

Development of Potentially Degradable Materials for Marine Applications. II. Polypropylene–Starch Blends

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SYNOPSIS

The effect of exposure of unstabilized polypropylene–starch blends, with or without a metal catalyst (e.g., cobalt (III) acetylacetonate), autooxidant (e.g., fatty acid), and a metal containing plasticizer (e.g., aluminum stearate) to the marine environment was studied for about six weeks at two different locations in New Jersey. Starch tends to absorb water. Unstabilized polypropylene degrades significantly during processing in air, as indicated by melt index values. Thus, for blends of unstabilized polypropylene–starch (no additives), prepared under controlled conditions and exposed to plain seawater, there seems to be no microbial activity or chemical degradation, as indicated by no surface erosion and practically no change in molecular weight and tensile properties. However, for unstabilized polypropylene starch blends containing metal catalyst, auto-oxidant, or plasticizer exposed under soft mud, surface erosion due to microbial activity is evident. In addition, chemical degradation due to the presence of degradative additives has been confirmed, as observed by a decrease in molecular weight and tensile properties. Changes in thermal characteristics of these blends after exposure to the marine environment have been studied.

INTRODUCTION

The presence of significant amounts of thermoplastic debris in the world's oceans is of great concern^{1–3} as it poses a hazard to marine life, including several protected species.⁴ Marine plastic debris consists of a predominant fishing-gear-related fraction⁵ and a smaller packaging-related fraction of plastics.⁶ As mentioned in our previous article⁷ in this series of development of degradable materials for marine applications, commercial fishing activities have created certain problems in the marine environment. Every year, fishing gear such as lobster pots and traps are lost or abandoned in the ocean, resulting in the possible loss of millions of entrapped creatures, which ultimately affects the economics of the fishing industry due to diminishing subsequent harvests. Our objective, therefore, is to develop degradable plastic materials that can be used in the assembly of fishing gear, specifically to fabricate

fasteners or ties, for holding one or more slats or panels on the traps. However, these materials would not be replacements for currently used plastic materials for marine applications except as mentioned above for fasteners and ties. The fasteners and ties fabricated from such materials are targeted to degrade within a reasonable time frame so as to open the traps by loosening the slats held by these fasteners.

Major pathways for degradation include (i) photodegradation, (ii) chemical degradation, (iii) attack by fungi and bacteria, and (iv) attack by invertebrates.⁸ For fishing gear or lobster pots and traps remaining under water, possible degradation routes⁹ are hydrolysis, chemical degradation, and slow biodegradation. Photodegradation is least likely to occur due to the absence of UV light at such depths. Therefore, the use of commercially available enhanced photodegradable polyethylene would not be suitable for this application.

Our attempts to develop marine degradable materials have centered around:

New degradable polymers
Modification of natural polymers

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Polymeric blends

Modifications of synthetic polymers.

Previously,⁷ we reported the effect of the marine environment on unstabilized polyethylene–starch and stabilized polyethylene–starch blends with or without a metal catalyst, autooxidant, and a plasticizer. In this paper, we consider the polymeric blends¹⁰ of unstabilized polypropylene–starch having varying starch content. The starch content is known to promote microbial degradation.¹⁰ Starch-based polyethylene films were formulated by Otey et al.^{11–14} and consisted of up to 40% starch. In 1973, Griffin^{15–17} introduced the concept of using corn starch as a filler to accelerate the degradation process. Maddever and Chapman^{18,19} discussed a method of rendering common polymers degradable through the use of a starch-based additive system. Cole and Wool et al.^{20–22} investigated the degradability of corn-starch-based polyethylenes and modeled the role of biodegradation by a (scalar) percolation theory. Based upon the work of Griffin,^{15–17} Archer Daniels Midland (ADM) Company developed a technology to make starch-based degradable plastics.

Even though a part of marine debris consists of well-stabilized, durable polypropylene components, the effect of the marine environment on unstabilized polypropylene and particularly its blends with starch has not been studied. In the present study, in addition to starch, a metal catalyst and an auto-oxidant to promote chemical degradation via the formation of peroxides have been included^{23,24} to achieve targeted disintegration of parts within a reasonable time frame. Various specimens from these formulations have been tested at two different locations in New Jersey.

The samples have been characterized before and after field testing with respect to any changes in sample weight, molecular weight, molecular weight distribution (MWD), morphology, and mechanical as well as thermal properties.

EXPERIMENTAL

The unstabilized polypropylenes, namely Profax 6501 [PP5] and Profax 6301 [PP3], were provided by Himont Company, U.S.A. Surface modified starch, Ecostar [ST], was received from St. Lawrence Starch Company, Canada. Aluminum stearate [AL] and cobalt (III) acetylacetonate [CO] were obtained from Strem Chemical, Inc., while fatty acid,

Industrene 4518 [FA], was from Humko Chemical Div., Witco Corporation. All materials were dried in vacuo at room temperature for at least 24 h prior to compounding.

A Haake-Buchler system 40 torque rheometer was used to prepare blends by melt mixing in air or nitrogen at 190°C and 60 rpm rotor speed. A total of 40 g vacuum-dried materials in varying ratios plus appropriate amounts of additives were blended for 9 min, removed immediately in the molten state, and cooled. All blends were then stored in a vacuum oven at room temperature until they were vacuum compression molded into sheets. The amount of either AL or FA and CO used was 1 and 0.5% by weight, respectively. Various formulations prepared are summarized in Table I.

All PP–ST blends thus prepared were vacuum compression molded into circular sheets of 5" diameter and about 50 mils thickness at 190.5°C (375°F) molding temperature. It may be noted here that the amount of sample required to obtain the same thickness of sheets increased as the starch content in the blend increased because the density of starch is higher than that of PP. The sheets were then cut into tensile test specimens of 2.5" length and 0.5" width (Dumbell shape, ASTM D638) by using a "Tensilkut" machine. Prior to field testing in the marine environment, all cut test specimens were measured for their thickness and width. The weights of all the samples were also recorded to monitor any weight change after exposure in the marine environment.

