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Miscibility and biodegradability of blends of poly(lactic acid) and poly(vinyl acetate)

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Poly(lactic acid) (PLA) was melt blended with poly(vinyl acetate) (PVA) using a single-screw extruder. The extruded films obtained were characterized for miscibility, physical properties, degradation and surface morphology. Differential scanning calorimetry showed that all the as-extruded films were amorphous, and that the blends were compatible as only one glass transition temperature was observed. Results obtained from physical property testing indicated that the blends exhibit synergism in the range of 5 to 30% PVA, probably due to some interactions taking place in that region. Enzymatic degradation studies showed that there was a vast difference in the weight loss of pure PLA samples and the 95/5 PLA/PVA blend. Surface tension results showed that this was due to the vast difference in the surface tension of the pure PLA films and the 95/5 blend. Deaged-free blends showed the maximum degradation, followed by aged-extruded and then deaged-fixed. Scanning electron micrographs showed that the mode of degradation differs for the aged and deaged samples. A uniform degradation pattern was seen in the case of deaged samples while the aged samples showed a non-uniform pattern of degradation.

(Keywords: PLA/PVA blends; miscibility; biodegradability)

INTRODUCTION

Lactic acid (lactate) is a natural molecule that is widely employed in foods as a preservative and a flavouring agent. It is the main building block in the chemical synthesis of the polylactide family of polymers[1]. Although it can be synthesized chemically, lactic acid is procured principally by microbial fermentation of sugars such as glucose or hexose. These sugar feed stocks can be derived from potato skins, corn and dairy wastes. The lactic acid monomers produced by fermentation are then used to prepare polylactide polymers[2]. Lactic acid essentially exists in two stereoisomeric forms, which give rise to four morphologically distinct polymers. The poly(lactic acid)s (PLAs), D-PLA and L-PLA are the two stereoregular polymers. D,L-PLA is a racemic polymer obtained from a mixture of D- and L-lactic acid, and *meso*-PLA can be obtained from D,L-lactide. The polymers obtained from the optically active D and L monomers are semicrystalline materials, but the optically inactive D,L-PLA is always amorphous[3].

Lactic acid has a hydroxyl group as well as a carboxylic group and hence can be easily converted into a polyester. These polymers have some potential advantages such as their high strength, thermoplastic behaviour, biocompatibility and availability from renewable sources, and have been classified as water sensitive since they degrade slowly compared with water soluble or water swollen polymers[4]. It is not at all surprising that, owing to the wide application of PLA in the medical industry, there has been extensive research on the *in vivo* and *in vitro* degradation of L-PLA[5]. Cha and Pitt[6] tested the degradability of L-PLA in a phosphate buffer and found a 66% loss in number-average molecular weight. Fukuzaki *et al.*[7] reported from results obtained from X-ray patterns that the hydrolytic degradation occurs mostly in the amorphous regions of PLA stereoisomers. PLA has been investigated for its enzymatic degradability previously by Williams[8], who exposed lactic acid to various enzymes such as bromelain, esterase, ficin, lactate dehydrogenase, pronase, proteinase K and trypsin, at varying pH levels and with different buffer solutions. It was concluded from this study that pronase, proteinase K and bromelain highly degraded PLA, while ficin, esterase and trypsin had little or no effects on the degradation of PLA. Reeve *et al.*[9] exposed PLA films with varying stereochemical compositions to the enzyme proteinase K and confirmed that PLA samples were completely degradable by proteinase K. They also concluded that the degradation rate of PLA is greatly affected by the stereochemical composition, and that proteinase K degrades the L-PLA preferentially over the D-PLA. It was, however, concluded that the dominant factor that led to the degradation of PLA over the stereochemical range studied was the degree of crystalline order[10].

Struick[11] has reported that physical ageing is a general phenomenon characteristic of the glassy state of

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all materials. It is also known that this process is thermoreversible, which means that, although a material has been physically aged, this ageing can be removed by simply heating the material above its glass transition temperature. The effects of physical ageing are important because they lead to changes in polymer properties as a function of time and temperature. Physical ageing normally occurs in the glassy state and can be attributed to relaxation of the molecules towards equilibrium. The effects of physical ageing on the viscoelastic spectrum and thermal properties of PLA have been investigated by Scandola and Celli[12]. Kobayashi *et al.*[13] studied the physical ageing of poly(vinyl acetate) (PVA) and determined a significant decrease in the per cent free volume at temperatures below 2°C for samples aged for up to 100 h. These effects tend to decrease above room temperature as the glass transition temperature of PVA is about 30°C.

