Biodegradability, Mechanical Properties, Melt Flow Index, and Morphology of Polypropylene/Amylose/Amylose-Ester Blends

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ABSTRACT: We blended polypropylene (PP) with amylose (AM) and/or dodecanoyl ester of amylose (DODAM) in an effort to make it biodegradable. The content of AM/DODAM was varied from 0 to 40% in the blends. The biodegradability, mechanical properties, melt flow indexes (MFIs), and morphologies of the blends were studied. Biodegradability increased with increases in AM/DODAM content. It was found to be dependent on DODAM content and was at a maximum in blends containing 40% AM + DODAM. Blends with no DODAM or 2.5% DODAM showed almost no adherence of the phases. Dispersion of AM improved in blends with 5% DODAM, and it showed satisfactory adherence to PP also. The tensile strength, elongation at break, and Izod impact strength decreased with increasing AM content. However, in blends with both AM and DODAM, all these properties, especially the elongation at break, showed improvements. The same trend was observed for MFI. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 1434–1442, 2002

Key words: biodegradable; esterification; compatibility; amylose; microbes

INTRODUCTION

Environmental pollution caused by the careless disposal of bioinert plastic materials is now a serious and critical problem all over the world. In the last few years, studies concerning the total or partial substitution of synthetic plastics by biodegradable materials have been increasing steadily and have proven to be very useful in the solution of the solid waste management problem of plastics, at least to some extent.[1–4] At present, the demand is that disposable items such as packing bags; milk, water, and soft drinks cartons; coffee and tea cups, and agricultural mulch films, must be biodegradable and should degrade into safe byproducts after use under normal composting conditions. One way of rendering biodegradability to otherwise inert synthetic polymers is by its partial substitution with a starch/amylose (AM) type of natural biodegradable polymer. Starch/AM, because of its easy availability in large quantities, low cost, and total biodegradability, has so far received maximum attention in the preparation of biodegradable plastics.[5]

Native starch/AM can be incorporated into synthetic nonbiodegradable plastic as an additive, or the plastic can be coextruded with them[6–9] to prepare a composite more biodegradable than the pure thermoplastic or to increase the biodegradation rate of the synthetic polymer. However, due to the hydrophilic nature of starch/AM, most of the blends have poor mechanical properties due to poor adhesion.

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The compatibility between the synthetic polymer and starch/AM, without the sacrifice of mechanical properties, can be improved mainly in two ways:

1. By introduction of a reactive functional group capable of H-bonding or reacting with starch/AM hydroxyls into the synthetic polymers. For instance, polyethylene (PE) copolymerized with acrylic acid,[10–12] vinyl alcohol,[13,14] and vinyl acetate[15] are good examples of compatabilizers to be used with PE–starch blends due to the H-bonds that can be formed with the OH groups of starch.
2. By replacement of the hydrophilic OH groups of starch/AM with hydrophobic groups through esterification reactions.

In this study, AM was esterified with dodecanoyl chloride to give dodecanoyl ester of amylose (DODAM) with a degree of substitution of 1.8. Then, we examined its use as a compatibilizer for polypropylene (PP)/AM blends and its effect on the mechanical, biodegradation, thermal, and morphological properties.

EXPERIMENTAL

Materials

PP (trade name KOYLENE 0030) was obtained from Indian Petrochemical Co. Ltd. (IPCL, Vadodara, India). The melt flow index (MFI) was 10. Commercial AM (70%) was obtained from Sigma Chemicals Co. (St. Louis, MO, USA). Dodecanoyl chlorides obtained from Aldrich Chemicals (Milwaukee, Wisconsin, USA) were reagent grade. Pyridine and absolute alcohol from E-Merck (Germany) were analytical grade.

Esterification

The esterification of AM was carried out by the modified method of Mullen and Pacsu.[16] The general procedure of esterification was as follows: AM was dried overnight in an oven at 105°C to remove moisture (final moisture $< 2\%$). Then, 20 g of this AM was placed in a double-necked flask fitted with a mechanical stirrer and a condenser. Subsequently, 150 mL of pyridine and a calculated amount of dodecanoyl chloride was added to prepare DODAM ester with a degree of substitution 1.8, which was determined by elemental analysis and an H-NMR technique.[17]

Blend Preparation

Blends were prepared by the melt mixing technique with a single screw extruder (Windsor SX-30), with a screw speed of 20–25 rpm. The temperatures of the feed zone, compression zone, and die were maintained at 170, 180, and 190°C, respectively. PP, AM, and DODAM were air dried at 80°C for 48 h before being fed into the extruder. The various compositions used for the study are given in Table I. Extrudates were water cooled and granulated with a granulator.