A Tinius Olsen tensile testing machine was utilized for tensile strength measurements at a testing speed of 2"/min with a gap separation of 1". A Carl-Zeiss optical microscope was used to observe any morphological changes, particularly on the surface, in reflectance mode under dark field with a polarizer

Table I Preparation of Polypropylene–Starch Blends

Series	Components	% Starch
G	PP5 : ST	0, 9, 15
H	PP5 : ST : AL : CO	0, 9, 15, 22, 30
I	PP3 : ST : AL : CO	15, 22
J	PP5 : ST : FA : CO	15

In identifying various batches of PP–ST blends, the number following the series letter (G, H, I, J) represents the percent starch by weight in a given batch. For example, batch H22 means that this batch contains 15% by weight starch along with other components (like unstabilized PP5, AL, and CO) as described above.

at magnification of 160. A Perkin-Elmer DSC-4 equipped with a System 4 Microprocessor Controller and a 3600 Data Station was utilized at a heating rate of 10°C/min and 20 cc/min N₂ flow rate to observe any changes in thermal behavior of the samples, particularly on the surfaces, before and after field testing. Isothermal DSC runs in N₂ and O₂ were also made to determine thermooxidative stability of virgin unstabilized PP. The DSC-4 was calibrated using Indium standard. A DuPont high-temperature GPC with Zorbax PSM bimodal columns (60S and 1000S) and an IR detector (3.45 μm) was utilized at 149°C. 1,2,4-Trichlorobenzene (TCB) was used as a mobile phase with a flow rate of 0.75 ml/min. A universal calibration method^{25,26} was used, employing narrow MW polystyrene standards. The solutions of surface cut samples were prepared at 140°C in TCB containing 0.2 wt % Irganox 1010 as the stabilizer. The dissolution time was kept to about 35–40 h to dissolve any aggregates that might have formed. The solutions were hot filtered through a Millipore type LSWG (5 μm) filter using a stainless steel Swinny filter unit prior to injection.

For field testing, a selected number of test specimens from each batch were tied 1–2" apart on a cable wire, the two ends being tagged with numbered aluminum plates for identification. These were kept in different plastic bottles with big holes cut in their walls, bottoms, and lids to allow free flow of seawater through them. The bottles were finally tied into a wooden cage for submerging. The field testing conditions at two different sites in New Jersey are listed in Table II. All samples from the field test were washed gently with cold tap water to remove any dirt, mud, and microbial deposits from the surface. The samples were then wiped and dried overnight in vacuo at room temperature and weighed. Any change in weight of samples from each batch (average of 4–6 specimens) before and after field testing was measured.

RESULTS AND DISCUSSION

To disintegrate PP-ST blends within 6–9 months in a marine environment, it is desirable to bring about chemical degradation of polypropylene by certain metal catalysts like cobalt (within the sample or in seawater) and autooxidants like corn oil or fatty acid, in addition to the possible biodegradation of the starch filler. According to Maddever and Chapman,¹⁹ for polyethylene-starch blends, degradation proceeds by two interactive mechanisms. Starch granules are attacked by microorganisms, such as fungi and bacteria (if present in seawater depending upon location), until they are completely consumed. This weakens the polymer matrix and greatly increases the surface area of the plastic. The second mechanism is a result of the formation of peroxides by the autooxidant when it comes into contact with metal salts present in seawater. These peroxides begin to degrade the polymer chain by an autooxidation mechanism in the presence of oxygen²⁴ in seawater. This second mechanism is tremendously enhanced by the increase in surface area provided by the first mechanism. Thus, overall, the material would degrade, the rate being dependent upon such factors as presence and type of microorganisms, temperature, presence of metal salts, concentration of polymer and active ingredients, polymer type, and the surface area and thickness of the article.

Preparation of Polypropylene-Starch Blends

As reported in our previous paper⁷ in this series, for stabilized polyethylene-starch blends exposed to the marine environment for six weeks in soft sludge, and coarse sand/shell (plain seawater) conditions at 59–86°F in the Gulf of Mexico locations, it was observed that there was practically no change in tensile properties and molecular weight. Thus, it was concluded that stabilized PE-ST blends, even in the

Table II Field Testing for PP-ST Blends (New Jersey Sites)

Batch	Exposure Time/Type	Depth (ft)	Temp. (°F)	Salinity (%)
G, GO (N ₂), GO (Air), G9, G15 ^a	36 d, coarse sand (plain seawater)	23–26	58–63	27
H22, H30, I15, I22, J15	36 days, soft mud	5–9	61–68	15–19

^a G, samples molded directly from virgin PP5 (no blending); GO (N₂), samples without starch molded after Haake run in N₂; GO (Air), samples without starch molded after Haake run in air.

presence of catalysts, would not degrade within 6–9 months in the severe marine environment. Perhaps it would take a long time before any significant degradation could be observed, since commercial stabilized polyethylenes are so formulated as to remain undegraded (to last) for many years. The same is true for commercial stabilized polypropylenes. Hence, in this study it was decided to investigate the effect of the marine environment on only unstabilized PP–ST blends. However, unstabilized PP is much more susceptible to thermooxidative degradation (during processing) than PE by virtue of the tertiary carbon on the backbone chain.

To examine the thermooxidative stability of unstabilized PP [both Profax 6501 (PP5) and 6301 (PP3)], isothermal DSC runs were made at 190°C in O₂ and 200°C in N₂. The comparative DSC scans for PP5 are shown in Figure 1, which clearly shows that in O₂ PP5 starts degrading instantly [almost zero oxidation induction time (OIT)], while in N₂ it shows no exothermic autoxidation up to 190 min, indicating that PP degrades more significantly in

O₂ than in N₂. PP3 showed similar behavior. This observation was further supported by the melt index (MI) measurements on virgin PP5 powder blended without any additives in a Haake machine at 190°C with 60 rpm rotor speed for 9 min in N₂ and in air. The MI in air (19.6 g/10 min) is much higher than in N₂ (4.8 g/10 min), again indicating significant degradation in air during processing. Thus, it was decided to prepare all PP–ST blends in N₂ during melt mixing in the Haake mixer. Compression-molded sheets of these blends were prepared in vacuo, so the only degradation possible is thermal degradation.

