Deterioration of Plastic Films under Soil Burial Conditions*

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Synopsis

The deterioration of polyolefin, poly(ethylene terephthalate), and polyamide films under soil burial conditions extending up to 32 months has been investigated. Based on changes in their elongation at break, the films can be ranked in order of increasing sensitivity to degradation: polyester $\simeq$ polypropylene < low-density polyethylene $\simeq$ high-density polyethylene < nylon 6.6. The degraded nylon 6.6 and polyethylene films were characterized by infrared and luminescence spectroscopy and scanning electron microscopy, as well as by wet analysis for hydroperoxides. From a comparison with the well-known oxidative sensitivity of nylon 6.6 in oxygenated water at slightly elevated temperatures, the rapid deterioration of nylon 6.6 film during soil burial was also concluded to be an oxidative process. The somewhat smaller, but significant, embrittlement of the polyethylenes studied could not be simply explained by thermal oxidation (with only trace oxidation products detectable) or microbiological attack (deterioration being unaffected by surface activation to enhance wettability).

INTRODUCTION

The microbiological processes which lead to the destruction of natural polymers such as cellulose (e.g., cotton) and protein (e.g., leather) during exposure to soil are well understood.[1,2] This deterioration of natural polymers is of great commercial importance, and can be reduced by special treatments.[3] However, for the commercialized synthetic polymers, there are conflicting claims regarding their sensitivity to microbiological attack.[4–16] The useful lifetimes (normally measured by embrittlement) of films and fibers prepared from synthetic polymers when exposed to soil are now of relevance to many areas. For example, plastic film is extensively used in contact with the soil in construction, as are geotechnical fabrics (nonwoven felts) for soil stabilization (in roads, dams, etc.). In both cases, long lifetimes are expected for these film and fabric products. Plastic film is also being increasingly used as an agricultural mulch to retain moisture, increase the soil temperature, and inhibit weeds. In the case of mulch films, the action of sunlight during the growing season causes partial degradation and embrittlement. Progressive biodeterioration of film fragments is predicted once the film is plowed into the top soil.[17] It is claimed that a similar approach can be used to destroy plastic litter.[7,18]

The literature on the biodeterioration of synthetic polymers is sharply divided between those suggesting that microbiological attack can only occur if polymers could be degraded (by UV, for example) to extremely short chain lengths[5,10] and those suggesting that synthetic polymers can also be metabolized at relatively high molecular weights.[6–8,13] The former conclusion is based on growth exper-

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iments with various organisms on precisely defined polymerlike oligomers of increasing molecular weight. Experiments indicating assimilation by microorganisms of polymers or partially degraded polymers have depended on, for example, the use of soil burial or pure cultures on ^{14}C labeled polymer.[7,13] In a series of publications on nylon 6 and cellulose acetate yarns, several Japanese researchers have also reported microbiological deterioration both from exposure to pure cultures[16] and from exposure to enzyme extracts from these organisms.[15,16] Other workers have concluded that nylon 6.6 is not biodegradable.[4,9]

In an attempt to resolve the controversy in this extremely important area, we have studied the effects of soil burial on the properties of various thin polymer films. The films have been characterized in terms of physical and chemical changes. Where severe deterioration was observed, the soil effects were compared with controlled chemical attack. Commercial synthetic polymers are predominantly much less wettable by water than the natural (cellulosic or protenaceous) polymers. This difference should inhibit attack by the aqueous enzyme systems of microorganisms.[14] To investigate the role of wettability, some film samples were surface activated by exposure to a corona discharge in various atmospheres prior to soil burial.

