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Microbial biodegradable potato starch based low density polyethylene

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Plastic materials remain in the nature for decades. Slow degradation of plastics in the environment caused a public trend to biodegradable polymers. The aim of this research was to produce the microbial biodegradable low density polyethylene with potato starch. Degradation of potato starch based low density polyethylene (LDPE) was investigated in soil rich in microorganisms for 8 months. Weight differences of polymeric samples before and after degradation in soil indicated soil biodegradation. Fourier transform spectroscopy (FTIR) approved the result. Scanning electron microscope (SEM) and weight change after 84 days' exposure to *Pseudomonas aeruginosa* confirmed degradation by microorganisms. In addition, potato starch based LDPE was exposed to 8 different kinds of fungi and the degradation was studied visually. Result confirmed the microbial biodegradability of potato starch based LDPE blend in natural and laboratory condition.

Key words: Low density polyethylene, fungi, biodegradable polymer, *Pseudomonas aeruginosa*.

INTRODUCTION

Synthetic polymers could not be degraded by present natural microorganism, so they remain in the environment. Growing consumption of polymeric materials caused the increase in solid waste production. In almost everywhere, plastic waste can be seen. Collection and disposal of solid waste costs and problems created. Landfills are occupied by plastic materials (Breslin, 1993). Production of biodegradable plastics is considered as a possible way to solve the solid waste problem (Ojomu et al., 2003). Compounding petroleum based polymers with natural polymers such as starch, cellulose, lignin, chitin and chitosan is a significant way to accelerate polymer biodegradation (Liu et al., 2003; Biikiaris et al., 1998). Research on biodegradable petroleum based polymer began in the 1970s (Chiellini, 2003). Biodegradable polymer during their usage must have same mechanical properties like synthetic polymers. However, they are finally degradable to low molecular weight compounds

such as H_2O and CO_2 but they are nontoxic byproducts in living microorganisms (Ikada et al., 2000). Microbial biodegradable plastics could be degraded into simpler particle such as CO_2 or water by microorganism's activities. Bacteria and fungi are attracted to polyethylene starch based blend (Rutkowska et al., 2002). Microorganisms break the polymeric chain and consume materials through aerobic and anaerobic process.

Low density polyethylene was used in huge scale for package and production of bags, composites and agricultural mulches (Raj, 2004; Wang, 2005). Microorganisms catabolized the end chain of polyethylene. Polyethylene is the hydrophobic polymer with high molecular weight; degradation of polyethylene takes a hundred years in nature (Labuzek et al., 2003). LDPE has a kind of carbon-carbon linkage that microorganisms cannot degrade easily.

Starch is an inexpensive materials used as a biodegradable additive. Starch is abundant, biodegradable and renewable; so appropriate for blending with synthetic polymers (Matzinos et al., 2001).

In food packaging section, starch based plastic is most considered. Plastic that contained starch did not have a

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negative effect on quality of food or other packed materials (Raj, 2003). Also, starch based plastic did not have a negative effect on the environment and also reduced the green house effect (Bastioli, 2001). Synthetic plastic takes a long time to degrade in nature. The use of starch as a biodegradable agent accelarated the time of degradation in the environment.

MATERIALS AND METHODS

Materials

Low Density Polyethylene (LDPE), with commercial grade (0200) was prepared from Bandar Imam petrochemical complex, Iran. Food grade potato starch was obtained from Alvand co. Iran. Glycerol with food grade was obtained from Merck co. Germany. Polyethylene grafted maleic anhydride (PE-g- Ma) was produced in Karankin Co., Iran. Olive oil was used as a moisturizer.

Compounding

Starch powder was plasticized with 25 wt% glycerol at 180 $^{\circ}$ C for 10 min. Samples were processed in HBI system (Haake Buchler Company from UK) with 60 rpm in 160 $^{\circ}$ C. Sample sheets (0.4 mm thickness) were prepared by using Hot Mini Press.

