EFFECTS OF INTENSIVE MICROBIAL METABOLISM ON STARCH-FILLED POLYETHYLENE FILMS IN CONTROLLED COMPOSTING WINDROWS

GIOVANNI VALLINI, ANDREA CORTI, ANTONIO PERA, ROBERTO SOLARO, FABIO CIONI, AND EMO CHIELLINI

CNR, Soil Microbiology Center and University of Pisa, Institute of Agricultural Microbiology, 56124 Pisa, Italy

Department of Chemistry and Industrial Chemistry, University of Pisa, 56126 Pisa, Italy

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Low density (LDPE) and high density (HDPE) polyethylene films filled with starch up to a maximum level of 20% by weight were tested for biodegradation under different environmental conditions. Composting windrows consisting of various putrescible waste and assembled for controlled biostabilization management under static conditions were used. The physical and chemical deterioration of the polyethylene-starch films exposed to a controlled composting environment were recorded and analyzed with respect to the different composting evolution and were compared with the data collected in pure culture systems and in bench scale tests simulating an aerobic biostabilization process. Evidences are presented on the partial removal of starch from the different films as a consequence of massive surface colonization by various microorganisms. Loss of starch is accompanied by a small but significant drop in the average molecular weight and decrement in mechanical strength. In the case of a composting trial experiencing prolonged severe temperature conditions, a small but spectroscopically detectable oxidation of the polyethylene matrix was also observed. Efficiency of the controlled composting systems can be claimed in assessing reproducible conditions in an accelerated biostabilization of putrescible matter and hence versatility in the evaluation of the degradation of plastic manufactures.

Polyolefins such as polyethylene with a degree of polymerization higher than 20 are particularly recalcitrant to microbial attack (1, 14, 26). Biodegradation of polyethylene as well as of many other thermoplastic polymers (e.g. polypropylene, polyvinyl chloride, polystyrene) has been indeed considered as a phenomenon to be
prevented until recent years. Therefore a wide variety of additives were and still are incorporated into the plastics in order to prevent environmental stress induced by abiotic and biotic agents. Among the latter, microorganisms play by far the most important role.

Nevertheless, since plastic wastes are more and more widespread in the environment and their permanence in natural habitats represents a potential hazard for biota, attention is now being given to the design and production of polymeric materials susceptible to microbial degradation. Making polyethylene “biodegradable” could be used for containers, packaging, shopping bags and other disposable products that otherwise should continue to overfill landfills or accumulate in soil, freshwater and sediments. Actually polyethylene represents, as both low density polyethylene (LDPE) and high density polyethylene (HDPE), more than 50% of the plastics in municipal solid waste where thermoplastic materials range altogether between 7 and 10% by weight (4).

Loading of starch into plastics is one approach used in polyethylene manufacturing to promote its biodegradability (12, 23). Microbes can utilize and remove the natural polymers embedded in the synthetic matrix (11, 16, 32). Exposure of the polyethylene bulk to weathering changes is supposed to be a consequence of starch degradation (19). In fact, once the starch is degraded, a wider surface area of the polymer will become exposed to possible microbial attack (6, 10).

Although plastics recycling from garbage is undoubtedly pursued because of the benefits in terms of both material and energy recovery and saving on disposal costs, polyethylene manufactures, especially films, are expected to continue to enter the unsorted stream of municipal solid waste for a long time.

This increases the need for further and more systematic research on the real behavior of degradable polyethylene during biological processes such as landfilling and composting, currently used for urban refuse treatment and disposal.

In recent years, experiments have been undertaken by several authors in order to expose polyethylene and plastic products to biological attack under conditions comparable to real environment situations (13, 22, 28). For degradation tests through soil burial experiments, a number of indoor and outdoor apparatuses have been described (2, 8, 21). Also composting biomass have been considered to confine polymeric films in matrices harboring intense microbial activity. However, only few studies have been carried out by following the fate of samples exposed to composting systems operating with large amounts of putrescible substrates (7, 17). Actually, the literature contains many reports of attempts to recreate the complex dynamics of compost stabilization in the laboratory (13). Evidences exist that in these cases the evolution of the process is somewhat erratic because of the lack of spontaneous increase of the temperature in the organic matter, due to mass-dependant biological self-heating. On the other hand, the only biodegradability tests carried out as a part of full-scale composting trials mainly refer to uncontrolled systems such as open heaps of gardening residues in which compost stabilization is achieved in several months.
In the last years, study has been undertaken aimed at the evaluation of the environmental degradation of polyethylene loaded with starch (15, 18, 25, 27). As a part of our continuing interest in this issue, the present paper investigates the biodegradability of different starch-filled polyethylenes in an intensive composting environment. This is represented by full-scale aerated static windrows formed with different putrescible wastes and carefully managed according to the Rutgers strategy (9) that allows for the starting material to be stabilized in a few weeks.

