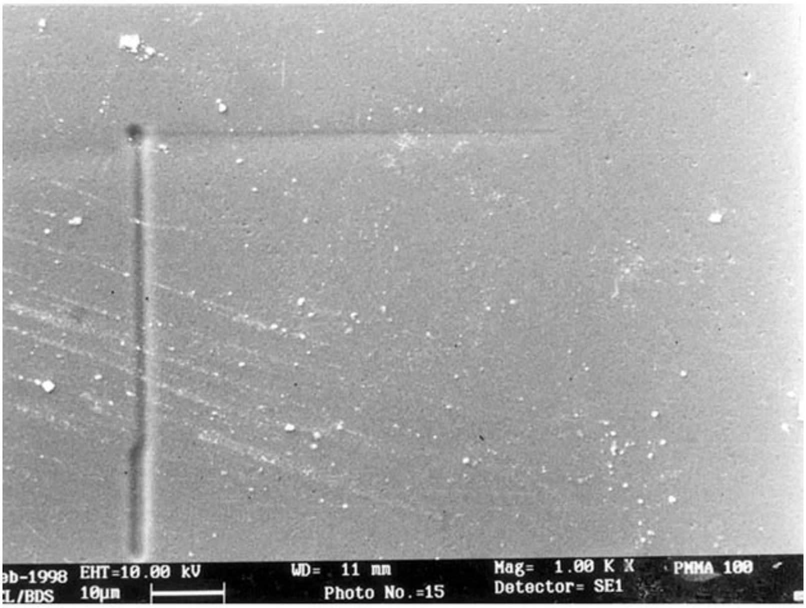
(g)

FIGURE 8 (*Continued.*)

that virgin PS remained unaffected by NaOH, while the StCn particles were selectively removed from the blend film. The morphology of the UV degraded films is exhibited in Figures 8f and 8g. Polystyrene films were hardly affected, whereas the blend films showed degradation on exposure to UV. The micrographs of the etched and the UV-degraded films support the uniform distribution of the disperse phase.

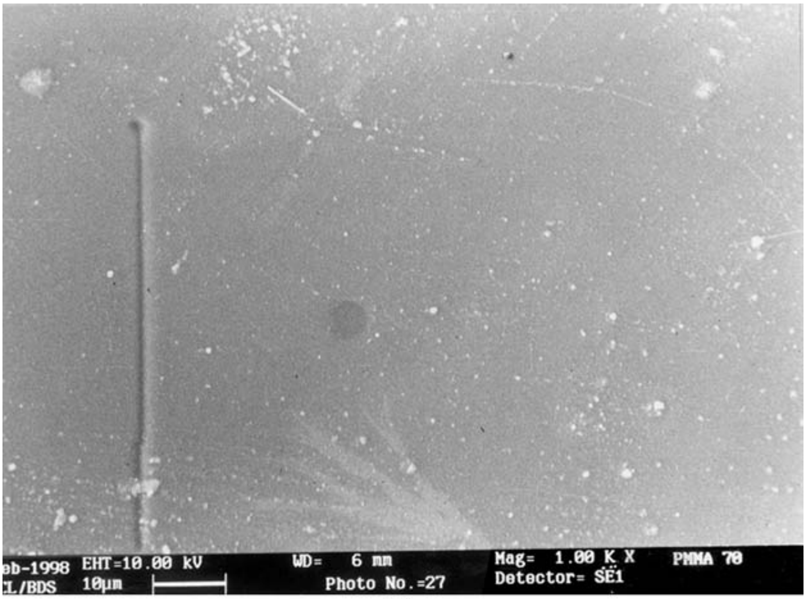
The SEMs of the PMMA/StCn blends (Figures 9a–9f), which were observed to be compatible in solution, do not clearly show the StCn particles. Moreover, etching with sodium hydroxide had no significant effect even on the blend film (Figures 10c and 10d). Photodegradation also led to the same observation (Figures 9e and 9f). Hence it may be possible that the StCn is molecularly dispersed in a continuous PMMA phase. Such a dispersion may protect the StCn against UV irradiation.

