Peroxide Oxidation and Compost-Induced Surface Changes in Degradable Plastics

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Abstract: This study examined degradation conditions of biodegradable and oxo-degradable plastics using non-biodegradable plastics as a control. Samples were subjected to different concentrations of hydrogen peroxide at different lighting conditions and showed residual peroxide titrated with permanganate initially decreasing before increasing over time. Oxidizable species are speculated to be produced by the degradation of the polymers. Scanning electron micrographs of strips of plastics mixed in a simulated compost heap showed that biodegradable plastics underwent more pronounced surface changes than non-biodegradable plastics. Thermomechanical analysis indicated biodegradable plastics to be more elastic after exposure to the experimental conditions and broke faster at a lower temperature. Attenuated total reflectance spectra did not indicate significant changes in the plastic strips over the six month period of the experiments.

Key Words: peroxide oxidation of plastic; biodegradable, oxo-biodegradable; thermomechanical analysis

1. INTRODUCTION

The aggravating role of indiscriminately disposed polymers in the effects of severe weather in our country impel us to continue our study on locally used plastic bags. There are two types of degradable plastics currently used for retail packaging in the Philippines: biodegradable and oxo-degradable. Biodegradable plastics degrade in the presence of microbes (Lazcano, 2007) and on the other hand, oxo-degradable plastics degrade under oxidative conditions (Thomas, 2010). We have previously shown by thermomechanical analysis and mass changes that biodegradable bags have higher sensitivity to uv radiation and higher temperatures as compared to plain LDPE (Janairo, 2013). Here we report results on simulated degradation conditions in a compost heap and in hydrogen peroxide. The effect of ambient natural light is also explored. The study is limited only to the abovementioned plastic samples. Comparisons were made using the following methods and parameters: (1) visual – using the Scanning Electron Microscope (thickness included), (2) peroxide oxidation for oxo-degradable and non-biodegradable plastic, through permanganate titration of residual oxidizable material and (3) mechanical properties (elongation, tension and shrinkage) – through the thermomechanical analyzer. Oxodegradable films were not subject to compost testing.
2. METHODOLOGY

The plastic samples were cut into 1×1 inch squares and labelled according to the experimental conditions they were kept in.

2.1. Peroxide Oxidation

To chemically induce oxidation, plastic strips were immersed in hydrogen peroxide using two concentrations: 0.1M and 0.5M. Small glasses were filled with 30ml peroxide solution and plastic strips were submerged in them. The containers were covered with saran wrap. Two batches were prepared for each concentration with half of the samples stored exposed to ambient light and the second half kept in the dark inside cardboard boxes in a cabinet. Peroxide blanks were also prepared with no plastic strips.

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<thead>
<tr>
<th>SAMPLES</th>
<th>LIGHT</th>
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<tbody>
<tr>
<td>Oxo-degradable</td>
<td>1LO</td>
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<tr>
<td>Non-biodegradable</td>
<td>1LNB</td>
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<td>Hydrogen Peroxide</td>
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1= 0.1 M H₂O₂; 5 = 0.5 M H₂O₂

To monitor plastic oxidation by peroxide, 5.0mL aliquot portions of the solution were periodically drawn and titrated with standardized potassium permanganate. 5.0mL aliquots were mixed with 15.0mL distilled water and 30mL 0.75M sulfuric acid in an Erlenmeyer flask. The samples were then titrated with potassium permanganate until the pink endpoint that persists for at least 20 seconds.

2.2. Composting Degradation

Compost was prepared by mixing 3.0 kilograms of dried leaves, 100 grams of rotting cabbage, and 100 grams of Folia Tropica® compost activator following a 30-1 Carbon-to-Nitrogen ratio. (Richard, 1996) The mixture was placed on top of a strainer placed upside down at the bottom of a bucket to ensure the aeration of the compost. The bucket was covered with perforated plastic to protect the compost from pests. This set up was stored in a cool and dry place. The compost was kept moist by spraying with water on the surface every other day for 1 month, and every 3 days for the succeeding months.

2.3. Scanning Electron Microscopy

SEM micrographs were measured on a Jeol JFC-1200. Snapshots at ×200 and ×500 magnification for each of the samples were taken for surface analysis. Thickness of the films were determined using ×1500 magnification.

2.4. Thermomechanical Analysis

A Shimadzu thermomechanical analyzer (TMA-60) was used to analyze the mechanical properties of the plastic samples. Treated plastic samples were cut into a smaller size approximately 15 × 4 mm to fit the die of the analyzer. This was placed between chucks at each vertical end and subject to an applied tensile load of 10 grams. Temperature was raised at a constant rate of 20°C per minute up to 130°C.