Field Testing: G-series Batches G, GO (N₂), GO (Air), G9, G15

The G-series blends (only PP5 and starch, no additives) were exposed for 36 d in coarse sand (plain seawater) having 27% salinity at 23–26' depth and temperature of 58–63°F at the New Jersey site. These samples showed no surface erosion after field

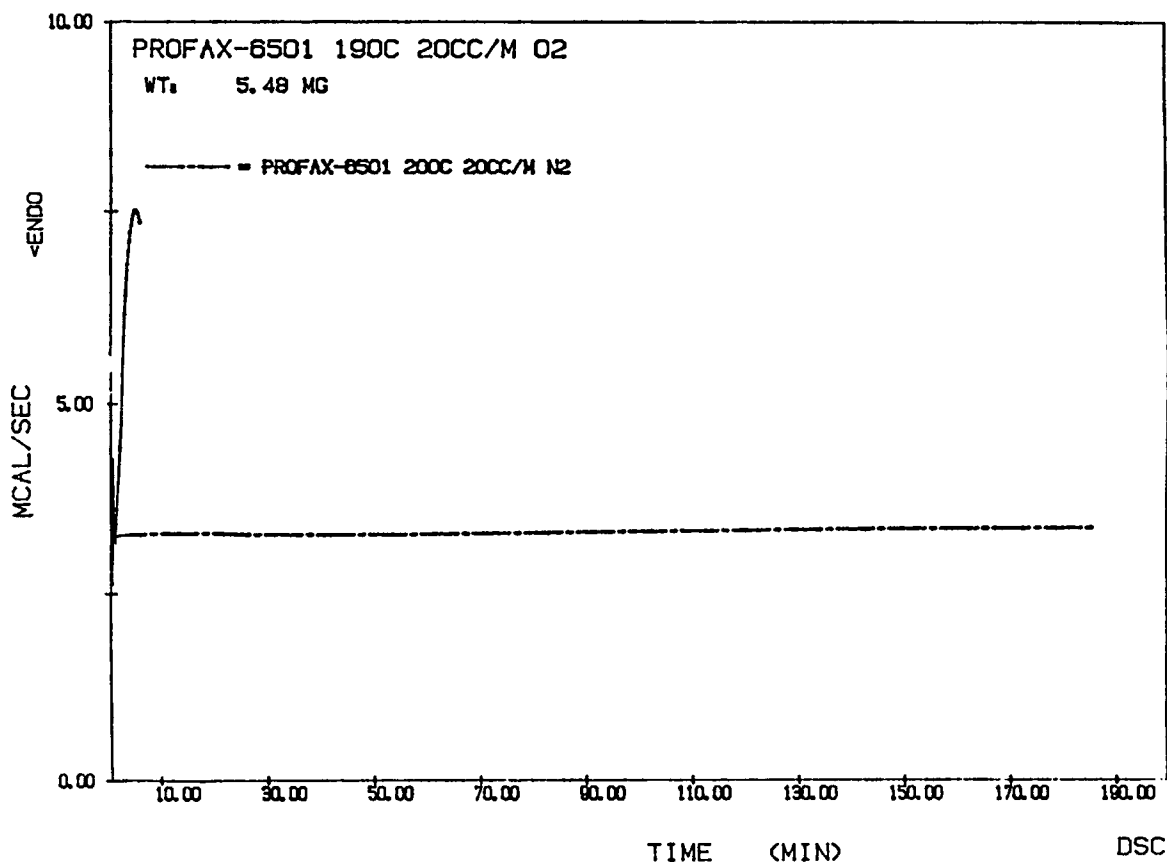


Figure 1 Isothermal DSC scans of unstabilized polypropylene (PP5) in (—) O₂ and (---) N₂.

Table III Percent Weight Change Data for PP-ST Blends

Batch	% wt Change
G (virgin PP5 powder)	+0.08
GO (N ₂)	+0.04
GO (Air)	+0.08
G9	+0.80
G15	+1.12
H22	-2.23
H30	-4.41
I22	-2.17
J15	-2.32

testing. Table III shows % wt change data for these samples after field testing. As observed from Table III, there is a weight gain, which increases with the starch content, indicating the tendency of starch to absorb water. Table IV shows for these samples practically no change in tensile strength and percent elongation. Typical DSC curves for the surface of sample G15 before and after field testing are shown

Table IV Tensile Data for PP-ST Blends

Batch	Tensile Strength (psi)		% Elongation	
	Before	After	Before	After
G	5,532	5,569	20.3	53.5
GO (N ₂)	5,616	5,529	12.7	10.0
GO (Air)	5,345	5,252	9.5	13.2
G9	4,894	4,889	18.5	21.4
G15	4,439	4,322	12.7	13.8
H22	1,660	1,202	2.4	1.7
H30	1,624	942	1.9	0.7
I15	1,809	1,326	1.7	0.9
I22	1,658	1,245	1.5	0.5
J15	2,937	1,810	2.9	1.7

in Figure 2, which also show practically no changes in thermal characteristics after field testing.