Sample Preparation

Samples were injection molded in a Windsor SP-1 type injection molding machine to obtain test specimens for measurements of the tensile properties and impact strength.

Measurements

Biodegradation

Microbes were isolated from soil and enriched with AM and DODAM 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 PP/AM/DODAM blends in granular form were surface sterilized with 0.1% (w/v) HgCl solution, washed repeatedly with sterile distilled

Table I Composition of Blends

PP (wt%)	DODAM (wt%)	Amylose (%)
100	—	—
90	—	10
80	—	20
70	—	30
60	—	40
90	2.5	7.5
80	2.5	17.5
70	2.5	27.5
60	2.5	37.5
90	5.0	5.0
80	5.0	15.0
70	5.0	25.0
60	5.0	35.0
90	10.0	—
80	20.0	—
70	30.0	—
60	40.0	—

water, dried at 60°C in an oven until a constant weight was reached, and exposed to a 2% (w/v) adapted consortia of soil isolated for 3 weeks at 30 ± 2°C under static conditions along with a uninoculated control for each treatment. Biodegradation was measured in terms of the 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 1*N* NaOH for 10 min for cell lysis. The soluble protein was estimated by the method of Lowry et. al.[18] with bovine serum albumin as the standard. The growth of the microbes on pure AM and DODAM was also compared to show that AM is a preferable carbon source over DODAM.

Tensile Properties

The tensile properties of the dumbbell-shaped specimens were measured according to ASTM D 638 procedure on an Instron (model 4301) machine at room temperature (25°C), 50% relative humidity, and a cross-head speed of 25 mm/min.

Impact Properties

The impact strength was measured by following the ASTM D 256 procedure on a FIE impact tester (model IT-0.42, falling hammer type). The specimens were 6.35 × 1.27 × 0.35 cm and had a 0.025-cm notch radius.

Morphology

The biodegraded and impact-fractured surfaces were examined with a scanning electron microscope (stereo scan, model S-360, Cambridge Instruments Ltd.), operated at 10 kV. The specimens were coated with 50 μm of thick gold film in an automatic sputter coater (Polaron) to avoid charging under an electrobeam.

MFI

The MFIs of PP and the blends were determined with 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.

RESULTS AND DISCUSSION

Biodegradation

The biodegradation of PP/AM and/or DODAM showed linear increases in weight loss (Fig. 1) and whole cell protein (Fig. 2) of these materials with proportionate increases in biodegradable AM/

