# Development of Potentially Degradable Materials for Marine Applications. III. Polyethylene-Polyethylene Oxide Blends*

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## SYNOPSIS

The effect of a simulated marine environment on unstabilized polyethylene–polyethylene oxide blends, having varying polyethylene oxide content (up to 40% by weight), with or without a metal catalyst (e.g., cobalt (III) acetylacetonate) and a metal containing plasticizer (e.g., aluminum stearate), has been studied for 10 weeks exposure time. In the absence of metal catalyst and plasticizer, phase separation of polyethylene oxide was quite evident visually after melt mixing and subsequent regular compression molding of polyethylene–polyethylene oxide blends. However, these blends rendered better and uniform mixing in the presence of metal catalyst and plasticizer. Since polyethylene oxide is a water soluble component of the system, % weight loss increased significantly with increase in its content after exposure to brine. These blends have been further characterized by tensile properties, optical and scanning electron microscopy, and thermal analysis in order to monitor mechanical as well as morphological changes.

## INTRODUCTION

In our previous articles,[1,2] we have described the need for developing degradable materials for marine applications, such as in the assembly of fishing gear, specifically to fabricate fasteners or ties for holding one or more slats or panels on the lobster pots or traps. However, these materials would not be replacements for the currently used plastics or other (wood) materials for marine applications, except as mentioned above for fasteners and ties. These materials are targeted to degrade within a reasonable time frame so as to open up the traps by loosening the slats held by the fasteners made from the materials. Thus, our attempt here is to address one of many problems related to marine debris,[3–8] which has been of great environmental concern recently.

Various pathways by which degradation can occur include, (i) photodegradation, (ii) chemical degradation, (iii) attack by fungi and bacteria, and (iv) attack by invertebrates.[9] For fishing gear or lobster pots and traps remaining under water, the possible degradation routes[10] are hydrolysis, chemical degradation, and/or slow biodegradation. Photodegradation is least likely to occur because of the absence of UV light at such depths where most of the pots and traps are being lost or abandoned. 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, modifications of natural polymers, polymeric blends, modifications of synthetic polymers.

Previously,[1,2] we have reported the effect of the marine environment on both unstabilized and stabilized polyethylene–starch and unstabilized polypropylene–starch blends having varying starch content, with or without a metal catalyst, auto-oxidant, and a plasticizer. The starch content is known to promote microbial degradation.[11] Starch based polyethylene films were formulated by Otey et al.[12–15]

and consisted of up to 40% starch. In 1973, Griffin[16-18] introduced the concept of using corn starch as a filler to accelerate the degradation process. Maddever and Chapman[19,20] have discussed a method of rendering common polymers degradable through the use of a starch-based additive system. Wool et al.[21-23] investigated the degradability of corn starch-based polyethylenes and modeled the role of biodegradation by a (scaler) percolation theory. Based upon the work of Griffin,[16-18] ADM (Archar Daniels Midland) Company has developed a technology to make starch-based degradable plastics.

In this paper, we consider the polymeric blends of unstabilized polyethylene–polyethylene oxide as having varying polyethylene oxide content. In our earlier work,[1,2] it was noticed that there could be very little or no microbial activity, for example, in plain sea water as compared to sludge/soft mud, depending upon the location. Therefore, at such locations (no microbial activity) starch played no role in biodegradation (by not being consumed by microorganisms). It was also observed in the case of stabilized polyethylene–starch blends[1] that there was appreciable degradation even in the sludge and relatively warmer ocean conditions of the Gulf of Mexico. In light of the above considerations, it was decided to use polyethylene oxide, a water soluble polymer. Upon exposure to water, polyethylene oxide would leach out of the polyethylene and leave a honeycomb-type structure that could crumble more easily than polyethylene. In the present study, in addition to polyethylene oxide, a metal catalyst and a metal containing plasticizer to promote chemical degradation via the formation of peroxides, have also been included[24,25] in order to achieve the targeted disintegration of parts within a reasonable time frame. The samples have been characterized before and after field testing with respect to any changes in sample weight, morphology, and mechanical as well as thermal properties.

## EXPERIMENTAL

The unstabilized low density polyethylene, namely DYNH-1 [PE], and two different grades of polyethylene oxide, viz., POLYOX WRPA-3154 [PEOW] and POLYOX WSRP N750 [PEON], were provided by Union Carbide. Aluminum stearate [AL] and cobalt(III) acetylacetonate [CO] were obtained from Strem Chemical Inc. All the materials were dried under vacuum at room temperature for at least 24 h prior to compounding.