EXPERIMENTAL

The following films were studied: polypropylene (PP, Enjay 25 μm thickness), low-density polyethylene (LDPE, du Pont 110 μm), high-density polyethylene (HDPE, du Pont 25 μm), poly(hexamethylene adipamide) (nylon 6.6, du Pont 25 μm) and poly(ethylene terephthalate) (PET, du Pont "Mylar," 25 μm). A second LDPE sample (12 μm, Union Carbide) was also examined, but in less detail than the 110-μm sample. However, very similar deterioration effects were observed in both samples and only the data for the thicker film is reported here. Films were Soxhlet extracted with acetone (48 hr) to minimize surface lubricants and soluble stabilizers or other additives. The detectable metals in the nylon 6.6 film were (in ppm by spark source mass spectrograph) Zn (0.1), Ni (0.1), Mn (0.2), Cr (0.7), Cu (2), Fe (3), and Ti (6), and in PP were Ti (85) and Al (35).

Soil burial of the films was carried out in flats containing an enriched garden soil held at tropical conditions (29 ± 1°C, 85% RH) as described in CGSB 4-GP-2, Method 28.3 (very similar to the ASTM recommended method AATCC 30-1974). Film samples (6 $\times$ 15 cm^2) were buried at random in 20 soil flats. They were removed periodically up to a total exposure of 32 months. The films were thoroughly rinsed in a stream of water, followed by immersion in distilled water until clear, and air dried. Neither abrasion nor detergents were used in the cleanup of the buried films.

For comparison with changes observed during burial, fresh nylon films were wet oxidized by immersion in aqueous reagents in a three-necked flask. Oxygen, air, or nitrogen was bubbled into the aqueous solutions via a sintered glass diffuser. The solutions were held at constant temperature with a heating mantle and stirred by a magnetic stirrer. The aqueous solutions used included either deionized water, distilled water, soil extract, or water buffered at pH 8.0. The soil extract had a pH 6.75, and contained dissolved transition metals (Fe, Ti, Mn, Cu, etc.).

Some film samples were exposed to a surface activation treatment prior to soil burial. This involved exposure of each film surface to a corona discharge in the anhydrous gases ammonia, carbon dioxide, or air (60 ml min^{-1} flow rate) for 200 sec in the apparatus described previously.[19] After treatment in NH_3 and CO_2, films were kept in the flowing treatment gas for 30 min to allow the decay of any reactive species before exposure to oxygen.

Changes in film wettability on corona treatment were measured by the sessile drop method. Contact angles for water drops before (and after) corona treatment in all atmospheres were PP 99° (50°), LDPE 90° (50°), HDPE 100° (45°), PET 74° (58°), nylon 6.6 63° (40°).

Tensile testing was performed on 2-mm strips, gauge length 1.25 cm, crosshead speed adjusted to give 30-sec breaks on an Instron model TTC tensile tester. Prior to testing the strips were conditioned for 48 hr at 20°C and 65% RH.

Infrared (IR) spectra were recorded on a Nicolet 7199 Fourier transform IR (FTIR) system. This instrument uses a Michaelson interferrometer to generate an interferrogram, which is transformed into an IR spectrum by the instrument's dedicated computer. The system allows addition of many scans to minimize noise, and manipulation of the stored spectra. Surface spectra were recorded by attenuated total reflection (ATR, KRS-5 reflection element, 45° incidence) as described previously.[20] Changes after exposure were clearly shown by spectral subtraction of the stored spectrum of each unexposed film from the spectrum of the exposed sample. Problems due to interference ripples in the spectra of the films were minimized by the use of a polarizer, and tilting the sample at the Brewster angle.[21] To measure low levels of products in film samples after soil burial, multiple layers (up to 32) were used in transmission IR measurements on films with low scattering levels (PP and LDPE).

For comparison with the products from treated nylon 6.6 films, IR spectra of model compounds were recorded in a solvent (methylacetamide) providing an environment similar to that found in the nylon matrix.

Changes in spectroluminescence were measured with a Farrand Mark I spectrofluorometer used in the phosphorescence mode on samples cooled at 77 K.