Unlike PMMA/StCn, the compatible blends of SAN/StCn (Figures 10a–10f) did not suggest molecular dispersion of the disperse phase. UV irradiation caused photodegradation in the blends, although pure SAN remained unaffected (Figures 10c and 10d). The morphology of

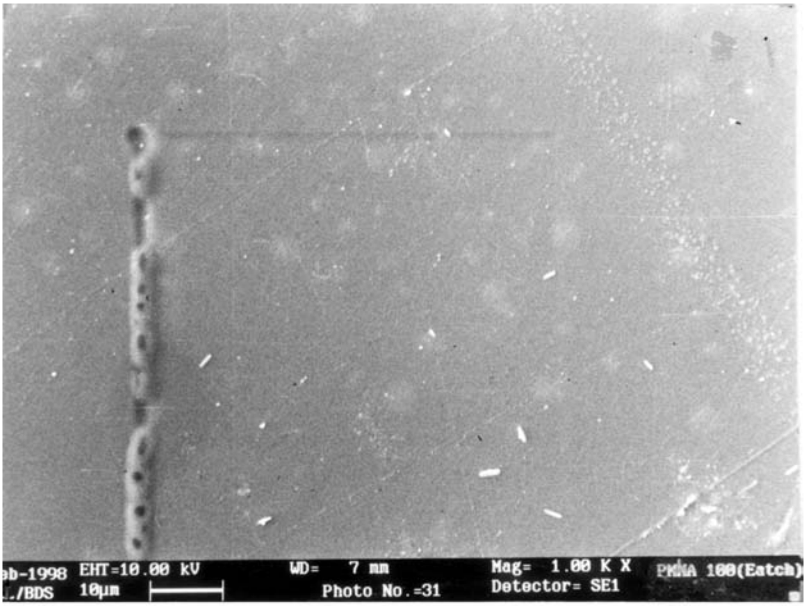


(a)

FIGURE 9 Scanning electron micrograph of PMMA/StCn. (a) 100/0, (b) 70/30, (c) 100/0, etched with 10% NaOH solution, (d) 70/30, etched with 10% NaOH solution, (e) 100/0, UV degraded, (f) 70/30, UV degraded.

