Biodegradability of Untreated and Microwave Treated Low Density Polyethylene-Totally Degradable Plastic Additives (LDPE-TDPA): A Preliminary Result

Soe Soe Than, Florinda T. Bacani, Susan A. Roces
Chemical Engineering Department De la Salle University-Manila, Philippines
2401 Taft Avenue, Malate, Manila, Philppines, 1004
Fax: (632) 524-0563
E-mail: bacanif@dlsu.edu.ph

Nguyen Xuam Sam
Department of Biotechnology and Molecular Biology, Hanoi University of Technology
No. 1, Dai Co Viet Road, Hanoi, Vietnam

Yasunori Tanji
Department of Bioprocess Engineering and Biotechnology, Tokyo Institute of Technology
4259 Nagatsuda, Midori-ku Yokohama 226-8501, Japan

Abstract: Locally available biodegradable plastic LDPE–TDPA is an alternative solution to the problem of plastic packaging waste and litter. The synergistic effect on LDPE–TDPA under microwave treatment were considered in this study in order to speed up its biodegradation. Heating thru microwave irradiation initially degraded the plastic first into molecular fragments. The resulting fragments eventually became readily accessible to biodegradation by the microorganisms in liquid medium under anaerobic condition and microbial resistance in solid agar nutrient using activated sludge withdrawn from wastewater treatment plant as inoculum.

Biodegradability assessment by biodegradation tests – closed bottle test in liquid anaerobic nutrient solution and petri dish screen test (polymer microbial resistance test)–are used to attribute the extent of biodegradation of untreated plastics and microwave–induced plastics. The biodegradability of untreated LDPE–TDPA and microwave induced LDPE–TDPA were compared. Results showed higher bioassimilation of microwave irradiated LDPE–TDPA after two weeks in liquid anaerobic condition, while original LDPE–TDPA did not show any significant bioassimilation. Based on the rating of ISO 846 both original and microwave irradiated LDPE-TDPA plastic polymers are rated 3 meaning no resistance microbial attacks containing nutritive substances is feasible. Microbial colonization was found in petri dish screen test in solid anaerobic condition after two weeks for both plastic films.

Key Words: LDPE–TDPA; biodegradation; microwave irradiation; biodegradable plastic

1. INTRODUCTION

Public awareness of the growing amount of plastics wastes as litter takes account of the proper disposal of plastics. Recycling is the alternative way of reducing these plastic wastes, but not all plastics are available for recycling due to difficulties in sorting and to the needs of particular interest for market demand. Another alternative waste disposal method for plastics is incineration. However, incineration and source reduction remain problematic as options since the burning process releases harmful, toxic pollutants into the environment.

Three types of degradable plastics have been introduced as technical solutions: (a) Photodegradable plastics (by action of natural light), (b) Oxidative-degradable plastics (by action of natural light or heat in air enhanced by mechanical stress), and (c) Hydrolytic-degradable plastics (by action of water known as hydrolysis).

Among these three, oxo–degradable technology using Totally Degradable Plastic additives (TDPA) incorporated in polyethylene facilitates its disintegration and subsequent biodegradation. TDPA have been formulated for conventional Low Density Polyethylene (LDPE) polymers by compounding additives based on transition metal ions, such as manganese (Mn), copper (Cu), iron (Fe), cobalt (Co), nickel (Ni), cerium (Ce), and on metal complexes, such as cobalt stearate and cerium stearate, at appropriate levels to provide enhancement to their oxidative degradation. These additives render conventional polyethylene (PE) susceptible to hydroperoxidation initiated by heat, UV light, or mechanical stress in the environment (Department of the Environment and Heritage, Australia, 2003).

It has been reported (Dupret et al., 2000; Chiellini et al., 2003) that thermal and/or photolytic abiotic treatment promotes the eventual biodegradation of both Low Density Polyethylene (LDPE) and LDPE containing pro-oxidant additives like Low Density Polyethylene–Totally Degradable Plastic Additives (LDPE–TDPA) by monitoring the initial variations in molecular weight and other structural parameters, such as tensile strength and degree of crystallinity. Thereafter, biodegradation is observed when degraded polymers are exposed to biotic environments. The biodegradation and microbial assimilation of LDPE–TDPA oxidized products when exposed to different environments become more significant for its ultimate mineralization. This cocurrent facilitation of abiotic and biotic treatments of LDPE–TDPA enhances the degree of biodegradation in the chosen environment.

