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# Influence of metal ion on the degradation of LDPE at the composting temperatures

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**SUMMARY:** Low Density Polyethylene(LDPE) films with additives that contain metal ions were subjected to accelerated degradation at simulated composting temperatures. The mechanical properties and viscosity-average molecular weight of the samples, during the degradation, were determined and the degradation mechanism was studied. The results show that the samples containing metal ion show considerable decreases. Percentage crystallinity of LDPE in the samples has changed obviously during the degradation. [POOH] increases during the early stage of degradation followed by a more or less flat maximum before it starts to decrease, but carbonyl index shows a polynomial increase during the degradation.

**Keywords:** polyethylene, metal ion, degradation, composting temperature

## Introduction

At present, more and more discarded plastic materials have become one of important factors that destroy the environments of oceans and lands due to their longevity and restrained the improvement of plastic industry, with the increasing output and application of plastic. Conventional techniques such as recycling and incineration for minimizing disposed problems of plastic waste have serious limitations and the materials sensitivity to e.g. biodegradation and/or photooxidation have limited to a small range. In the 1990s, it is believed that the composting technique, combined with the degradable plastic, is the most effective way to make the waste return to the nature, which supply new ways and methods to dispose of city solid waste. Most carbon-carbon main-chain containing polymers(e.g. PE) are oxidizable but biodegrade very slowly1). A reduction in molecular weight needs to take place before the material biodegrades at any appreciable rate. In polyethylene this reduction is achieved by either photo-oxidation or thermal oxidation. In a composting environment, thermal oxidation may be the dominant mode of degradation, since temperatures reached up to 80℃ over the life time of a compost2). Molecules that have been oxidized by the initial thermal oxidation are more easily degraded to smaller fragments. These fragments are more accessible to the micro-organisms in the compost. The objective of this study was to research the influence of usual transition metal ion(e.g. ferric and ferrous ions) on the degradability and degradation mechanism of PE.

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## Experimental

### Materials

PE/additives films with a thickness of 0.015~0.020 mm were used in this study. These films were made by conventional extrusion blowing using an SJ-40(s) extruder with a 40 mm screw of L/D 28:1 and a blow-up ratio of about 3:1. The die temperature was set to 185℃. The polymers used were LDPE(1F7B) acquired from the Beijng Yan-Shan Petrochemical Co.(China), and LLDPE(7042) obtained from the Da-Qing Petrochemical Plant(China). One of the samples was used as a control without additives while the others contained additives, which were introduced into the PE matrix in the form of a masterbatch in the amount of 10 wt.%. The additives consisted mainly of starch modified polyethylene(SME) supplied by the Tianjin Gie-Ming Degradable Resin Plant (China), oleic acid or ester(OA or OE) purchased from the local markets in Tianjin, and organic compounds with $Fe^{2+}$ or $Fe^{3+}$(ferrocene and ferric stearate) were made in our lab.

### Degradation Environments

The samples were all directly exposed to air in the oven at a simulated composting temperature e.g. 70℃ with a humidity of 60%. The aged samples were taken out and examined at regular intervals.

### Mechanical Properties Measurement

The mechanical properties of samples were measured by using a WD-5 Electronic Instron Tensile Strength Tester (Chang-Chun Testing Machine Plant II) according to GB1040-79. Five samples were tested for each film and the average value was obtained. All the tests were performed at ambient temperature of 25 ± 2℃.

### Molecular Weight Measurement

The viscosity-average molecular weight of samples was calculated by measuring the viscosity of its tetrahydronaphthalene solution at 80±0.05℃($K$=0.088ml/g and $\alpha$=0.635)[3). All the values were achieved by using the linear regression.

### Degradation Products Analyses

Carbonyl group and hydroperoxide in samples were analyzed by iodometric potentiometric titration(IPT)[4) and a NICOLET FTIR-170SX Fourier Transform Infrared(FTIR) Spectrometry. In the IR spectra, special interest was focused on the carbonyl regions at 1718 $cm^{-1}$, where Carbonyl absorbance was measured relative to the $CH_2$ scissoring peak at 1463 $cm^{-1}$ [5). All the measurements were performed with three or four samples.