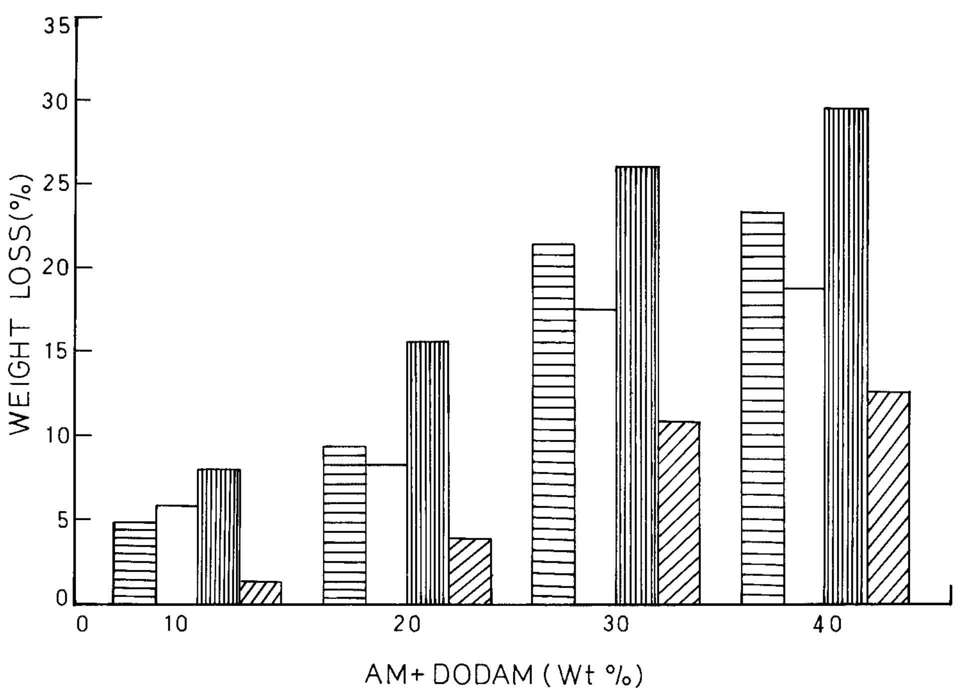


Figure 1 Weight loss of PP/AM/DODAM blends: (□) PP/DODAM, (□) PP/AM/DODAM (5%), (□) PP/AM, and (□) PP/AM/DODAM (2.5%).

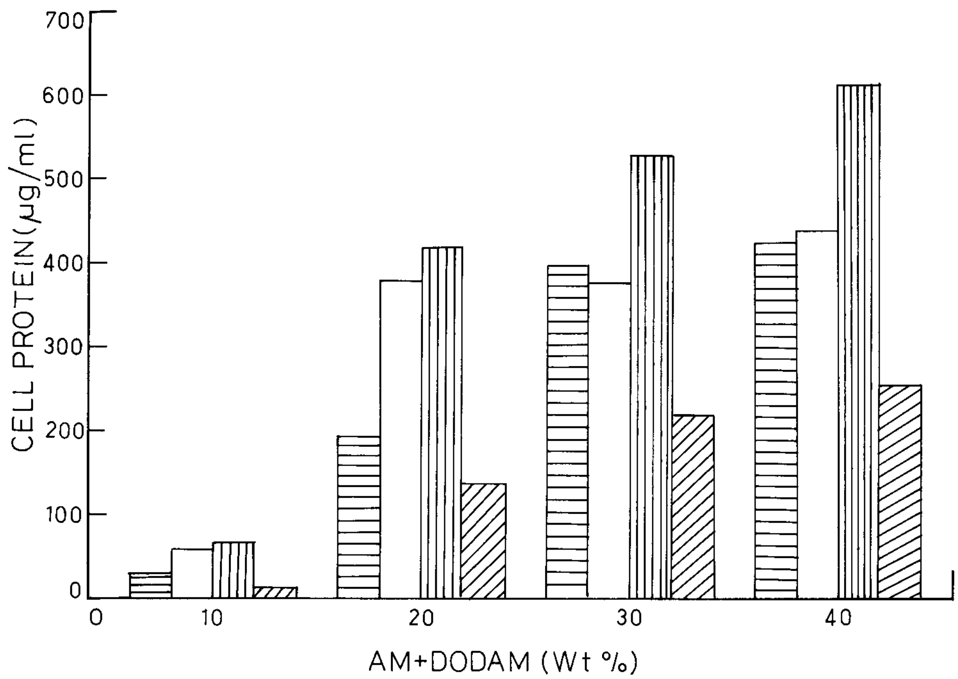


Figure 2 Cell protein of PP/AM/DODAM blends: (□) PP/DODAM, (□) PP/AM/DODAM (5%), (□) PP/AM, and (□) PP/AM/DODAM (2.5%).

DODAM in these blends. However, the biodegradation of these blends with 10., 20, 30, and 40% biodegradable components was found to depend on the DODAM content. The blends with 5% DODAM content always showed higher biodegradation rates. Blends containing only DODAM, however, responded poorly, which could be further substantiated by the poor growth of microbes with DODAM as the sole carbon source as compared to AM. This observation was supported by the higher growth of the isolates on pure AM compared to DODAM, as seen in Figure 3. The higher biodegradation rate of blends containing 5% DODAM may be attributed to the better accessibility of biodegradable groups at this particular proportion.

