

# Morphology, Thermomechanical Properties, and Biodegradability of Low Density Polyethylene/Starch Blends

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**ABSTRACT:** The biodegradability of low density polyethylene (LDPE)/starch and LDPE/starch/starch acetate (STAc) blends was tested and observed to be dependent on STAc content. The binary and ternary blends containing up to a maximum concentration of 30% starch were examined for their thermal, mechanical, and morphological properties. The blends with no STAc or 2.5% STAc show almost no adherence of two phases. With 10% STAc, dispersion of starch was observed to increase with some adherence to LDPE. Tensile strength, elongation at break, and Izod impact strength of the blends decreased with increased starch content. However, incorporation of STAc along with starch improved all these properties, particularly elongation at break and toughness. The melt flow index was also improved on partial substitution of starch by STAc. Maximum biodegradability was observed for the blends containing 30% (starch + STAc). Cell growth was observed to increase with increasing concentration of (starch + STAc) in the blends. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 2791–2802, 1999

**Key words:** low density polyethylene; starch; blends; biodegradation

## INTRODUCTION

Biodegradable plastics are very important in solving the solid waste management problem of plastics, especially for single use plastic items that are disposed of immediately after use. Packing bags; containers for milk, water, and soft drinks; disposable plastic cups; and agricultural mulch films must be biodegradable. A plastic with reasonable mechanical strength and good biodegradability may fulfill this requirement. Starch has received maximum attention in the preparation of biodegradable plastics and especially for one time

use plastics, because it is the most abundant degradable low cost natural polymer and it is available throughout the world. Partial substitution of synthetic plastic with materials like starch provides not only cheap filler but also biodegradation properties to the final products. However, starch by itself is unsuitable for use as a plastic because of its poor mechanical and thermal properties. To overcome this problem some solutions have been suggested such as chemical modification, addition of plasticizers, or blending with synthetic polymers.<sup>1</sup> In blends of starch with synthetic polymers such as low density polyethylene (LDPE), linear LDPE, polystyrene, and polypropylene, the hydrophilic nature of the former leads to poor adhesion (miscibility) with the latter, which are hydrophobic in nature. The addition of granular starch to these polymers was reported to reduce

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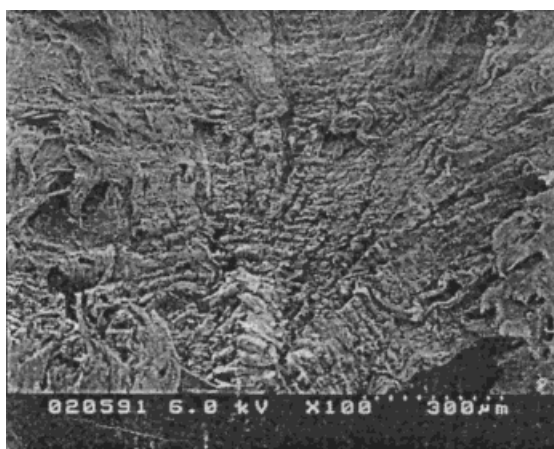
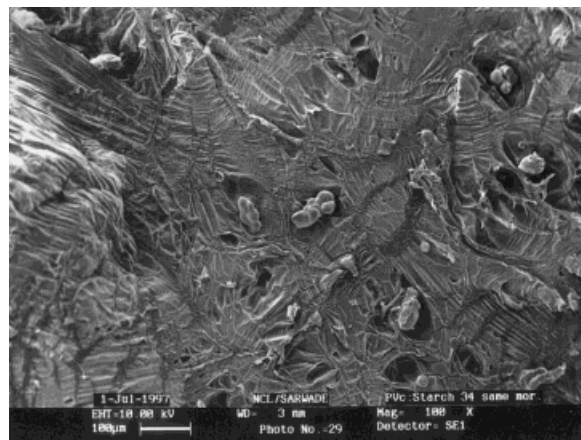
**Table I** Composition of Blends

Code No.	LDPE (wt %)	STAc (wt %)	Starch (wt %)
LDPE	100	—	—
A1	90	—	10
A2	80	—	20
A3	70	—	30
B1	90	2.5	7.5
B2	80	2.5	17.5
B3	70	2.5	27.5
C1	90	5.0	5
C2	80	5.0	15
C3	70	5.0	25
D1	90	10	—
D2	80	20	—
D3	70	30	—

the elongation, tensile strength, and impact properties.<sup>2</sup>

Hence, to enhance the compatibility between two immiscible polymers without sacrificing mechanical properties, a reactive functional group capable of hydrogen bonding or reacting with starch hydroxyls was introduced into synthetic polymers. For example, PE copolymerized with acrylic acid,<sup>3–10</sup> vinyl alcohol,<sup>11,12</sup> vinyl acetate,<sup>13</sup> or mixed with oxidized PE<sup>14</sup> was used for compatibilization between starch and LDPE.

Another method to improve the miscibility of phases in starch PE blends is the chemical modification of the hydroxyl groups of the starch to introduce hydrophobicity into it. Octenyl succinate starch metal ion complexes were combined

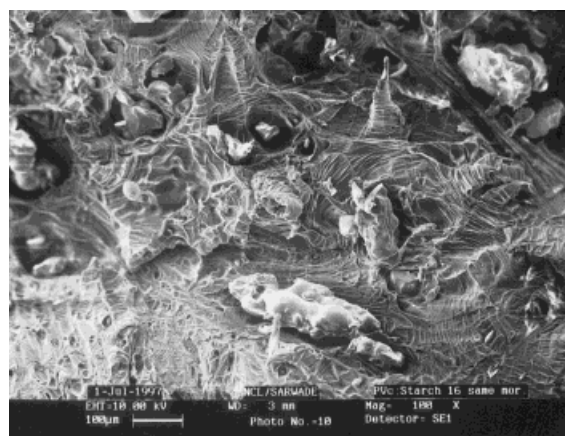
**Figure 1** SE micrograph of binary LDPE/starch blend (A1).**Figure 2** SE micrograph of LDPE/STAc/starch blend (B1).

with PE to create a biodegradable plastic with good tensile strength.<sup>15,16</sup> In the present study we examined the use of starch acetate (STAc) as a compatibilizer for LDPE/starch blends and its effect on mechanical and morphological properties.

## EXPERIMENTAL

### Materials

Grade 24FS040 LDPE [density of 0.923 g/mL and melt flow index (MFI) of 4 g/10 min] from Indian Petrochemical Co. Ltd. (Vadodara, India) and starch from Qualigenes (India) were used as received. The synthesis of modified starch as STAc (degree of substitution = 2.5) was reported earlier.<sup>17</sup>

**Figure 3** SE micrograph of LDPE/STAc/starch blend (C1).

### Blend Preparation

Potato starch air dried at 80°C for 48 h was used for the preparation of blends. A Berstroff ZE 25 twin screw extruder ( $L/D = 41$ ) fitted with a standard die with two 2-mm diameter holes was used for the preparation of blends. The temperatures of 1–10 zones were in the range of 130–180°C. The screw speed was kept at 175 rpm. The die temperature was 190°C. The binary and ternary blends were prepared by the single step extrusion technique. The various compositions used for the blends under study are given in Table I. Extrudates were water cooled and granulated using a palletizer.