Hydroperoxide yields were measured after film treatment with KI/2-propanol, and estimation of the I_3^- yield from its UV absorption at 360 nm as described previously.[22]

Film samples were examined by optical and scanning electron microscopy (SEM, Cambridge Stereoscan Mark II). Prior to microscopy, samples from soil burial were fixed so as to preserve any microorganisms on the surfaces. Fixation was carried out by immersion in Sabatini's cacodylate buffered glutaraldehyde solution (10%), followed by gradual dehydration in H_2O/ethanol solutions up to 99% ethanol.[23] The films were then critical-point dried. For SEM, ~20-nm coatings of gold were applied by vacuum evaporation.

RESULTS

Soil Burial Effects

In most applications envisaged for films or fibers, in contact with the soil, loss in tensile properties is the most relevant practical criterion. Tensile strength and elongation at break data for the five polymers are shown in Figure 1. From
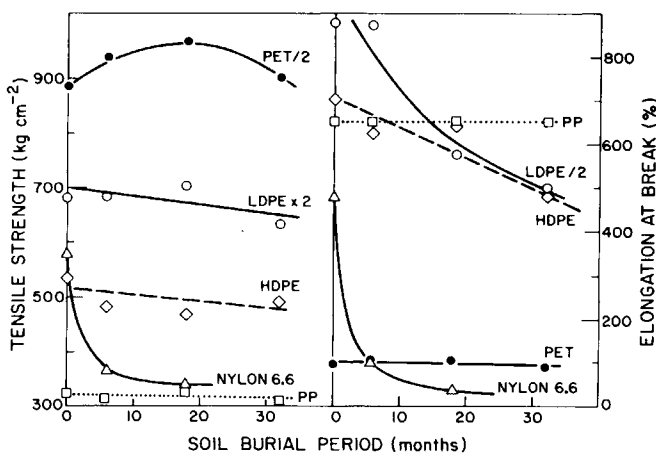
Fig. 1. Tensile strength and elongation at break of plastic films after soil burial.

their loss in physical properties, the films can be ranked in order of decreasing susceptibility: nylon 6.6 > LDPE $\simeq$ HDPE > PET $\simeq$ PP. Nylon is remarkably susceptible and PP surprisingly resistant. In most cases, elongation at break proved to be a much more sensitive indication of deterioration than tensile strength. Elongation is also found to be most indicative of the deterioration of unoriented polymers by, for example, oxidative processes.[24] Surface activation of the samples by corona discharge exposure did not produce any significant increase in susceptibility for any of the polymers despite the large increases in wettability, as well as formation of surface products, resulting from the treatments.

A key question is obviously the origin of the deterioration in mechanical properties observed for LDPE, HDPE, and especially nylon. Deterioration might result from attack by microorganisms or from the prevailing soil chemistry. The soil chemistry under our test conditions could possibly cause hydrolysis, oxidation, etc., and this soil chemistry will be extensively controlled by O_2 availability and microbiological action. In order to investigate the origin of the deterioration, film samples after varying periods of soil burial were extensively characterized for physical and chemical changes, with nylon 6.6 being most thoroughly studied.

Transmission and ATR IR detected negligible chemical change in PP, HDPE, and PET even after 32 months exposure, consistent with their generally small losses in physical properties. A comparison of bulk (transmission IR) and surface (ATR IR) changes in LDPE indicated that a low level of oxidation products (hydroxyl —OH and carbonyl >C=O) had accumulated throughout the samples during burial ([OH] $\simeq$ 1 $\times$ $10^{-2}M$; [>C=O] $\simeq$ 5 $\times$ $10^{-3}M$ after 32 months). Severe scatter from the opaque HDPE prevented the detection of low levels of oxidation products in multiple layers of film by transmission IR.