A Haake–Buchler System-40 torque rheometer was used to prepare PE–PEO blends, with and without aluminum stearate [AL] and a cobalt catalyst, by melt mixing in air at 150°C and 50 rpm rotor speed. A total of 40 gms of vacuum dried (for at least 24 h at room temperature) PE and PEO in varying ratios, plus an appropriate amount of additives were blended for 9 min, removed immediately in the molten state, and were cooled. All the blends were stored in a vacuum oven at room temperature, until they were compression molded into sheets. The amount of aluminum stearate and cobalt(III) acetylacetonate used was 1% and 0.5% by weight, respectively. Various formulations prepared are summarized in Table I.

A Carver press was utilized to prepare compression molded sheets of about 45–50 mils thickness from these batches of blends. An appropriate amount of a given blend sample was cut into small pieces using a cutter. The sample then was placed into a rectangular stainless steel mold (4 in. × 2.5 in. × 0.05 in.), having a Mylar (polyester) film as an upper and lower covering, ultimately being held between two aluminum plates with a smooth, flat surface. These plates (containing the sample in the mold between Mylar films) were then placed between the plates of the Carver press, preheated to 145°C, held there for 1.5 min in order to melt completely the sample; the pressure was then increased to 20,000 psi and was held there for another 4 min. The molded sample was then cooled down to room temperature by cold water passing through the plates of the press. It may be noted here that since the density of PEO was more than PE, the amount of sample required to fill out the mold completely (plus a little extra) was increased as the PEO content in the blend increased.

The regular compression molded sheets of PE–PEO blends were cut into tensile test specimens (Dumbbell shape, ASTM D 638) by using a "Ten-

**Table I  Preparation of Polyethylene [Pe]–Polyethylene oxide [PEO] Blends**

| Series | Components | % PEO |
| --- | --- | --- |
| A | PE | 0 |
| B | PE : PEOW | 10, 20, 30 |
| C | PE : PEOW : Al : Co | 10, 20, 30, 40 |
| D | PE : PEON : Al : Co | 10, 20, 30, 40 |

NOTE: In identifying various batches of PE–PEO blends, the number following the series letter (B, C, D) represents the % PEO by weight in a given batch. For example, batch D-30 means that this batch contains 30% by weight PEON along with other components (such as 1% and 0.5% by weight Al and Co respectively) as described above.

silkut" (International Electronics, Co.) machine. Prior to making test specimens, the sheets were cut into bars of 2.5 in. in length and 0.5 in. in width by using a two sided cutter with 0.5 in. bar width. Typical dimensions of the test specimens prepared were Length = 2.5 in., width at center = 0.230 in. and thickness = 0.050 in. All the test specimens cut were measured for their thickness and width at the center. The weights of all the samples were also recorded in order to monitor any weight loss after testing under aqueous conditions. Four samples from each batch were tied 1–2 in. apart from each other on a cable wire, one end being tagged with an aluminum plate for identification. The samples thus tied were kept in a stirred tap water bath with 10% salinity at room temperature.

After 10 weeks, all the samples from the saline solution were washed with cold tap water in order to remove any salt deposits from the surface. The samples were then wiped, dried for one week under vacuum at room temperature, and weighed. Any change in the weight of samples from each batch, before and after the treatment, was noted.

A Tinius Olsen tensile testing machine was utilized for tensile strength measurements at a testing speed of 2 inch/min with a gap separation of 1 inch for PE–PEO samples. The measurements were made on 4–6 specimens from each batch and the average value of tensile strength was considered.

A Carl–Zeiss optical microscope was used to observe any morphological changes, particularly on the surface, in reflectance mode under bright field at magnification of 160. Scanning electron microscopy (SEM) micrographs of a typical sample were also taken on SEM JSL-840 JEOL. 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 $N_2$ flow rate to observe any changes in thermal behavior of the samples, on the surface and in the bulk as well. The DSC-4 was calibrated using the Indium standard. A Tinius Olsen Extrusion Plastometer, model UE-4-78, was utilized for Melt Flow Index (MFI) measurements on some typical batches of PE-PEO blends to understand their rheological behavior.