One of the most widely employed methods to modify the properties of polymer resins is to blend them[14]. The most important factor that arises when considering polymer blends is whether the components of the blend system are miscible or not. One of the most commonly used methods to determine blend miscibility has been determination of the glass transition temperature (T_g) of the blend compared with the T_gs of the components in the blend. The main objectives of the present study are to investigate the effects of physical ageing and miscibility on the enzymatic degradation of PLA/PVA blends.

EXPERIMENTAL

Materials

PLA used in this study was supplied by Cargill Inc. (Ecopla Division, MN) with a weight-average molecular weight of 137 000 and 8% *meso* content (96% L). PVA was obtained from Union Carbide Corp., NJ with weight-average molecular weight of 187 000.

Methods

Processing. PLA and PVA pellets were dry blended in the following weight ratios: 100/0, 95/5, 90/10, 70/30, 50/50, 30/70 and 0/100, where the first number in these ratios represents PLA while the second represents PVA. These mixtures were then melt blended in a single-screw extruder (Brabender Inc.) with an L/D ratio of 25 : 1. In all, there were five heating zones. The first three represented the zones of the extruder, the fourth zone was for the adapter and the last one for the die. The films were extruded vertically downwards onto water-chilled rolls. A 102 mm (4 in) push–pull type of die was used. The thickness was maintained by adjusting the pick-up speed of the rolls. All the films had an average thickness of ~0.06 mm (0.0025 in).

Ageing, deageing and relaxation set-up. Three different conditions were employed to study the behaviour of the blends with respect to ageing, deageing and relaxation. The set-ups were as follows.

1. Aged-extruded: the films as-extruded were designated as aged-extruded. The direction of drawdown was referred to as the direction of orientation.
2. Deaged-fixed: two Teflon-coated aluminium plates were placed in an oven and heated to 70°C. The melt extruded film was then placed between the two plates and annealed at 70°C (above the T_g of PLA) for 15 min. The deageing time of 15 min was chosen after making sure, by differential scanning calorimetry (d.s.c.), that no crystallinity was being induced in the samples during the annealing process. The film placed between the two plates was under sufficient tension to prevent any relaxation along the machine direction.
3. Deaged-free: deageing was again carried out at 70°C for 15 min. Melt extruded film was pinned at the corners on a rectangular wooden block in a reverse U-shape so that the middle portion of the film was free standing. In this way, the middle portion of the film was free to relax since there was no restraining plate on top of the film. All the samples for analysis were cut from the middle portion of the film.

Thermal analysis. A dual-cell DuPont Differential Scanning Calorimeter (DSC) was used to determine the thermal transitions of the polymer blends. All the scans were carried out from −40 to 180°C at a heating rate of 10°C min^{-1}. The first and second scans were recorded in all cases and liquid nitrogen was used to quench the samples after the first scan.

Mechanical properties. Tensile testing of the films was carried out using an Instron 1137 tester with a 90.1 kg (200 lb) load cell following ASTM D882-90. The gauge length was maintained at 102 mm (4 in) and the thickness of each sample was measured before testing. The film width and crosshead speed were maintained at 25.4 mm (1 in) and 50.8 mm min^{-1} (2 in min^{-1}), respectively.

Scanning electron microscopy (SEM). SEM was carried out using an ISI electron microscope (ISI-IC 130) to study the surface morphology of the samples before and after enzymatic degradation. All the samples were sputter-coated with a thin layer of carbon.

Enzymatic degradation. Films with an approximate thickness of 0.06 mm (0.0025 in) and measuring 2.54 mm × 10 mm were placed in glass vials containing 5 ml of Tris/HCl buffer, 1.0 mg of proteinase K (Sigma Chemicals; lyophilized powder, 80% protein, 12.8 units/mg of solid) and 1.0 mg of sodium azide (Sigma Chemicals). The Tris/HCl buffer was prepared in such a manner that the pH was maintained at 8.6. A Barnstead NANO pure water purification system was used to purify the water used for the above solutions. The enzymatic degradation tests were carried out at 37°C in a rotary shaker maintained at 200 rev min^{-1}. For weight loss measurements, three replicate films in separate vials were removed at specified times. If the experiments lasted for more than 32 h, the enzyme solutions were changed every 32 h in order to ensure optimum enzyme activity. Once the time for the sampling was reached, the three vials were removed from the shaker. The films were removed from the vials and washed thoroughly with distilled water. These films were dried in vacuum [0.67 Pa (0.005 mm Hg)] for 48 h at room temperature and the weight loss measurements were then taken.

Surface tension analysis. The contact angle method was used to determine the surface tension of the films. The films were mounted on glass plates and a laser light was focused on the top of the films. An electropipette was used to dispense a drop of the liquid in order to measure the contact angle. The two liquids used for the measurements were water and diiodomethane (Aldrich Chemicals).

