Synergistic Effect of Photo- and Chemical Treatment on the Rate of Biodegradation of Low Density Polyethylene by Fusarium sp. AF4

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ABSTRACT: This work was focused on the possibility of accelerating the biodegradation process of low density polyethylene (LDPE). Comparative studies, between the properties of untreated LDPE pieces and those exposed to UV irradiation and nitric acid plus microbial culture treatment, were performed. The LDPE pieces were irradiated by UV light (254 nm wavelength) for 250 h and incubated with nitric acid (99.0%) at 80°C for 6 days. These pretreated LDPE pieces were used as sole carbon source in mineral salt medium and inoculated with the *Fusarium* sp. AF4, isolated from soil. The efficiency of the LDPE degradation depended on the growth phase in pure cultivation of the fungus. The changes in the structural properties of LDPE film because of UV-nitric acid and microbial treatment were determined by Fourier transform infrared spectroscopy (FTIR). It was observed that in case of UV and nitric acid treated LDPE, peaks appeared at 1710 cm^{-1} and 831, which were then reduced to 1708 cm^{-1} and 830 after microbial treatment, indicating breakdown of polymer chain. In this study, it was observed that a synergistic effect of UV-nitric acid and microbial treatment induced oxidation reaction that enhanced and accelerated the biodegradability rate of LDPE pieces. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 1466–1470, 2007

Key words: low density polyethylene; Fourier transform infrared spectroscopy; biodegradation

INTRODUCTION

During the past 20 years, there has been a continuous increase in the production of commodity and packaging plastic products such as polyolefin, accompanied by an ever-increasing amount of plastic waste. This is because such products accumulate in nature because of their resistance against chemical and biological degradation.[1,2]

The degradation of most synthetic plastics in nature is a very slow process that involves environmental factors, followed by the action of wild microorganisms.[3,4] Synthetic and natural polymers are normally not biodegradable until they are degraded into low molecular mass species that can be assimilated by microorganisms. Biodegradation must be preceded by an abiotic or biotic degradation that gives monomeric and oligomeric products.

Polyolefins, like polyethylenes (PEs) of high and low density, are primarily used in product packaging as sheets and thin films. They are hydrophobic hydrocarbon polymers, resistant to hydrolysis, and for this reason, they cannot hydrobiodegrade. The primary mechanism for biodegradation of polyolefins is the oxidation or hydrolysis by enzymes to create functional groups that improve its hydrophilicity.[5] Consequently, the main chains of polymer are degraded resulting in polymer of low molecular weight and mechanical properties are rather weak, thus, making it more accessible for further microbial assimilation.[6,7]

Hueck pointed out that PE needs to undergo some nonbiotic degradation before microbial attack because of its hydrphobicity and its large molecular dimensions.[8] Albertsson et al.[9] concluded that UV light or oxidizing agents, such as UV sensitizer, are needed at the beginning of biodegradation of inert materials such as PE and that biodegradation without them takes more than 10 years.[10] The radiation by UV or sunlight reduces the polymeric chain size of PE and form oxidizing groups such as hydroperoxides, peroxides, alcohols, ketones, and perhaps some aldehyde resulted from the partial oxidation of PE are present in small amounts, but they continue to undergo oxidation. The amounts of the intermediate products depend on whether the oxidation has been started by UV light. Ketone groups attached on PE molecules are decomposed by UV light and hydroperoxide groups are decomposed both by UV light and heat.[4,11,12] The combination of different environmental factors such as oxygen, temperature, sunlight, water, stress, living organisms, and pollutants, which

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are responsible for degradation of the polymer, may result in synergistic effects on the polymer degradation rate.[13,14]

In a long-term study on the biodegradation of ^{14}C-labeled PE, Albertsson and Karlsson[6] found that after 10 years of incubation in soil, <0.5% carbon (as CO_2) by weight was evolved from a UV-irradiated PE sheet. Nonirradiated PE emitted <0.2% carbon dioxide during the same time. Furthermore, no signs of deterioration could be observed in a PE sheet that had been incubated in moist soil for 12 years[15] and only partial degradation was observed in a PE film buried in soil for 32 years.[16]

