

Biodegradability of degradable mulching film in a laboratory-controlled composting test

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Abstract: A series of degradable films was prepared, and 2 formulas of polyethylene (PE) films with the highest degradable performance were experimentally determined. These films contained 3.43% and 0.44% stearate, and were denoted as PE-3 and PE-4, respectively. Their biodegradability was studied in a laboratory-controlled composting test using ordinary PE film (OPEF) as a control. Contrast composting experiments indicated that the biodegradability of untreated samples was very low, and that the biodegradation rates of PE films after natural aging were significantly higher. FT-IR analysis showed that OPEF changed little after the composting experiment, and that PE-3 and PE-4 showed a carbonyl absorption peak at 1720 cm^{-1} , whose intensity increased with increased composting time. Analysis of the viscometric-average molecular weight revealed that it changed little for untreated film but significantly decreased for aged films, especially PE-3, after the composting experiments.

Key words: Resulting polyethylene film, biodegradability, composting

1. Introduction

The advantages of polyethylene (PE) include its ease of production, high performance, and increased crop yield. Thousands of tons of PE are used worldwide in industry, agriculture, space exploration, high-energy-density batteries and electronic devices,¹ environmental studies, medical treatment, etc.² Additionally, the applications of PE products (mulch films, greenhouse coverings, and drip irrigation) are increasing. However, only some PE products can be recycled, such as greenhouse films, silage films, fertilizer sacks, and pipes. All other products are difficult to recycle for technical and/or cost reasons,³ especially mulching cultivation products in Xinjiang, where cotton sown areas have expanded to 1.33 million ha per year. Xinjiang has long hours of sunshine and low rainfall amount during the season of crop growth. Thus, mulching cultivation is applied for cotton planting, and the amount of PE films used is approximately 10^5 t each year.⁴ With increased film usage, residual films gradually accumulate in the soil^{5,6} and become solid trash that cannot be processed by microorganisms. In other words, they are not biodegradable and result in “white pollution”. PE modification can overcome these drawbacks, and has thus been extensively studied. The major challenge in PE material research is the development of suitable modification methodologies to improve the properties of PE,⁷ and some studies have

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focused on the biodegradation of PE-starch film. Under experimental composting conditions, a study on PE biodegradation characteristics has revealed that PE-starch blends have high biodegradability and that high starch content favors PE-starch biodegradation.⁸ The degradation of PE-starch blends in soil can proceed in 2 stages: (1) simple hydrolysis of the starch fraction without affecting the PE dry weight; and (2) starch degradation by microbial enzymes at the surface level, generating small splinters of the polymer blend and enabling PE assimilation by soil microbes.⁹ However, few studies have reported on the biodegradation of PE films containing ferric stearate under experimental composting conditions.

Natural degradation is an important process for polymer matrix degradation into organic waste.¹⁰ A biological approach, such as composting or digestion, is a good method for the management of biodegradable PE waste. Compared with traditional treatments such as landfills and incineration, composting is a microbiologically mediated process wherein biodegradable wastes or organic material are converted into humic substances. Thus, composting is used as an alternative technology, and the resulting product is valuable as high-quality manure for agricultural purposes.¹¹

The advancements in biodegradable PE have prompted efforts to develop official standards and laboratory test methods to evaluate the environmental impact of PE.¹² In the last 20 years, most research has focused on biodegradation under the following composting conditions: ASTM D6400, 2004; ASTM D6868, 2003; and UNI EN 13432, 2002.^{13–15} The biodegradation of plastics is based on the measurement of carbon dioxide evolution or oxygen consumption when the original polymer is exposed to controlled environmental conditions (e.g., soil and compost). Biodegradation is generally measured as the degree of mineralization, namely conversion into CO₂, which is considered the best way to confirm total biodegradability (i.e. the total conversion of organic carbon into inorganic carbon).⁹

Several film techniques^{16–21} have also been developed in recent decades, but they cannot be widely applied because of high cost or uncontrollable degradation. Previous studies have indicated that PE biodegrades <0.5% in 100 years and about 1% if pre-exposed to sunlight for about 2 years.²² Accordingly, in the present study, we developed degradable PE films containing 3.43% and 0.44% ferric stearate, hereafter denoted as PE-3 and PE-4, respectively. Under the specific climatic conditions in Xinjiang, PE-3 and PE-4 samples with dimensions of 50 cm × 60 cm were exposed on the soil surface for 1 month, and their biodegradation was examined by composting experiments. The films were then buried in soil after use.