### Differential Scanning Calorimetry

Differential Scanning Calorimetry(DSC) thermograms were recorded on a Universal V1.8M DSC-2010 differential scanning calorimeter at a heating rate of 10℃/min in a nitrogen atmosphere. Percentage crystallinity was calculated based on a heat of fusion of 293.1 J/g for 100% crystalline PE.

## Results and Discussion

### Degradation Characterization

The changes of the samples in Mη, and percentage elongation during the degradation are shown in Figures 1, and 2. It can be seen that the samples with Fe$^{2+}$ or Fe$^{3+}$ show almost immediate reductions in Mη within two months. Samples with only OA or OE also demonstrate reductions in Mη, but not as evident as that of the samples with Fe$^{2+}$ or Fe$^{3+}$, while the pure PE becomes very stable (From Fig.1).

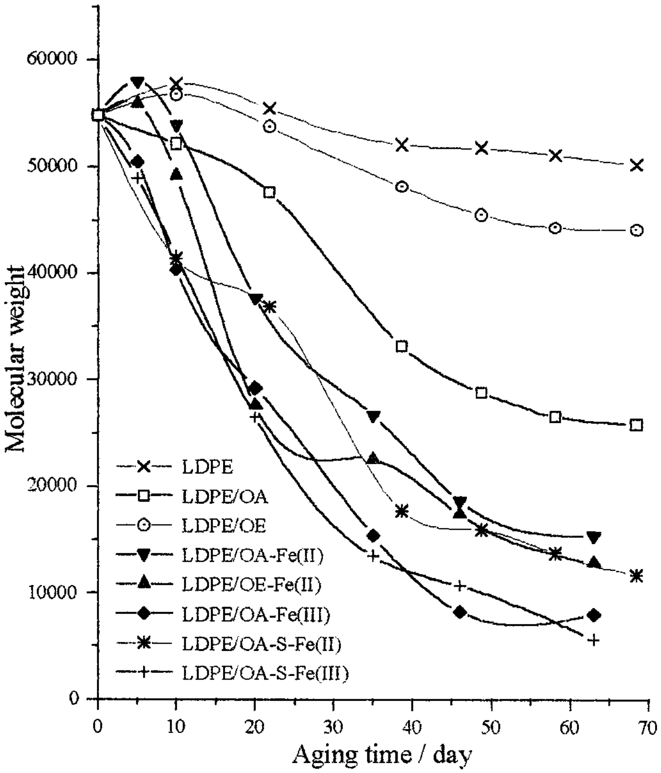


**Figure 1** Viscosity-average molecular weight changes with time for samples

Moreover, the corresponding mechanical properties, specifically percentage elongation, show the similar phenomena(Fig. 2). Those results indicate that metal ions in the system play an important role during the degradation of PE matrix. Incorporation of metal ions promotes the decomposition of hydroperoxide, an intermediate, and accelerates the degradation of PE matrix.