### Injection Molding

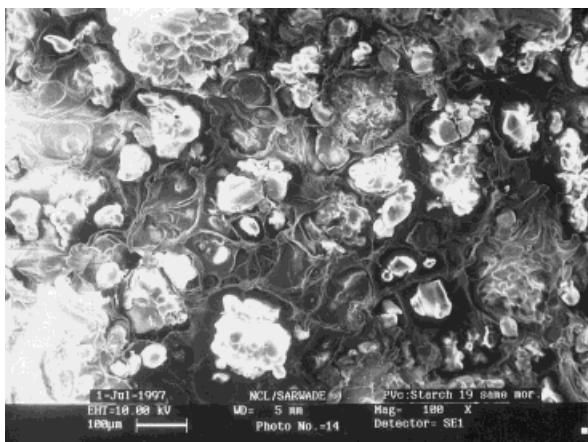
Pallets were dried in an air oven at 80°C for 24 h and injection molded in an Arburg 220-90-350 injection molding machine to obtain test specimens for measurements of tensile properties and Izod impact strength.

### Measurements

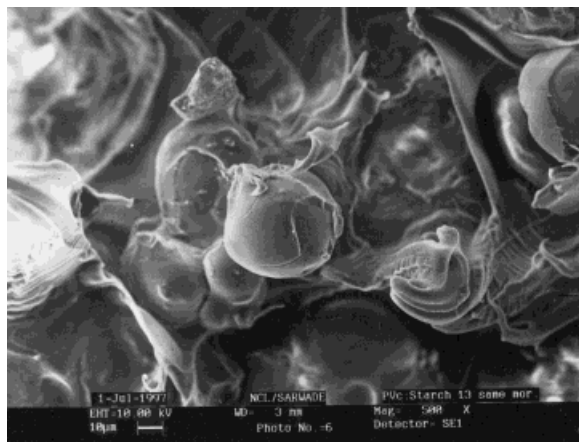
The tensile properties of the dumbbell-shaped samples were measured according to the ASTM D638 procedure on an Instron machine (model 4204) at 25°C, 50% humidity, and a crosshead speed of 25 mm/min.

The impact strength was measured by following the ASTM D256 procedure. The specimens were  $6.35 \times 1.27 \times 0.35$  cm and had a 0.025-cm notch radius.

The impact fractured surfaces and biodegraded films were examined using a Leica Cambridge



**Figure 4** SE micrograph of binary LDPE/STAc blend (D1).

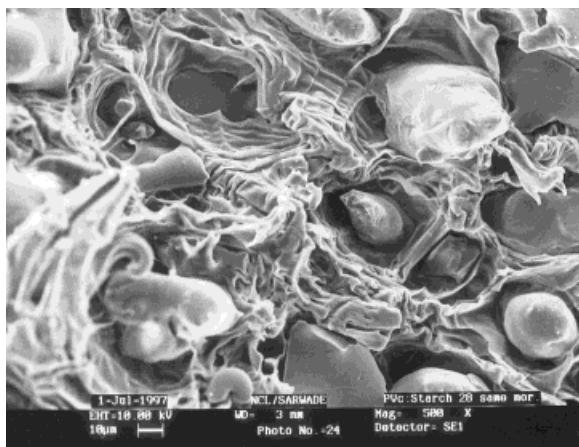


**Figure 5** SE micrograph of LDPE/STAc/starch blend (C2).

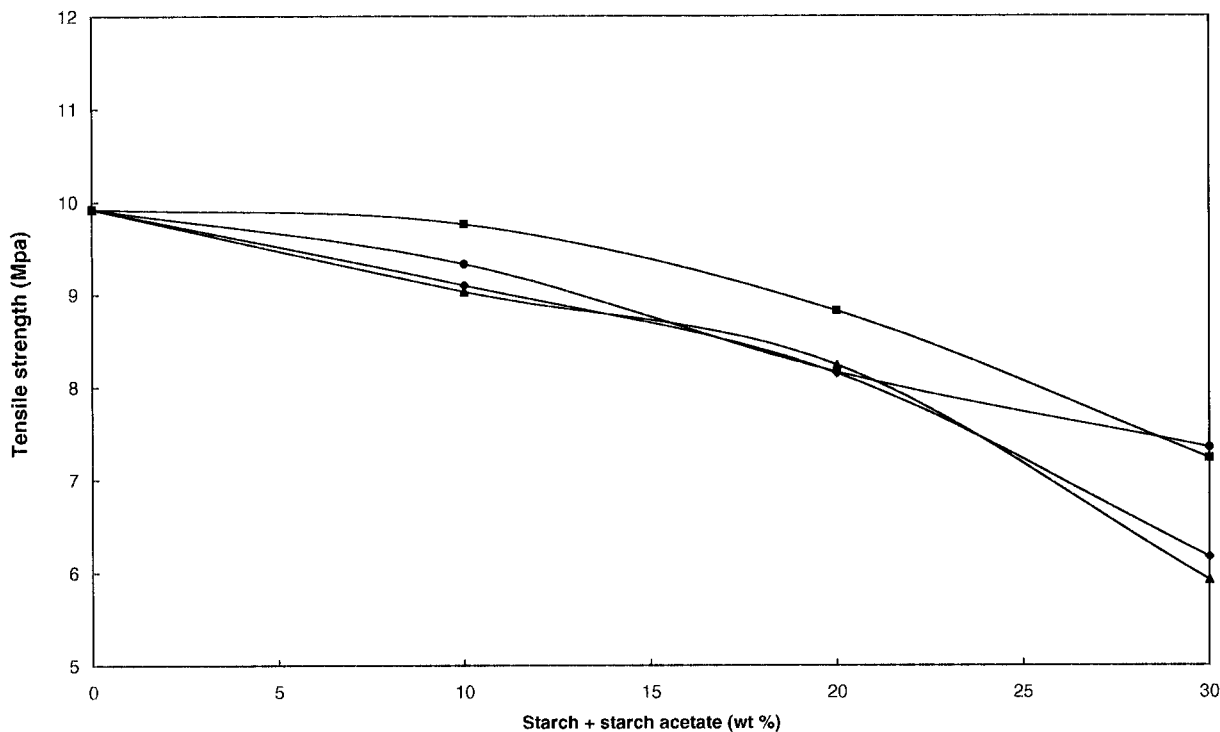
(Stereoscan 440, Cambridge, U.K.) scanning electron microscope operated at 10 kV. The specimens were coated with 50- $\mu$ m thick gold film in an automatic sputter coater (Polaron) to avoid charging under an electron beam.