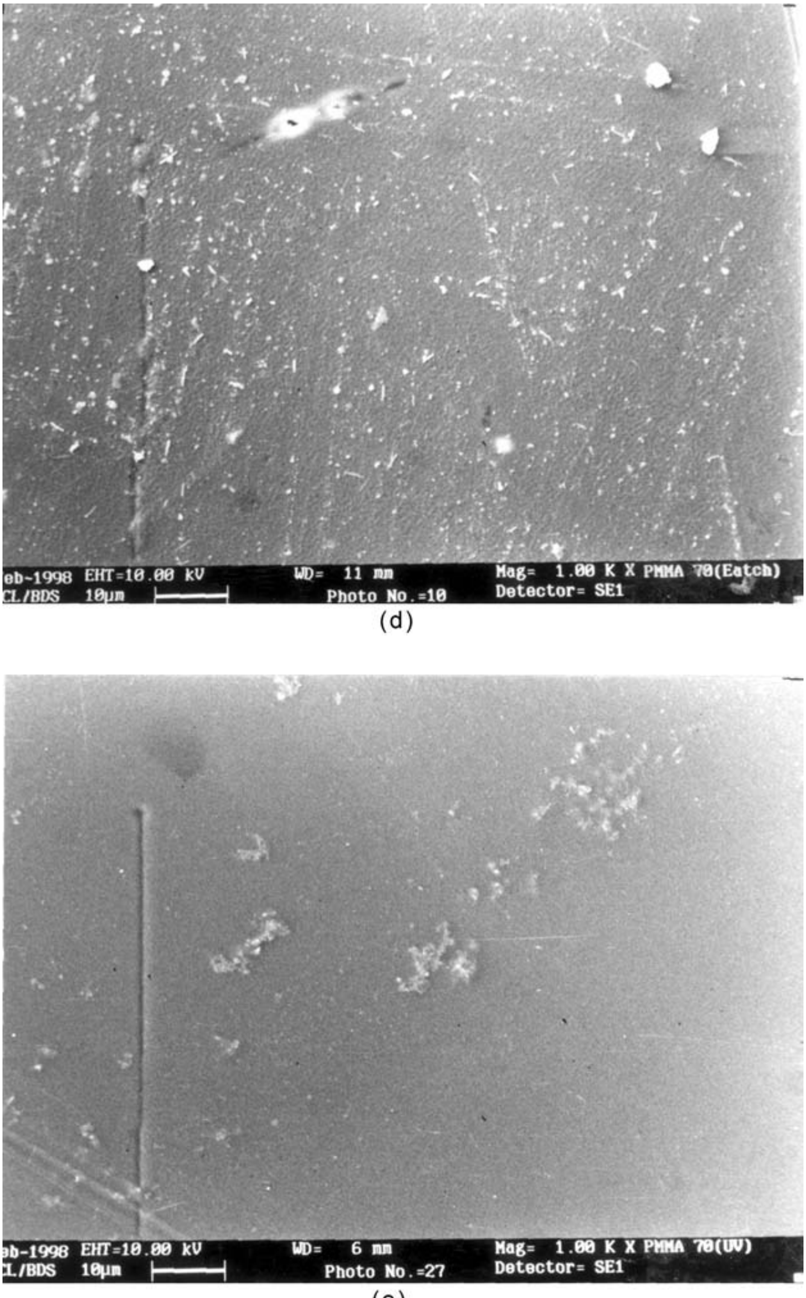


(b)



(c)

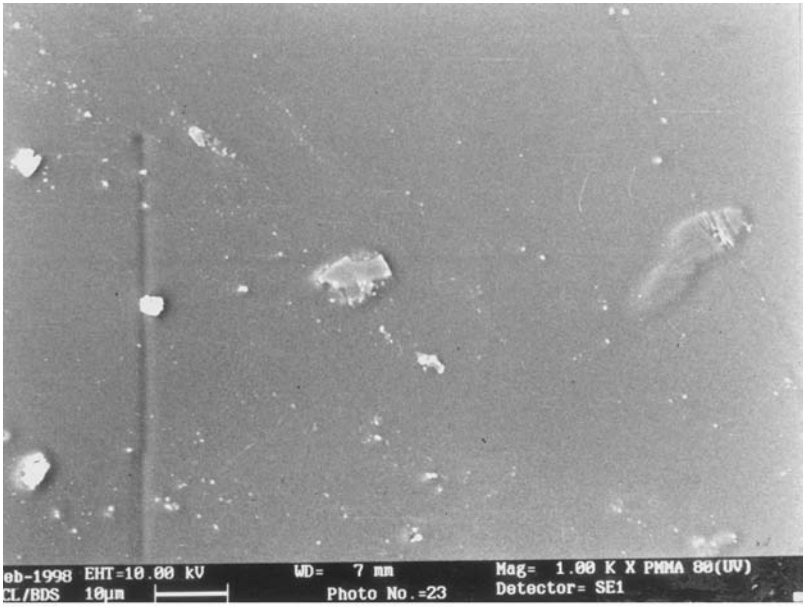
FIGURE 9 (*Continued*.)



(d)

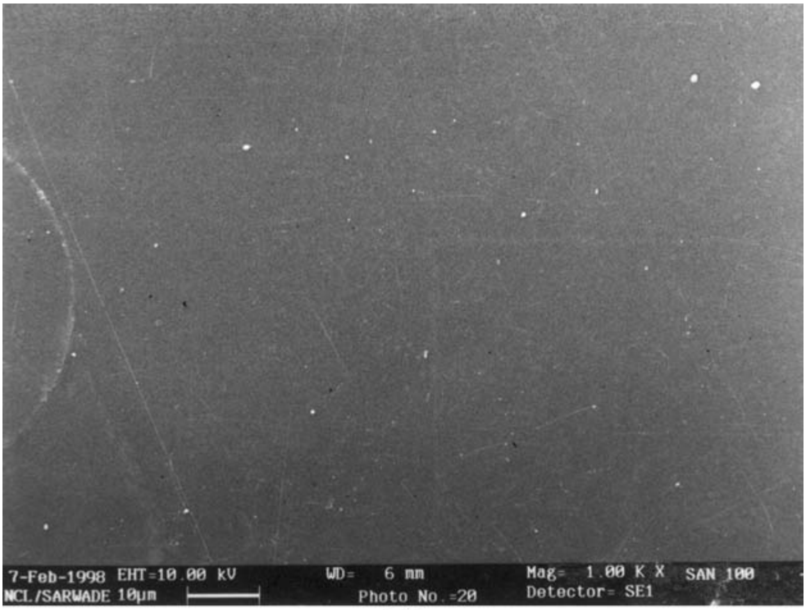
(e)

FIGURE 9 (*Continued.*)



(f)

FIGURE 9 (*Continued.*)



(a)

FIGURE 10 Scanning electron micrograph of SAN/StCn: (a) 100/0, (b) 70/30, (c) 100/0, UV degraded, (d) 70/30, UV degraded, (e) 100/0, etched with 10% NaOH solution, (f) 70/30, etched with 10% NaOH solution.