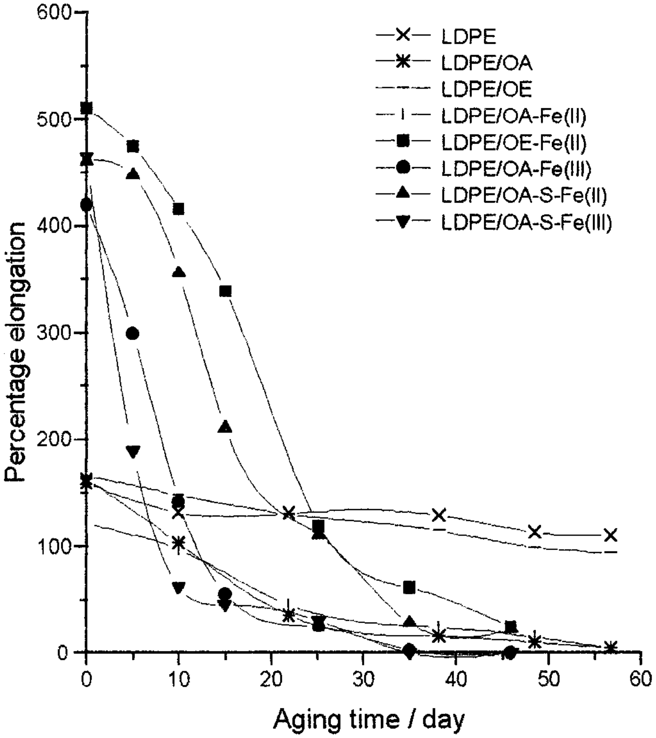


**Figure 2** Percentage elongation changes with time for samples

### Crystallinity Analyses

DSC thermograms for samples PE/OA-Fe(II) and PE/OA-Fe(III) during degradation, and the pure PE before degradation are shown in Figures 3 and 4. Figure 3 (a), for the pure PE, exhibits two distinct melting peaks with double arms: one at high temperature, about 118℃ (called the "HT" melting peak in this article), and the other at low temperature, about 100℃(the "LT" melting peak). The existence of two peaks in DSC thermograms from polyolefin blends has been observed by other authors[5,7]. The HT melting peak can be attributed to crystallization of the polymer chains of high molecular weight and low degree of branching while the LT melting peak is due to the less crystallizable, lower-molecular-weight, more highly branched chains [8]. Here the HT melting peak is assigned to the LLDPE fraction. For the two samples with ongoing the degradation, the intensities for left arm of LT melting peak and the right arm of HT melting peak increase while the others decrease. On the other hand, the intensity for the right arm of HT melting peak for sample LDPE/OA-Fe(III) shows a more apparent decrease than that for sample LDPE/OA-Fe(II), indicating that LDPE was more degradable in the presence of Fe(III).

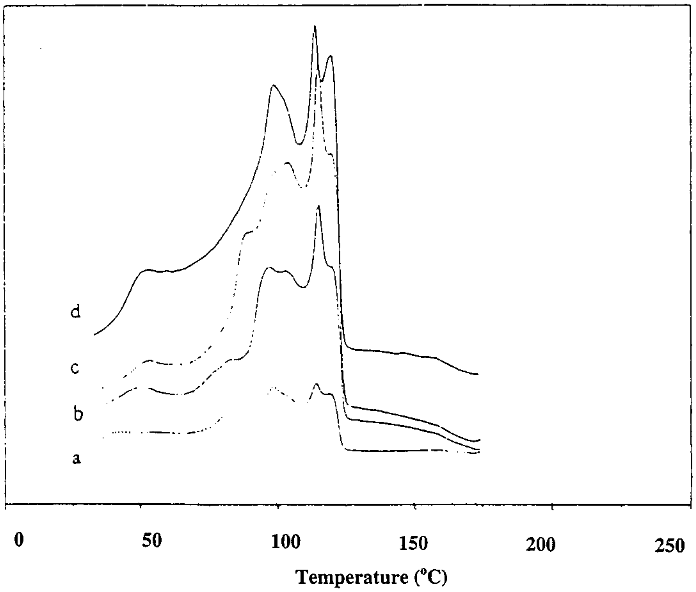


**Figure 3** DSC scans of Sample LDPE/OA-Fe(II) after degradation (a) original, (b) after 38 days, (c) after 57 days, and(d) original LDPE sample.

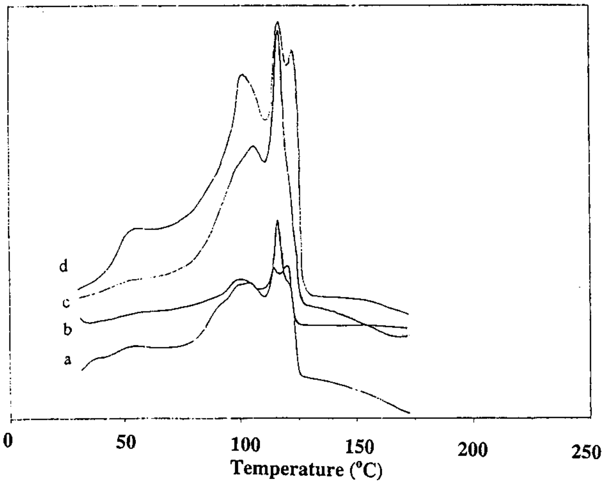


**Figure 4** DSC scans of Sample LDPE/OA-Fe(III) after degradation (a) original, (b) after 35 days, (c) after 63 days, and(d) original LDPE sample.

For the two samples with ongoing the degradation, the intensities for left arm of LT melting peak and the right arm of HT melting peak increase while the others decrease. On the other hand, the intensity for the right arm of HT melting peak for sample LDPE/OA-Fe(III) shows a more apparent decrease than that for sample LDPE/OA-Fe(II), indicating that LDPE was more degradable in the presence of Fe(III).