Figures 4–6 show the microbial and fungal growth on the blends of PP/AM/DODAM. The blends containing 5% DODAM as compatibilizer showed increasing growth of microbial colonies with increasing AM content (Figs. 4 and 5). However, blends containing 2.5% DODAM, 17.5% AM, and 80% PP showed fungal growth concentrated at various regions due to poor dispersion of the DODAM and AM. Similar types of results have been obtained with PE/starch blends by other authors as well.[19–23]

Mechanical Properties

Tensile Strength

The incorporation of AM and/or DODAM in PP caused a reduction in tensile strength of the blends for all the compositions studied. From the results shown in Figure 7, one can see that total replacement of AM by DODAM caused a lesser reduction in tensile strength. The blends containing 5% DODAM showed better tensile strength compared to the blends containing 2.5% DODAM.

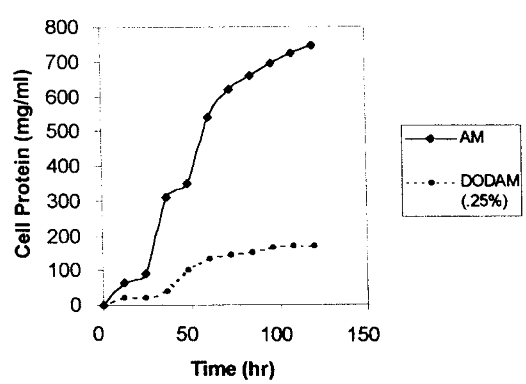


Figure 3 Growth of consortia on (–◆–) pure AM and (–●–) DODAM (0.25%) in terms of cell protein.

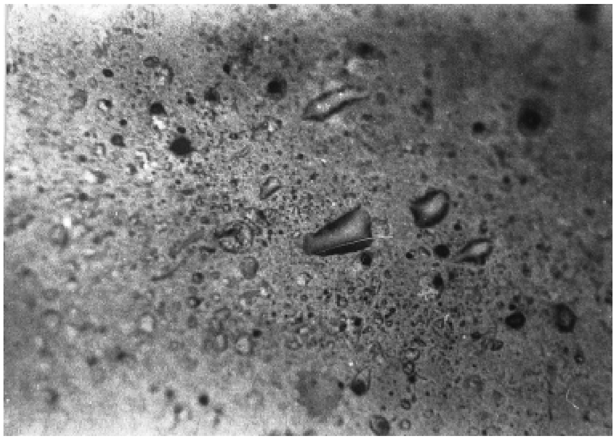


Figure 4 Scanning electron micrograph of the biodegraded film of the PP/AM/DODAM (90/5/5) blend.

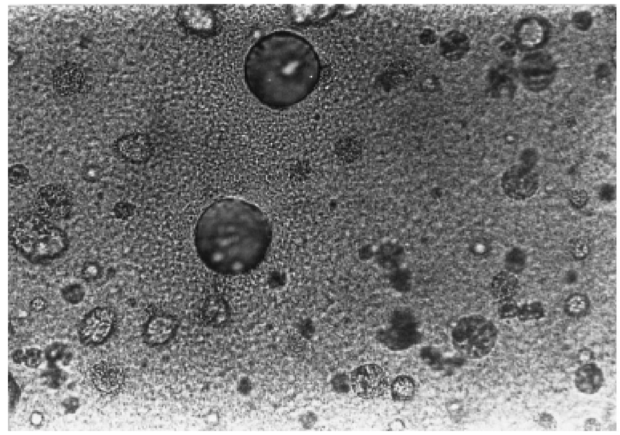


Figure 6 Scanning electron micrograph of the biodegraded film of the PP/AM/DODAM (80/17.5/2.5) blend.

This was probably due to the fact that blends with 5% DODAM showed comparatively better dispersion and, hence, better interaction between the phases. Scanning electron micrographs (Fig. 8) of tensile fractured samples of 80/20 blends with 2.5 and 5% DODAM confirmed this view. In the blend with 5% DODAM, the fracture surface was much smoother, whereas the blend with 2.5% DODAM showed holes from where a phase was pulled out, indicating poor bonding between the phases. Previous studies also showed that by reducing the hydrophilic nature of starch, the starch–polymer interaction could be improved.[24,25]

Elongation at Break

Figure 9 shows the variation of elongation at break with AM/DODAM percentage for various blend compositions. All binary blends containing only PP/AM showed lower elongations at break than PP alone. A drastic improvement was observed when AM was completely replaced by DODAM. In blends containing both AM and DODAM, elongation at break increased with increasing concentration of DODAM at all compositions. This may be attributed to the better interfacial interaction and improved plasticity of DODAM.