## RESULTS AND DISCUSSION

To achieve disintegration of PE–PEO blends within 6–9 months in the marine environment, it is desirable to bring about chemical degradation of polyethylene by certain metal catalysts, such as cobalt (within the sample or in sea water), auto-oxidants,

such as corn oil or fatty acid, and/or a metal containing plasticizer, such as aluminum stearate, in addition to the possible leaching out of PEO from the blend. According to Maddever and Chapman,[20] for polyethylene–starch blends, degradation proceeds by two interactive mechanisms. Starch granules are attacked by microorganisms, such as fungi and bacteria (if present in sea water, 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 auto-oxident when it comes into contact with metal salts present in sea water. These peroxides begin to degrade the polymer chain by an auto-oxidation mechanism in the presence of oxygen[25] present in sea water. 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, the surface area and thickness of the article.

As mentioned earlier, water soluble PEO would leach out easily from a PE–PEO blend exposed to the marine environment, regardless of the presence or absence of microbial activity. This would weaken the PE matrix, and also would provide the increased surface area needed for the second mechanism described above. Moreover, PEO disposed in water streams is plausible, since it is completely water-soluble and does not have any measurable biological oxygen demand, and possesses a low degree of oral, skin, or eye toxicity (as tested on rats or rabbits).[26] Also, both PE and PEO are flexible materials and are suitable for injection molding of flexible fasteners or ties to suit the needs of the present application.

### Preparation of PE–PEO Blends

As reported in an earlier article in this series,[1] for stabilized PE–Starch blends exposed to the marine environment for six weeks in soft sludge, and coarse sand/shell (plain sea water) 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–Starch blends, even in the presence of catalysts, would not degrade within 6–9 months in the severe marine environment. Perhaps it would take a very long time before any significant degradation could be observed, since commercial stabilized polyethylenes are so formulated as to remain
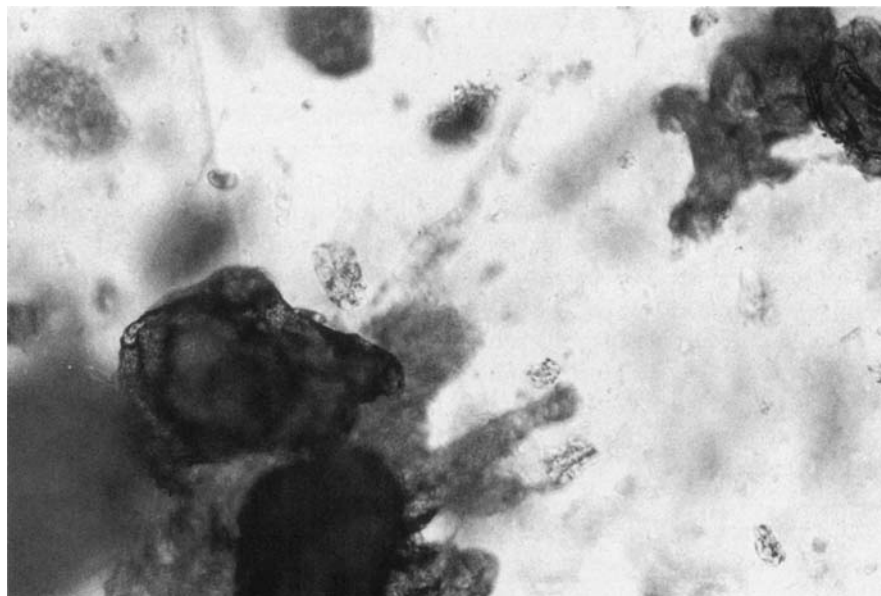
**Figure 1**  Optical micrograph of the surface of sample #B-10 showing phase separation of PEO (large agregates) in PE matrix blended at 120°C and 45 rpm, then compression molded at 145°C (×63).

undegraded (to last) for many years. Hence, in this study the effect of the simulated marine environment on only unstabilized PE–PEO blends was investigated.

In order to avoid or minimize bleeding of low melting PEO ($65 \pm 2°C$), initial trials to blend PE and PEOW were made at 120°C and 45 rpm rotor speed. However, phase separation was quite evident visually under these experimental conditions after melt mixing in Haake torque rheometer or subsequent compression molding at 145°C. Hence, final blends were prepared at 150°C and 50 rpm rotor speed, resulting in better mixing. In the presence of AL and CO, much better mixing of blends was observed.