Preparation of mould growth

The suspension was prepared in distilled water with 0.05% dioctyl sodium sulphosuccinate. Spore solution was put in sterile Petri dish. The polymer samples were immersed into suspension and then transferred to another sterile Petri dish and incubated in humidity greater than 90 at 30°C for 84 days. According to standards, 8 kinds of mould species that included *Aspergillus niger, Aspegillus terreus, Aureobasidium pullulans, Poecilomyces variotii, Penicillium funiculosum, Penicillium ochrochloron, Scopulariopsis brevicaulis and Trichoderma viride were used for test.*

Preparation of bacterial growth

Flat parts of polymer samples were cut into a square of 5×5 cm and placed on the surface of the nutrient agar in the Petri dish. *Pseudomonas aeroginosa* was cultured on nutrient agar medium in sterile condition. A bacterial suspension was prepared in the physiological saline and then sprayed on the samples. A piece of parafilm with dimensions of 4×4 was placed on it and was then incubated in humidity greater than 90 at 30 °C for 84 days.

Soil degradation

Samples were cut in strip shape and buried into soil for 8 months. The soil was a combination of *P. aeruginosa*, garden soil, leaf soil, compost and humus with bird fertilizer. FTIR test was performed on each sample before and after the soil was buried to confirm the biodegradability in soil environment.

Fourier transform spectroscopy (FTIR)

This test was performed using equinox 55 made by Bruker at 23 °C. The diameter of samples was 0.4 mm and the test was run

according to ASTM E 1252-07. The samples were scanned at 4 cm $^{\circ}$ 1 resolution.

Scanning electron microscope (SEM)

Surface of blends was observed by Oxford Instruments INKA Penta FET×3 scanning electron microscope at a voltage of 20 KV. Samples were fractured in liquid nitrogen, and then sputter was coated with gold.

RESULTS AND DISCUSSION

Soil degradation

Figure 1 shows the degradation of LDPE and LDPE/ potato starch in the soil. Plastic strips were buried in soil that consisted of compost, municipal waste, garden soil and P. aeruginosa; as an extra decomposer, that soil combination was a simulation of landfills. Soil environment contains different kind of microorganism and macroorganisms. Weight losses of polymer strips in the soil could be assumed as an indicator of biodegradation in the landfills or natural environment. Soil microorganisms attacked the polymer strips. First of all, microorganisms were attracted to the potato starch content of blends. Microorganisms consumed potato starch in the polymer matrix and caused a fracture in the LDPE chain. Because of the existence of maleic anhydride that made a chemical bond between LDPE and potato starch, degradation of potato starch caused a fracture in the polymer matrix and biodegradation of LDPE. Figure 2 shows a Fourier transform spectroscopy (FTIR) confirming the biodegradation in soil environment and the FTIR spectroscopy before and after degradation in soil.

FTIR exhibited some change in LDPE/potato starch after degradation in soil. The highest decrease in spectrum was observed at 1700 cm⁻¹ derived from carbonyl groups of potato starches. This reduction confirmed the degradation of LDPE/potato starch in soil. Maleic anhydride improved compatibility between non-polar LDPE and polar potato starches (Wang et al., 2005). Absorption band was between 1081- 1089 cm⁻¹ because of the weak hydrogen bond between starch and glycerol. Absorption band between 1081 and 1156 cm⁻¹ was derived from C-O-H stretching bond. Alcohol absorption band was 1070 – 1200 cm⁻¹ and this indicated a fast degradation rate of carbon chain (Labuzek et al., 2004).

Exposure to P. aeroginosa

Before and after the degradation test by bacteria, polymer samples were weighted. Table 1 shows the percentages of polymer weight loss during degradation by *P. aeroginosa*. Accordingly, pure LDPE had a little weight loss. The weight loss could be attributed to biodegradation



Time (months)

Figure 1. Weight loss of polymeric samples during 8 months soil burial.



Figure 2. Fourier transform spectroscopy (FTIR) of potato starch based LDPE (LDPE/potato starch) before and after degradation in soil.

 Table 1. Weight change of potato starch based LDPE after 84 days exposure to *P. aeruginosa*.

Samples	Weight lose (%)		
LDPE	0.43		
LDPE/ potato starches	2.19		

by *P. aeroginosa,* because carbon free media could degrade low density polyethylene (Agamuthu and Faizura, 2005).