The present study aims to evaluate the degradability of LDPE–TDPA through initial treatment using microwave irradiation and then through the action of microorganisms in liquid medium in anaerobic condition and microbial resistance in solid agar nutrient using activated sludge withdrawn from a wastewater treatment plant as inoculum.

2. MATERIALS AND METHODOLOGY

2.1 Materials

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 wastewater treatment plant of De La Salle University (DLSU), Manila.

A microwave labstation and domestic microwave oven with a maximum capacity of 950 W, a frequency of 2.45 GHz, and a 220-volt AC power supply, manufactured by Whirl Pool Company were used for the induction heating of the plastic film samples. The oven consists of two parts, a wave generator and a cavity. The cavity will generate heat when it is loaded. A teflon vessel reactor measuring 8×19 cm^2 will be placed inside the microwave oven cavity and assembled with a fiber optic thermometer that will enable temperature measurement.

2.2 Treatment of Plastic Films by Microwave Irradiation

Plastic films were cut into strips (15 x 3 cm) and irradiated in a Microwave labstation manufactured by Milestone at a temperature 70^0C, and 950 W for 4 h. After microwave irradiation, the films were then recut into smaller (3 x 3) strips.

2.3 Disinfection of Plastic Films

The untreated LDPE–TDPA and microwave irradiated LDPE–TDPA plastic strips were placed in a covered beaker containing sterile water and stirred for 30 min at room temperature. Each film was removed aseptically using forceps and transferred into a beaker containing 70% (v/v) ethanol and left for 30 min. Thereafter, the films were placed into sterilized petri dishes and dried overnight at 45^0C in an incubator. The films were then stored at room temperature.

2.4 Biological Treatment

2.4.1 Preparation of Inoculum

The freshly withdrawn activated sludge was filtered, washed twice with tap water, and decanted. Then, sludge was centrifuged at 3,000 rpm for 10 minutes. The inoculum solution was prepared to contain total solids of 1 g/l and used within 6 h of sampling.

The pH, Mixed Liquor Suspended Solids (MLVS) content, and Biological Oxygen Demand (BOD) value of the inoculum solution were measured using pH/conductivity meter and Dissolved Oxygen Meter.

2.4.2 Closed Bottle Test in Liquid Anaerobic Condition

The preweighed disinfected polymer films were added as sole carbon and energy source in a concentration range of approximately 100 mg/L with the exception of blanks (without polymers). The 250 ml Erlenmeyer flasks were filled with 95 ml of sterilized Mineral Medium (MM) solutions: 1 L of MM solution containing 1 ml of ferric chloride solution (0.25 g/L of $FeCl_3.6H_2O$), 1 ml of magnesium sulfate solution (22.5 g/L $MgSO_4.7H_2O$), 1 ml of calcium chloride solution (27.5 g/L $CaCl_2$), and 10 ml phosphate buffer solution (KH_2PO_4 8.5 g, K_2HPO_4 21 .75 g, $Na_2HPO_4.2H_20$ 33.4 g, NH_4Cl 0.5g) and 5 ml of sludge inoculum solution.

The aquatic reactors were tightly closed with sterilized rubber stopper and aluminum foil and incubated at 28°C in a rotary shaker at 140 rpm for 28 days. At intervals, each reactor was opened and measured for its dissolved oxygen concentration. The flasks were then closed and incubated again at 28°C in a rotary shaker at 140 rpm.

2.4.3 Petri Dish Screen Test in Solid Anaerobic Condition

The Petri Dish Screen Test followed ISO 846 and involved placing the plastic material on the surface of a mineral salts agar in a petri dish containing no additional carbon source. Petri dishes were sterilized in the autoclave at 121^0C for 30 min. Agar nutrient was poured into the sterilized petri dishes up to 6 mm deep. The preweighed disinfected test polymers were then placed on the solidified agar surface and 1 ml of the inoculum solution was sprayed both on the agar surface and on the test polymer using a sterilized atomizer. The petri dishes were sealed and incubated at a constant temperature range of 28–30^0C for 28 days were the growth were monitored and recorded for each week.

3. RESULTS AND DISCUSSION

The microwave irradiation of plastic films was done in a temperature controllable microwave labstation for 4 h as initial abiotic oxidation. The effect of microwave irradiation on the surface of the film can be seen clearly in Figures 1 and 2 that represent the original LDPE–TDPA and 4 h microwave irradiated LDPE–TDPA film.