Figure 1 shows an optical micrograph of the surface of sample #B-10 (PE–PEOW :: 90 : 10 by wt) that was blended at 120°C and 45 rpm, followed by compression molding at 145°C. Phase separation of PEOW (large aggregates) in PE matrix is quite evident from Figure 1. However, the optical micrograph of the surface of sample #C-10 (PE–PEOW : Al : Co :: 90 : 10 : 1 : 0.5 by wt), as shown in Figure 2, prepared at 150°C and 50 rpm followed by compression molding at 145°C, clearly shows much better dispersion of the components with no visual phase separation. This is probably due to polar interactions between PEO and carbonyl groups formed by oxidation of unstabilized PE during processing

(blending and compression molding) in air in the presence of metal catalysts such as cobalt and aluminum.[24–29] It should be noted here that commercial grade PEOW and PEON resins are stabilized against rapid oxidative degradation during thermoplastic processing conditions of 100–150°C.[30] Another probable explanation for better mixing of PEO with PE in the presence of catalysts such as cobalt and aluminum would be the fact that PEO resins have high binding efficiency for pigments, fillers, and metal powders[31] (as do CO and AL), and they form association compounds with a wide variety of materials including polymeric acids[27] (as do the ones that might have been formed during oxidation of unstabilized PE).[24,25]

Table II compiles the typical melt flow index data for PEOW, with and without Al and Co, and D-series blends after melt mixing in an Haake torque rheometer. It can be seen that PEOW, with or without AL and CO, had a very low MFI value, indicating poor flow characteristics. The Melt Flow Index value for PEOW with AL and CO is even smaller than for PEOW alone, probably due to crosslinking predominating over little degradation of stabilized PEOW. However, in the case of the D-series PE–PEOW blends, the MFI value increased with the increase in PEON content. This could be due to the increase in the lubrication effect of low melting PEON with an increase in its content.
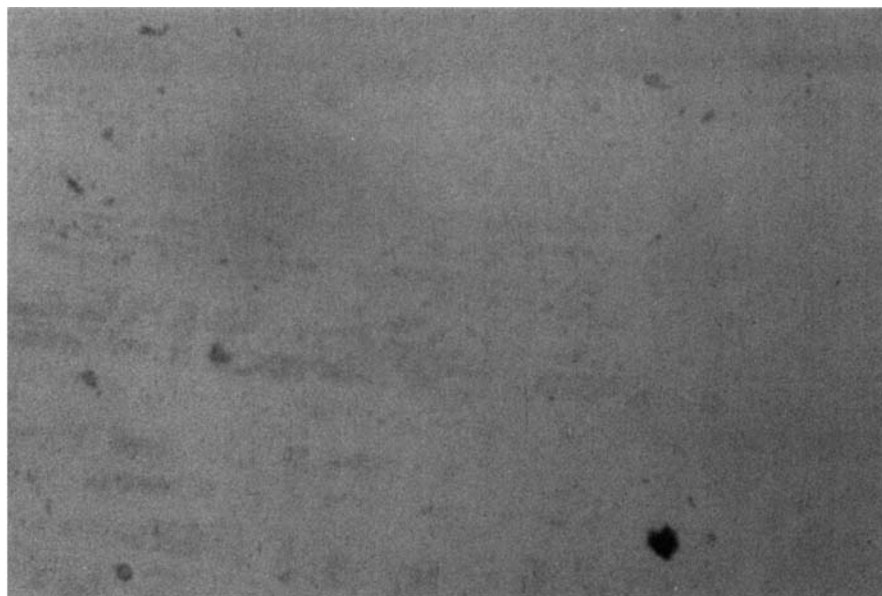
**Figure 2** Optical micrograph of the surface of sample #C-10 showing uniform mixing of the PE–PEOW blend, prepared at 150°C and 50 rpm, then compression molded at 145°C (×63).