Transmission IR also indicated a progressive accumulation of >C=O products in soil buried nylon 6.6 film (Fig. 2). A surface study by ATR IR showed that the >C=O products were not concentrated on the surface. The intense amide absorption of nylon 6.6 (at $\sim$1660 cm^{-1}) overlaps the absorptions due to >C=O products, which were only observed as a faint shoulder in the spectrum of each exposed film. The high photometric accuracy and low signal-to-noise ratio of
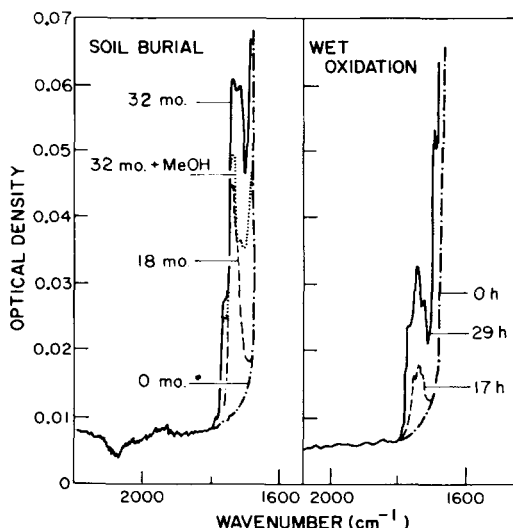
Fig. 2. IR spectral changes for nylon 6.6 after burial or wet oxidation. Values refer to hours (h) or months (mo.) of exposure. Wet oxidation carried out at 80°C in air-saturated water.

the FTIR system allows the meaningful subtraction of the spectrum of an undegraded nylon film from the spectrum of each exposed sample so as to make the >C=O product absorption clearly visible. The apparent intense absorption beginning at ∼1680 cm^{-1} in Figure 2 is, however, due to the failure of the subtraction procedure to remove the intense central zone of the amide band in the nylon film at the high-scale expansion employed.

When dissolved in methylacetamide, aliphatic carboxylic acids (e.g., butyric acid) were found to absorb at ∼1740 cm,$^{-1}$ backbone ketones (e.g., 3-pentanone) at 1720 cm,$^{-1}$ and aliphatic esters (e.g., methyl butyrate) at 1740 cm^{-1}. The acid group in the amide solvent absorbs well above the usual position for acids in nonpolar solvents (at ∼1708 cm^{-1}). This latter absorption is due to acid dimer, which is known to dissociate and exhibit a monomer absorption at 1740–1760 cm^{-1} in polar solvents.[25] From the IR changes observed after soil burial, the carbonyl products appear to be a backbone ketone (at ∼1720 cm^{-1}), with carboxylic acid and/or ester at 1740 cm^{-1}. The absorption after 18 months burial indicates [>C=O] $\simeq$ 5 × 10^{-2}M(ϵ_{1720} $\simeq$ 300M^{-1}cm^{-1}).[26] Soxhlet extraction with methanol for 15 hr caused a partial reduction in the >C=O absorption of the 32-month soil buried film, indicating the presence of some low-molecular-weight products.

Hydrolytic scission of the nylon backbone and oxidation can both be expected to produce various —OH and amino (—NH$_2$) groups. However, the —OH/—NH region (3600–3300 cm^{-1}) was obscured by absorbed water, which varied uncontrollably in quantity from sample to sample.

The accumulation of some >C=O products in nylon 6.6 was also confirmed by spectroluminescence changes, using the method which George and Browne[27] originally developed to detect the deterioration of nylon parachute canopies. Undegraded nylon 6.6 film shows a phosphorescence emission at 420 nm from an excitation maximum at ∼290 nm. This emission does not change during soil burial (or wet oxidation). A second phosphorescence at ∼455 nm from an excitation maximum at ∼295 nm is also detected in undegraded film. This latter

emission complicates the observation of the new emission from treated film, because after soil burial a strong phosphorescence at ∼455 nm (lifetime ∼0.8 sec) is detected upon excitation at a new absorption maximum of 310 nm (Fig. 3). George and Browne[27] reported a very similar phosphorescence at 460 nm (lifetime 0.7 sec at 77 K) from a 320-nm excitation for partially oxidized nylon fabrics. This emission has been attributed to α,β-unsaturated carbonyl groups, such as dienones.[28] Although exceptionally sensitive, the phosphorescence technique cannot be used to quantify emitting species because of the effects of the environment on emission intensity (due to quenching of the excited species). The IR absorption of any α,β-unsaturated carbonyl species present (at ∼1670 cm^{-1}) was obscured by the intense amide absorption of the nylon 6.6 so that an independent estimation of their concentration was not possible.

