BIODEGRADATION OF PLASTIC COMPOST BAGS UNDER CONTROLLED SOIL CONDITIONS

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Abstract

A degradation of compost bags strips made of supposedly degradable polyethylene and nondegradable low density and high density polyethylene were evaluated in soil mixed with 50% (w/w) mature municipal solid waste compost supplied from municipal refuse. Plastic films were buried during 15 months at room temperature in 2 L desiccator jars containing soil adjusted to 40% of maximum water holding capacity. Degradation of plastics was determined by the weight loss of sample, tensile strength, carbon dioxide production, chemical changes measured in infrared spectrum and bacterial activity in soil. The examined films can be ranged in order of decreasing susceptibility: degradable polyethylene >>> low density polyethylene > high density polyethylene.

Key words: biodegradation, compost bags, polyethylene

Introduction

Use of plastics in agriculture has increased the plastic litter problem in rural communities and there is significant effect to the plastic waste amount. Polyolefin derived plastics such as polyethylene are currently used in plastic films for garbage bags, mulching and compost bags. These plastics are characteristically inert and resistant to microbial attack and therefore they remain in the nature without any deformation for very long time. Due to the extensive agricultural activities in Turkey, the plastics using for these purposes are widely distributed to soil. The disposal of over 11 million tons of commercial synthetic plastic per year in Turkey has raised demand for degradable or biodegradable plastics as a means of reducing the environmental impact related to the waste management of plastics. Plastic film is being increasingly used as agricultural mulch to retain moisture, increase the soil temperature and inhibit weeds. Progressive biodegradation of film fragments is predicted once the film is plugged into the top soil. It is claimed that a similar approach can be used to destroy plastic litter.[1]

Research on degradable synthetic polymers begins in the early 1980's. The recognised lack of biodegradability of large volume of commercial polymers, particularly commodity plastics used in packaging (e.g. fast food), industry and agriculture, focused public attention on a potentially huge environmental accumulation and pollution problem that could persist for centuries.[2] Biodegradability of plastics has been proposed as a solution for the waste problem. Therefore there is growing interest in degradable plastics which degrade more rapidly than conventional disposable. One of the most commonly suggested uses for starch-based degradable plastics is for composting of lawn, garden and shrub litter, which could reduce the volume of material entering the landfills by up to 20%.[3] Interest in biodegradable plastics for packaging, medical, agricultural and fisheries applications has increased in recent years.[4,5]

Different degradable plastics have been developed.[4] In one development, plastics' inertness and resistance to microbial attack was reduced by incorporating starch and later prooxidants.[2,6,7] The degradation of polyethylene can occur by different molecular mechanisms; chemical-, thermal-, photo and bio-degradation. Some studies[3,4,8,9,10] have assessed the biodegradability of some of these new films by measuring changes in physical properties or by observation of microbial growth after exposure to biological or enzymatic environments, but mostly by CO_2 evolution.

Biodegradation is therefore considered as a subset of degradation, which is defined here as any physical or chemical change in a material caused by any environmental factor, including light, heat, moisture, wind, chemical conditions or biological activity. The field tests burying plastic samples in soil have been widely conducted for their biodegradation because of the similarity to actual conditions of use or disposal. The biodegradation of plastics proceeds actively under different soil conditions according to their properties, because the microorganisms responsible for the degradation differ from each other and they have their own optimal growth conditions in the soil.[4] The literature on the biodegradation of synthetic polymers is sharply divided between those suggesting that microbiological attack can only occur if polymers could be degraded to extremely short chain lengths, and those suggesting that synthetic polymers can also be metabolised at relatively high molecular weights.[10] A degradation of polymers may proceed by one or more mechanisms, including microbial degradation in which microorganisms such as fungi and bacteria consume the material. The degradation

mechanisms will vary depending on the polymers' environment and desired application. The biodegradability of plastics is desirable to be estimated in natural environment, where the wasted plastics are exposed as such.

The aim of this study was to investigate the degradation of disposable compost bags made of supposedly degradable polyethylene compared to the nondegradable low density and high density polyethylene, in controlled soil conditions.