Thermal analysis was carried out under a nitrogen atmosphere at heating rate of 10°C/min using a DSC 2910 (T. A. Instruments) over the temperature range of 25–250°C. The melting temperature ( $T_m$ ) and heat of fusion ( $\Delta H_f$ ) of the samples were obtained from the peak maxima and the area under the peaks, respectively. The percent crystallinity of the LDPE phase was calculated by using the following equation:

$$\% \text{ crystallinity} = \frac{\Delta H_f^*}{\Delta H_f^0} \times 100$$



**Figure 6** SE micrograph of LDPE/STAc/starch blend (C3).



**Figure 7** Tensile strength vs. weight percentage of starch: (■) LDPE/STAc, (▲) LDPE/STAc/starch (STAc = 5%), (◆) LDPE/starch, and (●) LDPE/STAc/starch (STAc = 2.5%).

where  $\Delta H_f^0$  is the heat of fusion for 100% crystalline LDPE and  $\Delta H_f^*$  is the heat of fusion obtained from the DSC studies for the blends.

The MFI of the LDPE and its blends was determined using a Davenport Rheometer. The capillary die length was 8 mm, the diameter was 2 mm, and the driving weight was 2.16 kg at 120°C.

### Biodegradation

Microbes were isolated from soil and enriched using native starch and STAc as the sole carbon sources in sterile synthetic Bushnell Haas medium (Hi Media Lab Pvt. Ltd., India). The adapted microorganisms were used for biodegradation of the blends. The polymer blends in granule form were surface sterilized with 0.1% (w/v)  $\text{HgCl}_2$  solution, washed repeatedly with sterile distilled water, dried at 60°C in an oven till constant weight, and exposed to a 2% (w/v) adapted consortia of soil isolated for 3 weeks at  $30 \pm 2^\circ\text{C}$  under static condition along with a uninoculated control for each treatment. Biodegradation was measured in terms of weight loss of the granules,

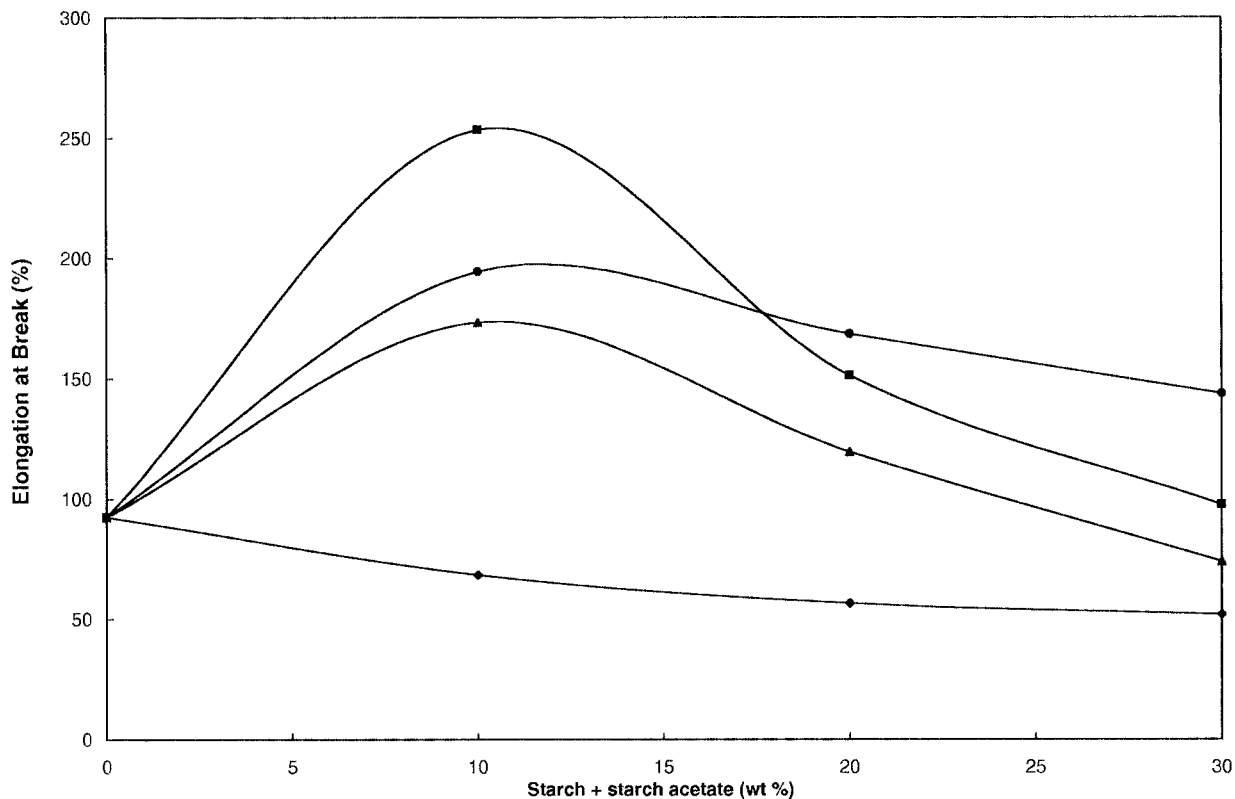
and microbial growth was measured in terms of the cell protein. After 3 weeks of incubation, 1 mL of the sample was withdrawn from each set and spun at 6000 rpm for 10 min and the cell pellet was boiled with 1N NaOH for 10 min for cell lysis. The soluble protein was estimated by the method of Lowry et al.<sup>18</sup> using bovine serum albumin as the standard. Growth of the microbes on pure starch and STAc was also compared to show that starch is a preferable carbon source over STAc. Films of selected blends were also subjected to the biodegradation study as described earlier. Incubation of the films was carried out for 30 days. Incubated films were analysed by SEM.

## RESULTS AND DISCUSSION

### Morphology

The morphology of the impact fractured surfaces of LDPE/starch and LDPE/STAc blends were examined through SEM.





**Figure 8** Elongation at break vs. weight percentage of starch: (■) LDPE/STAc, (▲) LDPE/STAc/starch (STAc = 5%), (◆) LDPE/starch, and (●) LDPE/STAc/starch (STAc = 2.5%).

The morphology of the impact fractured surfaces of ternary blends of LDPE containing 0, 2.5, 5, and 10% STAc and 10, 7.5, 5, and 0% starch is seen in Figures 1, 2, 3, and 4, respectively. As the concentration of STAc increases the dispersion of starch particles becomes more uniform and shows improved homogeneity and adherence to LDPE.

