

Modification of LLDPE Using Esterified Styrene Maleic Anhydride Copolymer: Study of Its Properties and Environmental Degradability

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ABSTRACT: Linear low-density polyethylene (LLDPE) was blended with decanol-esterified styrene maleic anhydride copolymer (MDESMA) with an aim to enhance the environmental degradability of polyethylenes. Styrene-maleic anhydride copolymer (SMA) was synthesized by precipitation polymerization, using benzoyl peroxide (BPO) as initiator. SMA was esterified with a long-chain monoalcohol, *n*-decanol, using methyl ethyl ketone (MEK) as solvent at 80°C to obtain monoesterified styrene-maleic anhydride (MDESMA). Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimeter (DSC), and thermogravimetric analysis (TGA) were performed to characterize SMA and MDESMA. IR spectra of MDESMA showed a decrease in intensity of peak responsible for carbonyl absorption of a five-membered ring anhydride group along with broadening of carboxyl O—H stretching peak. TGA showed two-stage degradation for SMA and MDESMA. LLDPE was blended with MDESMA in single-screw extruder

and blends were characterized thermally by DSC and TGA. A single endothermic melting peak of LLDPE/MDESMA blend was observed. Films of the blends, formed by compression molding, showed an increase in modulus of elasticity but a decrease in elongation at break with increasing concentration of MDESMA. LLDPE/MDESMA blend compositions when kept in phosphate/citric acid buffer solution (pH ~ 8) showed initial weight gain because of water absorption and subsequently loss in weight due to dissolution of soluble component of blends. Film samples of blends kept for soil burial also showed similar behavior. Contact-angle measurement of film samples of the blends showed an increase in value on soil burial, indicating degradation/dissolution of MDESMA. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 102–108, 2004

Key words: styrene-maleic anhydride; polyethylene; biodegradation; blends

INTRODUCTION

Plastic materials are generally resistant to environmental influences such as humidity or microbial attack. Polymers having a backbone solely made of carbon and hydrogen atoms fall under this category of plastics. Polyolefins form the major class of such polymers. Their low cost, high strength, and resistance to chemical and biological attack have led to their use in diverse application of which packaging is foremost. The amount of waste generated by the use of such inert material in packaging applications has markedly increased throughout the world in the last few years. Waste disposal is becoming a serious environmental problem, because of limited landfill capacity and incineration facilities. Problems such as these have led to the study of novel plastic materials, which can degrade to safer components in a desirable time frame under environmental conditions. Thus, a number of

studies on developments of synthetic biodegradable polymers such as polycaprolactone (PCL), polybutylenesuccinate/adipate (commercially known as Bionolle), and polyethylene adipate (PEA) have been done in the past few decades. However, the higher cost of these polymers has restricted their use in a large quantity in the packaging sector.

Postreactor modification by blending is an attractive technique by which superior material having desirable properties absent in parent polymers can be tailored. Thus, one convenient way to enhance waste management of polymeric material, used in packaging, is to blend nonbiodegradable polymers with biodegradable polymers. A number of studies have been done on blends of polyolefins with natural and synthetic biodegradable polymers. Starch-based plastics initially attracted some research interest,^{1–6} but difficult processing and poor mechanical properties of these blends have failed to excite its future prospects as packaging alternative. Polyethylene/PCL blends have attracted attention because of degradability of PCL. Kalfoglou⁷ studied the compatibility of low-density polyethylene with PCL. Study on PCL/polypropylene blends has shown that melt viscosities and composition of blends determine the phase structure and

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hence the rate of degradation of the blend system.⁸ Likewise, Zainuddin and coworkers studied the degradability and compatibility of polypropylene-ethylene copolymer and Bionolle. Polypropylene-grafted maleic anhydride was used as compatibilizers, which resulted in better blend compatibility and degradation.^{9,10} Studies of PE/PEA blends also revealed no miscibility between PEA and LDPE.¹¹ However, these poly blends have not become commercially successful because of the higher cost of the synthetic biodegradable polymer.