As listed in Table V, there is practically no change in MW of sample G15 before and after field testing. However, it should be noted here that even though

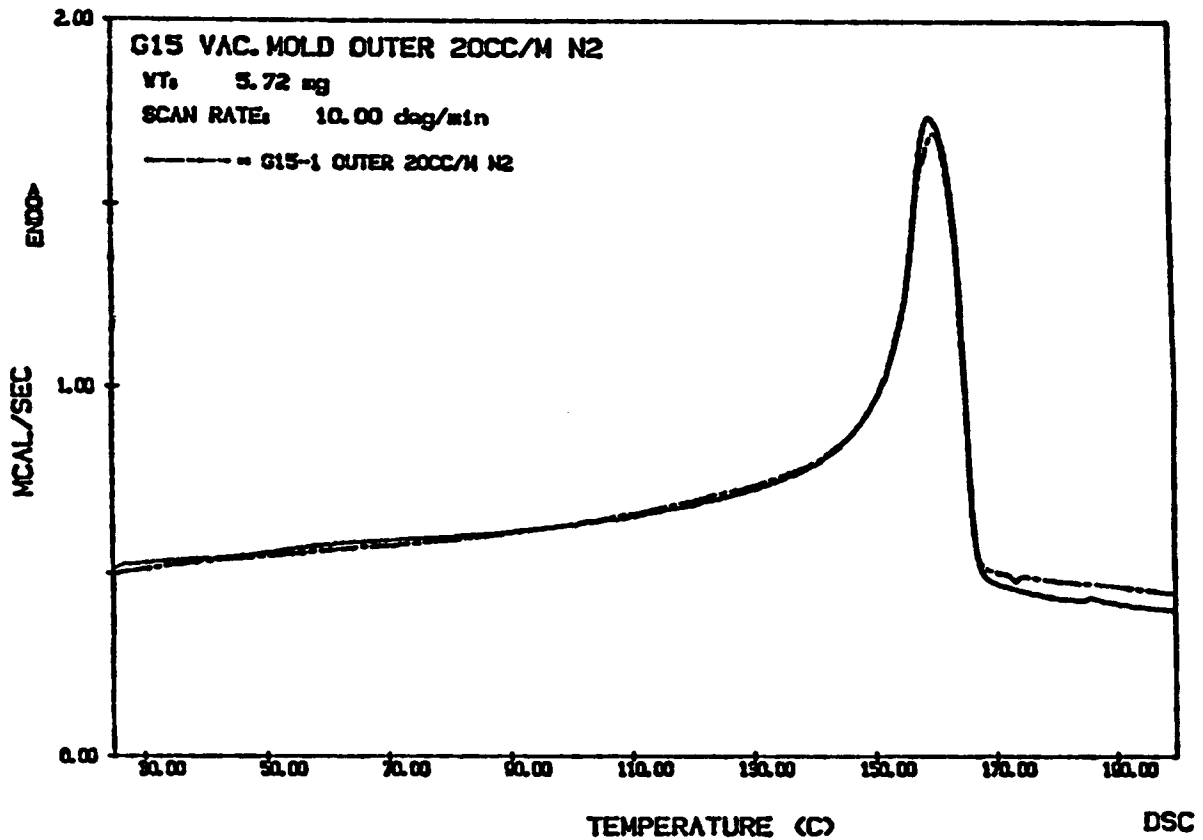
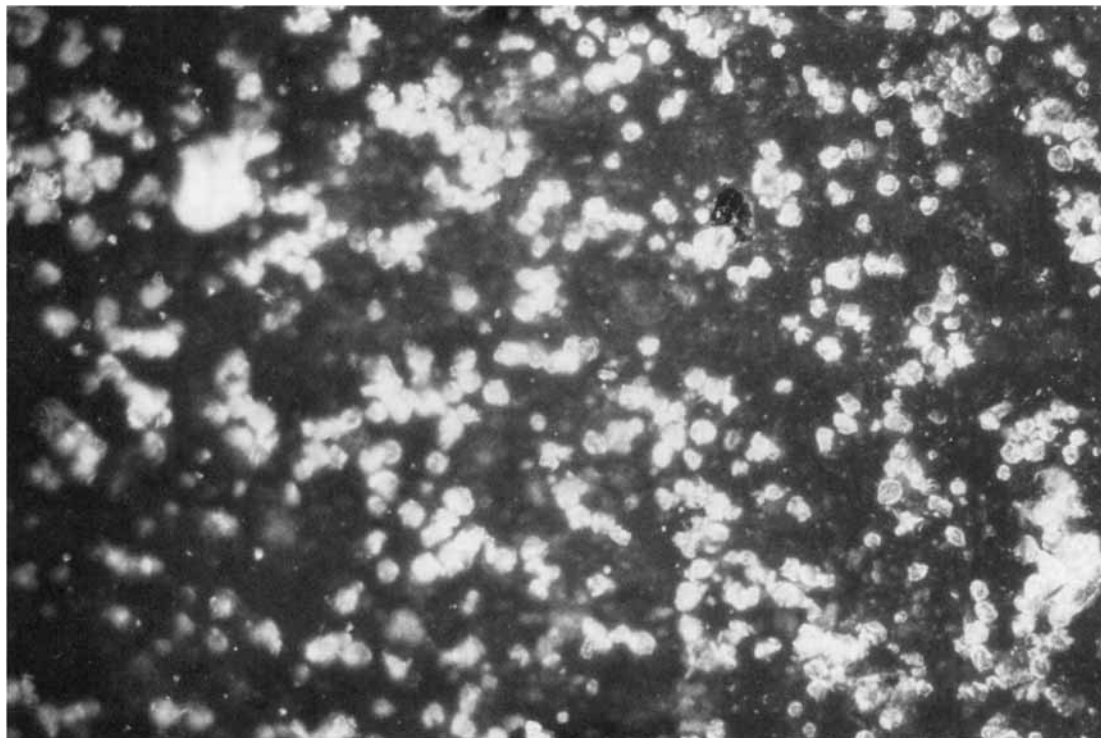
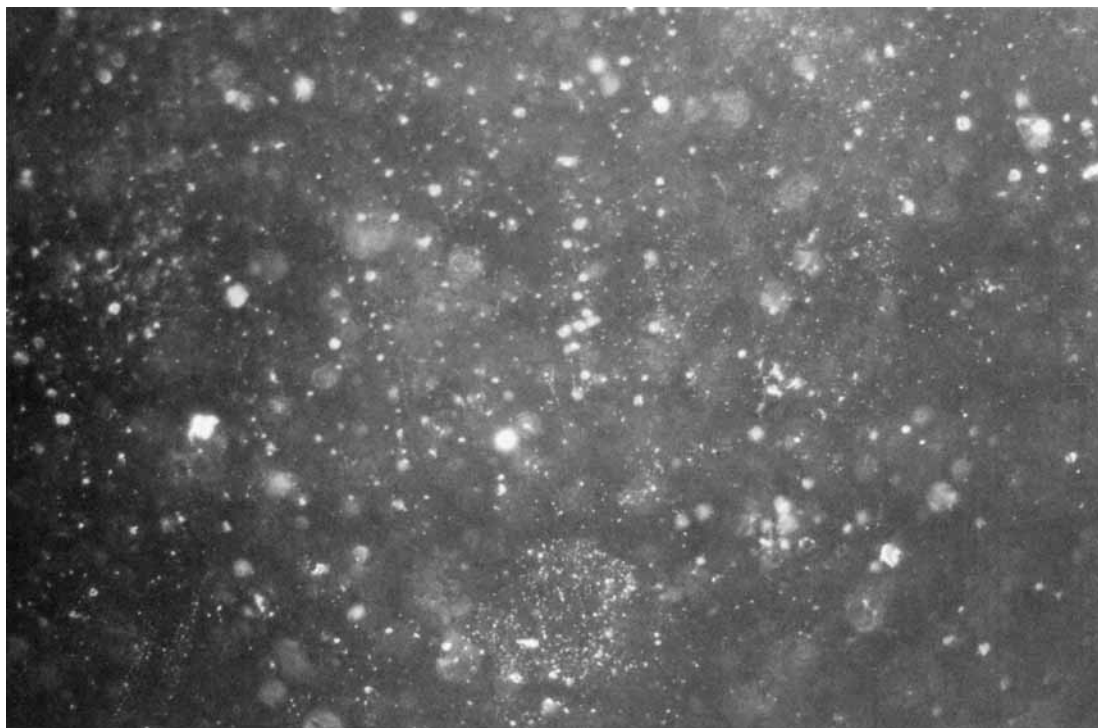