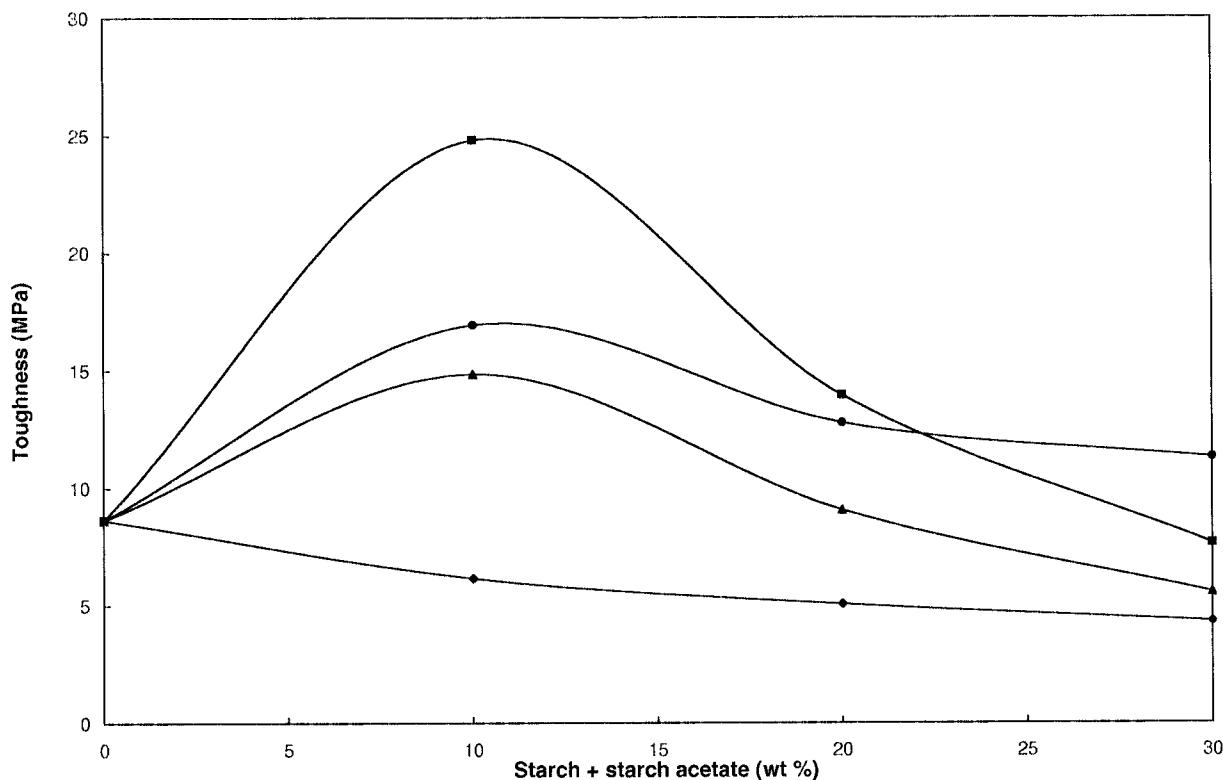
For LDPE/starch blends containing no STAc (Fig. 1) and only 2.5% STAc (Fig. 2) the dispersion of the starch particles was observed to be without any adherence to the matrix. It seems that LDPE formed a layer over the starch. However, with increased STAc (Figs. 3, 4) the particles were dispersed within the matrix with improved adhesion for the LDPE. Hence, the higher the percentage of STAc, the better the compatibility of the two phases.

Although STAc brings increased adhesion, this effect decreases with increasing starch concentration. This can be seen in Figures 3, 5, and 6 for the blends containing 5% STAc in 90/5, 80/15, and 70/25 LDPE/starch blends, respectively. Blends with 15% starch and 5% STAc show more firmly embedded particles that cannot be pulled out eas-

ily during the fracture process. However, Figure 6 shows the 25% starch and 5% STAc blend surface where cavities are seen that were created because of the easy pulling of particles.

### Tensile Properties

Incorporation of starch or STAc in LDPE reduced the tensile strength of the blends at all compositions. From the results in Figure 7 it is observed that if starch is completely replaced by STAc less reduction in tensile strength can be obtained. The variation of STAc (0, 2.5, or 5%) in the blend does not noticeably affect the tensile properties. This is particularly true for the 80/20 composition where morphological studies showed better dispersion and adhesion between the two phases. Earlier reports showed that by reducing the hydrophilic nature of the starch, starch-polymer interaction can be increased and hence tensile strength can be improved.<sup>19,20</sup> St-Pierre et al.<sup>21</sup> on the other hand did not observe any such improvement by replacing thermoplastic starch for starch in LDPE/starch blends.



**Figure 9** Toughness vs. weight percentage of starch: (■) LDPE/STAc, (▲) LDPE/STAc/starch (STAc = 5%), (◆) LDPE/starch, and (●) LDPE/STAc/starch (STAc = 2.5%).

Results obtained for elongation at break for various blends are given in Figure 8. All binary blends containing LDPE/starch showed lower elongation at break than LDPE alone. A drastic improvement was observed when starch was completely replaced by STAc in binary blends. With an increasing concentration of STAc the elongation at break increased at all compositions. This may be attributed to the improved plasticity of STAc.

In synthetic polymer blends the addition of the immiscible component to a ductile matrix generally decreases the elongation properties considerably at break point.<sup>22</sup> The elongation will therefore depend on the state of the interface in such cases.<sup>23</sup> The elongation at break decreased with increasing loading of starch in the blends, and the optimum was at 10% loading. Thus, improvement in elongation is an interesting feature of these blends and suggests that STAc behaves as a good interfacial modifier. The elongation data suggested that a good amount of adhesion of the hydrophilic starch to the hydrophobic LDPE was brought about by the addition of STAc.