Experimental

High density polyethylene (HDPE, 0.030 mm), low density polyethylene (LDPE, 0.042 mm) and polyethylene films containing 9% of starch and commercial prooxidant (autoxidizable fatty acid ester, catalytic agents and transition metals) additives (Naturegrad Plus, NP, 0.040 mm) were supplied from Petkim and Petroskey Plastics, Inc. Plastic strips were cut (2.54 x 15.24 cm) and placed in oven at 70 °C for 20 days in order to simulate the termophilic phase of a full scale composting process and to achieve material disinfection. Before the experiment, plastic films were aseptically kept for 2 days at 23 ± 2°C with a relative humidity of 50 ± 5%. Degradation of polyethylene compost bags strips made of HDPE, LDPE and NP were evaluated in soil mixed with 50% (w/w) of mature municipal solid waste (MSW) compost supplied from municipal refuse from the area of Ondokuz Mayis University, Samsun. Plastic films were buried during 15 months at room temperature in 2 L desiccator jars containing soil adjusted to 40% of maximum water holding capacity.

After a specified period of time, films were removed from the soil, thoroughly rinsed with tap water, following immersion in distilled water until it remained clear and drying in oven at 70 °C for 24 h. Samples were allowed to equilibrate to ambient temperature and humidity for at least 24 h before measurement. Biodegradation of the samples was followed by measuring the weight loss of samples, tensile strength, carbon dioxide (CO_2) production, chemical changes as seen from the infrared spectra and bacterial activity in soil.

The mass of each sample was measured before and after degradation using a Perkin-Elmer AD-4 Auto balance.

The most probable number (MPN) method by two tubes per dilution technique was used for enumeration of total viable bacterial counts in soil. The MPN method

involved decimal dilution of 1 mL of sample in tubes containing the basal medium (in g/L of distilled water: bacto-peptone 5.0; yeast extract 3.0; D-glucose 1.0; pH 6.0-6.5). Inoculated tubes were incubated for ten days at 25 °C. A pH drop and pink colour of methyl red indicator were taken as evidence of growth and these tubes were scored as positive. The MPN were estimated from the combination of positive and negative scores.[4] In order to examine the change of the activity of bacteria in soil during the test, colony forming units (CFU) of aerobic mesophilic heterotrophic bacteria were measured at appropriate intervals in the blank soil, by the dilution spread plate method using albumin agar medium and cultivation for 3 weeks at 25 °C.

Tensile testing was performed on 2 mm strips, gauge length 1.25 cm, cross-head speed adjusted to give 30 sec breaks on an Instron Model 4502 Universal (Instron Corporation, Canton, MA) Tensile Tester. Prior to testing the strips were conditioned for 40 h at 20 °C and 50% relative humidity.[11]

A modified Sturm test from the OECD test[4] and ASTM[12] procedures for testing of polymers were used to determine CO_2 release during the plastic degradation process. These methods were used to assess the biodegradation of plastic materials when exposed to soil or to measure additional biodegradation of the product of the controlled composting test upon exposure to soil. The material to be tested was exposed to soil in a desiccator jar. Alkali solution in an open beaker inside the desiccator was used to trap the CO_2 evolved, and a beaker of water maintained the humidity. Periodically, the vessel was opened to replenish the air with oxygen and replace the CO_2 trapping solution, which was titrated to determine the rate and extent of mineralization of the test material to CO_2.

The chemical changes of plastic films during experiments were evaluated by changes in the film infrared spectra measured on a Perkin Elmer IR, 1430 Radio Recorder. Polyethylene films were affixed directly to standard infrared sample plates. After their removal, samples were washed with deionised water and dried at 50 °C in a vacuum oven for 24 h before measurements.