The general objective of this study was to determine the aerobic biodegradability of PE-3 and PE-4 under controlled composting conditions. Ordinary PE film (OPEF) was used as a control. Some of our preliminary results are reported in this paper.

2. Experimental

2.1. Sample preparation and source materials

OPEF, PE-3, and PE-4 were processed at the Tianyuan Plastic Factory in the Fifth Division of Xinjiang Province. Samples were exposed on the soil surface in Shihezi. All test samples were in the form of thin films (2 cm × 2 cm; approximately 0.01 mm thick) with a sufficiently large area per weight to accelerate biodegradability. Microcrystalline cellulose (MCE), which has a particle size of less than 20 μm, was used as a positive reference control for biodegradability testing according to ISO 14855-1, 2004.²³

2.2. Compost characterization

Compost used for biodegradation testing was derived from municipal solid waste (Urumchi, Xinjiang). To remove large inert materials such as glass, stones, and pieces of scrap metal, the compost was sieved through a screen (0.9 cm). Water was added to the compost mixture prior to the test to ensure that the moisture content ranged within 50% to 55%, which was measured by drying the compost samples at 105 °C until the compost weight was constant.⁷ The pH of the compost was measured by mixing compost with deionized water at a weight ratio of 1:5 (A:B).

Compost parameters such as pH, volatile solids, total dry solids, moisture content, and carbon-to-nitrogen ratio were considered for monitoring the chemical properties of the inocula. These parameters were determined according to the following ISO standards: 10390, 2005; APHA 2540 E, 1989; APHA 2540 D, 1989; ASTM D2216, 1998; and ASTM D5373, 2002.^{24–28} The compost parameters are listed in Table 1.

Table 1. Main chemical properties of the tested compost and standards test methods.

Parameters	Inoculums before biodegradability testing	Standard test methods
pH	7.55	ISO 10390, 2005 Soil quality–determination of pH (water:inoculums = 5:1).
volatile solids %	33.39	APHA 2540 E, 1989 Fixed and volatile solid ignited at 550 °C
total dry solids %	58.90	APHA 2540 D, 1989 Total suspended solid dried at 103–105 °C
moisture content %	8.31	ASTM D2216, 1998 Standard test method for laboratory determination of water (moisture) content of soil and rock by mass
C analysis (g kg ⁻¹)	22.84	ASTM D5373, 2002 Standard test methods for instrumental determination of carbon, hydrogen, and nitrogen in laboratory samples of coal and coke.

2.3. Biodegradation testing

The degradability of biodegradable plastic films (OPEF, PE-3, and PE-4) and MCE was investigated under simulated aerobic degradation conditions. The aerobic degradation testing conditions were in accordance with ISO 14855-1, 2004. This standard is a general method of evaluating the ultimate aerobic biodegradability of plastics based on organic compounds under controlled composting conditions. The method involves the determination of the amount of carbon dioxide evolution and degree of plastic biodegradation. The test inocula were obtained from the compost of municipal solid waste and utilized as the microbial source in the biodegradability testing. These inocula were sieved to sizes of less than 10 mm.

The composting device used had 3 parts: (1) a CO₂-removal device, (2) a composting reaction device, and (3) a CO₂-absorption device. Three-liter jars were initially filled with 1200 g of compost and 200 g of sample in triplicate for 3 different mixtures: inocula without any added material (used as a blank control), inocula with MCE (used as a positive reference control), and inocula with test samples. All jars were placed in a water bath maintained at 58 ± 2 °C, and CO₂ was removed by adding saturated sodium hydroxide solution. By adding deionized water, a moisture content of 50%–55% and pH of 7.0–9.0 of the compost were achieved to ensure favorable conditions for the growth of compost microorganisms involved in the process. To

ensure uniform distribution of the humidity in the jar, aerobic conditions were maintained by supplying an uninterrupted humidified air stream and agitating the contents in the jars at least once a week. The theoretical amount of CO_2 (ThCO_2 , g) produced by the total oxidation of the tested sample was calculated by the following equation:²⁹

$$\text{ThCO}_2 = M_{TOT} \times C_{TOT} \times \frac{44}{12}, \quad (1)$$

where M_{TOT} (g) is the total dry solids of the PE sample initially added to the compost reactors, C_{TOT} (g g^{-1}) is the proportion of total organic carbon of the PE sample, and 44 and 12 (g mol^{-1}) are the molecular mass of carbon dioxide and atomic mass of carbon, respectively.