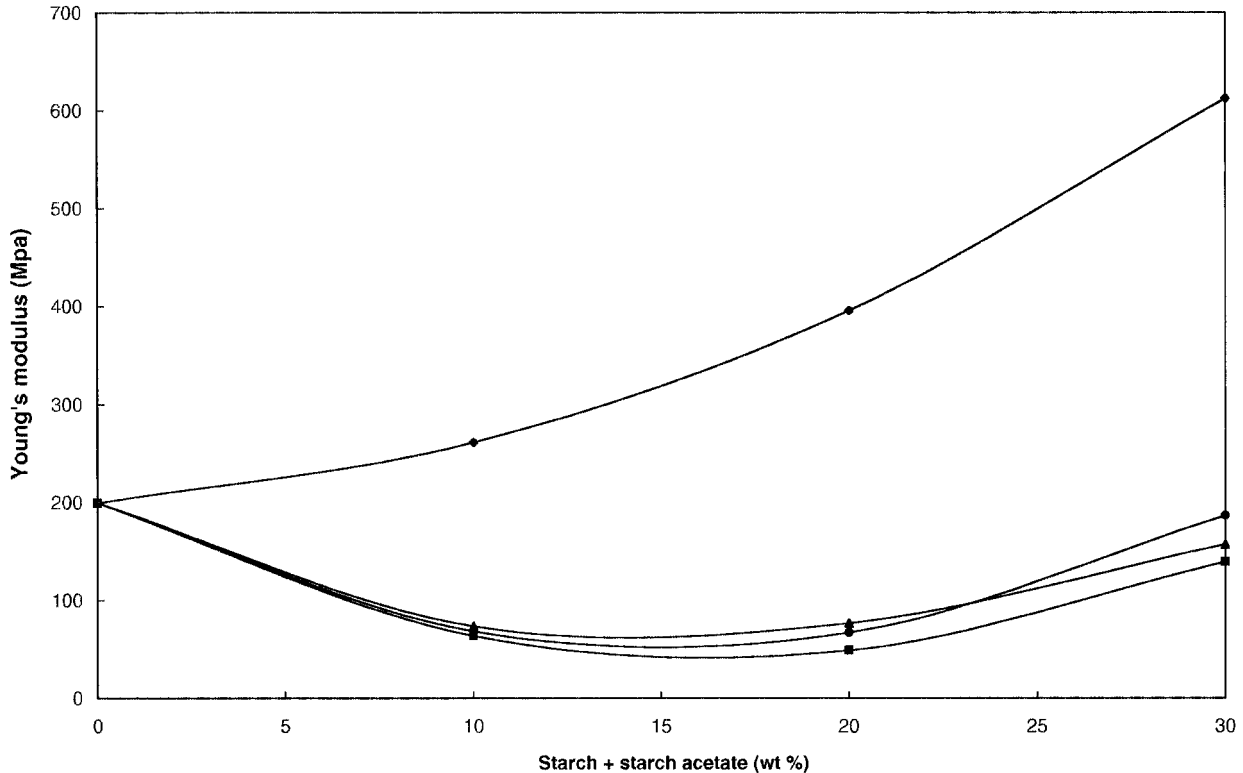
The toughness of the blends with respect to composition is expressed in Figure 9. It was also

observed here that incorporation of starch into LDPE decreases the toughness, but partial or complete replacement of starch by STAc in blends showed improved toughness at all compositions. However, maximum improvement was observed with the 90/10 blend composition. The improved toughness due to STAc can be assigned to the plasticizing effect of modified starch.

Crystallinity brings about an increase in modulus. The binary PE-starch blend shows an increase in modulus with increasing starch content (Fig. 10). This may be due to incorporation of the crystalline starch. On the other hand, the modulus of binary and ternary blends containing STAc is lower, which suggests a decrease in crystallinity of STAc compared to starch. The plasticizing effect of STAc decreases the crystallinity, which in turn decreases the modulus. We observed that constant deformation affects a high modulus material more than a low modulus material. Thus, it can be said that STAc is a better substitute for starch.

#### Impact Properties

The Izod impact strength of all the binary and ternary blends was lower than that of LDPE,



**Figure 10** Young's modulus vs. weight percentage of starch: (■) LDPE/STAc, (▲) LDPE/STAc/starch (STAc = 5%), (◆) LDPE/starch, and (●) LDPE/STAc/starch (STAc = 2.5%).

except for blends C1 and D1. Incorporation of STAc even at the 2.5% level could improve the impact strength of LDPE/starch blends to a considerable extent, which is a desirable observation for biodegradable materials. Thus, all the blends containing STAc showed better impact strength than the PE/starch binary blends as observed in Figure 11. This is because as the concentration of STAc increases, a better dispersion is achieved, which was observed in the SEM studies (Figs. 1–4).

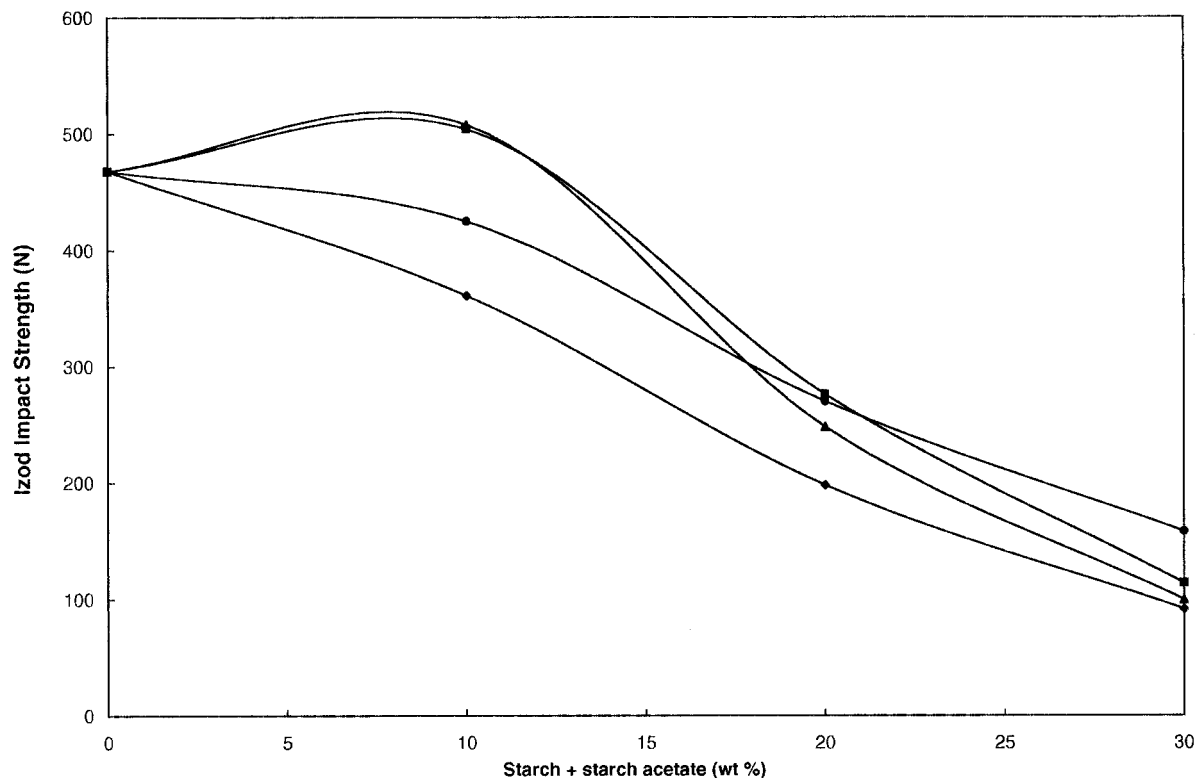
The observed high impact strength in the C1 and D1 blends can be explained by Figures 3 and 4 where rough surfaces of the dispersed particles can be seen, which indicates improved adhesion between the two phases. The decrease in impact strength with increasing starch content can be explained by the morphology as follows. Figures 3, 5, and 6 show an increase in the particle size as the amount of starch continues to increase. Also, the cavities in Figure 6 show that particles are pulled out of the LDPE matrix during impact testing due to poor adhesion in the 70 : 30 blend composition. Figure 5

shows that the particles of starch are just seated in the cavities with the 80 : 20 blend composition. In the 90 : 10 blend proportion (Fig. 3) the particles are properly embedded in the LDPE matrix, which is indicative of good adhesion between the blend components.