Biodegradation of PE has been studied extensively earlier,[17,18] but the results were based on PE blend with starch.[19,20] PE was claimed to be degraded but the extent could be extremely small. Other data describing degradation of PE-containing starch is questionable, and microbial metabolites may contaminate the PE surfaces and could be interpreted as degradation products of the parent PE.[3] It is widely accepted that the resistance of PE to biodegradation stems from its high molecular weight, its three-dimensional structure, and its hydrophobic nature, all of which interfere with its availability to microorganisms. It has been demonstrated that partial biodegradation of PE after UV irradiation,[14] thermal treatment,[21,22] or oxidation with nitric acid[23] is possible.

We have isolated microorganisms from soil that could degrade LDPE without needing compounds to be added for easier degradation. The purpose of this study was to attempt to correlate the loss of low molar mass oxidation products from the polymer with the growth of selected microorganisms on the surface of the polymer, photochemically oxidized by UV-nitric acid, respectively. The degradation of PE was monitored in terms of the growth of microorganisms.[8,14] The degradation is described here with the results of Fourier transform infrared spectroscopy (FTIR).

MATERIALS AND METHODS

Materials

The low density polyethylene (LDPE) granulates of density 0.921 g/cm^3, melting temperature 109°C, were obtained from Sigma-Aldrich, Germany. The PE granules were dissolved in xylene at high temperature and again recrystallized on cooling.

Irradiation of PE pieces with UV

A set of recrystallized pieces of LDPE were exposed to UV light (254 nm wavelength) for about 250 h.

Chemical treatment of UV-irradiated PE pieces

The UV-irradiated LDPE pieces were treated for 6 days with nitric acid (99.0%) at 80°C before being used as the sole carbon source in liquid medium inoculated by *Fusarium* sp. AF4.

Isolation of the microorganisms

The soil sample was inoculated in 100-mL nutrient broth and incubated at 37°C in an orbital shaker incubator at 120 rpm for 24–48 h to prepare the inoculum. About 10 mL of inoculum was added to 100 mL of mineral salt medium containing PE pieces [(g/L): recrystallized LDPE pieces 0.5, $(NH_4)_2SO_4$ 0.2, K_2HPO_4 0.5, KH_2PO_4 0.04, NaCl 0.1, $MgSO_4{\cdot}7H_2O$ 0.02, $CaCl_2$ 0.002, and $FeSO_4$ 0.001; pH was adjusted at 7]. The flasks were incubated at 37°C with shaking at 120 rpm for 3 months. Microbial treatment was given to both treated and untreated (control) LDPE pieces. The growth of the fungal isolate was observed on alternate days and also at the end of experiment.

Detection of PE degradation in liquid culture

FTIR (Bio-Rad Merlin) analysis was done to detect the degradation of LDPE in liquid culture on the basis of changes in the functional groups. LDPE pieces were mixed with KBr and made into a tablet, which was fixed to the FTIR sample plate. A spectrum was taken at 400–4000 wavenumbers cm^{-1} for each sample.

RESULTS AND DISCUSSION

A fungal strain that grew on LDPE was isolated from soil and identified and named as *Fusarium* sp. AF4.

The LDPE used in the experiment was treated by exposing it to UV light and also nitric acid. This pretreated polymer was then applied to microbial treatment using *Fusarium* sp. AF4 in a mineral salt medium containing treated plastic as a sole source of carbon and energy. Whereas, the control flask contained untreated plastic. There was 2.6% increase in growth of fungus as observed by the change in its dry biomass.

After microbial treatment, the structural changes in the polymer were determined by FTIR. FTIR image of untreated piece of polyethylene is shown in Figure 1. It was observed that in case of UV and nitric acid-treated LDPE, peaks appeared at 1710 and 831 cm^{-1} (Fig. 2). These two peaks corresponded to carbonyl group and formation of double bonds as a result of breakdown of polymer chain. Those peaks then reduced to 1708 and 830 cm^{-1} after microbial treatment (Fig. 3), indicated the break down of polymer chain and presence of oxidation products of LDPE.[24] According to Yamada-Onodera et al.,[25] absorbance at 1710–1715 (corresponding to carbonyl