Yet another way to tackle the waste management problem of packaging material comes from the use of water-soluble polymers. These polymers are expected to be biosoluble/biodegradable because of their hydrophilic nature. Thus, high molecular weight polyethylene oxide (PEO) is used in blends of polyolefins to make water-flushable films.¹² Styrene-maleic anhydride copolymer (SMA) may also be used in a similar way in packaging application. SMA is being used in a variety of applications such as paper and textile sizing, floor polishes, and coatings for medicine and packaging material.¹³ It has also been proposed to be used as a bioerrodable-biosoluble injectable nonocclusive contraceptive for males.^{14,15} Although SMA is a hydrophobic polymer and insoluble in water, it slowly swells in alkaline medium and ultimately gets solubilized because of hydrolysis of anhydride groups. The use of SMA-based polymers in packaging application may lead to enhanced waste management as these polymers should be slowly soluble in soil media, which are alkaline in nature. The present article investigates the possible usage of SMA as a biosoluble component in linear low-density polyethylene (LLDPE) blends. To impart compatibility with nonpolar LLDPE, SMA has been esterified with *n*-decanol, a long hydrocarbon chain alcohol. Postreactor modification of LLDPE by blending it with MDESMA and the study of its environmental degradability is the subject of the discussion in the current article.

EXPERIMENTAL

Materials

LLDPE (film grade F20S009, MFI 0.9), used for modification, was supplied by GAIL (India). Styrene used for synthesis of SMA was supplied by GS Chemicals (Mumbai, India). Styrene was made inhibitor free by washing with aqueous alkali solution (5%) and subsequently washing with distilled water to make it alkali free. Inhibitor-free styrene was dried over anhydrous sodium sulfate and used for synthesis. Maleic anhydride and benzoyl peroxide (BPO) from CDH (New Delhi, India), decanol, methyl ethyl ketone (MEK), and petroleum ether from Qualigen Chemicals (Glaxo-SmithKline Pharmaceuticals Ltd., Mumbai, India) were used without any further purification.

TABLE I
Mechanical Properties of LLDPE/MDESMA Blends

Sample No.	Composition (wt%)		Tensile strength (MPa)	Tensile modulus (MPa)
	LLDPE	MDESMA		
LLDPE	100	0	27 (7.5) ^a	109 (4.4) ^a
BIOD82	80	20	17 (1.7)	117 (11.9)
BIOD73	70	30	13 (2.2)	171 (13.5)
BIOD64	60	40	12 (0.9)	188 (23.1)

^a Values in parentheses indicate standard deviation.

Synthesis

SMA was synthesized by precipitation polymerization by using 1 : 1M ratio of styrene and maleic anhydride at 80°C for 3 h by using xylene as solvent and BPO as free-radical initiator in nitrogen atmosphere with continuous stirring. The reaction was carried out in a glass reaction kettle equipped with a glass mechanical stirrer, a nitrogen inlet tube, and a cooling condenser. The monomer mixture along with an initiator was added slowly over a period of 2 h to ensure controlled polymerization and the reaction was carried out for another 1 h to ensure complete polymerization. SMA was precipitated as a fine white powder during polymerization. SMA powder was filtered, washed with petroleum ether, and dried in a thermostat at 80°C. SMA (202 g) was then esterified with *n*-decanol (159 g) at 80°C by using MEK as solvent. The reaction was carried out for 2.5 h with continuous stirring. MDESMA was separated by distilling off the MEK and unreacted decanol was removed by washing the polymer with petroleum ether. MDESMA was dried in a thermostat oven at 80°C.

Characterization of SMA, MDESMA

FTIR spectra of SMA and MDESMA were taken by using a Nicolet spectrophotometer. Acetone solution of SMA and MDESMA was titrated against standardized ethanolic potassium hydroxide solution by using phenolphthalein as an indicator, to determine the acid value. DSC and TGA were performed in nitrogen atmosphere by using a DuPont Thermal Analyzer 910 DSC module at a heating rate of 10°C/min.

Preparation and characterization of LLDPE/MDESMA blends

LLDPE was blended with three different ratios of MDESMA in a single-screw extruder (Windsor L/D ~ 21) at 160°C, 20 rpm, and blends were abbreviated as BIOD blends. The MDESMA content was varied as 20, 30, and 40% in the blends and are listed in Table I.