The iodometric method can detect hydroperoxide groups (—OOH, a common product from polymer oxidation) at $\geqslant 1 \times 10^{-4}M$ concentrations in polymer films.[22] All nylon 6.6 samples, both buried and unburied, showed a similar —OOH level [$(3 \pm 1) \times 10^{-3}M$]. LDPE films showed a significant increase in —OOH level ($1 \times 10^{-4}M$ unburied, $1.3 \times 10^{-3}M$ after 32 months burial).

Analysis of the nylon 6.6 films by SEM and optical microscopy showed marked changes after soil burial. The unburied film showed a microspherulitic texture [Fig. 4(A)]. Extensive surface damage or restructuring was visible after burial [Figs. 4(B) and 4(C)]. This damage took the form of star-shaped cracks and interconnected crack networks. The latter were more visible by optical microscopy using transmitted light, implying that they were beneath the film surface. Very few microorganisms were visible after cleanup of the buried nylon film. Although these microorganisms were usually associated with some surface damage, from the SEM information it was impossible to decide whether this damage was associated with the presence of the organism or simply offered a fortuitous anchorage point.

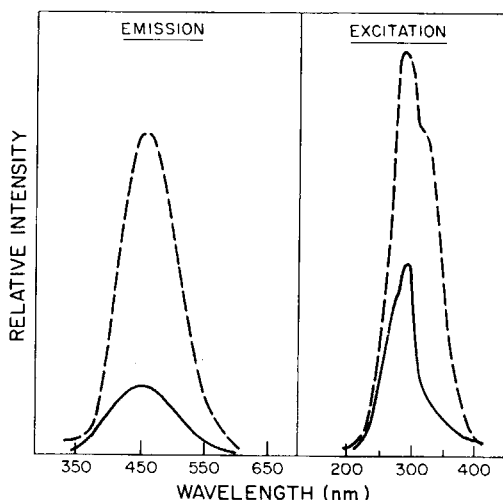To summarize the film characterization data, the embrittlement of the nylon

Fig. 3. Changes in nylon 6.6 phosphorescence on soil burial. Spectra recorded at 77 K. Emission spectra from excitation at 310 nm; excitation spectra for the emission at 455 nm. (——) Before soil burial; (– –) after 32-month burial.
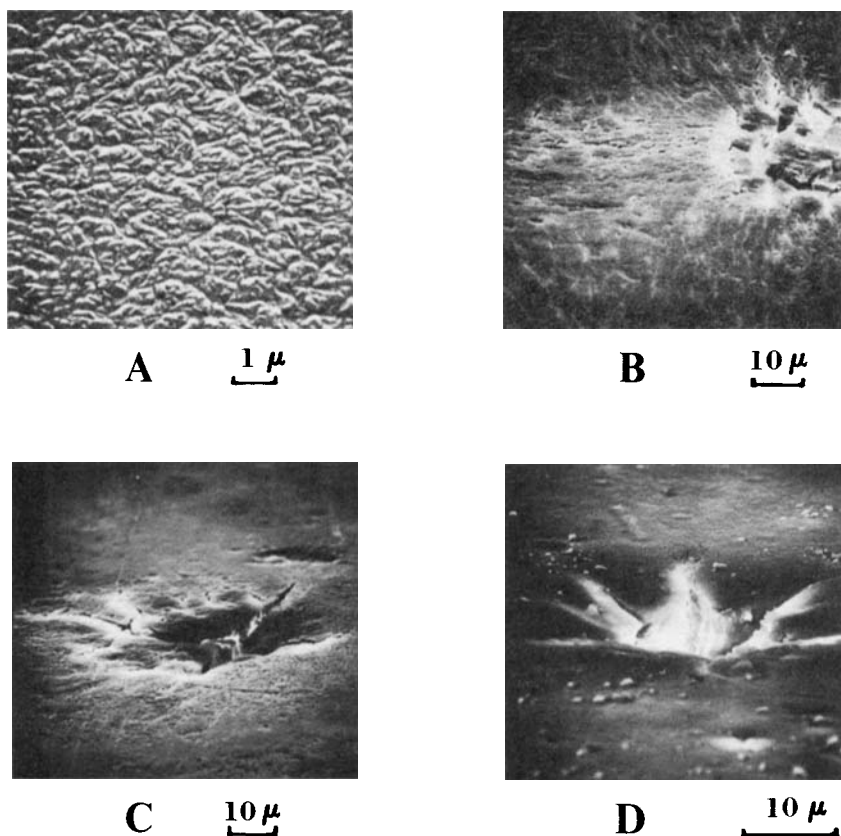
Fig. 4. Scanning electron micrographs of treated nylon 6.6 film. (A) untreated; (B), (C) after 32-month soil burial; (D) after 80°C wet oxidation in air-saturated water (24 hr). (A), (B) at normal incidence (90° to film surface); (C), (D) at ~60° incidence (i.e., oblique view).