MATERIALS AND METHODS

Characteristics of tested polymers. Investigations were carried out on low density (LDPE) and high density (HDPE) polyethylene samples filled with different amounts (0, 7.8, 12.8, 16 and 20% by weight) of Ecostar type (20) silanized corn starch. Starch loading was attained by melt extrusion at 150–180°C of appropriate mixtures of polyethylene with the corresponding polyethylene/starch master batch containing 40% by weight of starch.

Four samples (H1, H2, L1, and L2) contained also a 0.5% by weight of “White Master” consisting of polyethylene/calcium stearate/titanium dioxide in a weight ratio of 30:25:45. The polymer samples were supplied as thin films (50–100 μm) by Biodegradable International s.r.l. (Bari, Italy).

Two additional samples (100–200 μm films) of low density polyethylene filled with different amounts of unmodified corn starch (samples A and E, starch content 0 and 10% by weight, respectively) were supplied by EniChem Anic S.p.A. (S. Donato Milanese, Italy). These films contained also a 5% by weight of titanium dioxide. Starch loading was made by melt extrusion at 170–190°C of appropriate mixtures of LDPE with a master batch containing 20% by weight of corn starch.

Polymer samples were confined into actively composting organic matrices as 2×23 cm rectangular specimens cut out according to the ASTM D 882-B test (3). In a few cases, 2×5 cm and 2×10 cm specimens were used.

Composting trials. Composting runs were planned to simulate full-scale aerobic stabilization of putrescible materials. Static windrows with forced pressure ventilation of biomass by blowing air from the bottom and with feedback temperature control, were adopted in agreement with previous studies carried out at the Soil Microbiology Center in Pisa (30). Using the selected system, the process could be managed through the optimization of physicochemical and trophic parameters affecting microbial activity in the composting materials (31).

Four different composting windrows (Table 1) were formed to stabilize the following substrates: a) Chopped residues from pruning and garden waste mixed with fly ashes from coal power plants in the 90/10 weight ratio (Run CR1); b) The same organic residues as in a) added with only 5% by weight of fly ashes (Run CR 2); c) 40/60 (w/w) mixture of wood chips with shredded residues from restaurants and canteens (Run CR3); d) Mechanically sorted, putrescible organic fraction of
municipal solid waste (OFMSW) mixed in a weight ratio of 65:35 with the anaerobic effluent of a sea weed digester (Run CR4).

All windrows were arranged with 3 metric tons of substrate and their temperature, pH, moisture and microbial biomass dynamics were monitored throughout the composting process. Polymer specimens were fixed on stainless steel grids that were placed into the core of composting pile at 120 cm from the windrow top. Polymer samples were retrieved 50 days from the start.

The dynamics of aerobic microbial populations were evaluated by measuring the number of colony forming units (CFU) every 7 days by serial dilution of biomass samples on agar plates. Nutrient agar, Waksman agar and Malt extract agar containing 50 mg/l rifampicin were used as culture medium, respectively, for total bacteria, actinomycetes and moulds.

Microorganism isolation. L6c and L4c LDPE samples retrieved from the CR 3 composting pile and showing massive colonization of mycelial structure on the surface were washed with sterile water and then kept in a wet chamber at 55°C in an incubator. After 3 weeks incubation, abundant aerial hyphae developed on the plastic specimens allowing for isolation of a thermophilic mould by repeatedly streaking on Malt extract agar (Difco, Detroit, MI, U.S.A.) plates. The isolated mould was referred to as PSTFF1 strain.

Bench scale tests. (i) Putrescible organic matter: Experiments were carried out in rectangular polyethylene containers (28 × 14 × 16 cm) with a stainless steel grid located 3 cm from the bottom. The boxes were loaded with partially stabilized organic fraction of municipal solid waste, previously wetted up to saturation (60–70% water uptake). Rectangular plastic film samples (2 × 10 cm) were buried horizontally within the core of the organic substrate, then the loaded vessel was placed in a thermostat and heated for 50 days at 55°C, while a constant flow (150 ml kg⁻¹ min⁻¹) of humidified air was blown from the bottom. Moistened air was continuously blown from the bottom through the organic matrix to avoid drying of cultures and to maintain the environment under aerobic conditions.