Figure 2 DSC thermograms of surfaces of sample no. G15, (—) before and (---) after field testing.



(A)



(B)

Figure 3 Optical micrographs of the surface of sample no. G15, (A) after and B (before) field testing (NJ site) ($\times 160$).

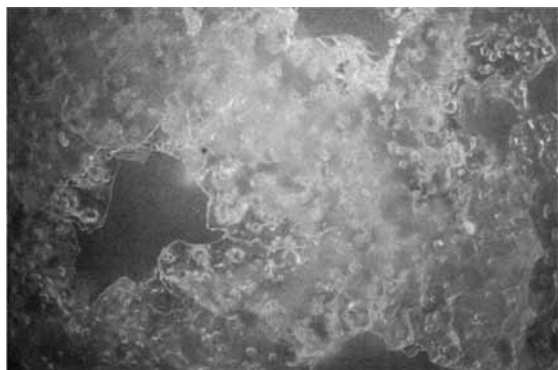
Table V GPC Data for PP-ST Blends

Batch ^a	M _w	M _n	M _w /M _n
G (PP5 powder)	254,400	68,400	3.72
G15 (B)	202,401	43,600	4.64
G15 (A)	199,500	45,200	4.41
H22 (B)	107,700	22,500	4.79
H22 (A) ^b	104,000	20,200	5.16
H30 (B)	126,900	20,500	6.2
H30 (A)	115,900	20,700	5.6
I15 (B)	177,300	32,400	5.47
I15 (A)	87,400	22,700	3.85
I22 (B)	97,600	20,800	4.7
I22 (A)	88,900	23,700	3.75
J15 (B)	195,200	27,800	7.0
J15 (A)	116,600	19,500	5.97

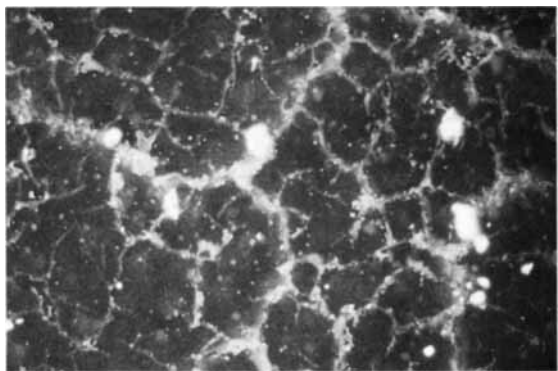
^a B, before field testing; A, after field testing.

^b Bulk sample; remainder are cut from the surface.

these blends were prepared under N₂ there seems some thermal degradation during processing as the MW of these blends is lower than unprocessed G (PP5 powder). Typical optical micrographs of the

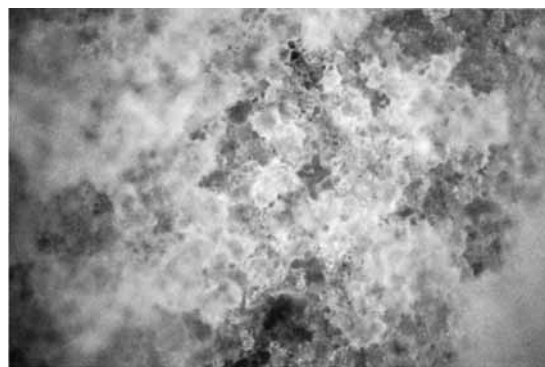


(A)

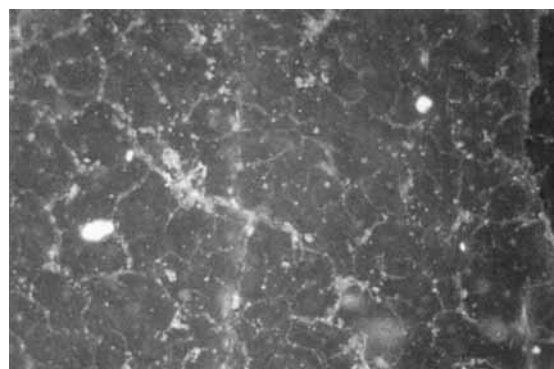


(B)

Figure 4 Optical micrograph of the surface of sample no. H22, (A) after and B (before) field testing (NJ site) ($\times 160$).