RESULTS AND DISCUSSION

Thermal analysis

Figure 1 shows the first d.s.c. scans of the melt extruded films. It is evident that all the films are amorphous. The broad halo in the wide-angle X-ray scattering patterns (not shown) also confirmed that the films were completely amorphous. An endothermic peak near the T_g should be noted in *Figure 1* which is a result of enthalpy of relaxation caused by physical ageing for pure PLA. The extent of physical ageing can be quantitatively followed by the area under the endothermic peak which incidentally decreases ($\Delta H_{PLA} = 1.56\,J\,g^{-1}$) as the amount of PLA in the blend decreases.

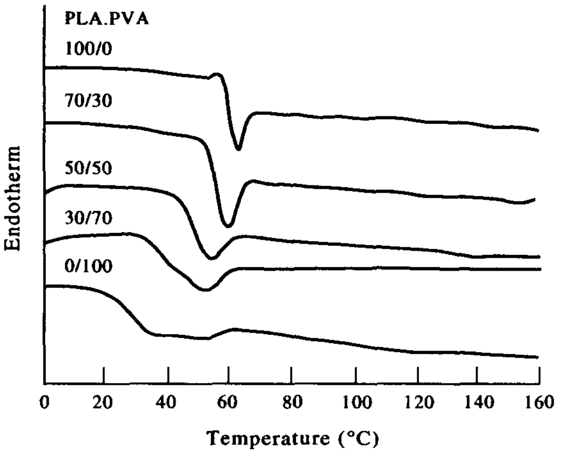

Figure 1 D.s.c. scans for the as-extruded PLA/PVA films (first run)

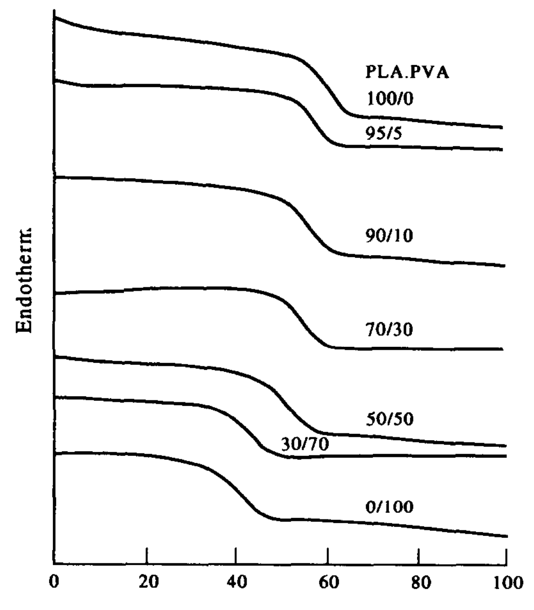

Figure 2 D.s.c. scans for the PLA/PVA films (second run)

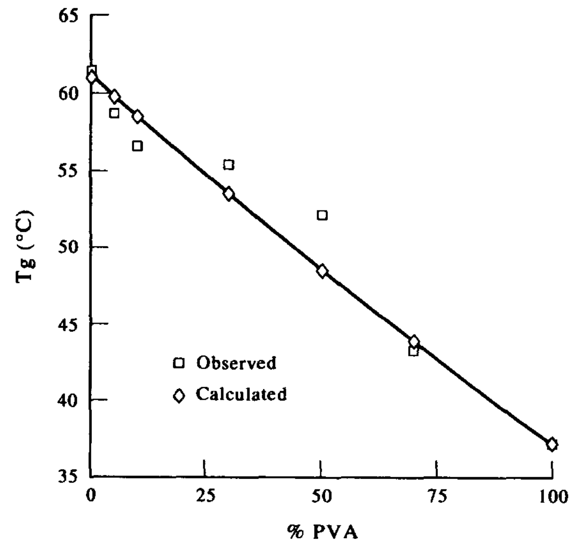

Figure 3 Glass transition temperature values as a function of % PVA for the PLA/PVA blends

Figure 2 shows the second d.s.c. scans of the PLA/PVA blends. A single T_g is observed for all blend compositions, which indicates that the PLA/PVA system is miscible. It should be noted that physical ageing is not observed in the second d.s.c. scans as all the samples were quenched and re-run immediately. The variation of the observed and calculated T_g (using the Fox–Flory equation[15]) as a function of per cent PVA in the blend is shown in *Figure 3*. The figure demonstrates a good agreement between the observed and calculated values. It is possible that the carboxyl groups of PLA interact with the α-hydrogens of PVA due to their proton-accepting and proton-donating properties, respectively. Such favourable interactions between polymers can lead to a miscible system. Similar results were also observed with the poly(hydroxybutyrate) (PHB)/PVA blend system[16].