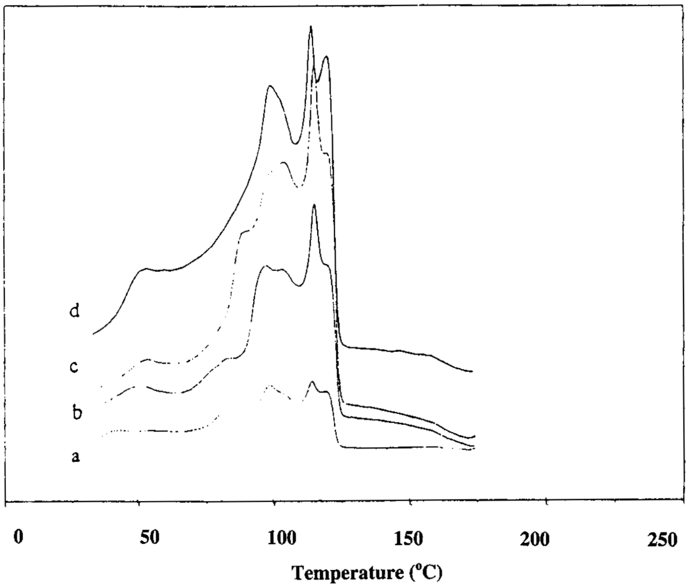


**Figure 3 DSC scans of Sample LDPE/OA-Fe(II) after degradation (a) original, (b) after 38 days, (c) after 57 days, and(d) original LDPE sample.**

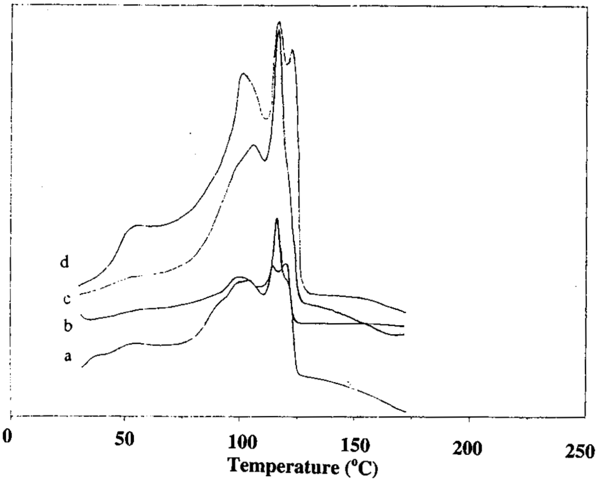


**Figure 4 DSC scans of Sample LDPE/OA-Fe(III) after degradation (a) original, (b) after 35 days, (c) after 63 days, and(d) original LDPE sample.**

Moreover, percentage crystallinities show obvious increases (Table 1). It is due to the formation of unbranched chain sections during chain scission, which crystallize at a higher temperature9).

**Table 1 The melting heat and percentage crystallinity of LDPE/additives systems(tested by DSC)**

| Samples | LDPE/OA-Fe(II) | | | LDPE/OA-Fe(III) | | | LDPE |
|---|---|---|---|---|---|---|---|
| Aging time / day | 0 | 38 | 57 | 0 | 35 | 63 | 0 |
| Melting heat / J/g | 22.5 | 58.8 | 94.9 | 57.2 | 125.91 | 176.6 | 112.7 |
| Crystallinity / % | 7.8 | 20.1 | 32.4 | 19.5 | 43.0 | 60.3 | 38.5 |

### Experimental Kinetics of Functional Groups

The formation of functional groups in LDPE/additives films during the degradation are shown in Figures 5 and 6. It can be seen that [POOH] increases during the early stage of degradation, then passes through a more or less flat maximum before it starts to decrease, which shows a typical S-shaped curve.