DSC and TGA of blends were performed in nitrogen atmosphere by using a DuPont Thermal Analyzer 910 DSC module at a heating rate of 10°C/min. Films of

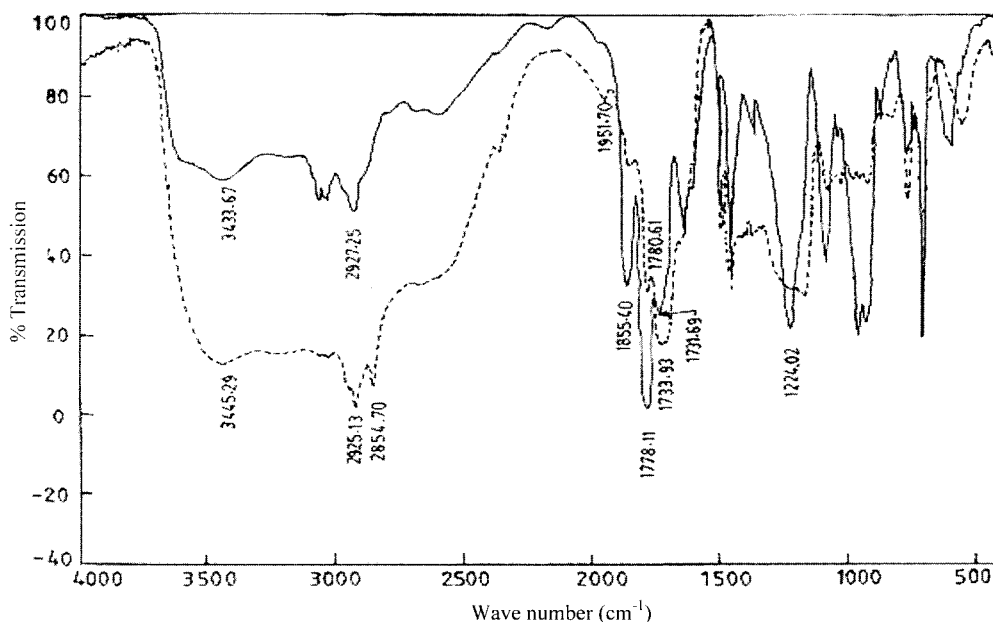


Figure 1 FTIR spectra of SMA (—), MDESMA (---).

LLDPE and the blend samples were made by compression molding at 160°C. Dumbbell-shaped samples were cut out with the help of a die from the films. Tensile properties of the samples were tested in a Zwick Tensile Tester. The jaw separation speed was maintained at 500 mm/min. Tensile strength, tensile modulus, and elongation at break were determined.

Test for environmental degradability

Effect of buffer solution (pH ~ 8)

Dumbbell-shaped samples were cut from the film of BIOD blend samples and weighed. Film samples of MDESMA were also weighed. Dumbbell-shaped samples could not be cut out from MDESMA films, as they were very brittle. The samples were then kept in a buffer solution (phosphate/citric acid) of pH 8. Samples were weighed periodically after every 10 days of immersion and percentage of weight change of the specimen was followed up to 80 days of immersion.

Outdoor soil burial test

Six film samples of each blend composition were kept in a tray with perforations all around the sides and bottom (for easy access of biotic environment) and were buried under soil. The soil pH was determined by checking the pH of aqueous soil solution. Two samples of each blend were taken out after every 20 days and washed clean with distilled water. Water adhering onto the samples were wiped off with filter paper and air-dried at room temperature for 5 min. Samples were weighed accurately and variation of

weight change with time was studied. After 60 days of burial, weight change was determined by using the above procedure. On the 60th day, samples were further buried for 90 more days and after completion of the stipulated period samples were taken out and percentage of weight change was also determined following the usual procedure of cleaning and drying.

Contact-angle measurement

The contact angle between a drop of distilled water and the surface of polymer specimens was measured at room temperature by using a contact-angle goniometer (rame-hart, Inc., USA). Films of LLDPE, MDESMA, and their blends, prepared by compression molding, were taken on separate clean glass slides and placed on the movable platform of the instrument. A drop of distilled water was deposited on the sample film with a syringe and the angle formed between water and solid surface called contact angle was measured by using a telescope. Contact-angle measurement of the films kept for soil burial for 150 days was also done. The results presented here were obtained by averaging the data measured as triplicate on at least three sample films of each polymer.