In synthetic polymer blends, the addition of the immiscible components to a ductile matrix generally decreases the elongation properties considerably at breaking point.[26] The elongation, therefore, depends on the state of the interface in such cases.[27] Here, elongation decreased with increasing load of starch in the blends, and the optimum was at 10% loading. Thus, improvement in the elongation with the addition of DODAM was an interesting feature of these blends and suggests

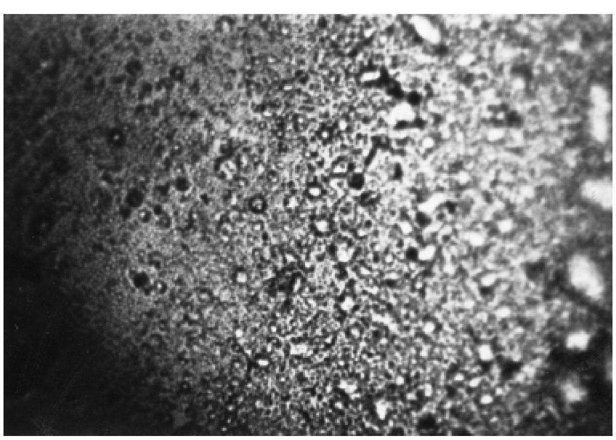


Figure 5 Scanning electron micrograph of the biodegraded film of the PP/AM/DODAM (70/25/5) blend.

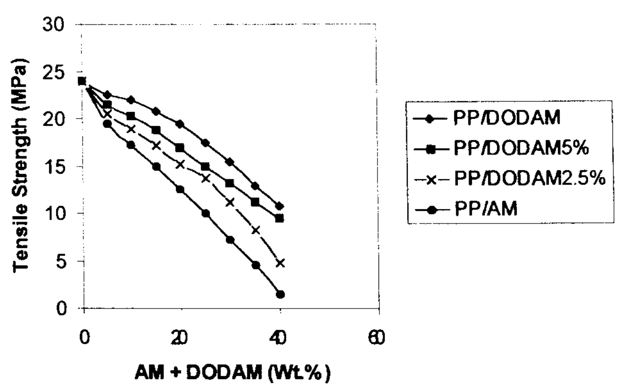
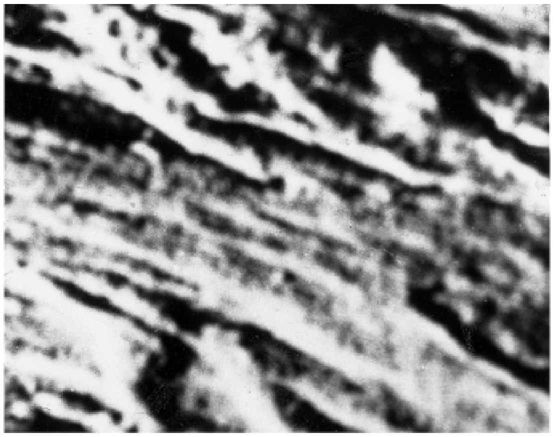
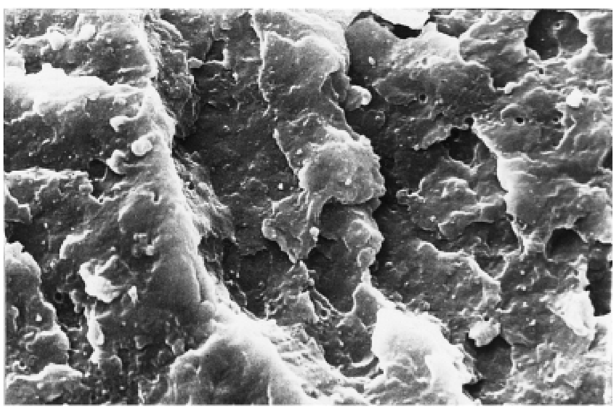


Figure 7 Variation of the tensile strength with the AM + DODAM content in the PP/AM/DODAM blends.