Results and Discussion

The weight loss of plastic films during degradation in soil amended with mature MSW compost is shown in Figure 1. The change of weight of LDPE and HDPE films

were not observed but the weight of NP film was reduced significantly - as much as 18%, after heat treatment. The weight loss of NP films in soil conditions started without an apparent lag phase and reached approx. 4% after four weeks of burial, which is consistent with the reported[13] mineralization of LDPE containing prooxidant additives. However, the weight loss of 36.0% achieved after 17 weeks showed no significant additional increase until the end of soil burial. The HDPE and LDPE showed a lag phase of 4 weeks, after which a slight weight loss (1.3 and 2.1%, respectively) was observed. Prooxidant transition metal combinations demonstrated the greatest effect on thermal degradation at 70 °C for 20 days. Upon activation by heat in the presence of oxygen, prooxidants produce free radicals on the polyethylene chain, which result in oxidation and a change in physical properties.
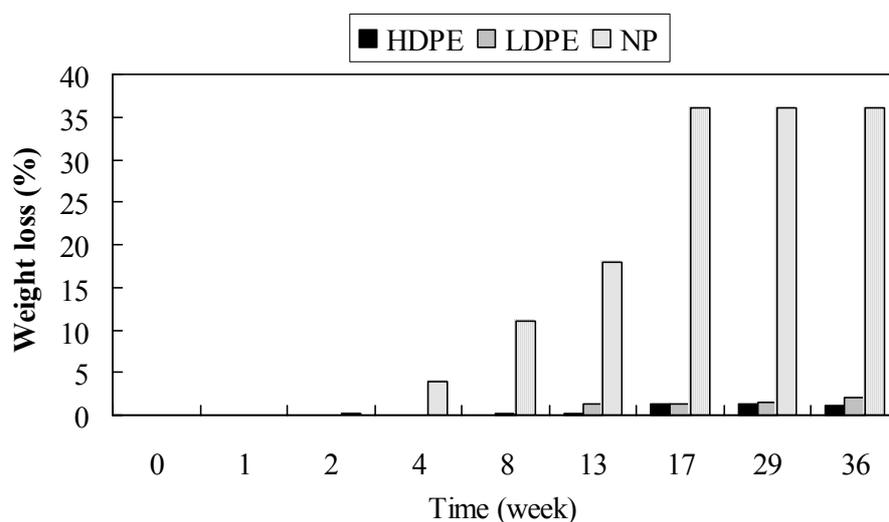
Figure 1. Weight loss (%) of high density polyethylene (HDPE), low density polyethylene (LDPE) and degradable polyethylene (NP) films during soil burial.

The microbiological process which lead to the destruction of natural polymers such as starch, cellulose and proteins during exposure to soil are well understood.[1,10] However, for the commercialised synthetic polymers, there are conflicting claims regarding their sensitivity to microbiological attack.[10] The useful lifetimes (normally measured by embrittlement) of films prepared from synthetic polymers when exposed to soil are now of relevance to many areas. The manner and rate of degradation of a polymer are dependent on the mechanism of degradation and on the acceleration of process. A variety of environmental factors such as oxygen, temperature, sunlight,

water, stress, living organisms and pollutants may affect the degradation of polymer.[10] Therefore, it is important from the viewpoint of soil microbiology to determine the biodegradability of plastics and microorganisms responsible for it in each soil condition for reaching the general conclusion on its biodegradability. Figure 2 shows the variation in the CFU of aerobic mesophilic heterotrophic bacteria and water content of the blank soil versus time.
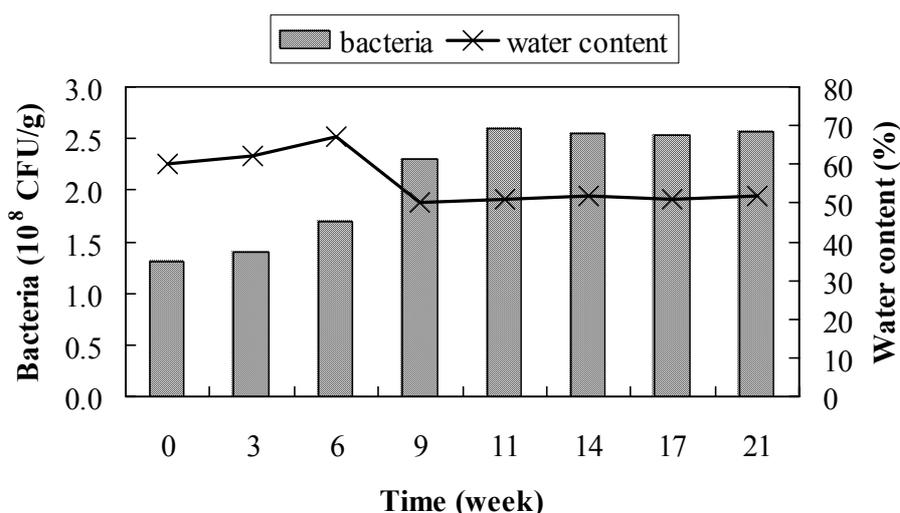