RESULTS AND DISCUSSION

Characterization of SMA and MDESMA

FTIR spectra of SMA and MDESMA are shown in Figure 1. FTIR spectra of SMA and MDESMA show the appearance of a peak at 1778 and 1855 cm^{-1} , which corresponds to carbonyl absorption of anhydride groups

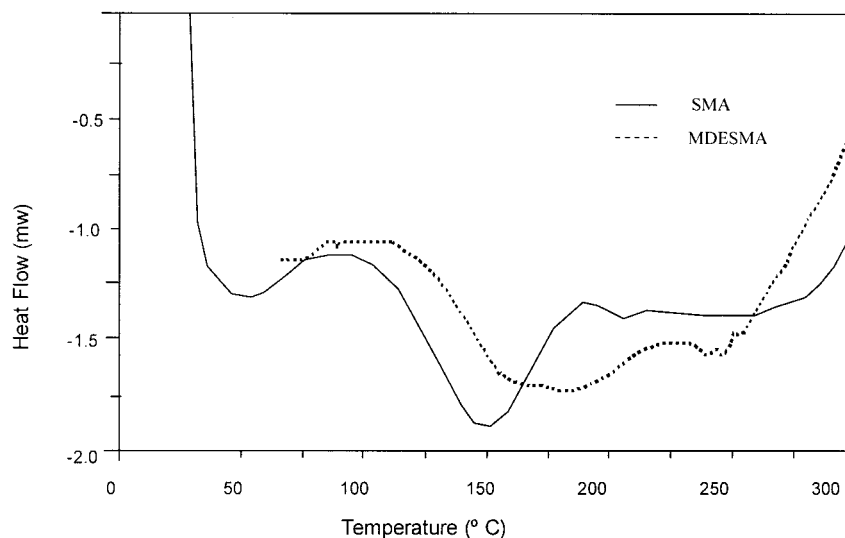


Figure 2 DSC thermograms of SMA (—), MDESMA (- - -).

in five-membered rings. A peak at 1224 cm^{-1} appears because of characteristic C—O—C stretching vibration in cyclic anhydride in which ring strain is involved. Peaks at $2500\text{--}3800\text{ cm}^{-1}$ correspond to —OH stretching vibration, which indicates SMA might have hydrolyzed to some extent. The shoulder appearing at 1731 cm^{-1} due to carbonyl of hydrolyzed —COOH group also supports this. FTIR spectra of MDESMA show a very prominent and strong absorption in $2500\text{--}3800\text{ cm}^{-1}$ regions, which can be attributed to esterification of SMA by 1-decanol and thus the formation of COOH group. Esterification of SMA is also supported by a decrease in intensity of peak at 1778 and 1855 cm^{-1} . In addition, the shoulder at 1731 cm^{-1} becomes more prominent in FTIR spectra of MDESMA, indicating a formation of carbonyl of carboxylic acid. Formation of esterified SMA is confirmed by the presence of these characteristic peaks.

Acid values of SMA and MDESMA were found to be 475 and 238, respectively. The acid value is halved on esterification, which indicates monoesterification in MDESMA.

DSC thermograms of SMA and MDESMA are shown in Figure 2. Endothermic transition at 150 and 175°C as seen in the thermograms of SMA and MDESMA, respectively, corresponds to cyclization of partial hydrolyzed SMA and MDESMA. The TGA curve of SMA and MDESMA is shown in Figure 3. The TGA data of MDESMA shows a major weight loss in the temperature range $175\text{--}250^\circ\text{C}$. This weight change is due to deesterification and liberation of decanol. No such weight loss is observed in SMA over this temperature range. Weight loss in the temperature range $250\text{--}420^\circ\text{C}$ is observed in both SMA and MDESMA, which is attributed to decarboxylation reaction. A similar study by Zeliaskow on thermal degradation study of SMA and hydrolyzed SMA also showed a similar

trend in degradation behavior of SMA and hydrolyzed SMA.¹⁶

DSC thermograms of all three blends and LLDPE are shown in Figure 4. Single-melting endotherms, which appeared in the DSC thermogram of blends, correspond to the melting of LLDPE.