6.6 is obviously associated with the cracking visible by SEM and optical microscopy. The detection of $>C{=}O$ products by IR and luminescence implies that a bulk oxidative process has occurred during burial, and might be associated with the embrittlement. For the less severely degraded LDPE, bulk oxidation products are also associated with the moderate embrittlement observed. Oxidative deterioration of many polymers is well known to lead to surface or bulk cracking and an associated embrittlement.[24] The rapid deterioration of nylon fibers under wet-oxidative conditions is particularly well documented.[29-32] In view of this fact, the wet oxidation of the nylon 6.6 film was examined, and changes compared with those observed under soil burial conditions.

Wet Oxidation of Nylon 6.6

Exposure of the nylon 6.6 film to wet-oxidative conditions led to a slight drop in tensile strength and a marked embrittlement (Fig. 5), as has frequently been reported previously.[29-32] Embrittlement rates at 80°C depended on the type of gas used to saturate the water, and increased in the sequence $N_2 <$ Air $< O_2$. Immersion beyond ~30 hr at 80°C caused complete fragmentation of the films
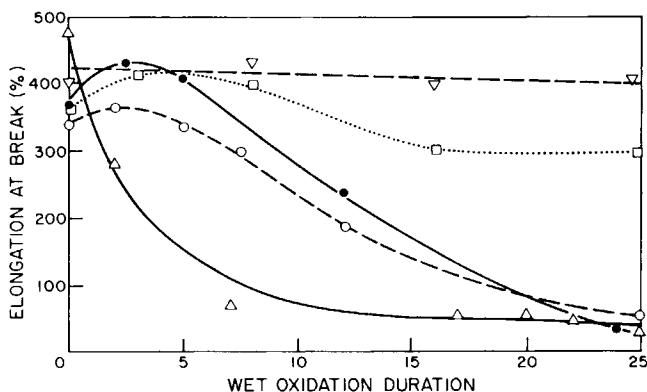
Fig. 5. Effects of wet oxidation on nylon 6.6 film elongation at break. $\triangle$, O_2 Saturated water at 80°C, duration in hr; ●, air saturated water at 80°C, duration in hr; □, N_2 saturated water at 80°C, duration in hr; O air saturated water at 50°C, duration in days; $\triangledown$, dry heat at 80°C, duration in hr.

in the gently agitated O_2-saturated water. In contrast, exposure to dry air at 80°C had only a slight effect on elongation at break. Contrary to the data of Vachon, Rebenfeld, and Taylor,[30] but supporting Mikolajewski, Swallow, and Webb,[29] little effect of pH was found, or of using solutions of varying dissolved transition-metal content (aqueous soil extract, distilled, or deionized water). However, only a quite narrow range of pH values was covered in our work (from soil extract pH 6.75 to a buffered solution pH 8.0).