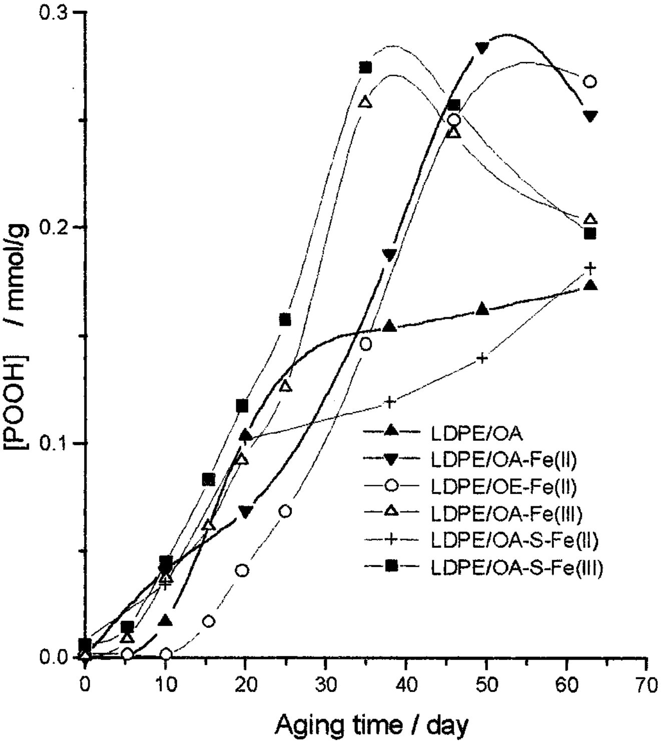
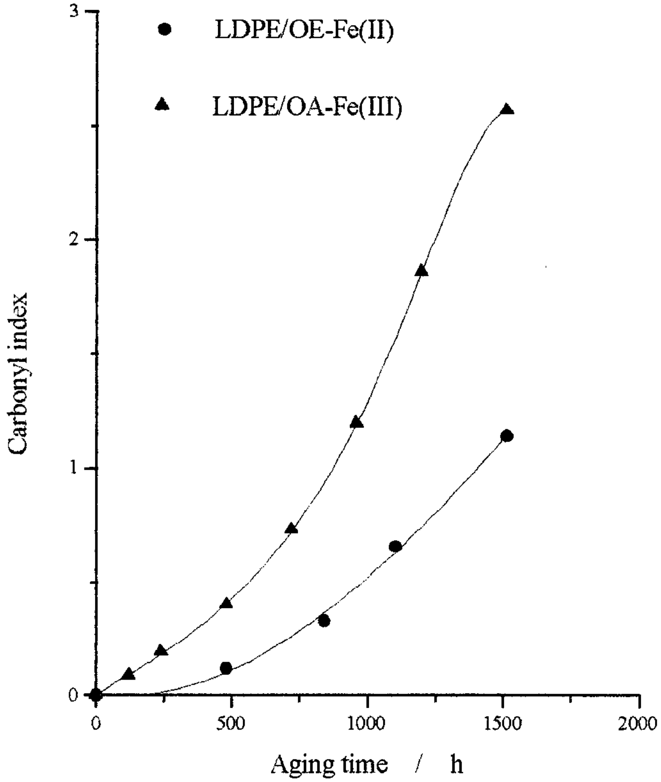


**Figure 5** Formation of hydroperoxides in samples during the degradation



LDPE/OE-Fe(II): $y=0.00517-0.00015t+7.9557E\text{-}7t^2-1.3069E\text{-}10t^3$

LDPE/OA-Fe(III) : $y=-0.00125+0.00089t-1.4541E\text{-}6t^2+5.21E\text{-}9t^3$

$-7.2728E\text{-}12t^4+5.5019E\text{-}15t^5-1.5848E\text{-}18t^6$

**Figure 6** Formation of carbonyl groups in samples during the degradation

However, in the initial stage, [POOH] in samples with $Fe^{3+}$ increases more greatly than that in samples with $Fe^{2+}$, which proves the results that samples with $Fe^{3+}$ degraded more obviously than samples with $Fe^{2+}$. At the same time, carbonyl index shows a polynomial increase during the degradation. The greater the rate of degradation, the more the number of high power's term exists in polynomial.

## Conclusion

1. PE films containing both oleic acid or ester and metal ion show obvious decreases, indicating that metal ions play an important role in the degradation of PE.

2. Percentage crystallinity of PE in samples with $Fe^{2+}$ or $Fe^{3+}$ has changed greatly during the degradation.
3. [POOH] increases during the early stage of degradation followed by a more or less flat maximum before it starts to decrease.

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