(ii) Sterilized substrate seeded with specific microbial inocula: Experiments were carried out in 3-l glass vessels filled with poplar (Populus canadensis) sawdust. The lignocellulose bulk was moistened with a liquid medium having the following composition: NH₄NO₃ 1.0 g, K₂HPO₄ 0.2 g, MgSO₄·7H₂O 0.05 g, CaCl₂·2H₂O 0.08 g, D-glucose 10.0 g, distilled water 1,000 ml. The bottles were autoclaved at 120°C for 20 min, then LDPE and HDPE samples filled with 20% starch, after sterilization by chemical disinfection (18), were placed within the poplar bulk. Each bottle was inoculated with massive cultures of PSTFF1 thermophilic mould. Incubation of the bottles was carried out in the dark at 55°C for 30 days. Moistened air was continuously blown into the ligno-cellulose bulk to assure oxidative conditions while avoiding excessive drying of the substrate.

Cleaning of untreated and retrieved samples. Original specimens and samples retrieved from degradation experiments were washed repeatedly with sterile distilled water, treated in an ultrasonic bath for 10 min, and dried under a vacuum at
50°C until the weight became constant. The weight of each specimen was averaged over at least three measurements.

**Acid attack of embedded starch.** Rectangular specimens of LDPE and HDPE samples loaded with 12.8 and 20% by weight of silanized corn starch were suspended under stirring in 250 ml of 10% HCl at 55°C until the weight became constant.

**Polymer extraction.** To remove starch, polymer samples were extracted with boiling toluene in a Kumagawa extractor under nitrogen atmosphere and in the presence of traces of 2,6-diterbutyl-p-cresol as a radical inhibitor. The hot toluene solutions were then coagulated into a large excess of methanol and dried under vacuum until the weight became constant.

**Molecular weight determinations.** Viscometric determinations were carried out at 135±0.1°C on decahydroneaphthalene solutions of the extracted samples by a Desreux-Bishoff dilution viscometer.

Gel permeation chromatography (GPC) analyses were carried out on polymer solutions of the extracted samples in 1, 2, 4-trichlorobenzene at 134°C by a Waters Liquid Chromatograph Model 150 equipped with a Gel H6 TCK column. Mono-dispersed polystyrene standards were used for calibration.

**FT-IR analysis.** IR transmittance spectra were recorded on polymer films by a Perkin-Elmer 1600 FT-IR spectrometer and by a Perkin-Elmer 1760X FT-IR spectrophotometer coupled with an on-line FT-IR microscope Spectratech TLAN II. Films of the extracted polymers were cast at 130°C by applying a 12 bar pressure for 72 s and then analyzed by a Perkin-Elmer 1600 FT-IR spectrophotometer. The number of vinyl and vinylidene end-groups per 1,000 carbon atoms was evaluated according to the procedure reported by Usami and Takayama (29).

**NMR analysis.** NMR spectra were recorded by a Varian Gemini 200 spectrometer in 5-mm tubes on 10% (w/v) trichlorobenzene/hexadeuterobenzene (9/1) solutions, at 110°C. 1H-NMR spectra were recorded at 200 MHz. Spectral conditions were as follows: size, 11,968 points; spectral width, 3 kHz; pulse, 30°; acquisition time, 2 s; number of scans, 1. 13C-NMR spectra were recorded at 50.3 MHz, under conditions of full proton decoupling. Spectral conditions were as follows: size, 23,936 points; spectral width, 15 kHz; pulse, 70°; relaxation delay, 1 s; acquisition time, 0.8 s; number of scans, 60,000. No weighing function was applied before the Fourier transformation.

**SEM analysis.** Scanning electron microscopy (SEM) analyses were performed using a JEOL T 300 apparatus.

**DMTA analysis.** Dynamic mechanical measurements were performed in the temperature range -25°C to 125°C using a Perkin-Elmer DMTA-7 instrument at a scanning rate of 4 K min⁻¹ and at 1 kHz frequency by using the extension geometry.
RESULTS AND DISCUSSION

Low density (LDPE) and high density (HDPE) polyethylene films loaded with starch at levels between 0 and 20% by weight were submitted to biodegradation tests under different controlled conditions. Full-scale composting windrows arranged with different putrescible wastes (CR1–CR4, Table 1) and in a few cases bench scale tests simulating an aerobic biostabilization process of solid organic matter and pure culture systems were used.