LDPE/potato starch showed significant weights loss. It

was determined that potato starches were the only source of carbon for microorganisms. As shown in Figure 3 part (b), black spot appeared on the surface of samples, which indicate the bacterial growth; but pure LDPE did not show any visible growth.

To ensure bacterial degradation, SEM test was done. Figures 4 and 5 display the scanning electron micrograph of pure LDPE and LDPE/potato starches blend after 84 days' incubation by *P. aeroginosa*. Scanning electron micrograph (SEM) confirmed the observation of bacterial growth and weights loss measurement. According to Figure 4, the surface of LDPE was smooth. As it is shown



Figure 3. LDPE/potato starch before (a) and after (b) 84 days of exposure to P. aeroginosa.



Figure 4. Scanning electron micrograph of LDPE after 84 days of exposure to *P. aeroginosa.*



Figure 5. Scanning electron micrograph of potato starch based LDPE after 84 days of exposure to *P. aeroginosa*.

in Figure 5, some holes and bores appeared on the surface of the LDPE/potato starch blend. These holes indicate the rate of biodegradation and confirmed the potato starches removal by *P. aeroginosa* function. Bores show the area attacked by microorganisms. Potato starch was used as a main source of nutrient by *P. aeroginosa*. Potato starch consumption by bacteria caused holes in the polymer matrix and eventually the degradation of the polymer. Because polyethylene grafted maleic anhydride made a chemical bond between potato starch and polyethylene backbone, biodegradation of potato starch

lead to accelerated LDPE biodegradation. These observations agreed with other researches (Rantanakamnuan and Aht-Ong, 2006).

Fungi growth

After 20 days of sample incubation, 20% of Petri dishes were covered by fungi growth. Samples were colonized by mould about 50% in the middle of the incubation period. Fungi colonized potato starch/LDPE surface more



Figure 6. Visual fungal growth on LDPE/potato starch blend after 84 days incubation.

than 80% at the end of the incubation as shown in Figure 6. After 84-days of incubations, LDPE strips did not exhibit color change or mould growth. This result is similar to other researchers' work on polymer degradation (Abdolrahman et al., 2006). Table 2 shows the fungal growth rate on the samples. As shown in Figure 4, more than 80% of samples were covered by mould growth.

Genus *Penicillum* could decompose hazardous materials and plastic (brukato and Wong, 1991). Genus *Aspergillus* is described as a decomposer of polyethylene, DDT and starches (Labuzek et al., 2004; Scherer et al., 1999). Potato starch in polymer blends had a digestible link for mould and fungi. Microorganisms recognized the potato starch carbon link as a nutrient source. Consumption of polar hydrophilic starch caused fracture in the polymer chain. Maleic anhydride created a link between two incompatible particles, so with starch removal, a gap appeared in the polymer chain. Through the gap, microorganism's had access to the carbon link of polyethylene; the result is the polymer biodegradation.

Conclusion

Growing concern about environment pollution leads to public trends usage of biodegradable polymers. Natural polymers were used as a biodegradable additive. In this work, potato starch was a selected biopolymer. Microbial biodegradation of potato starch based on low density polyethylene was examined under natural and laboratory condition. Potato starch/LDPE weight loss and FTIR test after the soil was buried were stimulated as biodegradation in landfills. Microbial degradation in laboratory by 8 kinds of fungi and exposure to *P. aeroginosa* was done and this

Table 2. Visual	examination	of LDPE/	Potato	starch	blends
during incubatio	n.				

Cultivation time (days)	LDPE	LDPE/ Potato starch
20	0	2
40	0	3
84	0	3

0 = No apparent growth under a nominal magnification of approximately $50 \times .$

2 = Growth plainly visible to the naked eye, but covers less than 25% of the test surface.

3 = Growth plainly visible to the naked eye and covering more than 25% of the test surface.

confirmed the microbial degradability of potato starch based LDPE. Scanning electron micrograph (SEM) after exposure to *P. aeroginosa* confirmed the potato starch removal of LDPE/potato starch blend. Existence of anhydride maleic created linkage between LDPE and potato starch, so consumption of potato starch in any environment caused a destruction of polymer matrix. Consumption of potato starch as a biodegradable agent initiates the biodegradation process. According to this research, potato starch based low density polyethylene is a microbial biodegradable polymer.

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