Mechanical properties

Tensile testing was carried out for the aged-extruded as well as the deaged-fixed samples in order to determine the effect of ageing on physical properties. *Figures 4* and *5* summarize the results for tensile strength at yield and per cent elongation, respectively, for all the blend compositions. It can be seen that for the aged-extruded 95/5, 90/10 and 70/30 blend compositions, there is a definite increase in the tensile strength. There is also an increase in the per cent elongation for the 95/5 composition in both the aged as well as the deaged samples. Kalfoglu[17] has studied poly(ethylene oxide)/PVA blend systems and observed a similar trend for the 80/20 blend composition. An increase in tensile strength for the 90/10 and 80/20 compositions was also observed for the PHB/PVA blend system[16]. In the case of the PLA/PVA system, the aged 95/5, 90/10 and 70/30 compositions show an increase in tensile strength, and the values are higher than that of an aged sample of pure PLA. The value for the 50/50 composition is almost the same as that of pure PLA. In case of the deaged samples, the 95/5 and 90/10 compositions exhibit tensile strength values higher than that of pure PLA. However, the

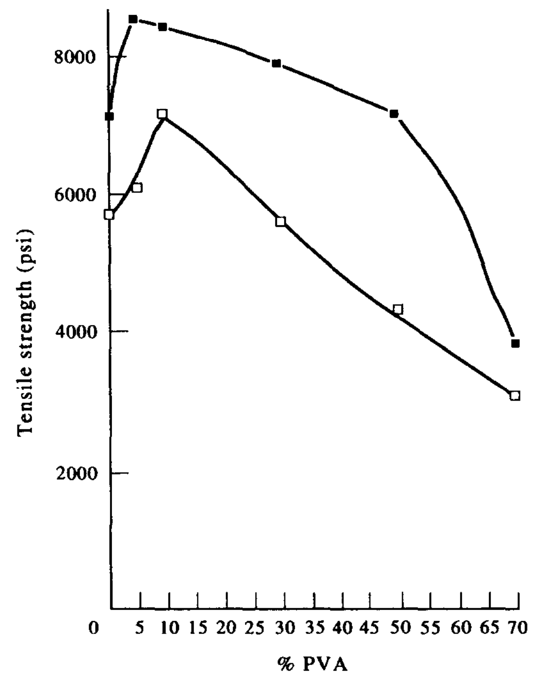

Figure 4 Tensile strength at yield as a function of % PVA for the aged-extruded (■) and deaged-fixed (□) PLA/PVA blends

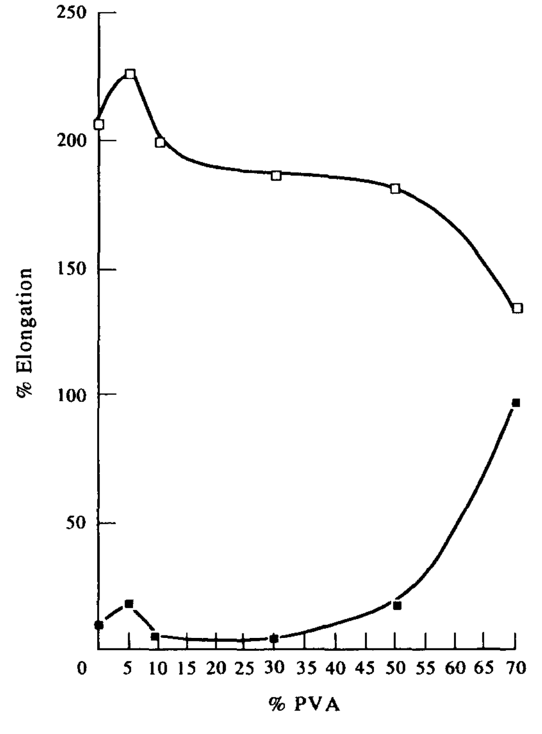

Figure 5 Per cent elongation at break as a function of % PVA for the aged-extruded (■) and deaged-fixed (□) PLA/PVA blends

tensile strength decreases for the 70/30 composition compared with that of pure PLA.

Physical ageing can have a dramatic influence on physical properties as it increases the relaxation times of the polymer chains due to the decrease in the free volume during the ageing process. The yield stress of the aged samples is higher than that of the deaged-fixed samples as there is a decrease in the segmental mobility of the polymer chains caused by the volume relaxation associated with physical ageing. It is also not surprising to observe an increase in the per cent elongation of the deaged samples (from 8.7 to 207% in the case of pure PLA films!) as the material becomes more flexible due to the increase in the free volume after deageing.

It was initially hypothesized that the increase in mechanical properties over the composition range 5–30% PVA could have been due to the effects of physical ageing. However, the trend of the properties remained unaltered even after deageing the samples. This leads us to believe that some kind of synergism exists in the PLA/PVA blend compositions containing up to 30% PVA, and indicates that the system is miscible in this particular range.