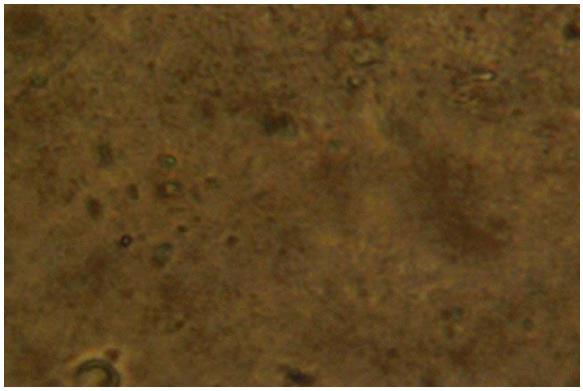

Figure 1. 100x microscopic photograph of LDPE–TDPA film

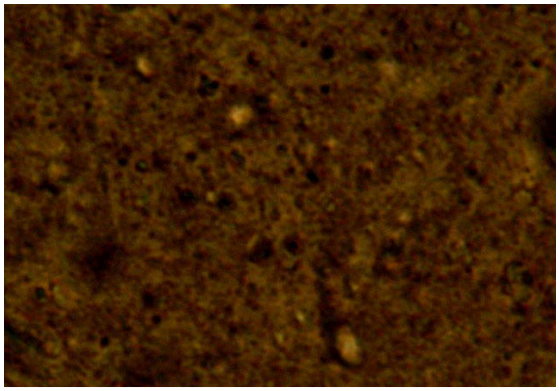

Figure 2. 100x microscopic photograph of microwave-irradiated LDPE–TDPA film

Fresh sludge utilized as inoculum for all biological treatment tests was collected from the aeration tank of wastewater treatment plant of DLSU. The main characteristics of the sludge used are shown in Table 1.

Table 1. Main characteristics of the sludge inoculum used

PH	6.84
MLVS(mg/l)	3274
BOD (mg/l)	0.92

Abiotically oxidized LDPE–TDPA and original LDPE–TDPA films were treated with activated sludge to evaluate their biodegradability by conducting closed bottle test and Petri dish screen test. The pH and dissolved oxygen content of each aquatic reactor in the closed bottle test including blank which contains inoculum and mineral medium without the test polymer were sampled on the 2^{nd}, 7^{th}, 14^{th}, and 21^{st} days. As can be seen in Figure 3, the pH profiles of LDPE–TDPA, microwave irradiated LDPE–TDPA, and the blank were decreased for the first two days. The sudden decrease of pH found in microwave–irradiated LDPE–TDPA had a value that ranged from 6.64 to 3.06 for the first week. A similar trend of decrease in pH for original film LDPE–TDPA and the blank was observed.

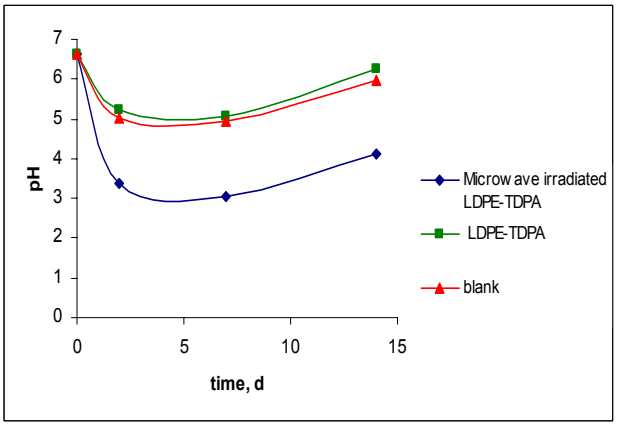

Figure 3. pH profile of Microwave treated LDPE–TDPA (♦), LDPE-TDPA (□), Blank (Δ) in closed bottle test