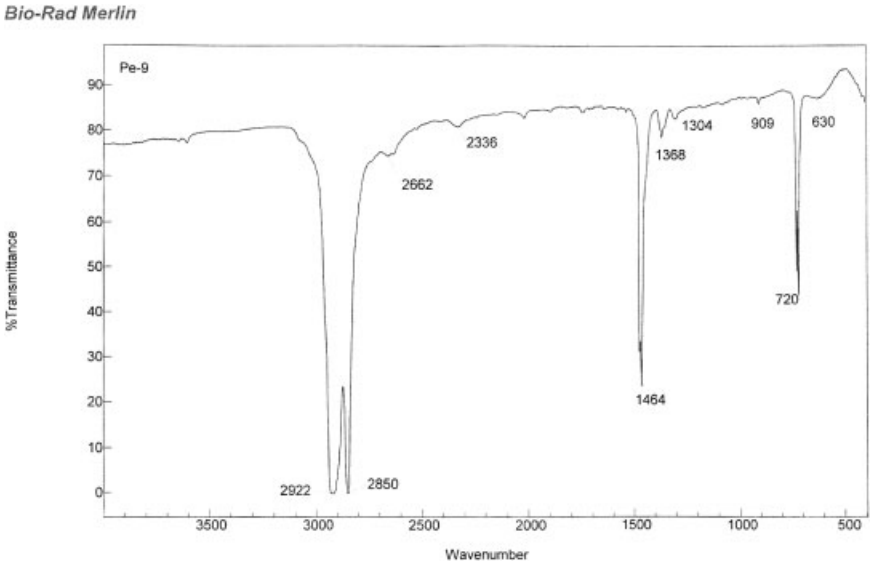

Figure 1 FTIR image of untreated piece of polyethylene.

compound), 1640, and 830–880 cm^{-1} (corresponding to —C=C—), which appeared after UV and nitric acid treatment, decreased during cultivation with microbial consortia. Typical degradation of LDPE and formation of bands at 1620–1640 and 840–880 cm^{-1}, attributed to oxidation of PE. In this study, there was no indication of breakdown of the bonds in case of untreated LDPE.

It is well-known that UV and nitric acid has a deterioration effect on many plastic materials, including LDPE. In our experiments, when LDPE pieces were exposed to UV, they underwent photodegradation, causing loss of mechanical properties/characteristics. The results of FTIR analysis showed that some of the double bonds of PE might be cut by fungal activity leading to degradation. As a sole carbon source, LDPE treated with hot nitric acid was degraded to lower molecular weight during cultivation with hyphae of the fungus. Albertsson et al.[9] concluded that carbonyl groups are produced by UV light or oxidizing agents and that these groups are main factors at the beginning of the degradation, being attacked by microorganisms that degrade the shorter segments of PE chains. Ohtake et al.[26] observed biodegradation of LDPE buried in soil for 32–37 years, which was promoted by UV irradiation. Albertsson and Karlsson[10] concluded that the biodegradation of inert material such as LDPE takes more than 10 years and that of degradable material containing UV sensitizers takes 2 years or less.

