# Evaluation of Biodegradability of Microwave-Irradiated Low-Density Polyethylene-Totally Degradable Plastic Additives (LDPE–TDPA) in Liquid Aerobic Environment

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## Abstract

Bioinert nature of throwaway plastic materials causes them to accumulate in the environment as litter. Recycling and incineration of such materials still remain in problematic as options since it is difficult in sorting plastics for recycling and burning process releases the irritant gases to the environment. Synthesis of biodegradable plastic such as Low-Density Polyethylene–Totally Degradable Plastic Additives (LDPE–TDPA) plastic polymer becomes a waste management option for polymer in the environment in recent years.

The combination of oxidation and biodegradation was considered to evaluate the degradability of LDPE–TDPA plastic. The initial oxidative effect on LDPE–TDPA through microwave irradiation enhanced its disintegration using a domestic microwave oven of 950 W at the frequency of 2.45 GHz and indicated 17.02% decreased value of its tensile strength. The resulted microwave induced plastic was accessible to biodegradation by the activated sludge microorganisms withdrawn from wastewater treatment plant in liquid aerobic environment.

The assessment of biodegradability of 28-day duration recorded that microwave-treated film mineralized 7% while 2.22% for untreated LDPE–TDPA in liquid aerobic medium. Surface morphological changes and weight losses of biodegraded plastic films showed the assimilation of activated sludge microorganisms based on SEM analysis. The biodegradation rate could be expressed by a simple first-order product curve and a sigmoidal curve applying iterative techniques of Table Curve window v2.0 software and the reaction rate constants were $9.7 \times 10^{-3}$ $day^{-1}$ for microwave-treated LDPE–TDPA and $9.0 \times 10^{-4}$ $day^{-1}$ for untreated LDPE–TDPA.

**Keywords:** LDPE–TDPA, microwave irradiation, activated sludge microorganisms, biodegradation rate constant

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## Introduction

Continuous use of large volume of synthetic polymers is becoming a serious environmental problem because of their throwaway products that accumulated in the environment. Their high molecular weight of synthetic nature inhibits the assimilation of microorganisms. Biodegradability, therefore, becomes an important parameter for plastic packaging materials. Biodegradable plastics such as plant based cellulosic plastic; bacterial based plastic, such as polyhydroxy β alkanoate (PHB); starch based plastic; and totally degradable prooxidant containing plastic; have been introduced in recent years.

Low density polyethylene–totally degradable plastic additives (LDPE–TDPA) plastic is designed to break down under the influence of thermal or ultraviolet light, before final biodegradation takes place through the activities of microorganisms. The direct incorporation of prodegradants, such as transition metal ions, polyunsaturated compounds, and metal complexes within the backbone of polyethylene (PE), facilitates disintegration and subsequent biodegradation.

Dupret, David, and Daro, 2000; Chiellini, Corti, and Swift, 2003 reported that thermal and/or photolytic abiotic treatment promotes the eventual biodegradation of LDPE containing prooxidant additives, by the cleavage of low molecular weight fragments that include aliphatic carboxylic acids, alcohols, aldehydes, and ketones. By monitoring the initial variations in molecular weight and other structural parameters, such as tensile strength and degree of crystallinity, abiotic treatment enhances the disintegration of LDPE. Thereafter, microbial assimilation of LDPE–TDPA oxidized products when exposed to different environments become more significant for their ultimate mineralization.

The present study was to evaluate the extent of degradability of LDPE–TDPA by carrying out the degradation process in two stages, namely, through: (1) abiotic oxidation by microwave irradiation; (2) followed by biotic microbial assimilation of the microwave–irradiated molecular fragments in liquid under aerobic condition.

## Materials and Methods

Low-Density Polyethylene–Totally Degradable Plastic Additive (LDPE–TDPA) plastic samples were obtained from Planet Friendly Plastics, Incorporation (PFPI), Philippines.

Activated sludge inoculum was withdrawn from the station 1 wastewater treatment plant of Yuchengco Building of De La Salle University (DLSU), Manila.

## Microwave Irradiation

Plastic films were cut into strips (3 x 15 cm) and placed into a teflon vessel, measuring 8 × 19 $cm^2$, and then put onto the turning disc (rotating reflector) inside the microwave cavity and irradiated under atmospheric pressure for four hours. After microwave irradiation, the films were recut into smaller (3 x 3 cm) pieces.