A



B

Figure 5 Optical micrograph of the surface of sample no. H30, (A) after and B (before) field testing (NJ site) ($\times 160$).

surface of sample G15 before and after field testing are shown in Figure 3. As can be seen from this figure, no cracks were observed on the surface before or after field testing. However, the surface after field testing shows more and bigger starch granules on the surface. It should also be mentioned here that, from Table IV, sample GO (Air) shows lower tensile strength and percent elongation than GO (N₂), which confirms that GO (Air) has degraded during mixing.

The G-series samples are the blends of only PP and starch with no autooxidant or metal catalyst. Based upon the above-mentioned observations, it appears at this point that there could be none or very little microbial action or chemical degradation of these samples under plain seawater.

Field Testing: H, I, J Series

The H, I, J Series blends (batches H22, H30, I15, I22, and J15) were exposed for 36 d in soft mud having 15–19% salinity at 5–9' depth and temperature of 61–68°F at the New Jersey site. From Table III it is interesting to note that there is a significant

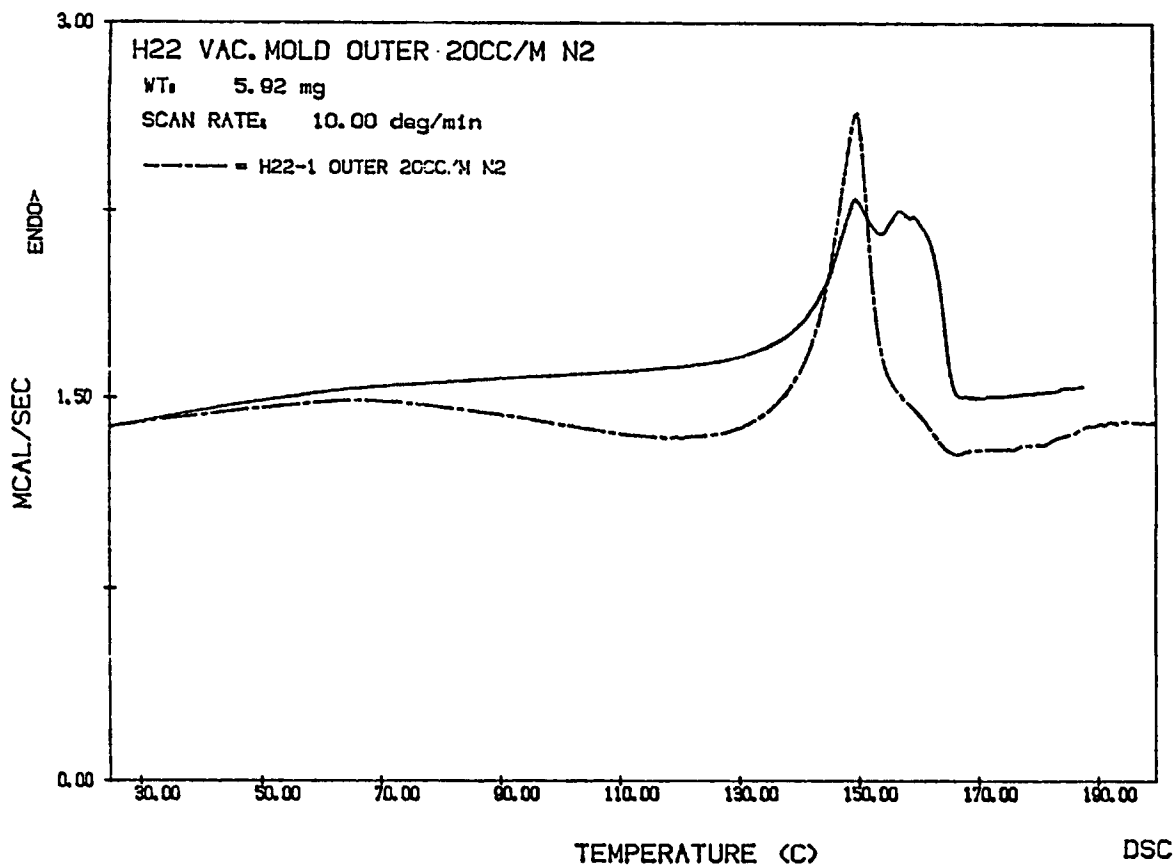


Figure 6 DSC thermograms of the surfaces of sample no. H22, (—) before and (---) after field testing (NJ site).