Evangelista et al. reported that 6–9 wt % of unmodified starch can be incorporated into industrial LDPE/starch blends with satisfactory mechanical properties.<sup>15</sup> However, we observed from the tensile strength and elongation studies that about 15–20% of STAc can be used to prepare blends with LDPE without much compromise in the mechanical properties.

#### MFI

Figure 12 gives the data on the MFIs of the binary and ternary blends. All the blends containing STAc showed higher MFIs than binary blends of LDPE and starch at all compositions, indicating improved homogeneity of the blends. Replacement of starch by STAc increases the MFIs of the blends, irrespective of the composition. A drastic



**Figure 11** Impact strength vs. weight percentage of starch: (■) LDPE/STAc, (▲) LDPE/STAc/starch (STAc = 5%), (◆) LDPE/starch, and (●) LDPE/STAc/starch (STAc = 2.5%).

increase of about 100% in the MFI was observed as the content of starch + STAc was increased from 10 to 20% and remained constant in the blends containing 20 and 30% starch/STAc. Once again this increase in the MFI can be attributed to the plasticizing effect of STAc, which improves the flow property and hence the processability of the blends.

### Thermal Properties

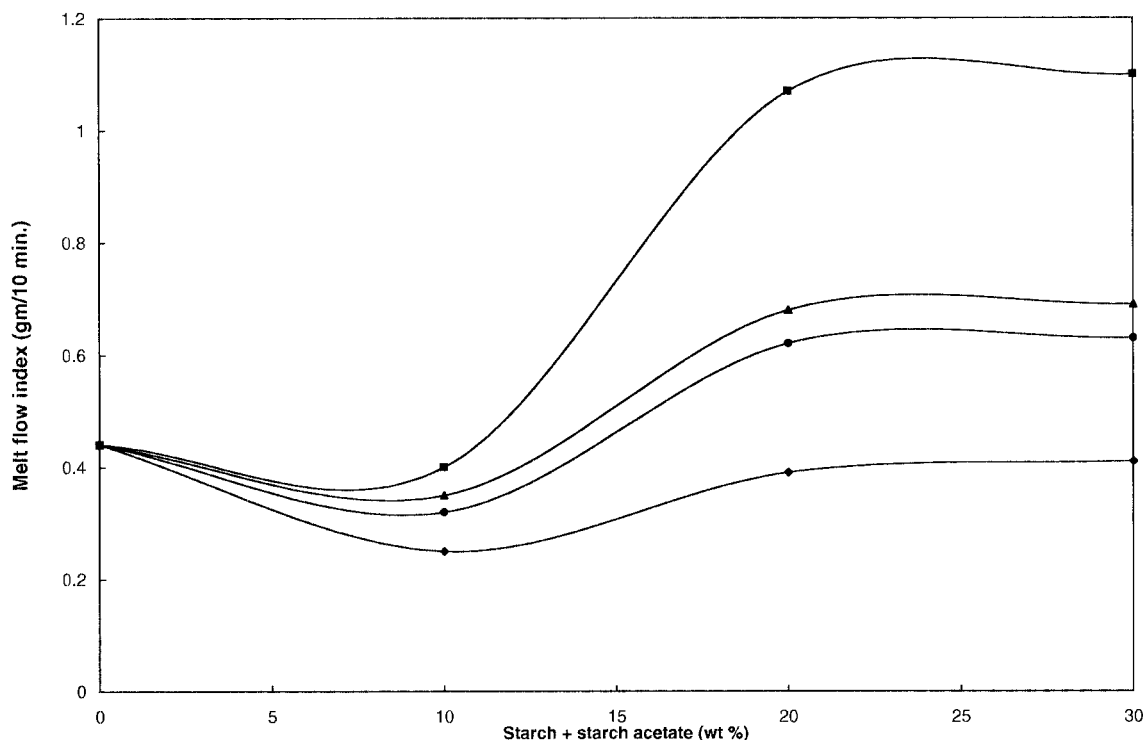
The melting temperatures of LDPE, STAc, and the blends determined from DSC thermograms are given in Table II. There is not much difference in the melting temperatures of the pure LDPE and STAc. Hence, the thermograms of the blends did not show two different melting temperatures for the components. No change was observed in the melting temperature of LDPE in any of the blends. The percent crystallinity of the LDPE phase in the blends (Table II) decreased. This decrease may have been due to the incorporation of starch/STAc, which hinders the close packing of the LDPE chains. The greater decrease of crystallinity in STAc containing blends supports the

presence of an interaction between the two blend components, which further reduces the close packing of the LDPE chains.

### Biodegradation

Recent studies of biodegradation of PE-starch blends<sup>1,24</sup> suggest that microbes consume starch and create pores in the plastic, leading to an increase in the surface area of the PE matrix, and provides susceptible groups for its biodegradation. Lee et al.<sup>25</sup> gave strong evidence to support reduction in the plastic integrity that was caused by microbial biodegradation of degraded plastics containing a prooxidant and 6% starch using a pure culture. Goheen and Woll<sup>26</sup> demonstrated biodegradation of binary polymer films containing different percentages of corn starch and LDPE in soil by monitoring starch removal. Thiebaud et al.<sup>27</sup> examined the biodegradation of LDPE/starch ester blends by measuring the weight loss due to removal of the starch component by microorganisms concomitant with the loss in integrity of the mechanical





**Figure 12** Melt flow index vs. weight percentage of starch: (■) LDPE/STAc, (▲) LDPE/STAc/starch (STAc = 5%), (◆) LDPE/starch, and (●) LDPE/STAc/starch (STAc = 2.5%).

properties, although the biodegradation observed with these composites occurred at a very slow rate.

Our studies with biodegradation of PE/STAc composites showed a linear increase in weight loss (Fig. 13) and whole cell protein (Fig. 14) of these materials with a proportionate increase in these composites of a biodegradable component like starch and STAc together.