In the case of composting experiments, the evolution of process conditions were constantly monitored in terms of temperature and pH profiles, level and type of microbial consortia, and C/N ratio. The trend of temperature variations recorded during the composting processes are represented in Fig. 1. It is worth mentioning that the peak temperature around 70°C was reached within a week and was maintained at that level for almost another week in the CR4 composting run. In the CR1 and CR2 runs, the maximum temperature never exceeded 50°C, limit recorded after 1 week in CR2 and between the fifth and sixth weeks in CR 1. In both cases, however, the peak temperature was maintained only for a relatively short time. In the CR3 and CR4 experiments, the pH slightly increased from weakly acidic (pH = 6.0–6.5) recorded at the beginning to reach a maximum value of about 8 throughout the biostabilization step. On the contrary, the initial alkaline pH of about 9–10 tended to approach neutrality during the biostabilization period in the CR1 and CR2 runs. A substantial drop in the carbon-to-nitrogen ratio was detected in all cases throughout the composting process.

The evolution of the overall microbial populations, as determined in the correspondence of samples location, are represented in Fig. 1. A common feature to the different composting experiments is that the microflora tended to increase within time. We must note the substantial increase of actinomycetes from $10^4$ cell/g dry weight up to $10^{10}$ cell/g dry weight after 10 days in the CR4 run, which however reached the highest temperature.

The samples retrieved from the various experiments were analyzed for weight loss and investigated for morphological and structural variations which may have occurred both at the bulk and the molecular levels.

Weight loss data of the samples retrieved from the full-scale composting trials are shown in Table 2. Weight loss was observed only in the samples loaded with

<table>
<thead>
<tr>
<th>Run</th>
<th>Composition (weight/weight)</th>
<th>C/N* (mol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CR1</td>
<td>Pruning and Garden waste/Fly ashes (90/10)</td>
<td>26.3</td>
</tr>
<tr>
<td>CR2</td>
<td>Pruning and Garden waste/Fly ashes (95/5)</td>
<td>35.0</td>
</tr>
<tr>
<td>CR3</td>
<td>Restaurant and Canteen waste/Wood chips (60/40)</td>
<td>23.9</td>
</tr>
<tr>
<td>CR4</td>
<td>OFMSW/Seaweed digested sludge (65/35)</td>
<td>16.0</td>
</tr>
</tbody>
</table>

* Organic carbon to total nitrogen content.
starch, with values ranging from 0.1 to 7.1%, and the highest values were observed for samples containing HDPE. In the starch-free polyethylene films and in a few starch-filled samples, a weight increase of up to 1.3% was observed and was attributable to either the presence of some inorganic debris or microorganism colonization not easily removable by the clean-up treatments used, or to hydration not fully removed from the polymer.

By assuming that the observed weight losses are associated with starch consumption, figures of starch loss ranging from 3 to 36% can be calculated.

A similar trend is clearly detected in the loss values observed in runs performed on HDPE and LDPE samples filled with 12.8 and 20% starch when exposed to a prolonged treatment with 10% hydrochloric acid at 50–60°C (Table 3). By considering the reported data in light of the percolation theory, as applied to starch
filled polyethylene films (24), one may infer a better accessibility of starch in the HDPE samples than in the LDPE samples. HDPE appears to be less prone than LDPE to allow homogeneous dispersion of the starch granules, at least when

Table 2. Weight losses of polyethylene samples at different starch contents after 50 days in composting piles.