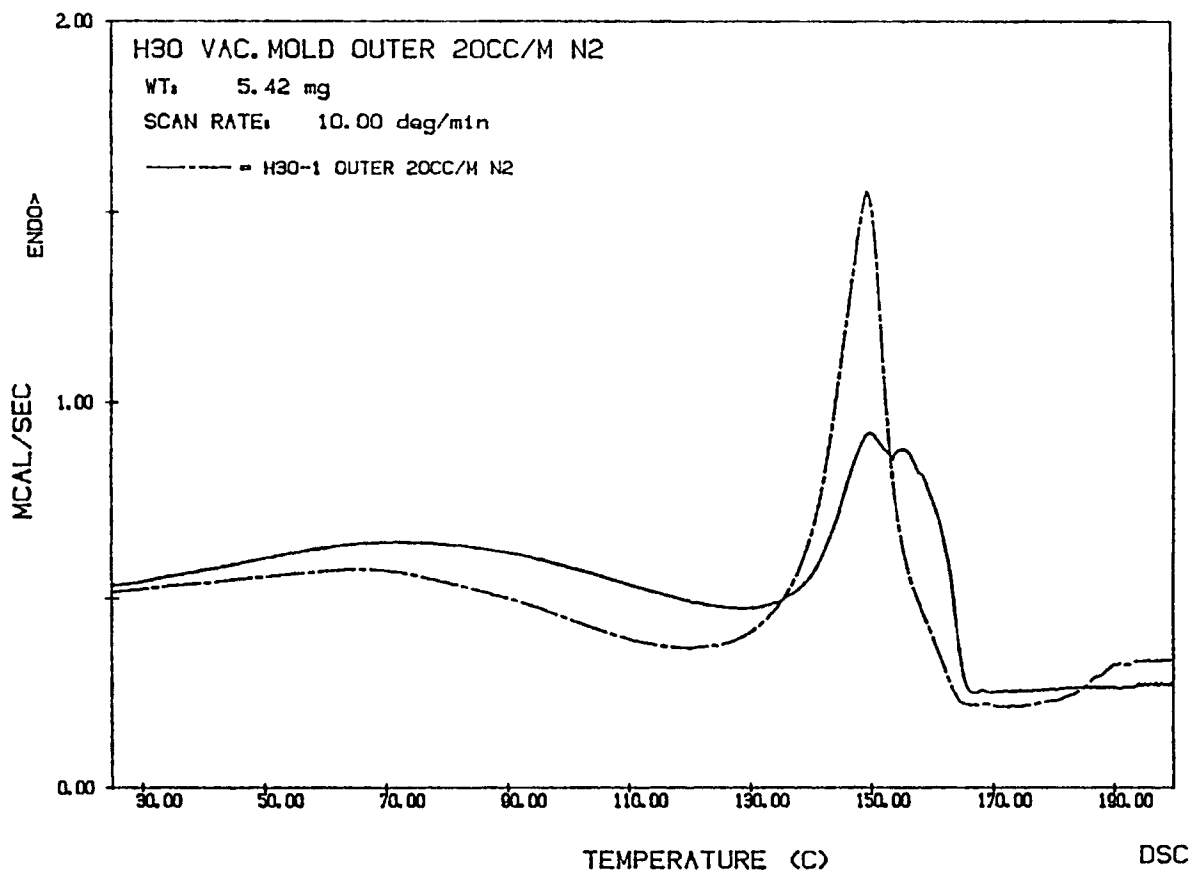


Figure 7 DSC thermograms of the surfaces of sample no. H30, (—) before and (---) after field testing (NJ site).

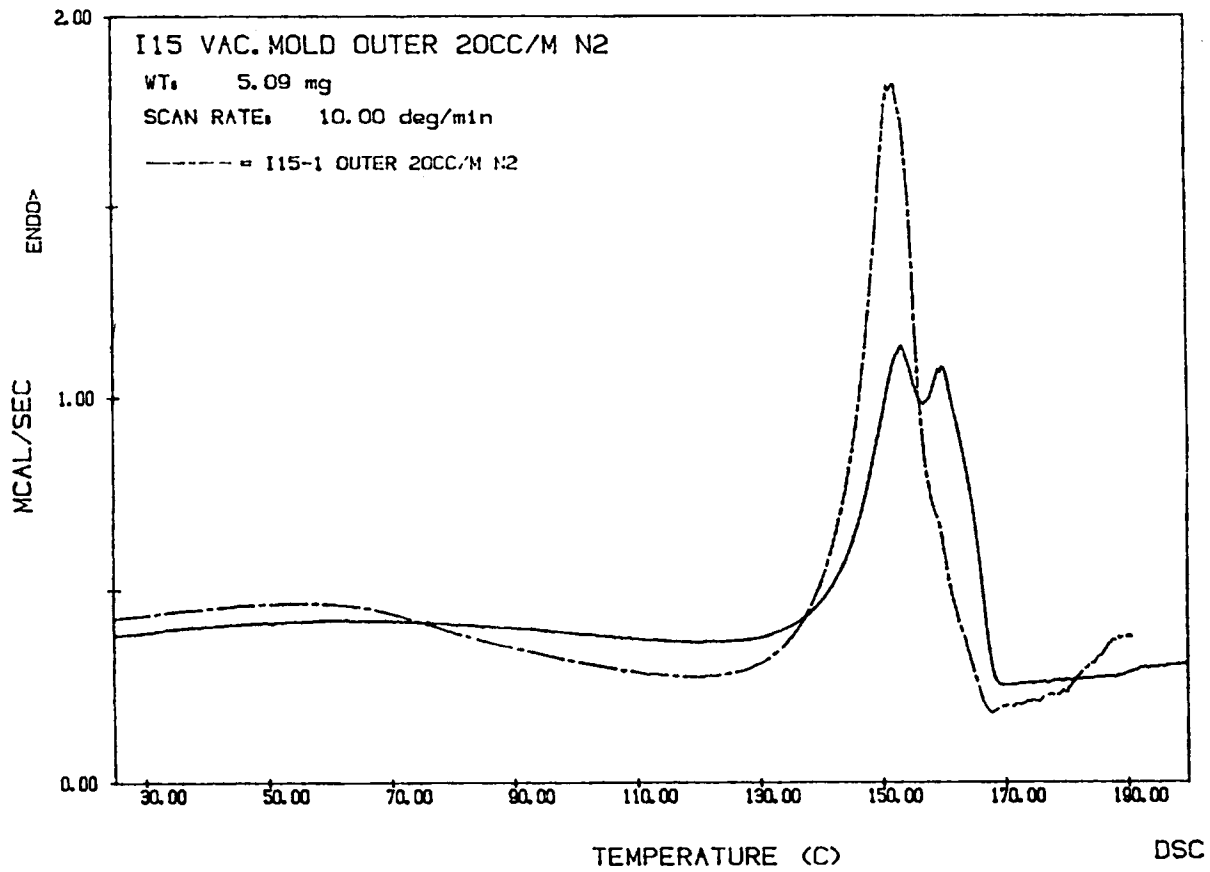


Figure 8 DSC thermograms of the surfaces of sample no I15, (—) before and (---) after field testing (NJ site).