(a)



(b)

Figure 8 Scanning electron micrographs of the tensile fractured samples of the 80/20 PP/(AM + DODAM) blends: (a) DODAM = 2.5% and (b) DODAM = 5%.

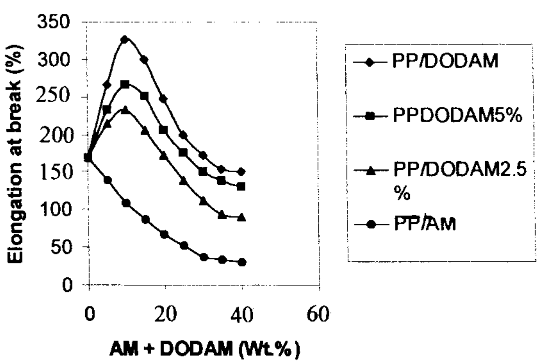


Figure 9 Variation of the elongation at break with the AM + DODAM content in the PP/AM/DODAM blends.

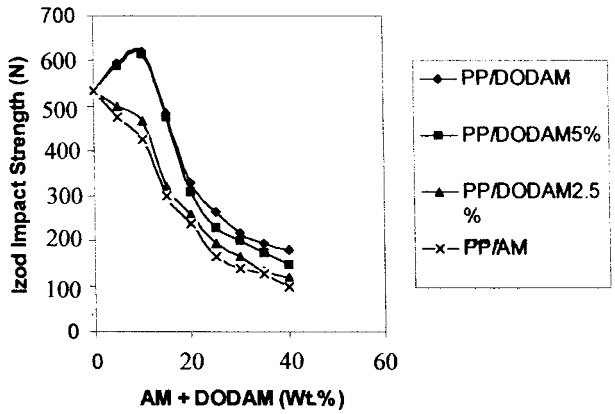


Figure 10 Variation of impact strength with the AM + DODAM content in the PP/AM/DODAM blends

that DODAM behaved as a good compatibilizer. The elongation data indicates that a good amount of adhesion of the hydrophilic AM to the hydrophobic PP was brought about by the addition of DODAM.

Impact Properties

The impact results are shown in Figure 10. The impact strength of all the blends was lower than that of PP, except for blends with only DODAM and with 5% DODAM. Incorporation of DODAM, even at 2.5% loading, could improve the impact strength of PP/AM to a considerable extent, which is an advantage in case of biodegradable materials. Thus, all blends containing DODAM showed better impact properties compared to PP/AM blends, as is clear from Figure 10. This is because

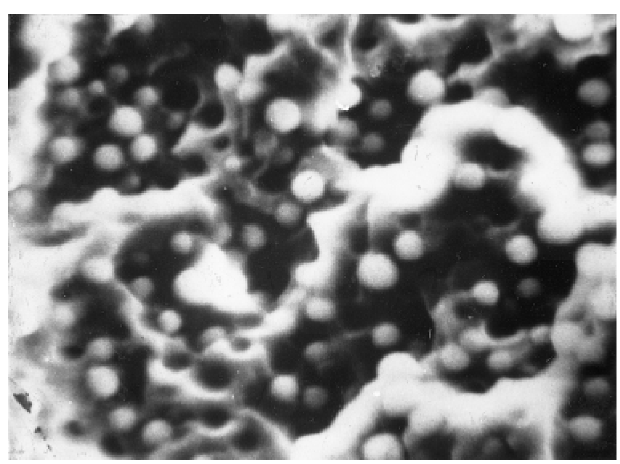


Figure 11 Scanning electron micrograph of the PP/AM (90/10) blend.

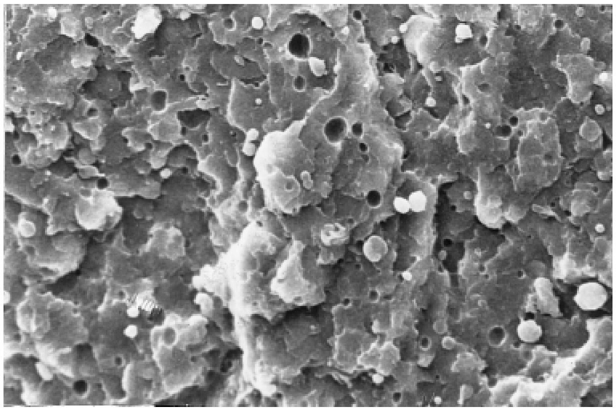


Figure 12 Scanning electron micrograph of the PP/AM/DODAM (90/7.5/2.5) blend.