An increase in elongation at break was observed for many nylon film samples in the first 2 to 3 hr of wet oxidation. A slight increase also occurred in N_2-saturated water which implies that some restructuring of the nylon occurred in 80°C water. Tensile strength data (not shown) for the nylon 6.6 films also showed a progressive decrease during wet oxidation. However, the changes were not as dramatic as the differences in elongation at break, paralleling the relative changes found after soil burial (Fig. 1).

Wet-oxidized film samples were examined by SEM and FTIR. Transmission IR changes were quite similar to those found in the soil buried films (Fig. 2) and no predominance of surface oxidation was detected by ATR. Similar star cracks and other features were also observed by SEM in both soil buried and wet-oxidized films [Figs. 4(C) and 4(D)]. Faint traces of the original microspherulitic texture were still visible on some film areas even after wet oxidation. Embrittled, wet-oxidized nylon film showed similar surface features when oxidized either at 50 or 80°C, although the rate of deterioration was ~20 times slower at 50°C (Fig. 5).

DISCUSSION

Although some specially synthesized nylon copolymers are reported to be biodegradable,[11] the commercial nylons (6, 6.6, and 6.10) are suggested to be resistant to microorganisms.[4,9,11] However, the sensitivity of commercial nylons to progressive oxidative attack at mild temperatures in the presence of O_2 has been frequently reported[29-32] and our soil burial data can readily be explained by this phenomenon. The stress–strain data (Fig. 1) and observed $>C\!=\!O$ groups

(from IR, Fig. 2; and phosphorescence, Fig. 3) are consistent with the nylon 6.6 film undergoing a progressive oxidative attack. The effects of purely wet oxidation [Figs. 2, 4(D) and 5] parallel those observed under soil burial conditions [Figs. 2, and 4(C)]. Even at 50°C, embrittlement is observed within 20 days, implying that the deterioration observed after ~10 months soil burial could well be an extension of the same process. Mikolajewski, Swallow, and Webb[29] have also observed the formation of carboxylic-acid-containing fragments from the IR of aqueous extracts of nylon fiber after severe degradation.

The level of carbonyl products observed in nylon 6.6 after 18 months soil burial is relatively close (within a factor of 2) to the level found in photodegraded film which had a similar low level of elongation at break (~60% remaining after ~480 hr xenon arc Weather-Ometer exposure).[33] The dominant carbonyl absorption in the IR spectra of photooxidized films was at ~1740 cm^{-1}, as found for the soil buried and wet-oxidized nylon 6.6 film (Fig. 2).

The mechanism of the rapid thermooxidative deterioration of wet nylon has not been fully explained in the literature, although catalysis by transition metal ions has been implicated.[29–31] Our data indicate little effect of ions in solution, but do not preclude the possibility of the significant transition metal content of the nylon itself playing a role. Mikolajewski, Swallow, and Webb[29] have proposed that Ti is a key source of oxidative instability in wet nylon, and Ti was the dominant transition metal (at 6 ppm) in our film samples. In addition, water alone is well known to have a dramatic effect on nylon 6.6 behavior, with T_g ranging from 107°C (dry) to −8°C (100% RH).[34]

Miner has examined the soil burial behavior of moldings of nylons 6 or 6.10 over an eight-year period.[35] The results indicated that nylon 6 was rapidly embrittled, whereas nylon 6.10 was largely unaffected. This result was explained in terms of the higher moisture uptake of nylon 6, but no study of the chemistry involved was reported.

Corona discharge treatment of the film surfaces prior to soil burial was employed to provide surfaces more readily wettable by aqueous media (e.g., contact angle of water on PP goes from 99° to 50° after air corona) and to modify the surface chemistry by introducing >C=O, —OH, or —NH$_2$ groups.[20] The large increase in wettability was expected to facilitate access of extra-cellular enzymes to the polymers.[14] In addition, the extensive changes in surface chemistry from the corona treatments[20] should have provided more readily metabolizable materials than the virgin polymers. The failure of surface modification to accelerate deterioration during soil burial is consistent with the observed embrittlement of nylon 6.6 and of both PE films resulting from purely chemical attack, rather than assimilation by microorganisms.