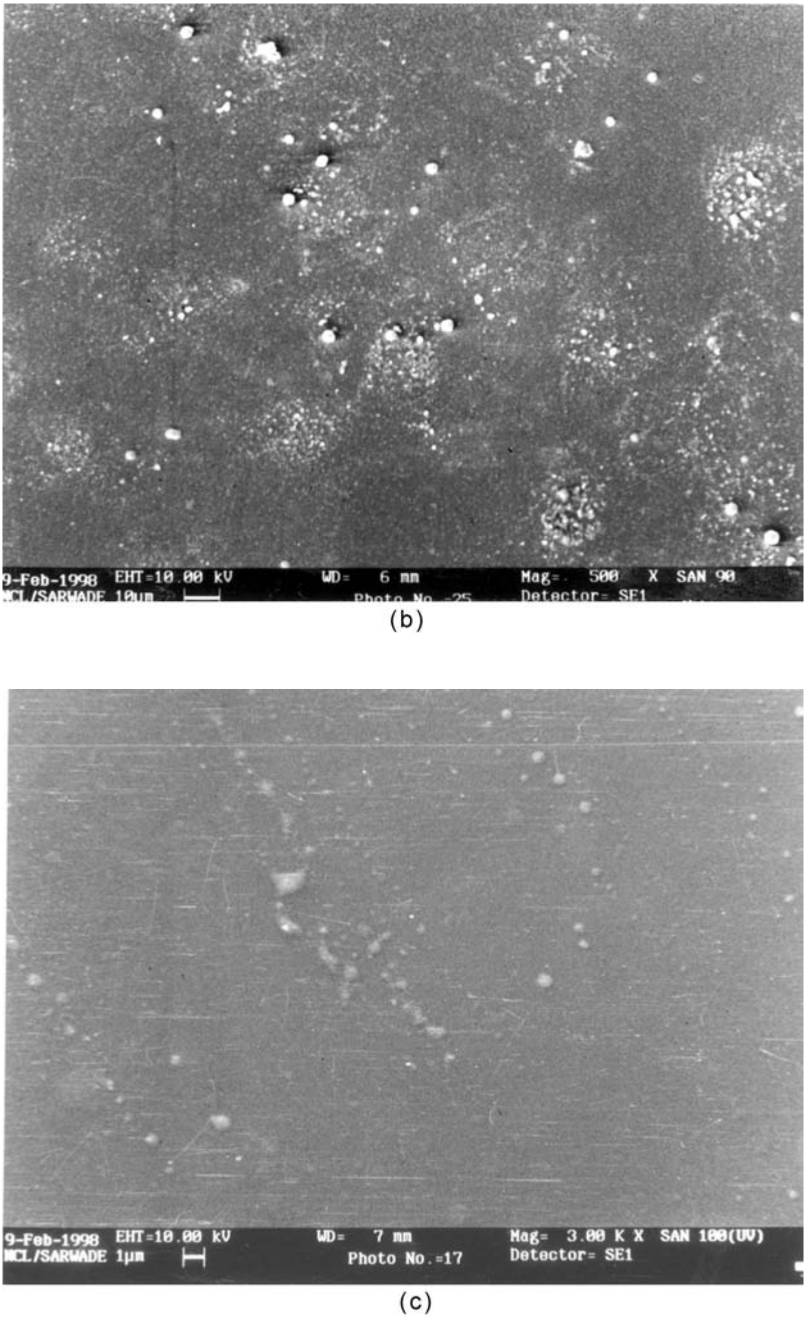


FIGURE 10 (*Continued.*)