The carbon dioxide evolved during the biodegradation test was captured by 20 g L^{-1} NaOH, which was regularly titrated with 0.1 mol L^{-1} standard HCl to the phenolphthalein and methyl red endpoint. The total amount of CO_2 evolution was calculated by referencing to the blank control reactor. The percentage of biodegradation (D_t) of the test film sample was calculated according to the following equation:²⁹

$$D_t = \frac{(\text{CO}_2)_T - (\text{CO}_2)_B}{\text{ThCO}_2} \times 100, \quad (2)$$

where $(\text{CO}_2)_T$ (g) is the cumulative amount of carbon dioxide evolved in each composting reactor containing a tested film sample, $(\text{CO}_2)_B$ (g) is the mean cumulative amount of carbon dioxide evolved in the blank reactor, and ThCO_2 (g) is the theoretical amount of carbon dioxide of the tested sample.

2.4. Molecular weight

The molecular weight of the samples was determined by viscometry. The film was dissolved in decahydronaphthalene, and the intrinsic viscosity $[\eta]$ was measured using an Ubbelohde viscometer at $135 \text{ }^\circ\text{C}$ in a thermostat-controlled oil bath with silicone oil as the medium. The viscosity-average molecular weight was evaluated by the following equation:¹

$$[\eta] = 46 \times 10^{-3} \times M_\eta^{0.73}. \quad (3)$$

2.5. FT-IR spectral analysis

FT-IR spectra were recorded with an AVATAR 360 spectrometer (Nicolet, USA). The growth of the carbonyl peak at 1720 cm^{-1} as a function of the compost time was used as a measure of the degradation degree.

3. Results and discussion

3.1. Biodegradability analysis

The biodegradable components of the film can eventually be mineralized into CO_2 and H_2O by microbes under aerobic conditions. Hence, biodegradation is generally measured as the degree of mineralization, namely conversion into CO_2 . The biodegradation behaviors of PE films are shown in Figures 1 and 2. The degradation rate of PE-3 was substantially faster than that of the others, as determined by comparing the degradation between untreated films and films insolated for a month under natural conditions after composting. After the composting experiment, the biodegradation of untreated OPEF, PE-4, and PE-3 samples was 0.08%, 0.12%, and 0.27%, respectively, and the insolated OPEF, PE-4, and PE-3 samples reached 1.51%, 2.37%, and 4.83%, respectively. Degradable films were exposed to the atmosphere to activate active substances (e.g.,

photosensitizers, free radicals, catalysts). These films not only had a certain degree of photodegradation, but also provided conditions for the thermo-oxidative degradation and microbial anaerobic digestion of PE films. The biodegradation rate of PE-3 increased with increased time, which may be caused by hot oxidation and/or humid oxidation of the part of the weak bond of polymer chain that can break and produce macroradicals. Then it acted on the oxygen to form hydroperoxide, which decomposed into free radicals under other predisposing factors. Subsequent disproportionation reaction of the macroradicals caused further degradation of the polymer chain, ultimately producing a large number of relatively stable products including alcohol and ketone. Meanwhile, the molecular weight of polymer also decreased and further became conducive to microbial degradation. The biodegradation rate of untreated PE-3 was slightly higher than that of the other untreated samples.

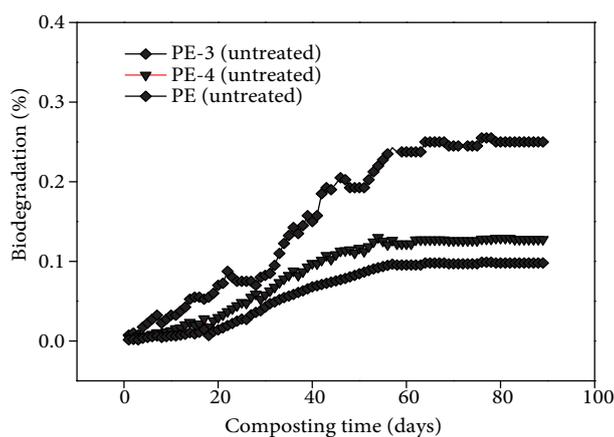


Figure 1. Evolution of the biodegradation of degradable polyethylene films without aging treatment.