## Biological Treatment

### Preparation of Inoculum

The freshly withdrawn activated sludge was filtered and decanted. The inoculum solution was prepared to 2:8 (v/v) with distilled water, aerated, and then used within six hours of sampling.

### Respirometric Test in Liquid Aerobic Degradation

Aerobic degradation test in liquid cultures followed ASTM 5209 (92) that presents the determination of aerobic biodegradation of plastic materials in the presence of municipal sewage sludge. The experimental setup can be seen in Figure 1. The plastic samples were the sole source of organic carbon in a cultivating aqueous medium. $CO_2$ produced was absorbed in a solution of alkali hydroxide and subsequently determined by titration. The exact amount of test polymer (70 mg/L) was added to 2 L Erlenmeyer flask bioreactor containing the Mineral Medium (MM) solutions of g/L ($KH_2PO_4$ 8.50, $K_2HPO_4$ 1.75, $Na_2HPO_4.H_2O$ 33.30, $NH_4Cl$ 1.70, $MgSO_4.7H_2O$ 8.550, $CaCl_2$ 27.50, $FeCl_3.6H_2O$ 0.25) along with 75 ml/L of inoculum solution. The total final volume in each bioreactor was 1 L.

The aquatic reactors were incubated at room temperature with agitation using magnetic stirring for 28 days. To control carbon dioxide-free air to the test system, it consisted of three parts: two $CO_2$ scrubbing flasks containing 100 ml of 5 N NaOH solution to trap $CO_2$ from the entering air and a third flask with 100 ml of deionized water to humidify the air. The air flow was maintained at 50–100 ml/min and $CO_2$ free-air was distributed from the bioreactors to the third part of $CO_2$ post-trapping flasks that are connected in series. Each post-trapping flask contained 30 ml of 0.5 N KOH solution.

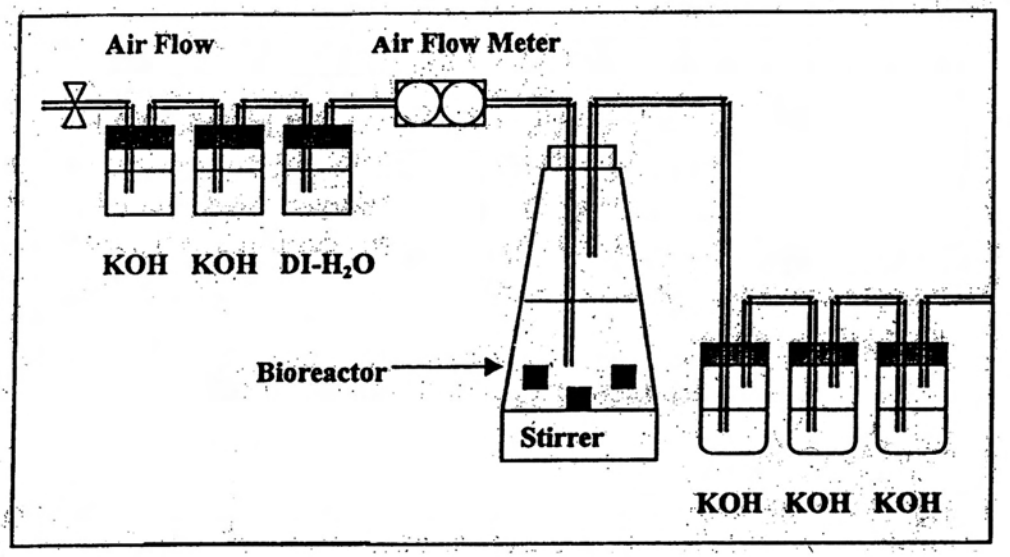


Figure 1 Experimental Setup for Liquid Aerobic Environment

The $CO_2$ produced in each bioreactor reacted with the KOH in the post-traps and precipitated as $K_2CO_3$. The quantity of $CO_2$ produced was determined by titration of the excess KOH with a standard solution of 0.5 N HCl using phenolphthalein as indicator. The carbon dioxide produced in the test material was corrected by subtracting the titration of the test materials and the blank (Equation (1)).