Mechanical properties of LLDPE/MDESMA blends

Tensile properties of the neat LLDPE as well as for blends are tabulated in Table I. Variation of elongation at break with MDESMA content in the blend is shown in Figure 5. There is an improvement in tensile modulus on addition of MDESMA in LLDPE. Tensile modulus increases by 72.5% in the BIOD64 blend in comparison to that of LLDPE. Tensile strength and elongation at break of the blend decreases with an increase in MDESMA content. Tensile strength of BIOD64 drops by 55.5% and elongation at break decreases by 43.8%, when compared to LLDPE. Tensile properties of MDESMA was not done because of brittleness of the sample. This also explains lowering of tensile strength and elongation at break with an increase in the amount of MDESMA in the blend samples.

Environmental degradability test

Effect of buffer solution

Weight change of the samples kept in phosphate/citric acid buffer solution ($\text{pH} \sim 8$) is expressed as a percentage with respect to the weight of the initial sample taken. MDESMA sample in general showed very high water absorption in buffer solution. After 30 days of immersion in the buffer solution, 400% increase in weight of the sample was noted. After 60

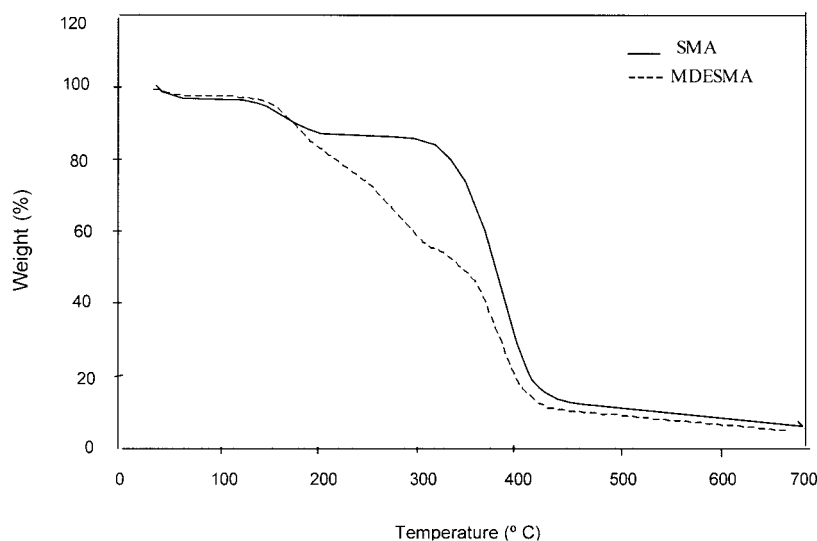


Figure 3 TGA curves of SMA (—), MDESMA (---).

days, the sample swelled enormously and fragmented into pieces and thus could not be retrieved for weighing. Weight change for blend samples was followed up to 80 days and the plot of the same as a function of days of immersion is shown in Figure 6. No change of weight was observed in LLDPE samples over the total period of testing. However, BIOD blend samples showed initial gain up to 50 days and subsequent loss in weight. Initial weight gain may be attributed to water absorption by $-\text{COOH}$ group of MDESMA. Subsequent weight loss is due to dissolution of already swelled polymer in the buffer solution. The water absorption is found to be more in BIOD64 than

the other two blends (i.e., BIOD73 and BIOD82). This is due to greater accessibility of MDESMA in BIOD64 to buffer solution. A weight change of 6% is noted in BIOD64 samples. Loss of weight of samples starts after 40 days in the case of BIOD73 and BIOD64 and starts after 70 days for BIOD82.

Soil burial test

Outdoor soil burial of film samples showed a similar trend as in the case of buffer solution (i.e., initial gain of water by the samples followed by weight loss in each of them). The variation in weight of the samples