**Table II  Melt Flow Index (MFI) Data for PE–PEO Blends at 190°C**

| Sample | Melt Flow Index (g/10 min) |
| --- | --- |
| PEOW (neat) | 0.44 |
| PEOW (with AL, CO) | 0.06 |
| PE | 2.21 |
| D-10 | 2.70 |
| D-20 | 4.18 |
| D-30 | 19.04 |

**Table III  % Weight Loss Data for PE–PEO Blends**

| Batch | % Weight Loss (Avg.) |
| --- | --- |
| A (Pure PE) | 00.00 |
| B-10 | 1.8 |
| B-20 | 3.76 |
| B-30 | 11.65 |
| C-10 | 0.23 |
| C-20 | 0.24 |
| C-30 | 11.04 |
| C-40 | 27.36 |
| D-10 | 0.19 |
| D-20 | 0.85 |
| D-30 | 16.36 |
| D-40 | 26.40 |

## Simulated Marine Environment Testing of PE–PEO Blends

Various batches of PE–PEO blend samples, as listed in Table I, were exposed to a simulated marine environment (stirred tap water bath with 10% salinity) at room temperature for 10 weeks. Table III lists wt % loss data for these samples. As can be expected,

**Table IV  Tensile Strength Data for PE–PEO Blends**

| Batch | Tensile Strength (psi) at Break | |
| --- | --- | --- |
| | Before | After[a] |
| A (pure PE) | 1464 | 1362 |
| B-10 | 1300 | 1219 |
| B-20 | 1190 | 997 |
| B-30 | 895 | 654 |
| C-10 | 1254 | 1214 |
| C-20 | 1032 | 1027 |
| C-30 | 900 | 794 |
| C-40 | 749 | 447 |
| D-10 | 1210 | 1166 |
| D-20 | 1198 | 1101 |
| D-30 | 725 | 646 |
| D-40 | 563 | 436 |

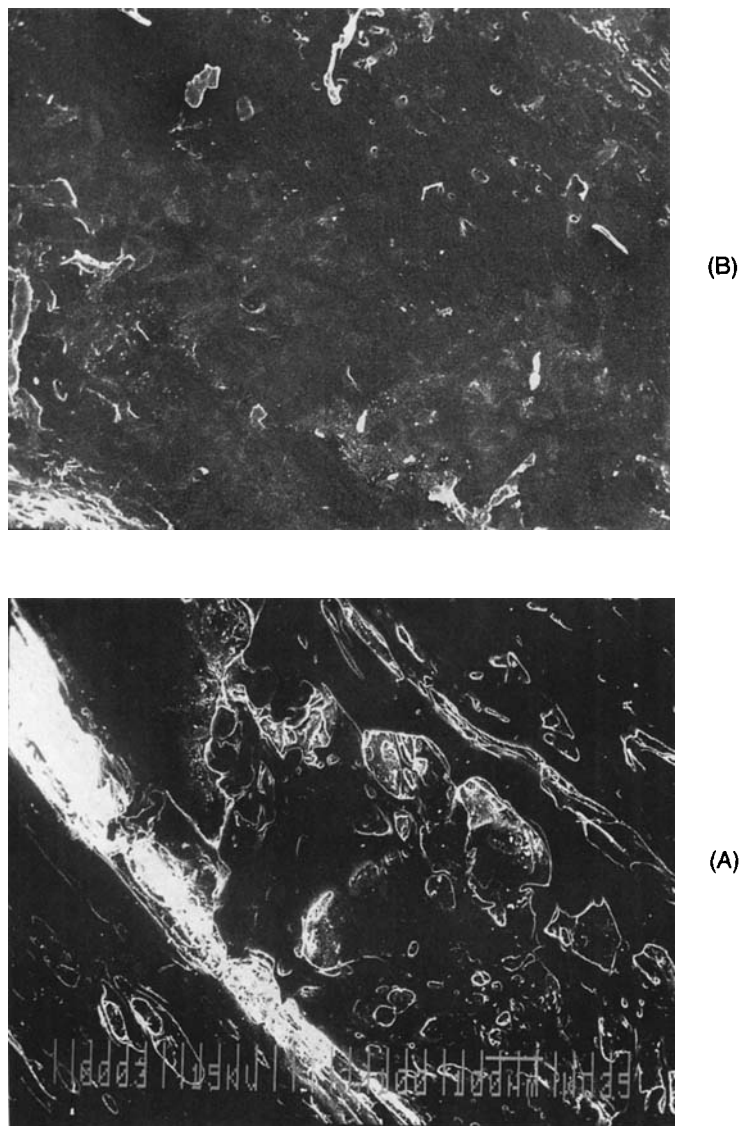[a] After 10 weeks' exposure to simulated marine environment (stirred tap water bath with 10% salinity at 25°C).