Enzymatic degradation

All the melt extruded films of pure PLA, 95/5, 90/10 and 70/30 PLA/PVA blends, and pure PVA were subjected to proteinase K treatment for the enzymatic degradation studies.

Figure 6 shows the normalized weight loss as a function of time for all the aged-extruded films. Pure PLA films were exposed to the enzyme for 10 h and the normalized weight loss was calculated at different times. The blends were exposed to the enzyme for a period of 64 h and the normalized weight loss was calculated for the samples removed every 8 h. It is seen from the figure that after 10 h, pure PLA showed a weight loss of $\sim$52% corresponding to a normalized weight loss of $\sim$29.5 g mm^{-2}. Reeve *et al.*[9] observed that if the films were exposed to the enzyme for a weight loss of >60%, the films turned into minute irrecoverable particles. The same was true for the melt extruded samples tested in our experiments and hence all degradation for pure PLA was limited to a time period of 10 h.

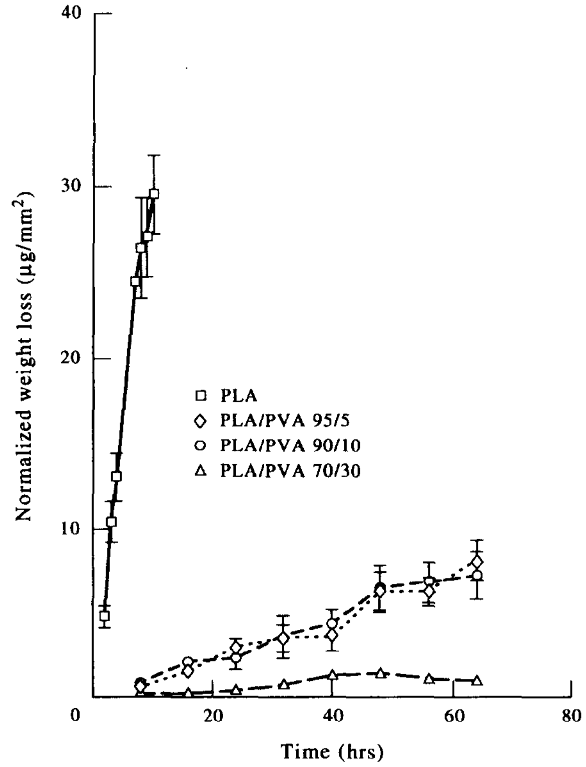

Figure 6 Normalized weight loss as a function of time for the aged-extruded PLA/PVA blends

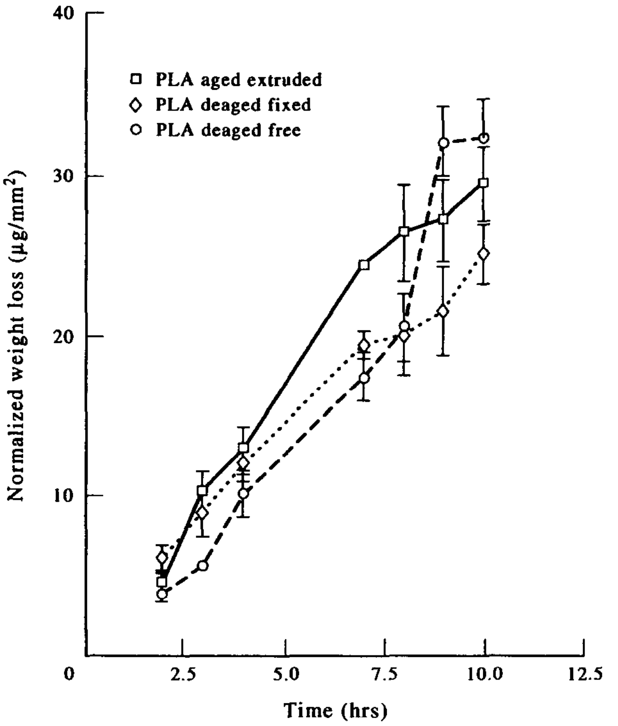

Figure 7 Normalized weight loss as a function of time for pure PLA films after different treatments