<table>
<thead>
<tr>
<th>Sample</th>
<th>PE (type)</th>
<th>Starch (%)</th>
<th>Total weight (mg)</th>
<th>Run</th>
<th>Weight loss</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(mg)</td>
</tr>
<tr>
<td>H0a</td>
<td>HDPE</td>
<td>0</td>
<td>680.4</td>
<td>CR1</td>
<td>3.9</td>
</tr>
<tr>
<td>H6a</td>
<td></td>
<td>20.0</td>
<td>425.5</td>
<td>CR1</td>
<td>30.2</td>
</tr>
<tr>
<td>H0b</td>
<td></td>
<td>0</td>
<td>220.6</td>
<td>CR2</td>
<td>-0.1</td>
</tr>
<tr>
<td>H6b</td>
<td></td>
<td>20.0</td>
<td>143.2</td>
<td>CR2</td>
<td>10.2</td>
</tr>
<tr>
<td>H0c</td>
<td></td>
<td>0</td>
<td>1,557.6</td>
<td>CR3</td>
<td>-1.8</td>
</tr>
<tr>
<td>H1c</td>
<td></td>
<td>7.8</td>
<td>1,001.9</td>
<td>CR3</td>
<td>28.1</td>
</tr>
<tr>
<td>H2c</td>
<td></td>
<td>12.8</td>
<td>1,169.5</td>
<td>CR3</td>
<td>15.0</td>
</tr>
<tr>
<td>H3c</td>
<td></td>
<td>7.8</td>
<td>851.1</td>
<td>CR3</td>
<td>16.7</td>
</tr>
<tr>
<td>H4c</td>
<td></td>
<td>12.8</td>
<td>1,148.1</td>
<td>CR3</td>
<td>27.4</td>
</tr>
<tr>
<td>H5c</td>
<td></td>
<td>16.0</td>
<td>946.8</td>
<td>CR3</td>
<td>42.7</td>
</tr>
<tr>
<td>H6c</td>
<td></td>
<td>20.0</td>
<td>1,198.0</td>
<td>CR3</td>
<td>69.7</td>
</tr>
<tr>
<td>L0a</td>
<td>LDPE</td>
<td>0</td>
<td>250.7</td>
<td>CR1</td>
<td>0.3</td>
</tr>
<tr>
<td>L6a</td>
<td></td>
<td>20.0</td>
<td>596.1</td>
<td>CR1</td>
<td>19.0</td>
</tr>
<tr>
<td>L6b</td>
<td></td>
<td>20.0</td>
<td>191.9</td>
<td>CR2</td>
<td>5.4</td>
</tr>
<tr>
<td>L0c</td>
<td></td>
<td>0</td>
<td>642.5</td>
<td>CR3</td>
<td>-1.9</td>
</tr>
<tr>
<td>L1c</td>
<td></td>
<td>7.8</td>
<td>1,195.4</td>
<td>CR3</td>
<td>-0.4</td>
</tr>
<tr>
<td>L2c</td>
<td></td>
<td>12.8</td>
<td>1,286.7</td>
<td>CR3</td>
<td>12.5</td>
</tr>
<tr>
<td>L3c</td>
<td></td>
<td>7.8</td>
<td>1,401.2</td>
<td>CR3</td>
<td>14.2</td>
</tr>
<tr>
<td>L4c</td>
<td></td>
<td>12.8</td>
<td>1,332.5</td>
<td>CR3</td>
<td>5.0</td>
</tr>
<tr>
<td>L5c</td>
<td></td>
<td>16.0</td>
<td>1,364.6</td>
<td>CR3</td>
<td>17.6</td>
</tr>
<tr>
<td>L6c</td>
<td></td>
<td>20.0</td>
<td>1,373.3</td>
<td>CR3</td>
<td>61.0</td>
</tr>
<tr>
<td>A</td>
<td></td>
<td>0</td>
<td>326.6</td>
<td>CR4</td>
<td>-4.1</td>
</tr>
<tr>
<td>E</td>
<td></td>
<td>10.0</td>
<td>633.0</td>
<td>CR4</td>
<td>-0.8</td>
</tr>
</tbody>
</table>

* Based on 3–5 specimens.
* Based on the sample total weight.
* Based on starch content.
* Sample containing 0.5% by weight of White Master.

Table 3. Weight losses of polyethylene samples at different starch contents after 5 days in 10% HCl at 50–60°C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>PE (type)</th>
<th>Starch (%)</th>
<th>Total weight (mg)</th>
<th>Weight loss</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(mg)</td>
</tr>
<tr>
<td>H4e</td>
<td>HDPE</td>
<td>12.8</td>
<td>670.0</td>
<td>36.8</td>
</tr>
<tr>
<td>H6e</td>
<td></td>
<td>20.0</td>
<td>693.9</td>
<td>105.0</td>
</tr>
<tr>
<td>L4e</td>
<td>LDPE</td>
<td>12.8</td>
<td>805.6</td>
<td>20.7</td>
</tr>
<tr>
<td>L6e</td>
<td></td>
<td>20.0</td>
<td>879.1</td>
<td>46.1</td>
</tr>
</tbody>
</table>

* Based on three specimens.
* Based on the sample total weight.
* Based on starch content.
comparable processing conditions were adopted for the formulation of the blends. It is important to note that starch removal by a chemical attack in the samples submitted to a composting treatment should be negligible if any, as the pH in the composting windrow never reaches values lower than 6.