$$Z_n = Z_{blank} - Z_{test} \quad (1)$$

Where: $Z_n$ is calculated ml of HCl needed to titrate the $CO_2$ generated solely from the test material
$Z_{blank}$ is mL of HCl used to titrate the blank, and
$Z_{test}$ is mL of HCl used to titrate the test substance

$CO_2$ evolved in milligram is obtained by multiplying the HCl titration. Theoretical carbon dioxide ($TheoCO_2$) is calculated by using the molecular weights of $CO_2$ and C, and the amount of substance in the sample according to the following equation:

$$\text{The } CO_2 = \text{Weight of carbon} \times \frac{44\ (molecular\ weight\ of\ CO_2)}{12\ (molecular\ weight\ of\ carbon)} \quad (2)$$

Then, the degree of mineralization can be expressed as:

$$\text{Mineralization level} = \frac{mg\ of\ CO_2\ produced}{TheoCO_2} \quad (3)$$

## Scanning Electron Microscope

The surface morphology before and after being subjected to microwave irradiation and biological degradation was observed using JEOL JSM-5310 Scanning Electron Microscope. The samples were sputter-coated with gold before examination.

## Kinetic Study

The kinetic degradation rate during biotic process was expressed by a first order product standard curve using the equation, (1 ) $y = a(1 - e^{-k(t-t_{lag})})$, and the logistic function described by sigmoidal curve using the equation, (2 ) $y = a + b(1 - e^{-(t-t_{lag})/d})$, which are represented by the nonlinear regression models. They were used extensively to describe microbial growth and degradation kinetics in a batch system (Larson, 1996; Hoffmann, 2003). All parameters were estimated by iterative techniques using least squares analysis and the convergence algorithms provided in Table Curve 2D. The good agreement was then observed with the correlation coefficients ($R^2$) by fitting the actual data to the model.

## Results and Discussion

The LDPE–TDPA is low-density polyethylene films containing totally degradable plastic additives that were produced locally by Environmental Planet Friendly Inc using oxo-biodegradable technology. A maximum four

hours of microwave irradiation showed 17.02% decrease in tensile strength from 14.1Mpa and no change in elongation at 25mm. Untreated and microwave-treated LDPE–TDPA plastic samples were then exposed to controlled laboratory environment under aerobic condition using fresh activated sludge from station 1 wastewater treatment plant. Activated sludge is a mixture of microorganisms involving bacteria, protozoa, and higher microorganisms such as rotifers. The pH of activated sludge could affect the enzymes that generate the biochemical reaction in the bacteria in activated sludge. The pH range in present sludge was at an optimum level of 6.84-7.2 that is proper for the microorganisms in activated sludge and the BOD was below 10 mg/L.

Throughout the aerobic degradation process, the whole system was checked for air leakage. $CO_2$ free-air was ensured to enter the bioreactors by changing new alkaline solutions and testing with a drop of phenolphthalein indicator. Moreover, the clumping or adsorption of the test material to the walls of the test vessel was avoided. The evolution of $CO_2$ by microorganisms was evaluated as a measure of biodegradation (mineralization). The converted $CO_2$ from carbon is absorbed in the post trap of potassium hydroxide solutions and excess potassium hydroxide is determined by titration method.

The cumulative $CO_2$ evolution is presented in Figure 2. The figure shows that the growth of microorganisms in microwave-treated LDPE–TDPA reactor entered a relatively long lag phase of two days while in the LDPE–TDPA reactor lasted until the $5^{th}$ day when they were introduced in single batch medium. After the lag phase the microorganisms in microwave-treated LDPE–TDPA bioreactor metabolized and produced an increased amount of $CO_2$ until the $28^{th}$ day. For the untreated film containing bioreactor, $CO_2$ evolved to gradually increase value until the $19^{th}$ day, thereafter, a sudden increase in $CO_2$ evolution occurred on the $20^{th}$ day and a stable amount of $CO_2$ was found until the $28^{th}$ day. It was observed that the total amount of $CO_2$ evolved for microwave-treated LDPE–TDPA was 16 mg on the $28^{th}$ day whereas untreated LDPE–TDPA was 5.54 mg.