2.5. IR Spectroscopy

Attenuated total reflectance IR spectra were obtained on a ZnSe crystal using a Nicolet 6700 FT-IR Spectrometer.

3. RESULTS AND DISCUSSION

Results of the titration of residual oxidizable material in the peroxide solutions over 70 days are plotted in Figure 1. For the peroxide control, the expected results show decreasing amounts of peroxide both in the dark and in ambient light. The photosensitive nature of peroxide however is seen in that there is less peroxide for the samples exposed to light than those kept in the dark. Solutions kept with the polymers on the other hand show decreasing peroxide up to 25 days afterwards followed by generally increasing oxidizable material.
This is in keeping with the radical nature of the oxidation process of these polymers. Over time, as more of the polymers are oxidized, radicals may accumulate. Supporting this speculation is the higher amounts of permanganate required for the samples kept in the dark. Photo-induced reactions could cut the buildup of radicals and result in the smaller quantities detected. This is true for both films, indicating that in peroxide, no advantage is gained by the oxodegradable plastic.

Comparison of the photomicrographs of the films after 7 and 70 days in peroxide with control samples do not show much difference over the time period but vary greatly with the control. Samples exposed to peroxide show edges that are flaking or spongy and have started to swell as evidenced by increase in thickness.

While other micrographs show decreases, the thickening is observed in more of the oxo-degradable films than in the non-biodegradable. This is also more evident in samples exposed to light than those kept in the dark, once more indicating dependency on photochemical reactions. Unravelling of the polymer chains may cause it to bulk up and absorb water.
Fig. 3 shows some of the micrographs of the films after 180 days in the compost. As seen in the x500 images, the films being compared are not that similar. The biodegradable plastic is thicker and rougher on the surface compared to the nonbiodegradable. The biodegradable films also appear to be layered in contrast with the nonbiodegradable. As such only comparisons with control may be relevant. Doing so however shows that both films indicate changes in terms of flaking, and increased specks, ridges and grooves after the six months that the plastic samples were in the compost. The changes are more pronounced in the biodegradable material. While this indicates a positive difference in favour of the biodegradable, the six month duration which would be sufficient for the turnover of composted material is not enough even for the biodegradable films. The difference in the films are seen on the microscopic scale. The films, though macroscopically rougher in texture and more brittle, are essentially intact.

Fig. 4. Polynomial trend lines for breaking temperatures plotted against time for oxodegradable films exposed to hydrogen peroxide solutions.

The breaking temperatures at 10 g tensile load in the thermomechanical analysis ranged from 106-112°C for both oxodegradable and nonbiodegradable plastics, bracketing the 110°C melt transition, T_m of LDPE. This is reasonable as the melt transition is the temperature at which the polymer loses its crystalline structure and starts melting. As the polymer therefore starts to melt, the constant load pulling on it begins to stretch the polymer until its breaking point. Oxodegradable
films broke within a narrower temperature compared with the nonbiodegradable. The temperatures however do not show linear correlations with time of exposure to hydrogen peroxide. Tentative quadratic trend lines were plotted to magnify any correlations. While non-biodegradable plastic were inconsistently affected by peroxide, exhibiting both generally increasing and decreasing temperatures over time, the oxodegradable films broke at initially decreasing temperatures the longer they were soaked in peroxide. Exposure to light also generally resulted in lower breaking temperatures than samples that were kept in the dark. No apparent consistent effect however is observed between the two concentrations of peroxide used.

Elongation values show inconsistent response for the nonbiodegradable films. Oxodegradable films on the other hand show reversing trends in elongation with time, initially becoming less flexible with early exposure to peroxide before elongating more the longer it is exposed.

IR spectroscopy did not reveal much difference between the oxodegradable and nonbiodegradable samples before and after the peroxide oxidation and the composting treatment. Only the characteristic peaks of polyethylene were detected suggesting that changes in the structure within the time frame of the experiments are either insignificant or too small relative to the hydrocarbon chain to be detected.

4. CONCLUSIONS

The biodegradable and oxodegradable plastics so labelled in retail packaging in the Philippines do react to a higher degree than ordinary low density polyethylene in the accelerated peroxide oxidation and simulated composting conditions as indicated by thermomechanical analysis and scanning electron microscopy. Initial composting simulation indicates however that even after 6 months, the changes remain microscopic and the desired degradation on the bulk level has not been effected. Refinement and variations on compost conditions need to be performed to establish optimum conditions that would break down these materials in the real world in as short a time as possible.

5. REFERENCES