Figure 2. Colony forming units (CFU) of aerobic mesophilic heterotrophic bacteria per g of dry weight and water content (%) in studied soils.

The percentage of water content of soil ranged between 65 and 50% during the whole period of monitoring. The bacterial growth rate had a maximum at six weeks and then decreased. Cell growth was strongly inhibited by LDPE and HDPE. After an increase during the first nine weeks of monitoring, bacterial number in the blank soil was kept at constant value until the end of test period. An increase of bacterial population correlated with the signs of disintegration of mechanical properties of NP films, indicating the role of biotic component in degradation process.

For the NP and LDPE samples after three weeks of experiment the pH values of the MPN media ranged between 3.5 and 4.5, but stayed unchanged (6.0-6.5) for HDPE samples. The pH drop was caused by an accumulation of organic acids and gases released as a result of biodegradation. At the lowest pH at which the maximum CO_2 evolution occurred, fungi grow well with the optimal lignolytic activity.[4] It was reported that polyethylenes are susceptible to degradation by fungi.[10] Therefore, except bacterial

activity, it is probable that fungi also played an important role in the biodegradation of tested NP and LDPE samples .

In most applications envisaged for films or fibers in contact with the soil, loss in tensile properties is the most relevant practical criterion to determine its degradation.[1] Tensile strengths for compost bag samples are shown in Figure 3.
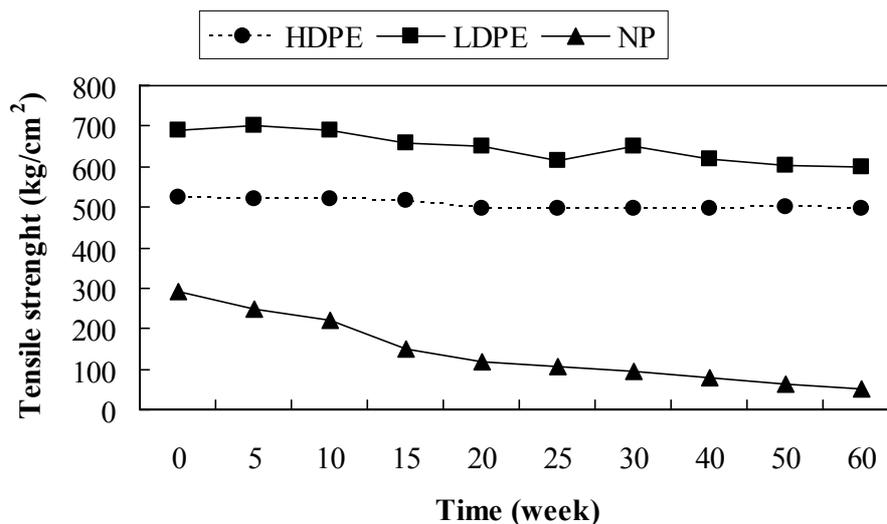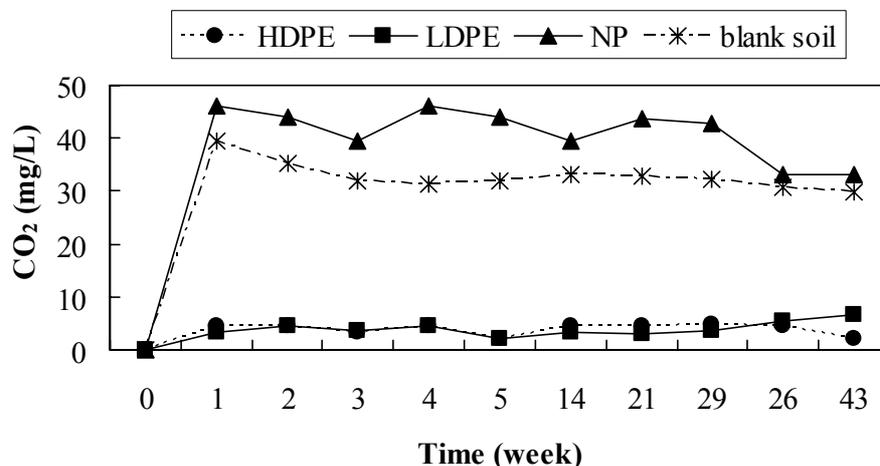