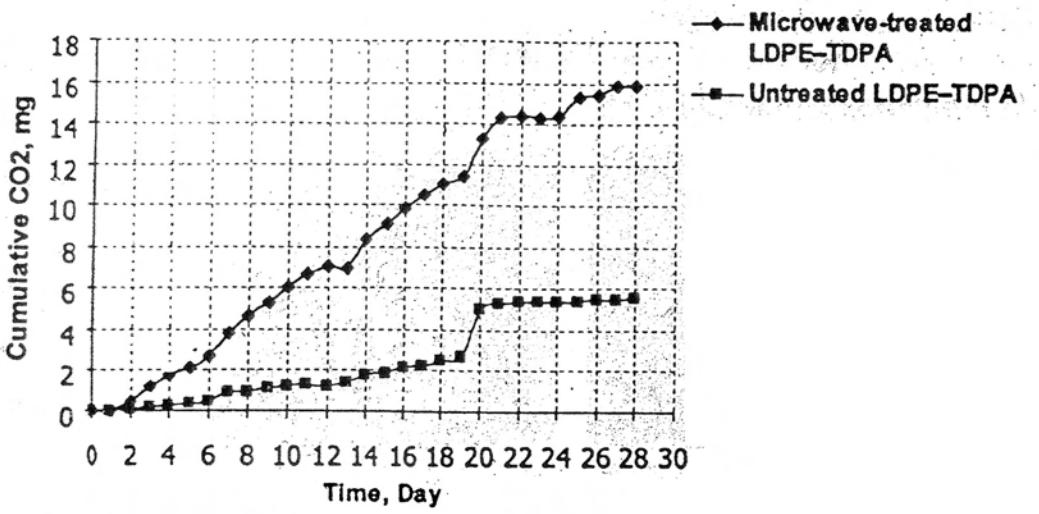


Figure 2. Cumulative $CO_2$ Evolution

Based on the actual carbon content of the added plastic samples, the conversion of carbon to theoretical quantity of $CO_2$ evolution can be computed for each sample. By the correlation of cumulative $CO_2$ produced and theoretical $CO_2$, the mineralization of polymer plastics can be expressed. The carbon content of LDPE–TDPA was 79.085% (weight) based on the study of Chiellini, Corti, and Swift in 2003.

Figure 3 represents the mineralization of each plastic sample. For a readily biodegradable chemical substance it should produce greater than 60% of its theoretical total within 28 days and the biodegradation should reach 10% within 10 days (Seal, 1995). It was apparent that biodegradation or mineralization of both plastic films could not reach the said conditions within 28 days. However, results indicated that microwave-treated LDPE–TDPA reached 7% mineralization while untreated film showed 2.22% mineralization.

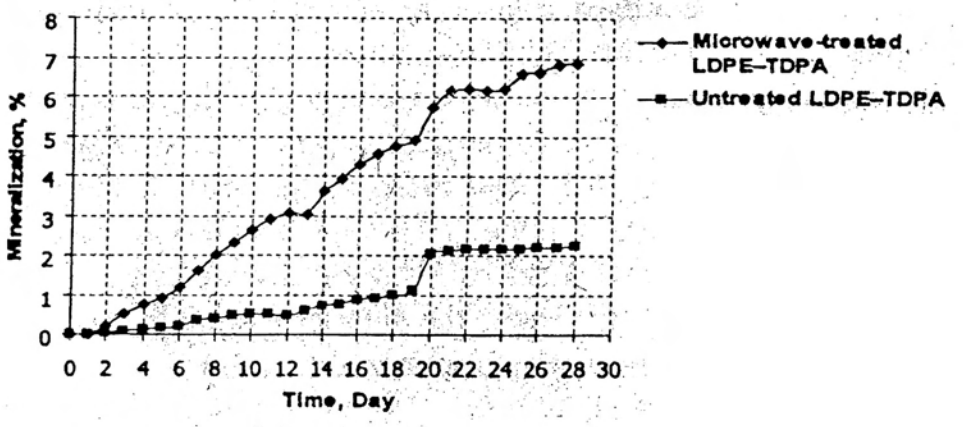


Figure 3. Mineralization of Plastic Films