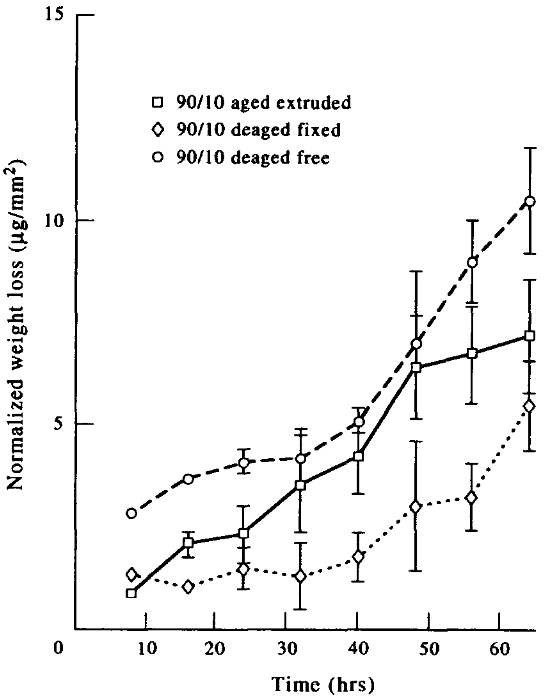

Figure 8 Normalized weight loss as a function of time for 90/10 PLA/PVA films after different treatments

The results observed from the enzymatic degradation for the aged-extruded samples show that although pure PLA showed a weight loss of ∼52% after 10 h, the 95/5 PLA/PVA blend showed almost no weight loss ($1.55\,\mathrm{g\,mm^{-2}}$) after 16 h and minimal weight loss ($8.11\,\mathrm{g\,mm^{-2}}$) after 64 h. The normalized weight losses observed in the 95/5 and 90/10 PLA/PVA blends are almost the same, while the normalized weight loss of the 70/30 composition is almost insignificant ($0.94\,\mathrm{g\,mm^{-2}}$) after 64 h. Pure PVA was tested for 64 h and showed no weight loss, suggesting that it is completely inactive towards the enzyme. Controls were maintained for all the samples tested. They showed no weight loss, indicating that the films are inactive towards the buffer solution and that no hydrolytic degradation occurs during the experiment.

The relaxation study for the deaged-fixed and deaged-free samples was done in order to observe the effects of physical ageing and induced orientation (during extrusion) on degradation. *Figure 7* compares the normalized weight loss as a function of time for pure PLA films after different treatments. It can be seen from the figure that, although initially the deaged-free films tend to show less weight loss than the aged-extruded and deaged-fixed films, the weight loss increases dramatically after 8 h. The deaged-free films have their molecules unoriented and relaxed with more free volume between the polymer chains. It is possible that this could lead to the increased weight loss after 8 h, as the enzymes have an easy access to degrade the polymer chains. It is difficult to explain the reasons for the increased weight loss for the aged-extruded samples in comparison to the deaged-fixed samples. The deaged-fixed samples tend to show a lower degradation than the deaged-free samples. This may be due to the fact that the enzymes are restricted to follow a definite path due to preferential molecular orientation for the fixed samples, thereby inhibiting excessive degradation.

Figure 8 shows the normalized weight loss as a function of time after different treatments for the 90/10 blend films. It is clear from the figure that the deaged-free films exhibit maximum degradation while the deaged-fixed films exhibit the least degradation.

Doi and Kumagai[18], in their study of miscible PHB/PVA blends, observed that the 74 PHB/26 PVA blend composition initially degraded and then was completely inactivated. This was attributed to the fact that the concentration of PVA may have increased on the surface after the films were initially degraded and therefore further degradation ceased in the films. The same could be happening with our PLA/PVA blended films. Several experiments were conducted to verify the influence of small amounts of PVA and other morphological changes on degradation of the 95/5 PLA/PVA blend.

Table 1 shows the normalized weight losses for 95/5 PLA/PVA films after different treatments. The aged-extruded 95/5 film was sanded with a sandpaper on both sides to polish it. This was done in order to observe the change in the degradation pattern by removing the first few layers from the film surface. To observe the effect of crystallinity on degradation of the 95/5 blend, the film was annealed at 90°C for 90 min. The film was kept between two plates to prevent any relaxation during the annealing process. A d.s.c. scan of the annealed sample showed a melting point at 140°C and the heat of fusion of the melting endotherm was $32\,\mathrm{J\,g^{-1}}$. This indicated that the sample was crystalline after the annealing process. The film prior to the annealing process was amorphous, as confirmed from the first d.s.c. scan of the aged sample.

The deaged-free films showed the maximum weight loss while the annealed films showed the least weight loss. It can be seen from *Table 1* that the trend in the

Table 1 Normalized weight loss of 95/5 PLA/PVA melt extruded films after different treatments

Time (h)	Normalized weight loss (μg mm^{-2})				
	Aged-extruded	Deaged-fixed	Aged-polished	Annealed	Deaged-free
8	0.448	1.2	1.79	0.8	2.42
16	1.55	1.19	2.99	0.88	3.1
24	2.93	1.19	2.38	0.96	3.1
32	3.46	2.03	2.87	1.31	5.53
40	3.5	2.7	4.21	1.5	7.83
48	6.2	2.93	6.41	1.7	8.07
56	6.14	3.0	5.21	1.76	9.79
64	8.11	5.62	6.69	1.96	10.6