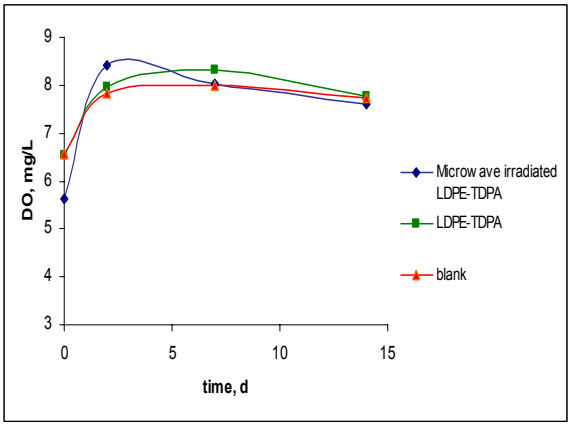

Figure 4. Dissolved oxygen concentration of Microwave treated LDPE–TDPA (♦), LDPE–TDPA (□), Blank (Δ) in closed bottle test

From Figure 4 it is apparent that there was an increase in dissolved oxygen in the first two days indicating the adaptation of microorganisms in the activated sludge to its new environment. After two days the descent dissolved oxygen (DO) value occurred for the blank, LDPE–TDPA and microwave–irradiated LDPE–TDPA films; however, a stable amount of DO was observed for the blank. During the degradation process, the aerobic microorganism in activated sludge consumed oxygen which resulted in the decrease in asymptotic DO value of 7.615 mg/l during sampling on the 14^{th} day.

The amount of dissolved oxygen depends on the temperature, amount of oxygen taken out of the system by respiring microorganisms, and the amount of oxygen put back into the system by agitation and aeration. The increased in the dissolved oxygen, is an indicative of higher concentration of microorganisms present in the system (Spanjers et al., 1998). Upon biodegradation, the polymer was converted into the biomass, CO_2, and eventually secondary products. Oxidation of the polymer to CO_2 results mainly from the tricarboxylic acid cycle pathway typical of aerobic bacteria metabolism. The tricarboxylic acid cycle uses O_2 as the terminal electron acceptor and is referred to as oxidative phosphorylation that allows the aerobic bacteria energy source and uses the main part of consumed O_2. Therefore, O_2 consumption and oxidation of the substrate to CO_2 are closely related (Lefebvre, et al., 1995).

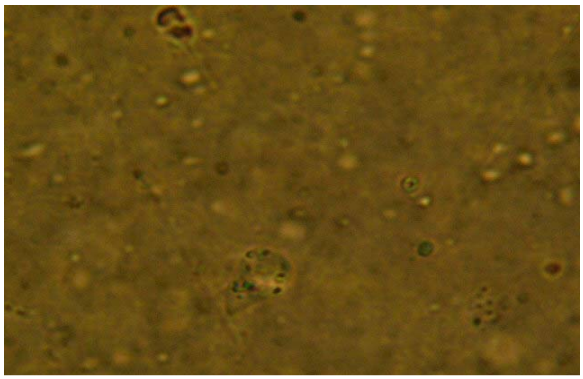

Figure 5. 100x microscopic photography of microbial attacks on the surface of LDPE–TDPA film in closed bottle test after two weeks

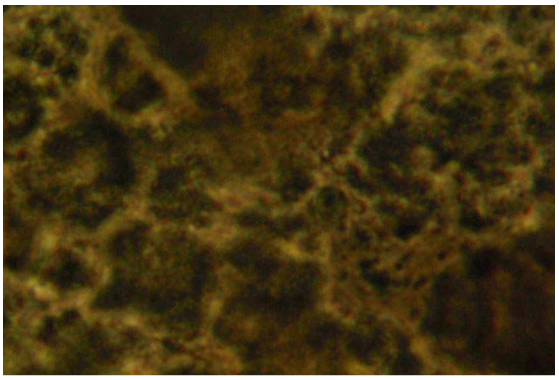

Figure 6. 100x microscopic photography of microbial attacks on the surface of microwave–irradiated LDPE–TDPA film in closed bottle test after two weeks

The microbial resistance of original LDPE–DPA and microwave–irradiated LDPE–TDPA film was determined by exposure of film surface to activated sludge in a solid anaerobic media of Petri dish agar plates. Weight loss and surface morphology changes were assessed weekly for the 7^{th}, 14^{th} and 21^{st} day. Weight loss of LDPE–TDPA first occurred during the sampling on the 7^{th} day whereas no apparent weight was observed in microwave–irradiated LDPE–TDPA. For the first week a little colonization was observed on the surface of both plastic films. After two weeks however, maximum colonization and microbial attacks were clearly seen under a microscope as shown in Figures 7 and 8.