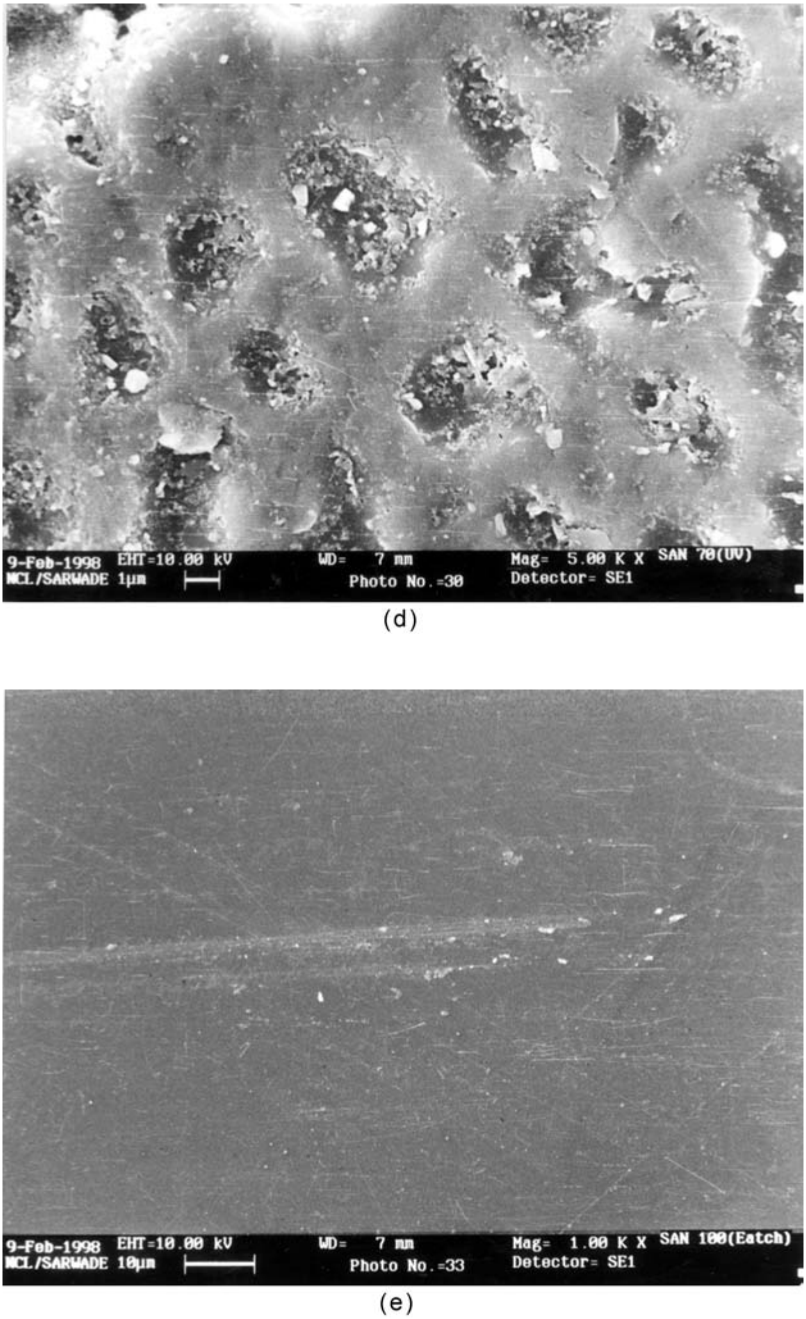
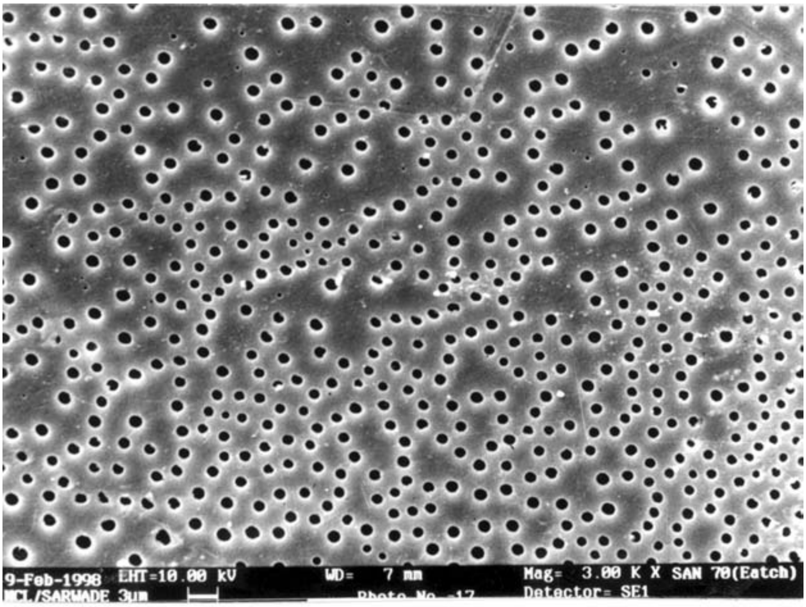