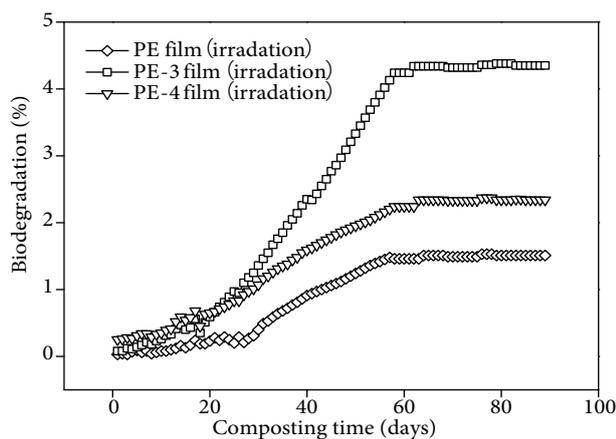


Figure 2. Evolution of the biodegradation of degradable polyethylene films after natural aging.

3.2. Viscometric-average molecular weight analysis

The M_v variations in the film samples before and after composting are shown in Tables 2 and 3. M_v of unhandled PE-film samples before and after composting minimally changed, but those of PE-3 and PE-4 samples after composting were slightly lower. M_v of unhandled OPEF, PE-4, and PE-3 samples was 0.88%, 10.12%, and 16.63%, respectively, and M_v of the insolated OPEF, PE-4, and PE-3 samples was 7.69%, 31.69%, and 38.95%, respectively, before degradation. Part of the weak bond of the polymer chain ruptured, and the molecular weight slightly decreased in the hot and humid oxygen environment. M_v of the insolated films further decreased, especially PE-3, which may be due to the added 3.43% FeSt₃ that triggered a PE photodegradation reaction, which led to PE chain fracture and promoted molecular weight decrease. Broken PE chains became low-molecular-weight substances that favored microbial digestion or decomposition. Meanwhile, PE underwent oxidation by producing radicals that further propagated to form hydroperoxide, and the main chain further caused rupture, which generated macromolecular aldehydes and/or transformed into ketone macromolecules.³⁰ With the synergistic reaction of light oxidation and thermal oxidation, the molecular carbonyl group promoted the rupture of the polymer chain to decrease M_v .

3.3. FT-IR spectra

Structural changes were investigated by recording the FT-IR spectra of the PE films under the same conditions. The FT-IR spectra of PE films before and after composting under the same environment are shown in Figures

3–8. Figures 3–5 show that the infrared spectrum of untreated samples did not change much after composting compared with before composting. PE-3 and PE-4 showed hydroxyl absorption peaks ranging from 3500 cm^{-1} to 3400 cm^{-1} . However, the absorption peak intensity was very weak, which can be attributed to the absorption of hydrogen peroxide, for PE-3, PE-4, and OPEF, which showed a carbonyl absorption peak at 1720 cm^{-1} after composting. A comparison with untreated film samples before composting indicated that the films were indeed biodegraded, although very poorly. The absorption level of the carbonyl group can characterize the depth of PE degradation. Figures 6–8 show that the carbonyl absorption peak of samples after light treatment appeared at 1720 cm^{-1} , which increased in intensity with increased composting time. This finding also showed that the PE carbon chain gradually broke and produced carboxylic compounds.

Table 2. Viscometric-average molecular weight (Mv) of mulching film with untreated before/after compost.

Original samples	Mv before composting ($\times 10^4$)	Mv after composting ($\times 10^4$)
PE-3 film	4.81	4.01
PE-4 film	4.84	4.35
OPEF	4.57	4.53

Table 3. Viscometric-average molecular weight (Mv) of mulching film with natural aging before/after compost.