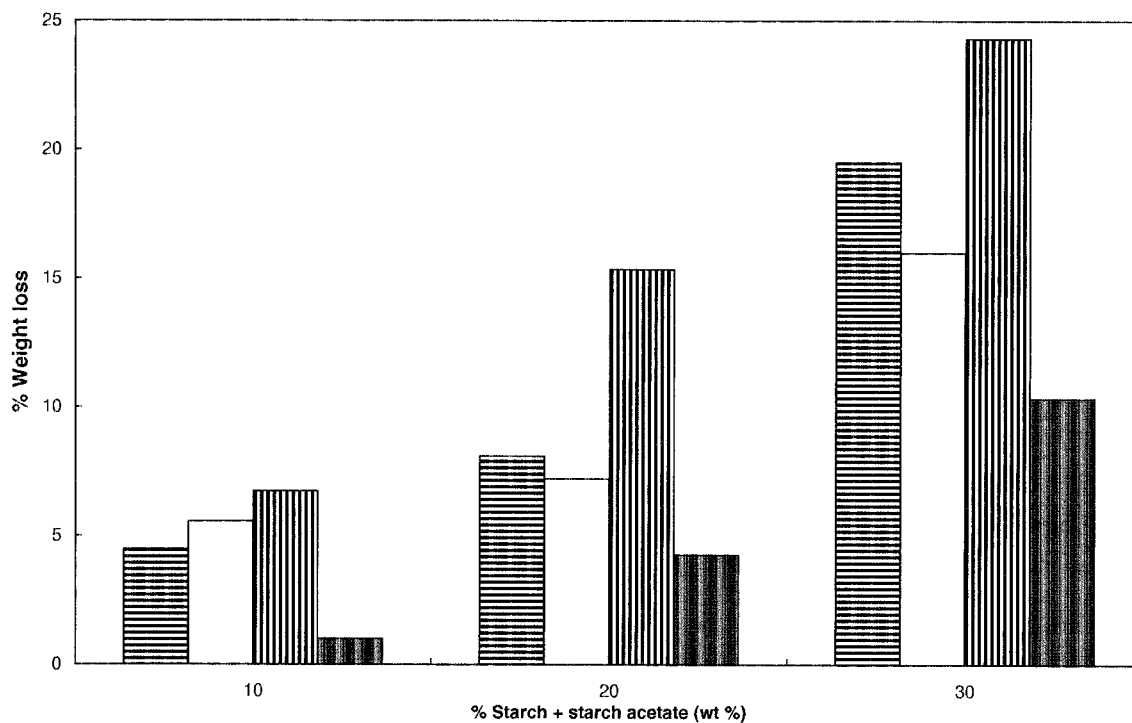
However, biodegradation of these composites depended on the proportion of the STAc within

the biodegradable component (starch and STAc) in the blends with 10, 20, or 30% biodegradable components. The blends with a 5% STAc concentration always showed high biodegradation. Blends containing only STAc, however, responded poorly, which can further be substantiated by poor growth of the microbes with STAc as the sole carbon source compared to starch.<sup>27</sup> This observation is supported by the higher growth of the isolates on pure starch compared to STAc as seen in Figure 15. The higher biodegradation of blends with 5% STAc substitution could be attributed to the better accessibility of biodegradable groups at this particular proportion.

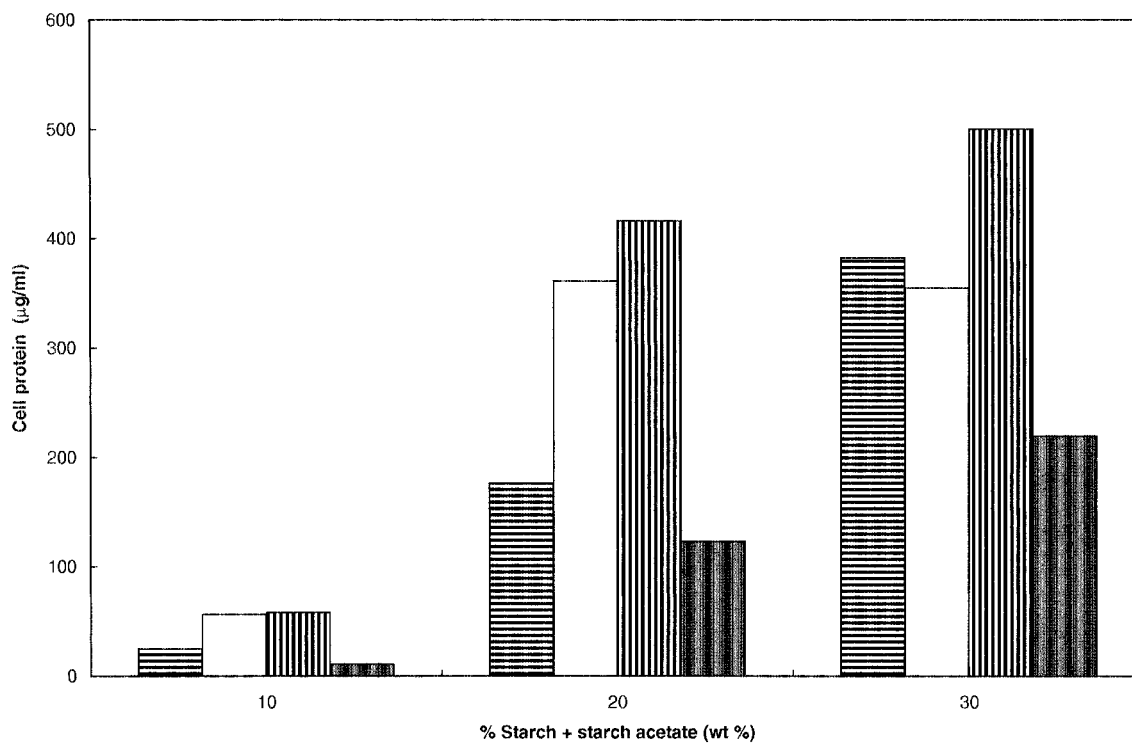
Figures 16–18 show the microbial and fungal growth on the ternary blends of LDPE/STAc/starch. Blends containing 5% STAc as a compatibilizer showed increased growth of microbial colonies with the increased concentration of starch (Figs. 15, 16). However, blends containing 2.5% STAc, 17.5% starch, and 80% LDPE showed fungal growth concentrated at various regions due to poor dispersion of the STAc and starch.