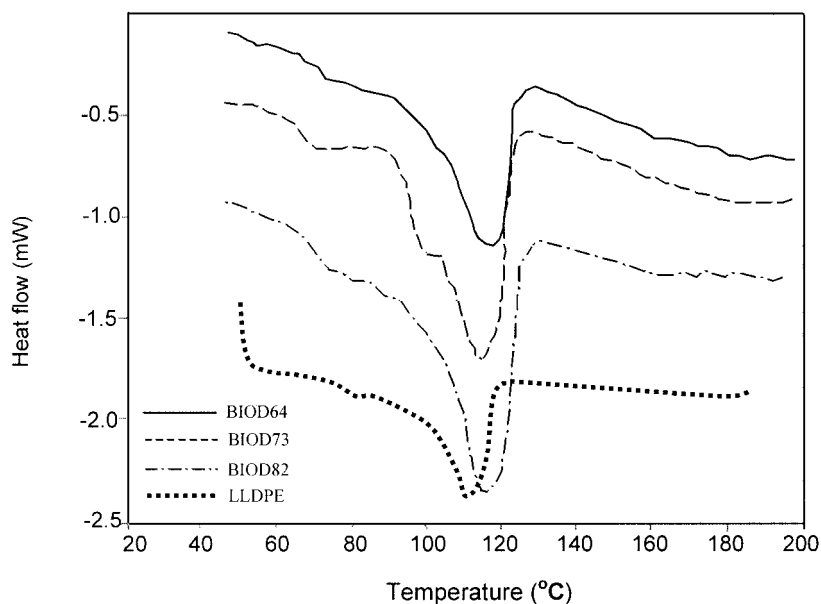


Figure 4 DSC thermograms of LLDPE/MDESMA blends: BIOD64 (—), BIOD73 (---), BIOD82 (-·-·-), LLDPE (···).

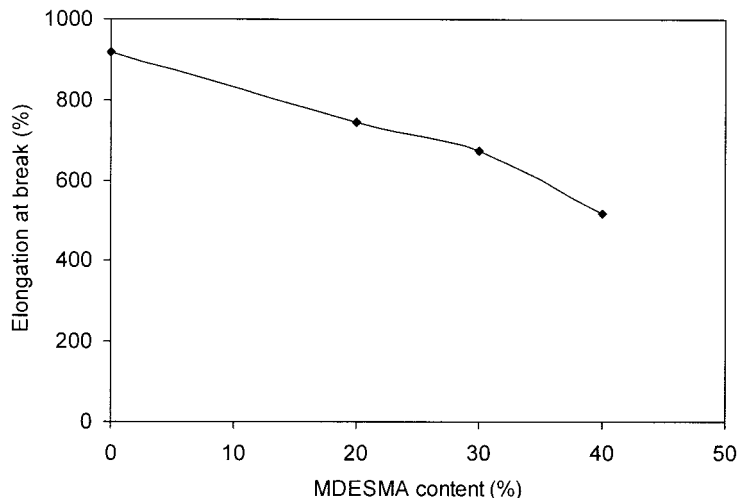


Figure 5 Variation of elongation at break (%) in LLDPE/MDESMA blends

as a function of number of days of burial is shown in Figure 7. No weight change was observed for LLDPE samples over the entire period of soil burial. BIOD64 and BIOD73 showed an increase in weight up to 40 days of burial and subsequent weight decreases. However, BIOD82 samples started to gain weight only after 40 days of burial and there was no weight loss even after 60 days of burial. BIOD82 samples took a longer time to absorb water, which may be reasoned because of a greater amount of LLDPE, thereby making the blend more hydrophobic. On prolonging the soil burial of the samples evaluated at the 60th day for a further 90 days, the blend samples were observed to show a decrease in weight. Rate of decrease in weight became slower after 60 days of burial.

Contact-angle measurement

The contact-angle measurements, carried out on the samples, indicate how the materials change in terms of

hydrophilicity or hydrophobicity and thus changes in wettability of the surface, on exposure to soil burial. Table II gives the results of contact-angle measurement before and after 150 days of soil burial. Contact-angle measurements revealed that MDESMA is more hydrophilic than LLDPE. This is expected as MDESMA contains carboxylic acid groups, which has greater affinity to water than any C—C and C—H bonds of LLDPE. Also, hydrophilicity of blends increases on increasing the amount of MDESMA in blend, as indicated by lowering of contact angle. The contact angle of all the blend samples buried under soil for 150 days showed higher values compared to unburied samples for same blend compositions. This indicates that water affinity is gradually lowered on soil exposure. This may be attributed to removal of MDESMA from the blend samples because of dissolution and/or degradation. This is also supported by weight-loss measurement. Thus, contact-angle mea-