Samples after aging	Mv before composting ($\times 10^4$)	Mv after composting ($\times 10^4$)
PE-3 film	2.67	1.63
PE-4 film	2.84	1.94
OPEF	3.64	3.36

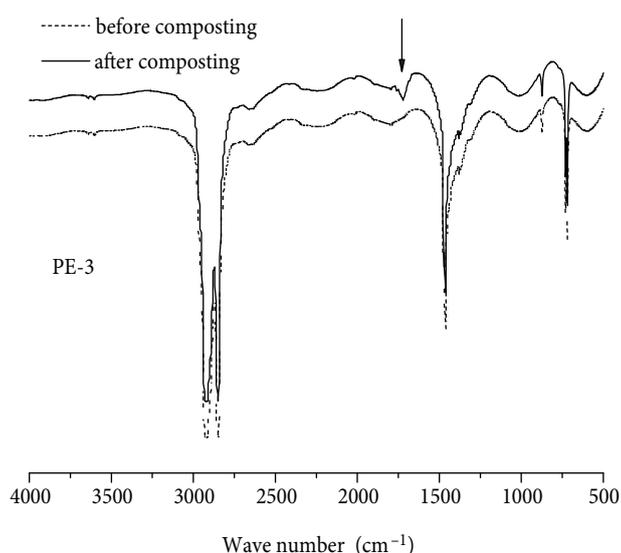


Figure 3. FT-IR spectra of degradable PE-3 film without any aging treatment.

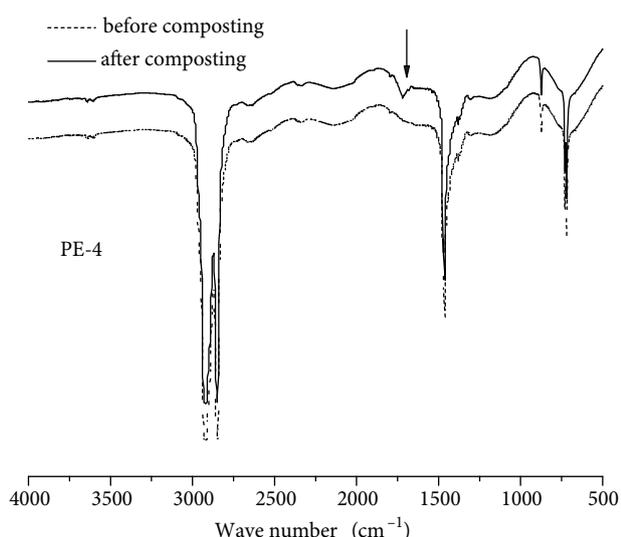


Figure 4. FT-IR spectra of degradable PE-4 film without any aging treatment.

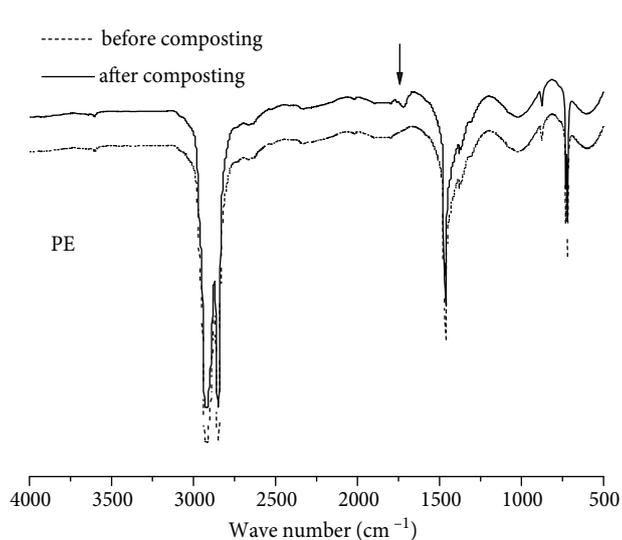


Figure 5. FT-IR spectra of degradable PE film without any aging treatment.