Table 2 Results of surface tension analysis

Composition PLA/PVA	Surface tension (dynes cm^{-2})
100/0 (Aged-extruded)	43.5
95/5	21.75
90/10	20.6
70/30	16.2
0/100	24.85
100/0 (Deaged-fixed)	40.4

degradation pattern after different treatments was as follows:

Deaged-free > Aged-extruded > Aged-polished > Deaged-fixed > Annealed

The aged-polished film showed higher degradation than the deaged-fixed film. This could be due to two possibilities, the first being that all the aged films showed greater degradation than the deaged films and the second being that there is definitely more PVA on the top layers of the film. It was hence decided to anneal the films to induce crystallinity and cause phase separation. Annealing the film reduced the weight loss even further. This could have been due to the induced crystallinity in the film preventing degradation, since the enzyme is known to preferentially attack the amorphous regions of PLA. The fact that the films did not show a higher rate of degradation leads us to believe that the two components are miscible and that adequate phase separation could not be achieved even after annealing the films for 90 min.

Surface tension analysis

Surface tension measurements were carried out using the contact angle method since surface tension could influence the degradation behaviour of the films. The two liquids used were water and diiodomethane, and the results obtained from the surface tension analysis are summarized in *Table 2*. There is a vast difference in the surface free energy of the pure PLA film (43.5 dynes cm^{-1}) and the 95/5 blend system (21.75 dynes cm^{-1}). The adhesion characteristics of the pure film were definitely much greater than those of the 95/5 blend system. This indicates that the enzyme was possibly able to adhere to the surface of the pure PLA film more easily. However, due to the high lubricity of the 95/5 blend film, adhesion of the enzyme to the film surface was possibly reduced. This may explain the reason for the low weight loss of the 95/5 blend system compared with that of pure PLA. The surface tension values obtained for the 90/10 and 70/30 blends are lower than those of pure PLA and 95/5 blend, and their corresponding degradation results are also low. The deaged-fixed PLA film has a slightly lower surface tension than the aged-extruded samples and this corresponds with the lower degradation of the deaged-fixed film.

Scanning electron microscopy

The films were observed by SEM for the aged-extruded and the deaged-fixed conditions. SEM micrographs were taken of the pure PLA films after they had been exposed to the enzyme for 8 h, while the micrographs of the blend systems were taken after the films had been exposed to the enzyme for 56 h. *Figures 9a–f* present the results. The aged-extruded PLA films (*Figure 9a*) exposed to the enzyme for 8 h showed degradation along the machine direction and also in isolated regions of the film. This indicates that the enzyme shows a non-uniform pattern of attack in the aged-extruded samples. However, in the case of the deaged-fixed sample (*Figure 9d*), it is clearly seen from the micrograph that the mode of degradation is more uniform and there is a 'web-like' structure formed throughout the film. This indicates that the degradation pattern varies in case of the aged samples and the deaged samples. The non-uniform degradation behaviour could be one of the reasons why the aged-samples showed higher degradation than the deaged samples. The holes observed in the aged sample are large and seem to penetrate through the thickness of the film.

Figures 9(*b* and *c*) and (*e* and *f*) represent the micrographs for the aged-extruded and the deaged-fixed 95/5 and 90/10 PLA/PVA films that were exposed to the enzyme for 56 h, respectively. The non-uniform degradation pattern can be seen for the aged sample whereas the deaged film shows a relatively uniform pattern. Also, the micrographs show that the degradation in these films is only on the surface.

It is possible that, due to the decrease in the segmental mobility of the polymer chains caused by the volume relaxation associated with physical ageing, there is formation of a morphological structure that is in a non-equilibrium state. Therefore, degradation of the aged-films is non-uniform due to random attack of the enzyme in different regions of the films. However, when the samples are deaged, there is an increase in the free