Our observation of some embrittlement of HDPE and LDPE during soil burial (Fig. 1) and our observation of bulk oxidation products (from transmission IR and —OOH determination) appear inconsistent with microorganism attack on polymers, which can be reasonably expected to be a surface phenomenon. Oxidation could result from the slow oxidation of the LDPE in the presence of contaminants from the soil. Griffin has observed a rapid oxidation of LDPE under warm-compost conditions, because of absorption of peroxidized fats and oils, and suggested that this may be the source of all detected polyolefin oxidation.[12] However, this mechanism appears unlikely in normal soil burial (as opposed to municipal waste) where the oil and lipid content is very low. Guillet

et al.[6,7] and Albertsson[13] have concluded that the emission of $^{14}CO_2$ from ^{14}C labeled polymers under soil burial conditions confirms direct microorganism attack on the polymers. However, these data could also be explained by slow oxidative processes made visible by a highly sensitive analytical technique (^{14}C labeling). For example, Albertsson[13] has recently reported similar steady rates of $^{14}CO_2$ evolution from labeled LDPE in the presence of a microorganism and nutrients, or distilled water, or nutrient sterilized with silver nitrate. In the first system, an initial burst of $^{14}CO_2$ production occurred, which might have resulted from attack on low-molecular-weight LDPE fractions as originally suggested by Nykvist.[8] In addition, the results of Potts et al.[5] and Colin et al.[10] indicate that direct microorganism attack is only likely for linear alkanes or even linear ketones less than C_{36} in length, although Haines and Alexander have proposed that alkanes up to C_{44} can be attacked by microorganisms.[36]

One disturbing feature of our polyolefin embrittlement data deserves mention. It is that the soil burial effects on tensile properties increase in the sequence PP < HDPE $\simeq$ LDPE, which is the converse of the sensitivity of these unstabilized polymers to all other oxidative processes, whether initiated by heat, light, or γ rays. In fact, this sequence is consistent with reported low rates of micro-organism attack on branched, low-molecular-weight alkanes as compared to linear alkanes,[5] although the presence of residual antioxidant in PP or of some efficient initiator of oxidation in the PE samples could also explain the results. Furthermore, the level of products detectable by IR after 32 months soil burial of LDPE (e.g., ~5 × $10^{-3}M$ carbonyl species) is an order of magnitude below the level found in the same LDPE film after photooxidation with a xenon arc to give the same level of elongation at break (1000% residual elongation).[33]

Although prolonged acetone extraction is expected to remove most additives (especially phenolic antioxidants) from the polyolefins, it is possible that traces of an effective antioxidant persist in PP and cause its resistance to soil burial. However, by UV spectroscopy, we have found that extraction reduces the level of phenols in polyolefin films by a factor of ~20 (to below the detection limit). Thus, our own data do not allow a clear differentiation between chemical and microbiological effects during soil burial. Monk has previously reported that PP films are resistant to soil burial, although experiments only extended over five months.[37]

PET is well known to undergo deterioration by hydrolysis at high tempera-tures. However, this process is expected to be very slow[38] at the pH (6.75) and temperature (29°C) of our soil exposures.

CONCLUSIONS

Our results on nylon 6.6 and LDPE have some important practical implica-tions. The widely held belief of the inertness of (undegraded) polyethylenes in contact with soil under aerobic conditions is apparently invalid. Progressive embrittlement will occur and could have serious effects, for example, where LDPE is used as a long term liquid/moisture barrier. Our results for nylon are not surprising in view of previously published work on nylon deterioration. Although fiber deterioration can be expected to be slower than that for (unor-iented) film, the use of nylon either alone or in mixtures (bicomponents) for geotechnical fabrics appears unwise, unless adequate precautions are taken to retard wet-oxidative deterioration.

Within the time scale of our experiments, PET and PP appear to possess high resistance to soil burial conditions.

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