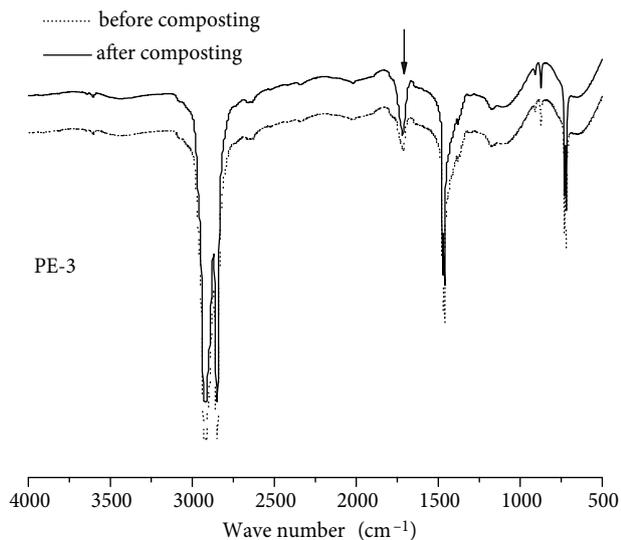


Figure 6. FT-IR spectra of degradable PE-3 film after natural aging.

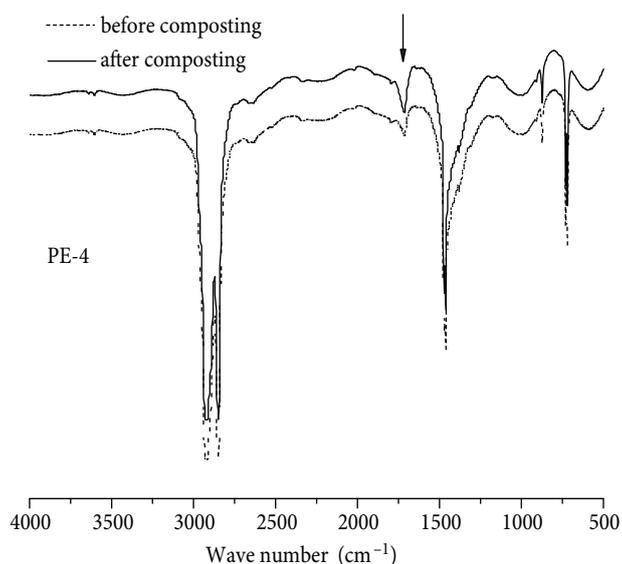


Figure 7. FT-IR spectra of degradable PE-4 film after natural aging.

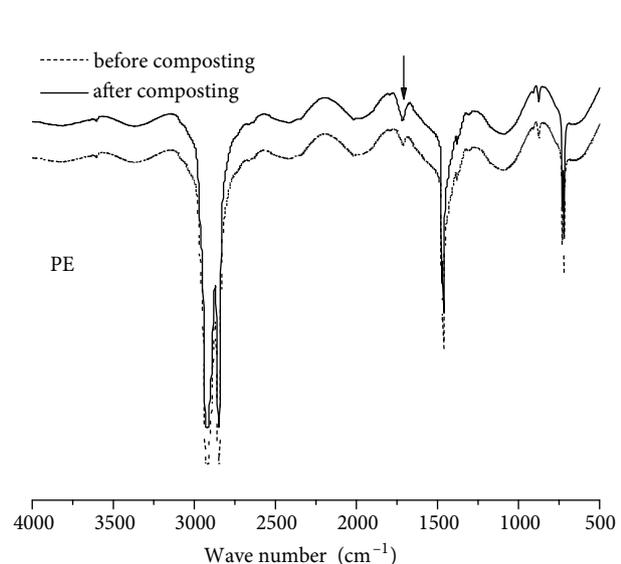


Figure 8. FT-IR spectra of degradable PE film after natural aging.

4. Conclusions

Highly biodegradable films were prepared. The biodegradability of untreated samples was very low, and the biodegradation rates of PE films significantly increased after natural aging. M_v analysis revealed that it slightly changed for untreated films but significantly decreased for aged films, especially PE-3 ($M_v = 38.95\%$ before degradation), after composting experiments. In the FT-IR spectra of PE films after the composting experiments, untreated PE-3, PE-4, and OPEF samples showed a carbonyl absorption peak at 1720 cm^{-1} , whose intensity increased with increased composting time, especially for PE-3. Thus, the films were indeed biodegraded.