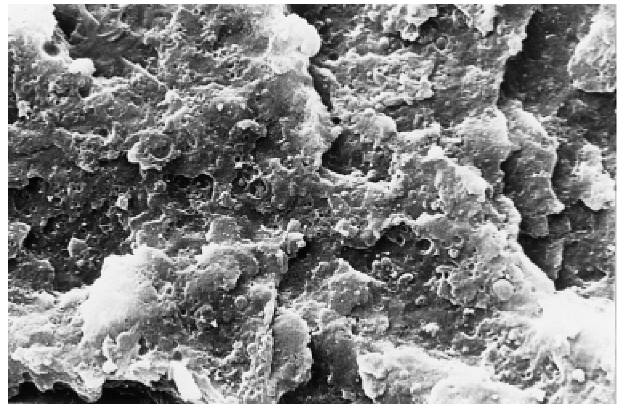


Figure 14 Scanning electron micrograph of the PP/DODAM (90/10) blend.

as the concentration of DODAM increased, a better dispersion was achieved, which was observed in the scanning electron microscopy studies (Figs. 11–14).

The observed high impact strength in the blends with only DODAM and 5% DODAM can be explained as shown in Figures 13 and 14, where the impact fractured surfaces show very good dispersion of the phases, indicating improved adhesion between the phases. The decrease in impact strength with increasing AM content can be explained by the morphological studies. Figures 13, 15, and 16 show an increase in the particle size as the amount of AM increased. In addition, the holes in Figure 16 show that particles were pulled out of the PP matrix during impact testing due to poor bonding in the 70/30 blend composition. Figure 15 shows that the particles of starch were just seated in the cavities in case of 80/20 blend compositions. In the 90/10 blend (Fig. 13), the particles were properly embedded in the PP matrix, which indicates good adhesion between the blend components.

When the results of the mechanical studies are considered, we may conclude that addition of 10–20% biodegradable AM/DODAM, with a minimum 5% DODAM, will give PP blends with satisfactory biodegradability without much compromise in their mechanical properties.

Morphology

Figures 11 and 12 show the morphology of blend surfaces with 0 and 2.5% DODAM. Here, the AM particles were distributed in globular form, without any adherence to the PP matrix.

However, with increased DODAM (Figs. 13 and 14), this globular nature disappeared, and a more uniform, homogeneous blend resulted, indi-

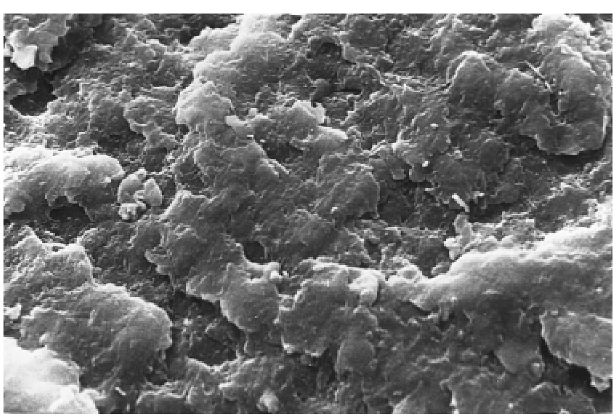


Figure 13 Scanning electron micrograph of the PP/AM/DODAM (90/5/5) blend.