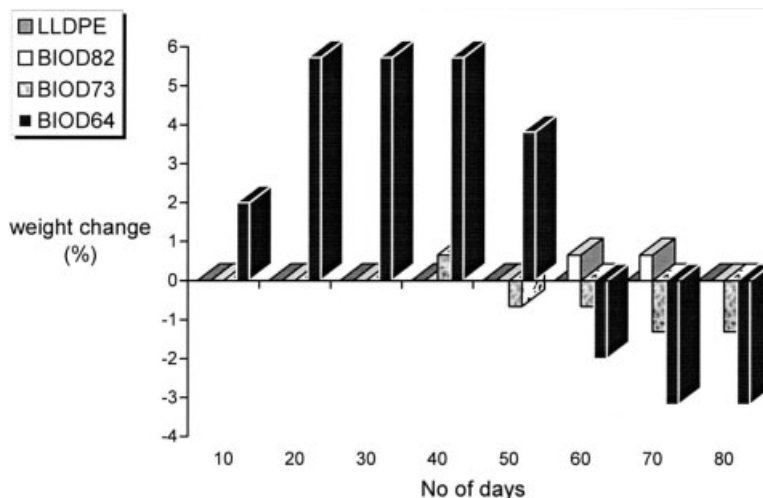


Figure 6 Variation in weight change of LLDPE and LLDPE/MDESMA blend samples in buffer solution: BIOD64 ■, BIOD73 □, BIOD82 □, LLDPE ■.

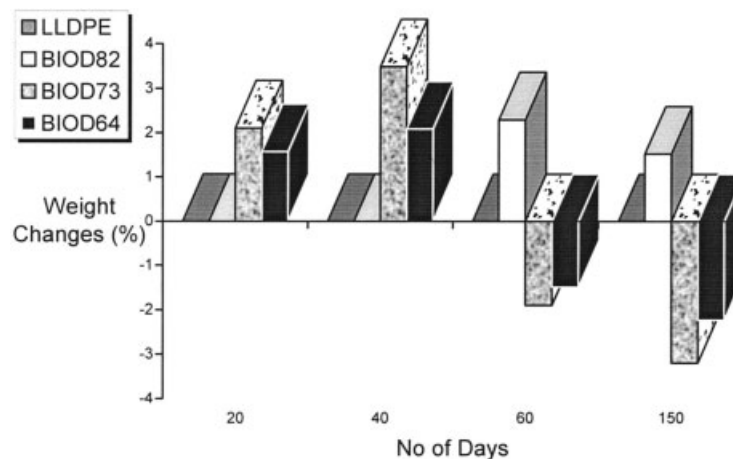


Figure 7 Variation in weight change of LLDPE and LLDPE/MDESMA blend samples kept under soil: BIOD64 ■, BIOD73 □, BIOD82 □, LLDPE ■

surements give an indirect method of knowing surface degradation/dissolution of these systems.

CONCLUSION

LLDPE was modified by blending with MDESMA to improve its environmental degradability. Tensile modulus improved on addition of MDESMA, whereas tensile strength and elongation at break showed a decline. Environmental degradation tests based on soil burial and contact-angle measurement revealed that BIOD64 and BIOD73 blends absorb water for the initial 40–50 days and thus show an increase in weight. Subsequently, these blends lose weight because of dissolution of MDESMA. However, BIOD82 showed much less and delayed water absorption, which is believed to be due to inaccessibility of MDESMA to soil or to buffer solution, because of a higher percentage of LLDPE in the blend. These degradation tests suggest that esterified SMA could be blended with

LLDPE to improve its waste management characteristics. Further studies in this direction are in progress.

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TABLE II
Contact Angles of LLDPE and Blend Samples

Sample No.	Contact angle	
	Before soil burial	After soil burial (150 days)
LLDPE	79.0 (0.5) ^a	77.0 (0) ^a
MDESMA	50.4 (0.5)	—
BIOD82	65.8 (0.6)	71.0 (3.6)
BIOD73	59.1 (2.0)	65.3 (3.7)
BIOD64	56.6 (2.0)	69.0 (4.0)

^a Values in parentheses indicate standard deviation.