In no case was weight loss accompanied by a macroscopic variation at visual

![](image)

**Fig. 2.** SEM micrographs (A, 530×; B, 3,500×) of an LDPE sample (L6c) filled with 20% starch after 60 days exposure to a real composting environment (Run CR3).

For reference, a 10-μm bar is given in the micrograph.
and stereomicroscopic observations. Scanning electron microscope (SEM) analyses carried out on the samples retrieved from the full-scale composting treatment, clearly revealed consumption of the starch granules present on the surface, accompanied in all cases by deterioration of the polyethylene matrix in proximity to these granules (Fig. 2). No substantial differences are detectable between the LDPE- and HDPE-based samples, apart from the lower homogeneity of the distribution of starch granules in the HDPE-based samples. SEM observation of the samples after removal of surface layer about 15-μm thick using a microtome indicated that starch granules embedded within the core of polymeric films did not experience any significant attack (Fig. 3). It appears, therefore, that at least under the adopted environmental conditions no massive invasion of the polyethylene bulk by microorganisms occurs.

Mechanical-dynamic analyses (DMTA) performed on some of the HDPE samples with different starch content before and after exposure to the composting environment, provided the following indications.

The real part of the mechanical modulus recorded at the same temperature (Fig. 4A) steadily decreases as the starch content increases, and a drop of one order of magnitude is detectable going from the unloaded sample H0c to the H6c sample filled with 20% starch. An analogous trend is detectable in the decrease of temperature corresponding to the onset \( T_{MD} \) of a marked drop in the modulus. An extrapolated 95°C value can be estimated for H6c sample, as compared to a value of \( T_{MD} = 115°C \) in the HO sample.

An overall drop in the modulus is observed at any temperature going from...
untreated samples to those retrieved from the compost pile (Fig. 4B). This drop is accompanied by a displacement toward lower values of $T_{MD}$, was a minimum value of 80°C being recorded in the H6c sample having the highest content of starch. Within the limits of the fairly low number of cases analyzed, one may infer that the composting treatment produces a substantial decrease of the plastic character of polyethylene matrix that tends to assume a viscoelastic character at a lower temperature. This behavior can be attributed either to a decrease in the molecular weight accompanied by a broadening of the polydispersity, as detected by GPC analysis (Fig. 5), or to a plasticizing effect played by starch metabolites or by lipophilic cellular debris possibly entrapped within the polyethylene matrix made less impervious by the thermal treatment experienced in the composting pile. A concomitance of the two phenomena could also be possible. A definite, experimentally substantiated explanation is still pending, as even a self-plasticizing effect due to polyethylene thermal oxidation cannot in principle be ruled out.

Two LDPE (L0c and L6c) and two HDPE samples (H0c and H6c), as retrieved from the composting treatment and after extraction in boiling toluene,
were submitted to high temperature GPC analysis and the GPC traces were compared with those of the corresponding untreated samples. In all cases, a slight displacement of the overall molecular weight distributions toward lower molecular weights, accompanied also by small changes of their profile is detected in going from the untreated to the composted samples (Fig. 5). As a consequence, a decrease of the average molecular weight is evaluated with a substantial increase of the polydispersity index. Indications can thus be gained that fragmentation of polyethylene backbone occurred during composting treatment. At present, there is no firm evidence regarding the role of either direct microbial attack or the effects of ageing due to temperature and chemical oxidation.