**Table II** Melting Temperature ( $T_m$ ) and Percent Crystallinity of LDPE in Various Blends

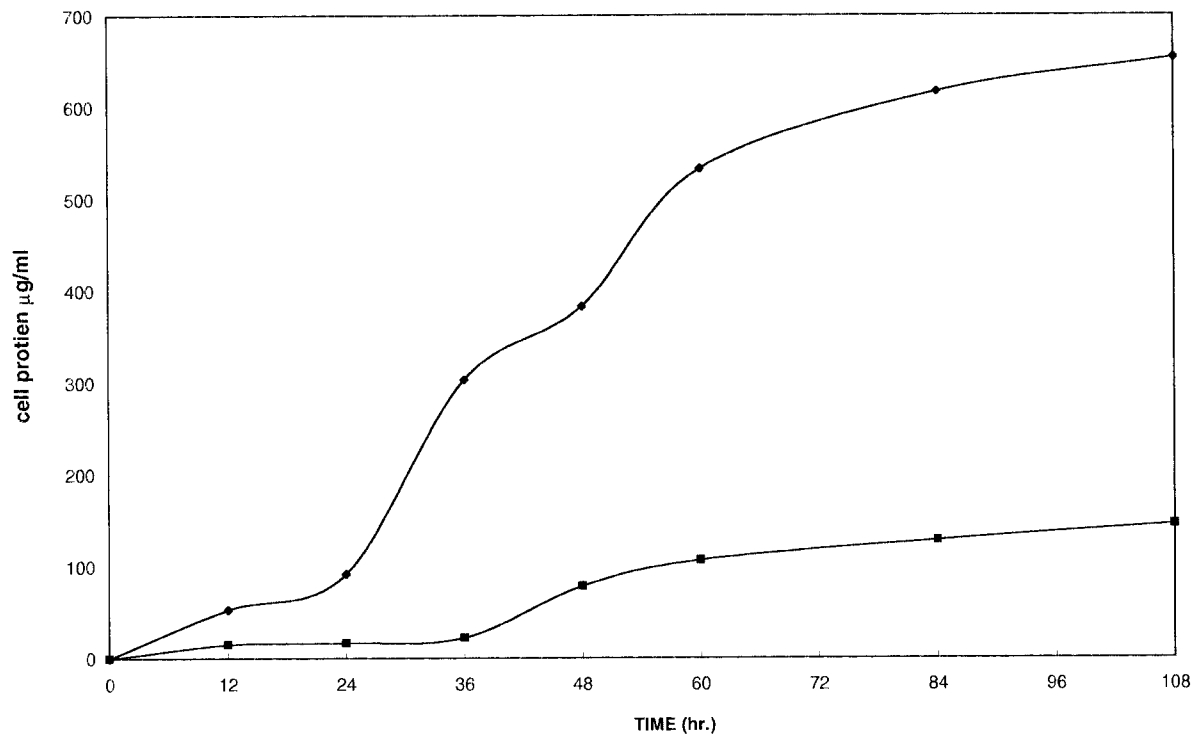
Blend Code	$T_m$ (°C)	Crystallinity (%)
LDPE	111.77	33.74
A3	111.87	19.43
B3	111.76	17.00
C3	111.65	16.71
D3	110.81	14.36
STAc	108.77	—



**Figure 13** Weight loss of LDPE/STAc/starch blends: (■) LDPE/STAc, (▨) LDPE/STAc/starch (STAc = 5%), (▤) LDPE/starch, and (□) LDPE/STAc/starch (STAc = 2.5%).



**Figure 14** Cell protein of LDPE/STAc/starch blends: (■) LDPE/STAc, (▨) LDPE/STAc/starch (STAc = 5%), (▤) LDPE/starch, and (□) LDPE/STAc/starch (STAc = 2.5%).

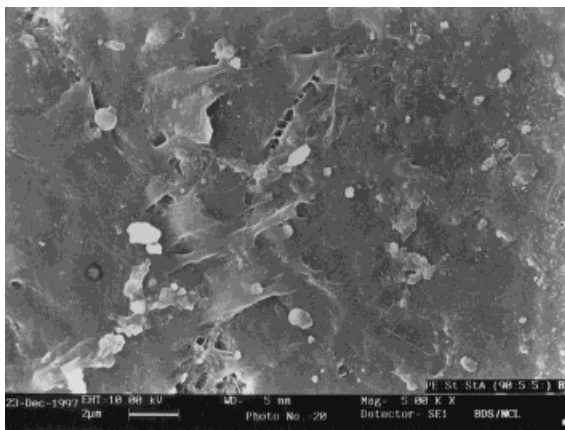


**Figure 15** Growth of consortia on ( $\blacklozenge$ ) pure starch and ( $\blacksquare$ ) STAc (0.2%) in terms of cell protein.

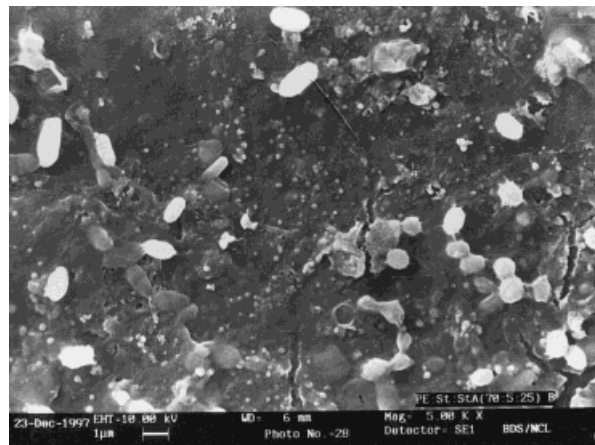
## CONCLUSIONS

The acetylation of starch makes it hydrophobic and enhances its mechanical properties, thus making it favorable for blending with LDPE. Therefore, blends containing STAc exhibit better and more interesting mechanical properties than those of LDPE/starch binary blends. Overall, 90/10 LDPE/STAc blends showed optimum me-

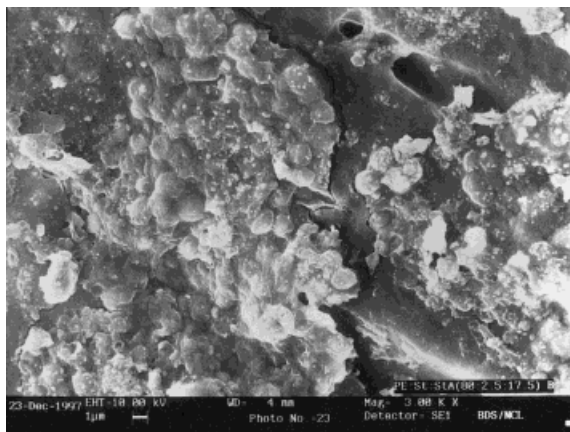
chanical properties. The biodegradation studies showed that STAc exhibited a somewhat lower rate of degradation than native starch. Maximum biodegradation was observed in blends containing 5% STAc substitution at all blend compositions. Thus, the biodegradability of the blends may be greatly influenced by the relative availability of the biodegradable component in the blend. SEM



**Figure 16** SE micrograph of biodegraded film of LDPE/STAc/starch blend (C1).



**Figure 17** SE micrograph of biodegraded film of LDPE/STAc/starch blend (C3).



**Figure 18** SE micrograph of biodegraded film of LDPE/STAc/starch blend (B2).

analysis of the films indicated surface growth and colonization of bacterial and fungal cultures.

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