**Figure 3**   SEM of the surface of sample C-40 (B) before and (A) after testing (×100).

batch A (only PE) showed no weight change. However, in batches B, C, and D, which have, varying PEO content, wt % loss increases with an increase in the PEO content. There has been a significant drop in wt %, particularly for samples with 30–40% PEO. It may be noted here that PEO resins are completely soluble in water at all temperatures except near the boiling point. At or near the boiling point they precipitate and, thus, exhibit inverse solubility in water. The addition of salts to water will also decrease the solubility of the resin.[26] This is important because in the marine environment % salinity varies depending upon the location.

Tensile strength data for various batches of PE–PEO blends, before and after testing, have been compiled in Table IV, which also show a significant drop in tensile strength particularly for samples with 30–40% PEO content. Table IV also shows a significant decrease in tensile strength, both before and after testing, with an increase in PEO content. Thus, for the initial strength of fasteners or ties for lobster pots, one has to compromise between strength and PEO content. Figures 3 and 4 show typical scanning electron micrographs of the surfaces of samples C-40 and D-40, respectively, before and after testing. It can be clearly seen from these figures that the surfaces of these samples have been eroded after testing due to leaching out of PEO content, leaving a porous PE matrix with increased surface area. Figure 5 shows a typical comparison of DSC scans
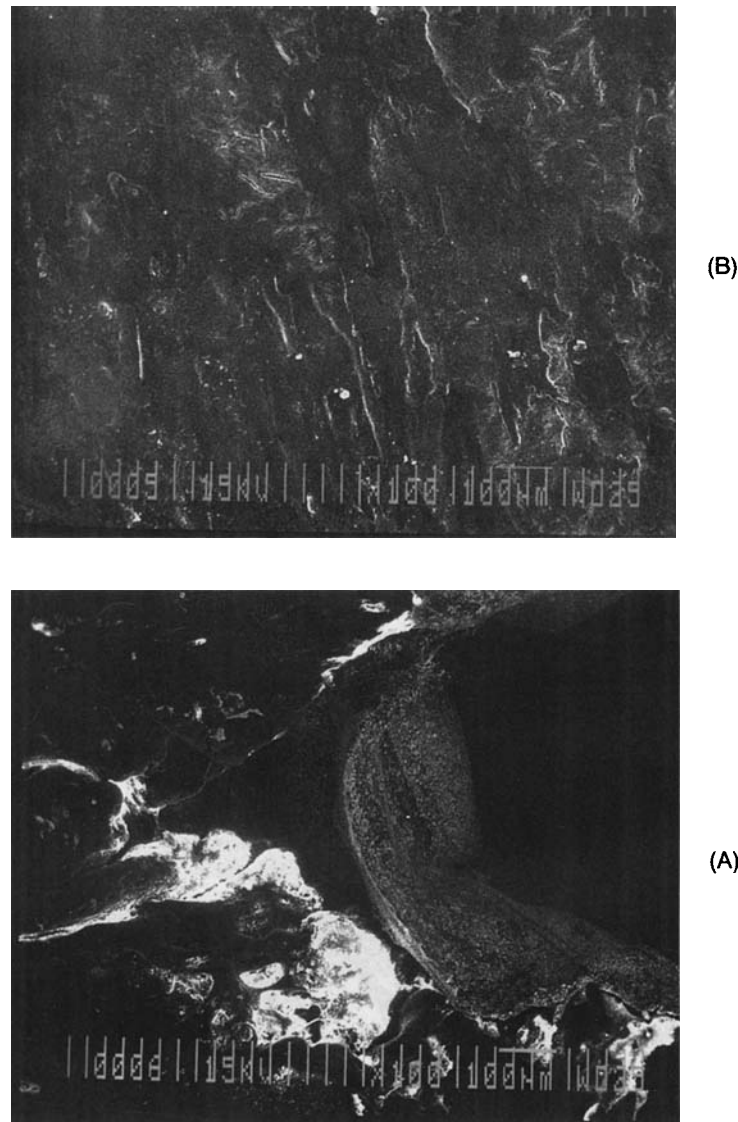
**Figure 4**    SEM of the surface of sample D-40 (B) before and (A) after testing (×100).

of sample D-30 as (i) surface before exposure, (ii) surface after exposure, and (iii) bulk after exposure. It is interesting to note that the low melting peak (due to PEO) present before exposure is completely absent in the DSC scan after exposure, indicating a complete leach out of PEO from the surface. However, the relatively small low melting peak in the bulk sample after exposure indicates the presence of some PEO. This also indicates that the process of leaching out of PEO is diffusion controlled and/or PEO is not a continuous phase. That is, some PEO aggregates are surrounded by PE domain with water not being able to penetrate into them, depending upon the thickness of the article. Higher loadings of PEO probably would enable the forma-

tion of a continuous PEO matrix under the given processing conditions.