Figure 3. Tensile strength of high density polyethylene (HDPE), low density polyethylene (LDPE) and degradable polyethylene (NP) films during soil burial.

NP was remarkably susceptible (82.76% loss of tensile strength), while HDPE and LDPE remained relatively resistant (5.33 and 13.04% loss of tensile strength, respectively). According to the loss in physical properties, the films can be ranged in order of decreasing susceptibility: NP >>> LDPE > HDPE. The hydrophobicity of polyethylene is the main reason of its resistance to microbial enzymatic systems.[12] It is likely that the starch in NP films allowed water adsorption and provided suitable conditions for microbial colonization and degradation of starch and esters, resulting in the disintegration of NP. Degradation of mechanical properties might result from attack by microorganisms or from the soil chemistry and it will be controlled by microbiological activity and CO_2 production. Figure 4 shows the biodegradation curve of films in soil as CO_2 produced.

The CO_2 evolution of NP compost bags reached to 46.2 mg CO_2/L within 28 days. While NP bags biodegraded extensively, negligible CO_2 evolution was recorded for the other polyethylene films. How the CO_2 evolution in blank soil was much higher than in soils containing HDPE and LDPE films, it could be claimed that the presence of these

nondegradable materials inhibits the biological activity of soil. The growth of soil microorganisms and CO_2 evolution occurred simultaneously.


Figure 4. Carbon dioxide production during the biodegradation of high density polyethylene (HDPE), low density polyethylene (LDPE) and degradable polyethylene (NP) films and in blank soil.

Infrared spectrum comparing the non-degraded and degraded polyethylene compost bags showed no significant chemical changes except for NP samples (Figure 5).

The infrared spectrum stayed unchanged for HDPE samples. After a period of burial the carbonyl absorption band for LDPE and NP extending from 1625 to 1850 cm, indicating various types of oxidation products formed during the biodegradation of polyethylene. The appearance of the carbonyl peak (1720 cm) and more double bonds (1650 cm) for NP samples (Figure 5b) is in agreement with the biodegradation mechanism of polyethylene.[10,11,13] The infrared spectrum for starch also absorbs in this region and therefore, much of the 1400-1800 cm absorbance may be due to the absorption of enzymes and proteins onto the remained starch granules in NP. However, there was a loss of C-O absorption bands (960-1290 cm), indicating removal of starch from the plastic film.[4] The starch contained in NP samples is preferentially removed leaving the polyethylene network.

Degradation of NP could be achieved through a combination of microbial and chemical processes, especially when prooxidants or organometallic additives were present in the starch-plastic blend.[8] The control films that went trough the thermal pre-treatment but were not exposed to the soil burial, did not show a significant change of