FIGURE 10 (*Continued.*)



(f)

FIGURE 10 (*Continued.*)

the etched films showed that the virgin SAN remained unaffected by NaOH, while the StCn particles were selectively etched from the blend film (Figures 10e and 10f).

The PVC/StCn blends (Figures 11a and 11b), also showed similar morphology. The micrograph of etched blend film also showed uniformly distributed StCn particles as observed in SAN/StCn blend (Figure 11b). However, the particle size of StCn in SAN was found to be much smaller than that in the PVC/StCn and PS/StCn blends. This may be due to the better compatibility between SAN and StCn.

Biodegradation

From soil degradation studies it was observed that pure PMMA, SAN, PS, and PVC showed no weight loss whereas the order of weight loss in blends was found to be $70/30 > 80/20 > 90/10$. Hence, the percent degradation increases with an increase in the weight percentage of StCn in all the blends, indicating that starch ester is preferentially removed, leaving the matrix of synthetic polymer. Rapid and substantial weight loss was observed in films containing 30% StCn, which

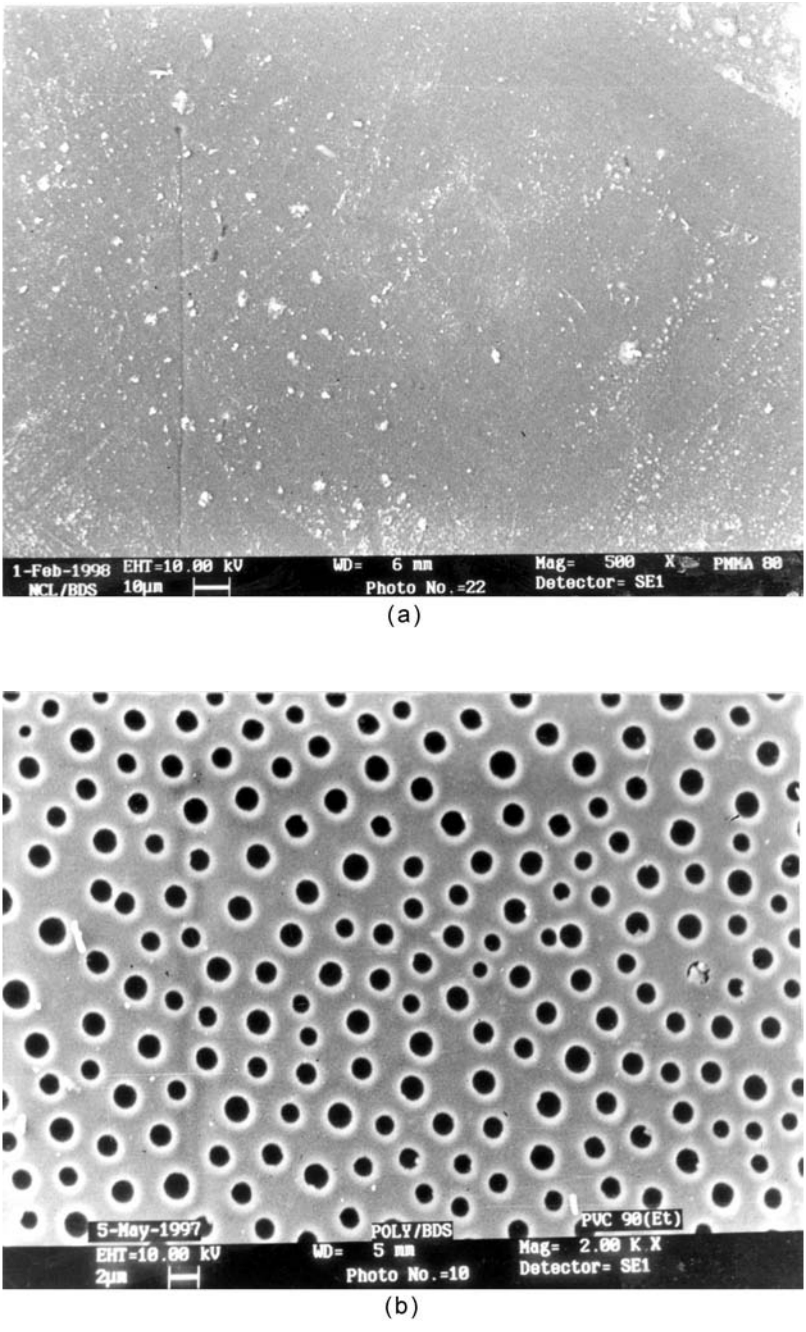


FIGURE 11 Scanning electron micrograph of PVC/StCn. (a) 90/10, (b) 90/10, etched with 10% NaOH solution.

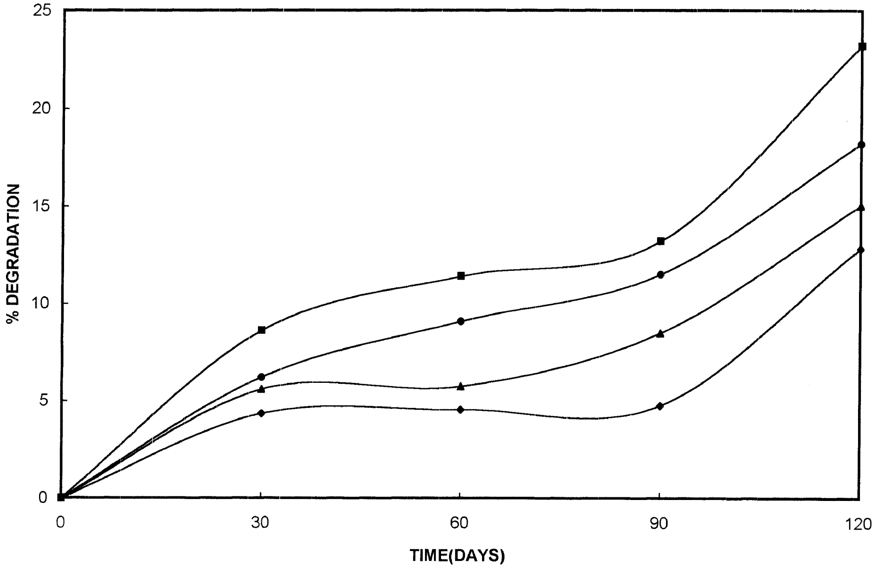


FIGURE 12 Percent degradation vs time for blends. ◆: PMMA/StCn, ■: PS/StCn, ▲: SAN/StCn, ●: PVC/StCn.

is due to the greater accessibility of starch to microorganisms in these films.

The results of soil degradation of the 70/30 blends are given in Figure 12. At the end of four months the percent degradation of 70/30 blends of StCn with PMMA, SAN, PVC, and PS was found to be 13%, 15%, 18% and 23% (Figure 12) respectively. The incompatible blend showed higher weight loss than the compatible ones.

CONCLUSIONS

The PVC/StCn and SAN/StCn blends were found to be compatible and PS/StCn incompatible from the experimental results of viscometric and density measurements. This observation was supported by the heat of mixing data and SEM. However, the results of polymer-polymer interaction parameters ($\Delta\mathbf{B}$, $\Delta\mathbf{b}$ μ and α) were in conflict with the experimental results. Thus, it can be concluded that starch cinnamate is compatible with the synthetic polymers, which are polar in nature (PVC, PMMA and SAN), but incompatible with PS, which is a non-polar polymer. The blends under study also show potential as biodegradable polymers. Biodegradation studies showed that the less compatible the blends by solution techniques, the higher their weight loss. Photodegradation studies showed that incorporation of StCn in synthetic polymer accelerated the UV degradation, although pure polymers are unaffected by UV radiations.

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