After composting and careful rinsing with water, all samples were submitted to an FT-IR investigation prior to any further treatment. Some of the samples
retrieved from composting CR3 showed two new absorption bands around 1,740 and 1,245 cm\(^{-1}\), attributable respectively to the C=O stretching and C-O-C asymmetric stretching of an aliphatic ester group (Fig. 6). Their optical density decreased with the starch content and the two bands could not be detected in the starch-free sample. This behavior bears out a more or less direct correlation between the oxidative attack and the presence of starch within the polyethylene matrix. \(^1\)H- and \(^13\)C-NMR spectra (Fig. 7) allow for evaluating at maximum a 0.5% oxidation of the polyethylene matrix. It is worth mentioning that apparently the number of methyl groups present at a level of 20 per 1,000 carbon atoms is not affected by the composting treatment and the oxidation seems, therefore, to take place either at the level of the polymer backbone or in the correspondence of fairly long-chain branches. Saponification experiments carried out on composted samples after removal of residual starch confirmed the nature of the oxidation functional moiety but did not establish the relative position of the ester groups in the oxidized polyethylene matrix.

No apparent oxidation was detected in the analyzed samples retrieved from the other composting windrows, that in any case never reached and maintained temperatures as high as those recorded in CR3 run (peak 85°C, over 75°C for 2 weeks). The observed oxidation of polyethylene matrix, limited to only one composting pile, could be related either to a specific microbial attack or to physical-chemical processes promoted by the higher temperatures reached and maintained for an extended length of time. This appears to agree with the findings of degradation studies of polyethylene-starch films carried out in uncontrolled composting windrows (17).

To isolate thermophilic microorganisms present on the treated samples, one L6c specimen retrieved from the CR3 composting pile was maintained in a wet chamber at 55°C. Microorganism colonies developed after 3 weeks’ incubation
were identified as a filamentous fungus, apparently belonging to a single species according to microscopic and macroscopic observation. The isolated microorganism once cultivated on Malt broth was transferred into an aerated wood flour containing sterile untreated L6 specimens and the relative weight loss of the sample after 28 days incubation at 55°C in the dark, as compared with a sterile control, was evaluated to be about 1%. However, no carbonyl absorption band was observed in the relevant FT-IR spectrum.

Bench scale experiments were carried out to gain information on the feasibility of lab-scale simulations of full-scale composting processes and hence on the possibility of evaluating the activity of microbial strains isolated on samples retrieved from composting windrows. Experiments were carried out on polyethylene films containing 20% starch (samples L6d and H6d) in putrescible organic
matter having a composition analogous to that of the CR4 pile. The weight losses recorded under these conditions were 1 and 4%, respectively, which was lower than the values detected for the same samples in composting piles. FT-IR spectra recorded on the retrieved specimens did not show any appreciable oxidation of the polyethylene matrix.

These findings further substantiate that in a full-scale composting plant a more complex mechanism is affecting the starch consumption and the observed deterioration of the exposed polyethylene-starch films.

CONCLUSIONS

The results were collected of a fairly extensive investigation undertaken on the composting degradation of polyethylene-starch films originating from different sources with a starch content of 0 to 20% by weight. A variety of full-scale composting windrows based on different putrescible organic matters and managed under controlled conditions was chosen for the investigation.

Depending upon the nature of the polyethylene matrix and on the starch content, variable drops in the weight of the exposed compost samples compared with the corresponding starting weights were detected.

The observed weight losses were found to be essentially due to the consumption of the starch granules occurring almost exclusively at the surface level. Once the starch granules are removed by the microorganism attack, holes and cracks are generated on the surface of polyethylene matrix thus increasing its surface-to-volume ratio. Starch consumption, at least in the composting pile that, in the thermophilic step, reached and maintained a temperature of about 75°C for a prolonged length of time, was accompanied by a weak oxidation of the polymer matrix whose possible metabolic and/or physical-chemical pathway is still unknown (5).

It is worth mentioning that removal of starch in composting-exposed samples is accompanied by a slight decrease of the average molecular weight and in some cases by a broadening of the molecular weight distribution. These changes are probably responsible for the Young's modulus drop observed by mechanical-dynamical analysis in going from the untreated to the corresponding exposed samples.

The starch removal recorded in degradation tests carried out at bench scale level on putrescible organic matter and in axenic cultures of a filamentous fungus showed that all cases well below the levels observed in full-scale composting pile.

The efficiency of full-scale composting systems operating under controlled conditions can be thus evidenced, as compared to the bench-scale systems and real composting piles operating however under uncontrolled conditions, even for much longer times (17).

In addition to the inherent practical benefits connected with the possibility of rather quick and reproducible investigation on biodegradation of different materi-
als, one may stress the potential of this technique which allows the dynamics of complex microbial physiological groups acting on the test materials to be controlled.

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