## CONCLUSIONS

Unstabilized PE–PEO blends without any additives show phase separation upon melt-mixing. In the presence of a catalyst like Cobalt and Aluminum, good dispersion of PEO in the PE matrix has been observed. This is probably due to polar interactions between PEO and carbonyl groups, formed by oxidation of PE in the presence of metal catalysts. PE–PEO blends containing 30–40% PEO showed significant weight loss (11–27%) after exposure of 10 weeks in saline solution, thereby weakening the
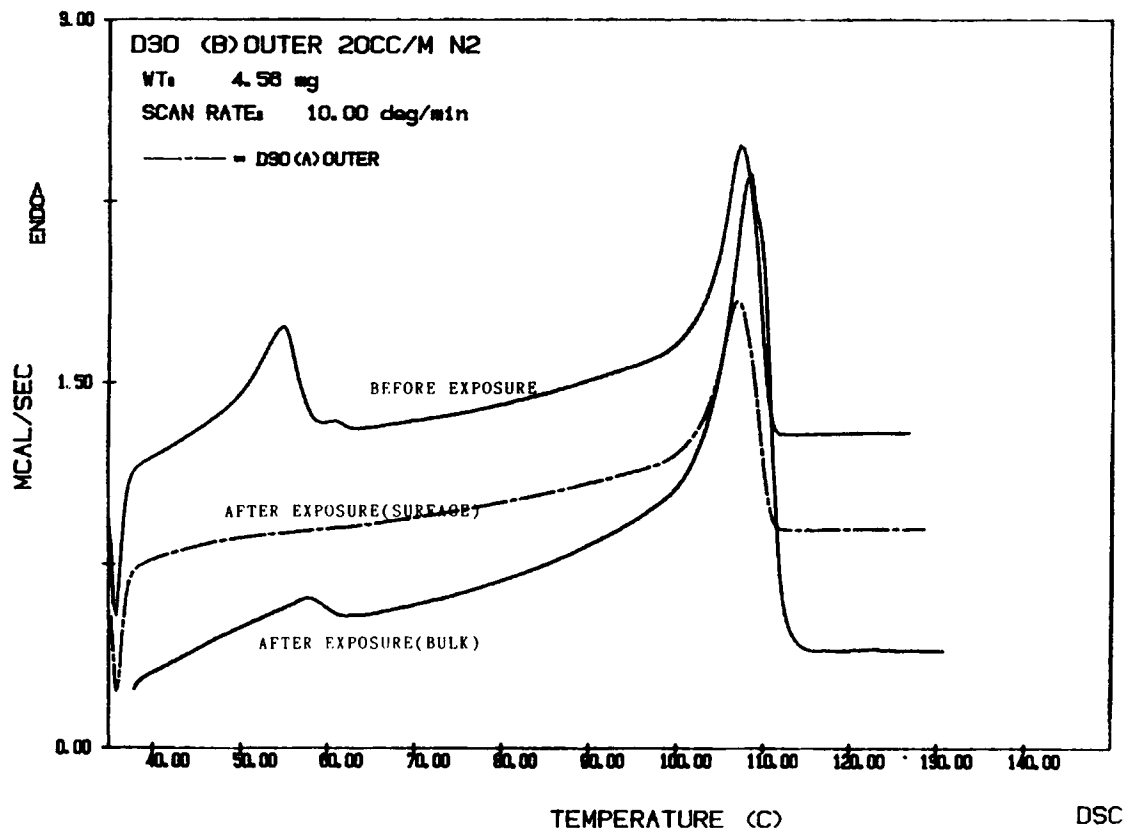
**Figure 5**  Comparison of DSC scans of sample D-30 before and after the testing.

specimens. DSC thermograms of surfaces of samples, before and after exposure, clearly indicate that PEO has been leached completely from the surface, thus eroding and weakening the samples. However, DSC of the bulk sample after exposure indicates that there is still some PEO present in the bulk. Tensile strength of PE–PEO blends after exposure to saline water decreased significantly, particularly for samples with 30–40% PEO content. It appears at this point that degradation for PE–PEO blends is very controlled. The materials are flexible and it should be possible to injection mold flexible fasteners to suit our needs.

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