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References

1. Rauf, A.; Baloch, M. K.; Durrani, G. F. *J. Chem. Soc. Pakistan*. **2010**, *32*, 168–171.
2. Gautam, R.; Bassi, A. S.; Yanful, E. K. *Appl. Biochem. Biotech.* **2007**, *141*, 85–108.
3. Briassoulis, D.; Dejean, C. *J. Polym. Environ.* **2010**, *18*, 384–400.
4. Zhao, C. X.; He, W. Q.; Liu, S.; Yan, C. R.; Cao, S. L. *J. Arg - Environ. Sci.* **2011**, *30*, 1616–1621.
5. He, W. Q.; Yan, C. R.; Zhao, C. X.; Chang, R. Q.; Liu, Q.; Liu, S. *J. Arg - Environ. Sci.* **2009**, *28*, 533–538.
6. Zhang, J. H.; Jiang, P. A.; Shen, Y. X.; Wang W. G.; Su H. Y. *Xinjiang. Agr. Sci.* **2010**, *47*, 1656–1659.
7. Zhang, X. Q.; Gozukara, Y.; Sangwan, P.; Gao, D.; Bateman, S. *Polym. Degrad. Stabil.* **2010**, *95*, 2309–2317.
8. Wang, Y. Z.; Yang, K. K.; Wang, X. L.; Zhou, Q.; Zheng, C. Y.; Chen, Z. F. *J. Polym. Environ.* **2004**, *12*, 7–10.
9. Siotto, M.; Sezenna, E.; Saponaro, S.; Innocenti, F. D.; Tosin, M.; Bonomo, L.; Mezzanotte, V. *J. Environ. Manage.* **2012**, *93*, 31–37.
10. Tosun, I.; Gonullu, M. T.; Arslankaya, E., Gunay, A. *Bioresource Technol.* **2008**, *99*, 6143–6149.
11. Ganjyal, G. M.; Weber, R.; Hanna, M. A. *Bioresource Technol.* **2007**, *98*, 3176–3179.
12. Siotto, M.; Tosin, M.; Innocenti, F. D.; Mezzanotte, V. *Water Air Soil Poll.* **2011**, *221*, 245–254.
13. ASTM D6400 Standard specification for compostable plastics. ASTM: West Conshohocken. **2004**.
14. ASTM D6868 Standard specification for biodegradable plastics used as coatings on paper and other compostable substrates. ASTM: West Conshohocken. **2003**.
15. UNI EN 13432 Requirements for packaging recoverable through composting and biodegradation-test scheme and evaluation criteria for the final acceptance of packaging. **2002**.
16. Aminabhavi, T. M.; Balundgi, R. T. *Polym. Plast. Technol. Eng.* **1990**, *29*, 235–262.
17. Scott, G.; Wiles, D. M. *Biomacromolecules*. **2001**, *2*, 615–622.
18. Grif?n, G. J. L. *Polymr. Degrad. Stabil.* **1994**, *45*, 241–247.
19. Huang, Y. Y.; Jia, X.; Li, D. Q.; Shang, J. J.; Zhang, X. M.; Wang, J.; Liu, Z. Y. *J. Shihezi University*. **2012**, *30*, 239–242.
20. Orhan, Y.; Buyukgungor, H. *Int. Biodeter. Biodegr.* **2000**, *45*, 49–55.
21. Sastry, P. K.; Satyanarayana, D.; Rao, D. V. M. *J. Appl. Polym. Sci.* **1998**, *70*, 2251–2257.
22. Khabbaz, F.; Albertsson, A. C. *J. Appl. Polym. Sci.* **2001**, *79*, 2309–2316.
23. ISO 14855-1 Determination of ultimate aerobic biodegradability of plastic materials under controlled composting conditions-Method by analysis of evolved carbon dioxide. **2004**.
24. ISO 10390 Soil quality-determination of pH. **2005**.
25. APHA-AWWA-WPCF 2540 E Fixed and volatile solid ignited at 550 °C. **1989**.
26. APHA-AWWA-WPCF 2540 D Total suspended solid dried at 103-105 °C. **1989**.
27. ASTM D2216 Standard test method for laboratory determination of water (moisture) content of soil and rock by mass. **1998**.
28. ASTM D5373 Standard test methods for instrumental determination of carbon, hydrogen, and nitrogen in laboratory samples of coal and coke. **2002**.
29. Leejarkpai, T.; Suwanmanee, U.; Rudeekit, Y.; Mungcharoen, T. *Waste Manage.* **2011**, *31*, 1153–1161.
30. Seeba, M.; Servens, C.; Pouyet, J. *J. Appl. Polym. Sci.* **1992**, *45*, 1049–1056.