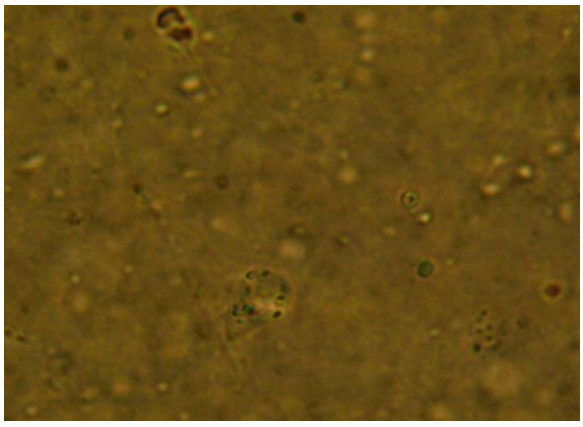

Figure 7. 100x microscopic photograph of microbial attacks on the surface of LDPE–TDPA film in petri dish test after two weeks

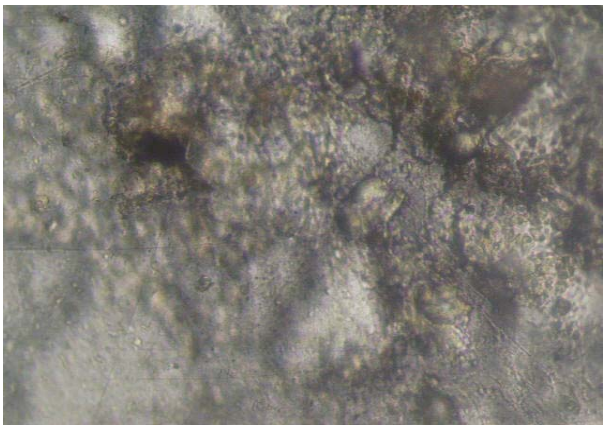

Figure 8. 100x microscopic photograph of microbial attacks on the surface of microwave–irradiated LDPE–TDPA film in petri dish test after two weeks

4. CONCLUSIONS

Biodegradability assessment by biodegradation tests – closed bottle test in liquid anaerobic nutrient solution and petri dish screen test (polymer microbial resistance test)–are used to attribute the extent of biodegradation of untreated plastics and microwave–treated plastics. The biodegradability of untreated LDPE–TDPA and microwave treated LDPE–TDPA were comparable. Results showed higher bioassimilation of microwave irradiated LDPE–TDPA after two weeks in liquid anaerobic condition, while original LDPE–TDPA did not show any significant bioassimilation. Preliminary results are indicative that heating thru microwave irradiation of plastic can cause abiotic oxidation that initially degraded the plastic first into molecular fragments. The resulting fragments became readily accessible to biodegradation by the microorganisms. The biodegradability can be assessed in starving mineral medium using activated sludge where the degraded polymer is the sole carbon source. Further confirmatory level testing should be performed under relevant conditions.

REFERENCES

Chiellini, E., Corti, A., and Swift, G. (2003) Biodegradation of Thermally-Oxidized, Fragmented Low-Density Polyethylene, *Polymer Degradation and Stability 81*, 341–351.

Dupret, I., David, C., and Daro, A. (2000) Biodegradation of Polyester-amides Using a Pure Strain of Microorganisms or Parpain II Polymer, *Polymer Degradation Stability 67*, 605.

Final Report to Department of the Environment and Heritage, Australia. (2003) *The Impact of Degradable Plastic Bags in Australia.*

ISO 846. (1997) Determination of Behavior Under the Action of Fungi and Bacteria, *Petri dish Screen Test*, International Standard 846: 1997, International Organization for Standardization (ISO), Geneva, Switzerland.

Lefebvre, F., Daro, A., and David, C. (1995) Biodegradation of Polycaprolactone by Microorganisms from an Industrial Compost of Household Refuse. Part II, *Degradable Polymers, Recycling, and Plastics Waste Management,* Edited by Ann-Christine Albertsson and Samuel J. Huang, Marcel Dekker, Inc., 280.

Seal, J. K. (1995) Test Methods and Standards for Biodegradable Plastics, *Degradable Polymers*, Edited by Gerald Scott and Dan Gilead, Chapman & Hall, 116–129.

Spanjers, H., Vanrolleghem, P. A., Olsson, G., and Dold, P. L. (1998) *Respirometry in Control of the Activated Sludge Process: Principles*, published by the International Association on Water Quality, Scientific and Technical Report Series, 7–10.