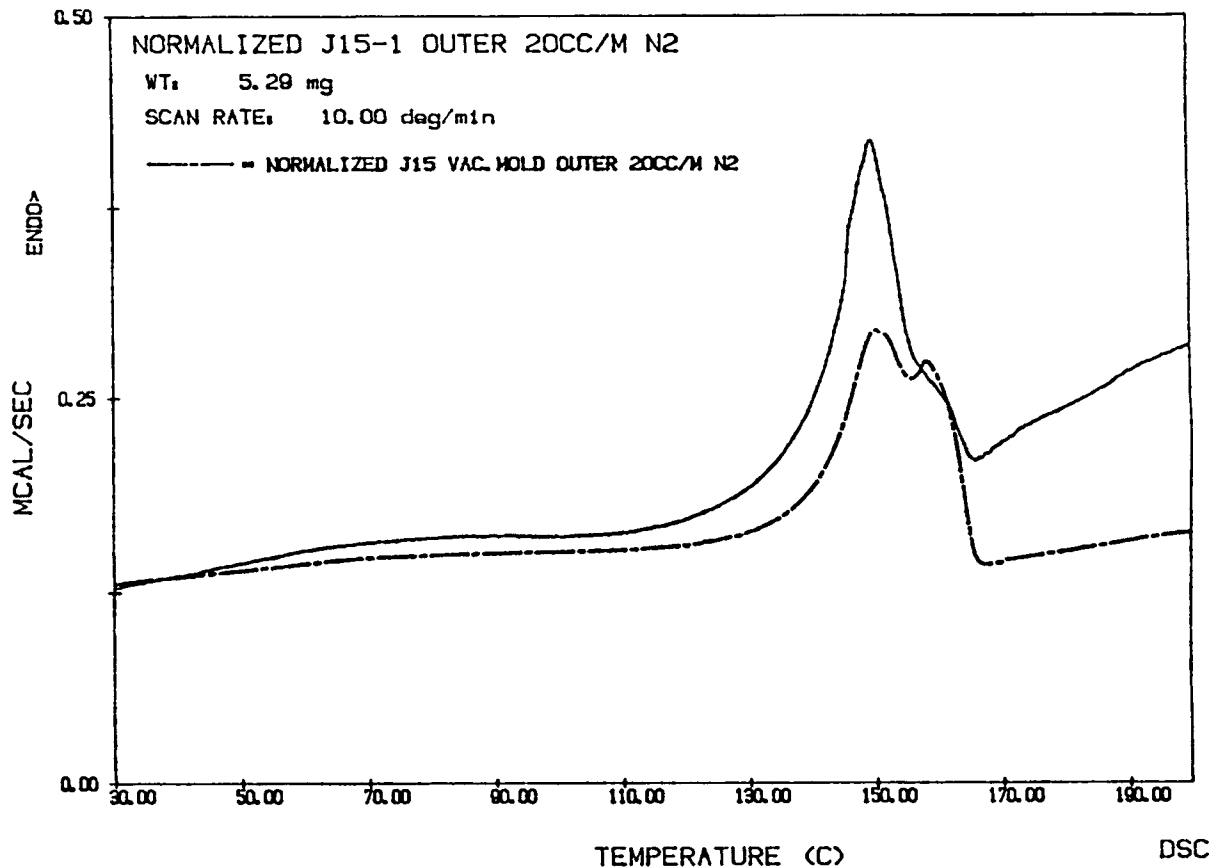


Figure 9 DSC thermograms of the surfaces of sample no J15, (—) before and (---) after field testing (NJ site).

weight loss during this short exposure in soft mud in contrast to C-series⁷ (PE-ST) and G-series N.J. samples exposed to plain seawater. These samples (H, I, J series) were discolored and eroded at many spots on the surface, indicating probable high microbial activity in soft mud due to the presence of starch. This seems to confirm that there could be no or little microbial activity in plain seawater as compared to that in soft mud. Table IV shows a significant drop in tensile properties of these samples. They also show a significant drop in MW in Table V. It may be noted that there was a significant drop in MW during processing, in the presence of autooxidant and metal catalyst, as the MW of unprocessed PP5-powder (G) is very high when compared to its blends.

Figures 4 and 5 show typical optical micrographs of the surfaces before and after field testing for samples H22 and H30, respectively. As can be seen from these figures, the surfaces before testing show microcracks that are absent on PE-ST (C and D-series⁷) blends. However, both samples H22 and H30 after field testing show a dramatic change on the surface with macrocracks, voids, and starch granules coming out quite clearly. Typical DSC curves for the surfaces of sample S H22, H30, I15, and J15 before and after field testing are compared in Figures 6, 7, 8, and 9, respectively, which show a significant change in thermal characteristics after field testing. The low melting peak before testing could be due to lowering of MW of PP during processing and the starch could be acting as a plasticizer, thereby lowering the melting point. After the field testing, the high melting peak appears only as a small shoulder while a low melting peak predominates. This may be due to a decrease in MW and change in crystallinity. Considering all these observations, it appears that the extent of microbial activities depends upon the location.

CONCLUSIONS

As unstabilized PP degrades appreciably during processing in air by virtue of its tertiary carbon, PP-ST blends should be prepared in inert atmosphere like N₂. Starch tends to absorb water. In the absence of any microbial activity (as observed in plain seawater), starch does not seem to play any role in bringing about the disintegration of the samples. However, in the presence of high microbial activity (like in soft mud/sludge), it could play an important role. Again, the extent of microbial activity varies with location. In absence of any additives (like MC, AO, or PL), unstabilized PP did not show any sig-

nificant chemical degradation in the marine environment. Hence, to bring about significant degradation within 6-9 months a metal catalyst like cobalt, an autooxidant like a fatty acid, and a metal containing plasticizer like aluminum stearate are desirable. As was the case with PE-ST blends,⁷ cobalt appears to be an effective catalyst for chemical degradation of PP in the marine environment. As there might be none or little microbial activity at certain locations (as observed at two different N.J. locations), the use of polymeric formulations having hydrolyzable groups along the backbone chain or slow dissolving water-soluble polymers are highly desirable.²⁷

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