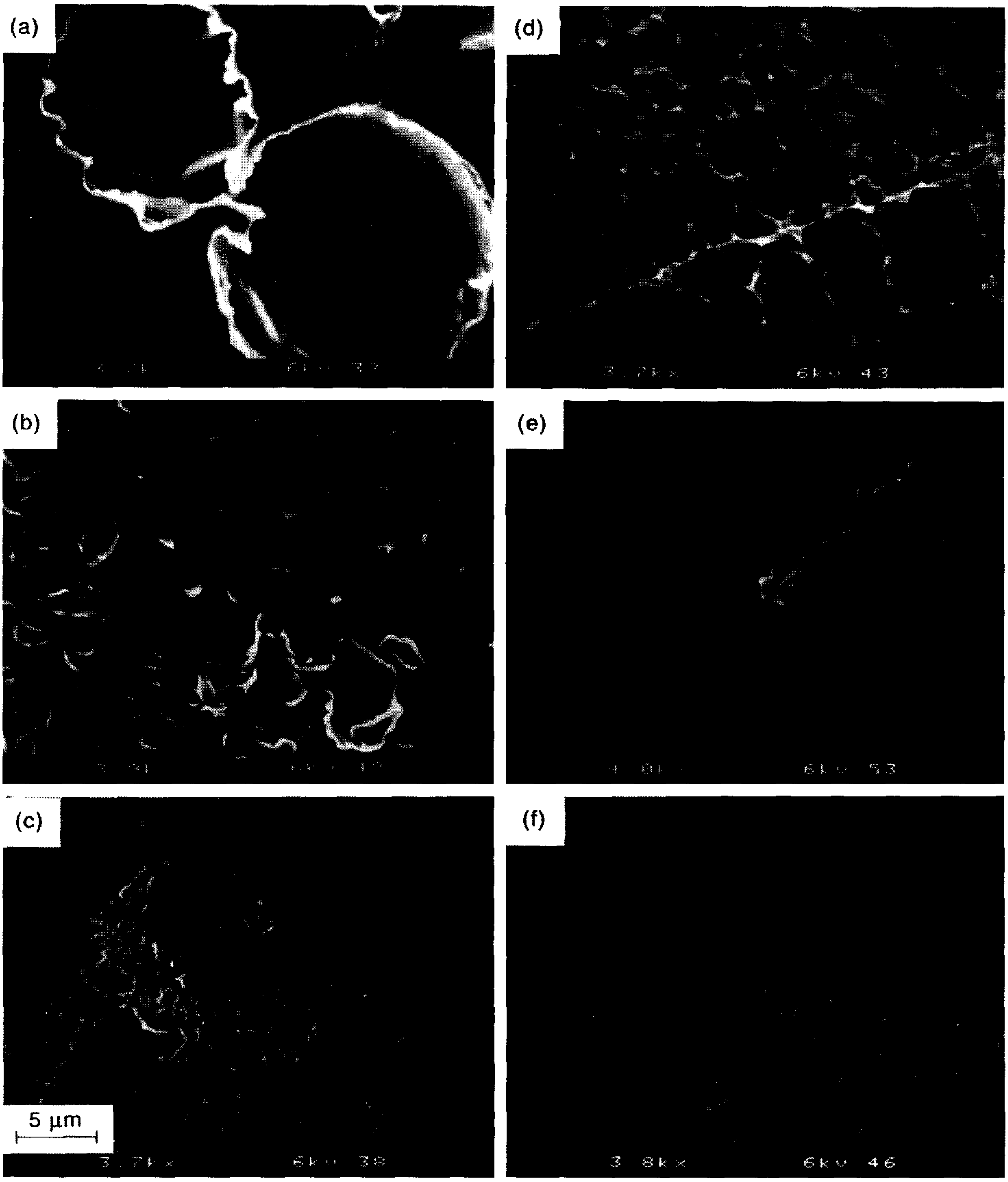

Figure 9 Scanning electron micrographs of degraded films: (a) aged-extruded PLA film after 8 h; (b) aged-extruded 95/5 PLA/PVA film after 56 h; (c) aged-extruded 90/10 PLA/PVA film after 56 h; (d) deaged-fixed PLA film after 8 h; (e) deaged-fixed 95/5 PLA/PVA film after 56 h; (f) deaged-fixed 90/10 PLA/PVA film after 56 h

volume and the samples are in an equilibrium state. This may allow the enzyme to enter the film without encumbrance and may cause the degradation to occur more uniformly than in the aged films.

CONCLUSIONS

D.s.c. results showed a single glass transition temperature for all PLA/PVA blend compositions, indicating that PLA and PVA form miscible blends. The PLA/PVA blends exhibit higher values of tensile strength between 5 and 30% of PVA. Per cent elongation is also seen to increase for the 95/5 blend. On deageing the blend system this trend was observed still to exist, which indicates that the improvement in physical properties was not due to physical ageing, but rather to some positive interactions between the two polymers in that particular blend composition.

Results obtained from enzymatic degradation indicated that the addition of PVA to PLA resulted in a dramatic decrease in the degradation rate. The deaged-free and annealed samples showed the highest and the lowest degradation, respectively. There was no significant difference between the weight losses of samples treated differently.

The surface tension analysis indicates a possible explanation for the difference in the rates of degradation between pure PLA and 95/5 PLA/PVA. There was a vast difference in the surface tensions of the two, with pure PLA showing a higher surface tension which may provide better adhesion for the enzyme.

The SEM analysis showed that the aged samples had a non-uniform pattern of degradation while the deaged samples had a more uniform pattern. The difference in the rate of degradation between the aged and deaged films can be attributed to this phenomenon.

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