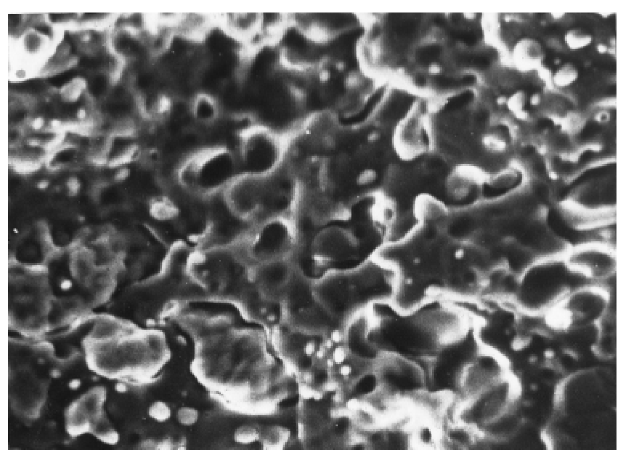


Figure 15 Scanning electron micrograph of the PP/AM/DODAM (80/15/5) blend.

cating better adhesion to the PP matrix. Hence, the higher the percentage of DODAM was, the better the compatibility of the two phases was.

Although DODAM acted as a compatibilizer and enhanced the adhesion between phases, this effect was found to decrease with increasing concentration of AM. This may be justified from Figures 15 and 16, which show the morphology of blends with 5% DODAM in 80/15 and 70/25 PP/AM blends, respectively. Blends with 15% AM and 5% DODAM (Fig. 15) showed a clear fracture without much roughness, indicating good bonding between the phases. However, in the blend with 25% AM and 5% DODAM (Fig. 16), the particles were scooped out during impact fracture, leaving deep cavities, which is indicative of poor adhesion of the phases.

MFI

The variation of MFI with the percentage of AM + DODAM is shown in Figure 17. All the blends with DODAM exhibited higher MFIs than did binary blends of PP/AM at all compositions, indicating improved homogeneity of the blends. The MFI increased on the replacement of AM with DODAM, irrespective of composition. A drastic increase of more than 100% in MFI was observed as the AM + DODAM content increased from 10 to 20% and remained constant in blends containing 20 and 30% AM/DODAM.. This increase in MFI can once again be attributed to the plasticizing effect of DODAM, which improves the flow property and, hence, the processibility of the blends.

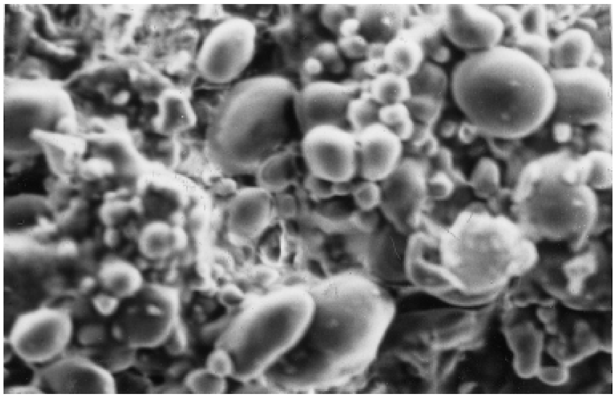


Figure 16 Scanning electron micrograph of the PP/AM/DODAM (70/25/5) blend.

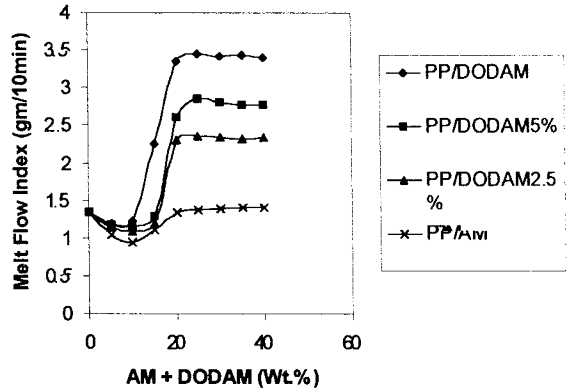


Figure 17 Variation of the MFI with the AM + DODAM content.

CONCLUSIONS

The acetylation of AM induces hydrophobicity, making it suitable for blending with PP. Thus, PP blends containing DODAM as such or as a compatibilizer along with pure AM exhibited better and more interesting mechanical properties than those of PP/AM blends. Optimum mechanical properties were shown by the 90/10 PP/DODAM blend. However, the biodegradation studies showed that the rate of biodegradation was somewhat lower in the case of DODAM compared to pure AM. Maximum biodegradation was observed in blends containing 5% DODAM substitution at all blend compositions. DODAM also had a positive influence on the MFIs of the blend systems. It improved the homogeneity of the blends, thus improving the flow properties and processibility of the blend systems.

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