the measured material parameters. The thermal pre-treatment probably promoted the prevailing biological process of disintegration of the NP films. It is evident from the results, that degradation of HDPE and LDPE in the natural environment posses a serious environmental concern due to their slow degradation rate. A new generation of environmental friendly polyethylene, such as tested NP containing 9% of starch and prooxidant additive, are highly recommended for use, since its degradation in environmental conditions is much faster. After five months of soil burial, a significant degradation of NP was achieved, as indicated by loss of weight (36%) and tensile strength (59%), CO_2 production, changes in infrared spectrum and total viable bacterial count activity. Moreover, the degradation of NP continued up to 15 months of monitoring. Nevertheless, full mineralization of NP still remains to be determined.
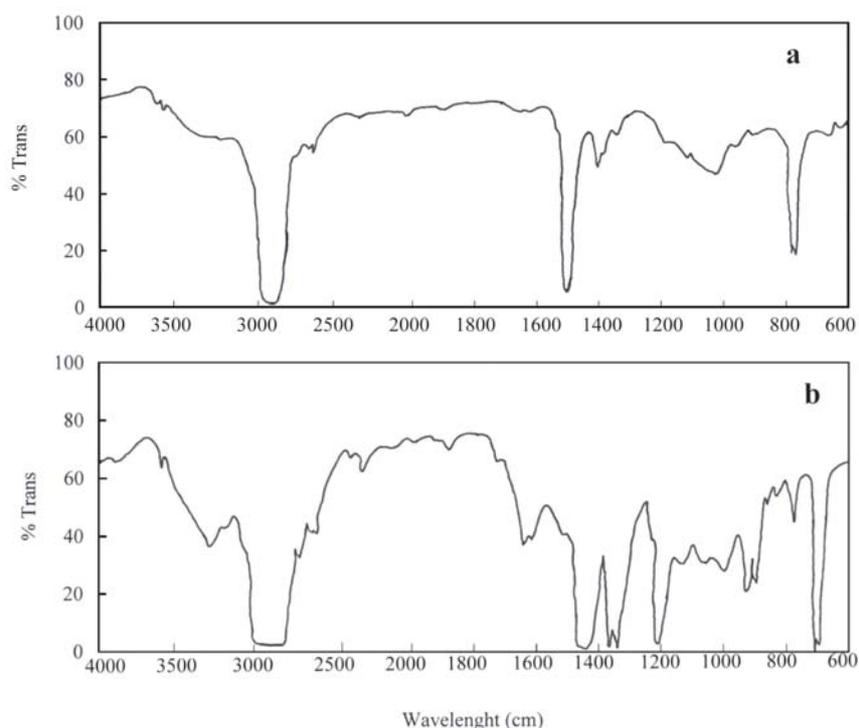
Figure 5. Infrared spectrum of degradable polyethylene (NP) films before soil burial (a) and after 60 weeks of soil burial (b).

Conclusions

Within the time scale of our experiments, HDPE appears to possess a high resistance to soil conditions. The LDPE materials recovered from the soil demonstrated very little degradation, indicated by lower changes in tensile strength and infrared spectrum and total viable bacterial count activity. An extensive degradation was observed for recovered NP plastic compost bags. At the end of experiments, the NP

films were colourless. The starch contained in NP samples was removed after 90 days leaving the polyethylene network. In NP, polyethylene polymers, starch granules and an autoxidizable fatty acid ester generate peroxides which chemically attack the bonds in the polymer molecules reducing the molecular chains to a level where they can be consumed by microorganisms. At the same time, the starch granules are biodegraded by the microorganisms present in soil. The increased surface area produced by this action and subsequent fragmentation of the product enhances the autoxidation of the polymer. Other mechanisms which play significant role are physical damage due to the microorganisms, biochemical effects from the extracellular materials produced by the microorganic activity. Moreover the rate of degradation is affected by environmental factors such as moisture, temperature and biological activity. Degradation of NP was indicated by loss of weight and tensile strength, CO_2 production, changes in infrared spectrum and total viable bacterial count activity.

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Povzetek

A degradation of compost bags strips made of supposedly degradable polyethylene and nondegradable low density and high density polyethylene were evaluated in soil mixed with 50% (w/w) mature municipal solid waste compost supplied from municipal refuse. Plastic films were buried during 15 months at room temperature in 2 L desiccator jars containing soil adjusted to 40% of maximum water holding capacity. Degradation of plastics was determined by the weight loss of sample, tensile strength, carbon dioxide production, chemical changes measured in infrared spectrum and bacterial activity in soil. The examined films can be ranged in order of decreasing susceptibility: degradable polyethylene >>> low density polyethylene > high density polyethylene.