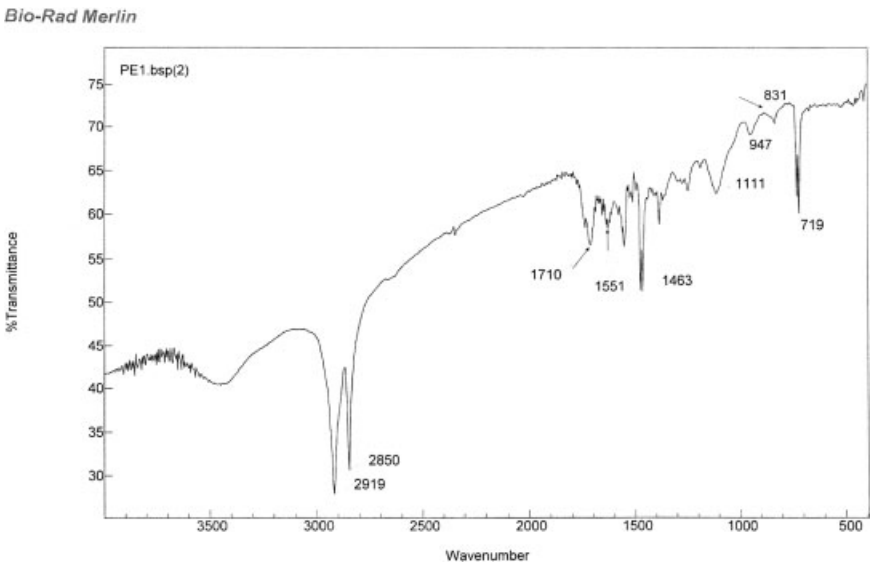

Figure 2 FTIR image of UV and nitric acid treated polyethylene piece.

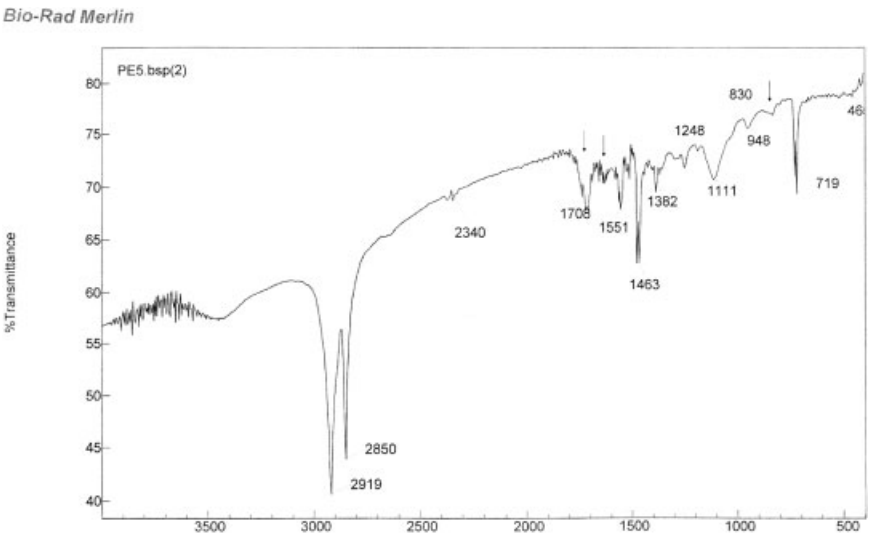

Figure 3 FTIR image of UV, nitric acid, and microbial treatment polyethylene piece.

LDPE without irradiation or the nitric acid treatment described in Materials and Methods section had no functional groups. Recrystallization does not cause the addition of functional groups. The microorganisms grew better in the liquid medium containing irradiated LDPE than that with not irradiated PE.

The photo-oxidation of LDPE is characterized by an induction period in which oxygen uptake, that is responsible for intermediate product formation includes hydroperoxides, peroxides, alcohols, and ketones. With increasing the exposure time, the oxygen uptake increases and the rate of formation of intermediate products increases leading to rapid increase in carbonyl group concentration. In this stage, the photoirradiation on LDPE is mainly caused by slightly chain scission, which resulted in chain orientation in the form of shorter, more readily crystallizable.[27] Cornell et al.[14] concluded that photo-oxidative degradation of polymers does not always facilitate progressive attack by microorganisms, because the oligomer fractions produced during photo-oxidation may support microbial growth, but polymers with a high molecular weight resulted in little or no growth.

CONCLUSIONS

A fungal strain, *Fusarium* sp. AF4, was isolated and identified, which utilized LDPE as the sole carbon source. The fungus grew better in the mineral salt medium with pretreated pieces of LDPE (which had carbonyl groups) when compared with untreated LDPE (which had no carbonyl groups). The decrease in the absorbance corresponding to carbonyl groups and —C=C— suggested that some of the double bonds of carbon in LDPE were cut by *Fusarium* sp. AF4. The results of this study indicated that biodegradation rate could be enhanced by exposing LDPE to UV and nitric acid treatment and followed by microbial treatment. This encourages in the sense that at least some degradation is happening. It suggests that further studies in sufficient details with modified procedures and microbes including other parameters are required.

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