

Study on Degradation Mechanism of Polyethylene Films Containing Additives with Metal Ions at a Simulated Composting Temperature

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ABSTRACT: In this article, the degradation mechanism of PE films containing additives with metal ions at a simulated composting temperature has been studied. The hydroperoxide concentration [POOH] in the films was traced quantitatively by using the iodometric potentiometric titration, compared with Fourier transform infrared spectrometry (FTIR). The results show that [POOH] increases during the early stage of degradation, followed by a more or less flat maximum before it starts to decrease. At the same time, similar results are obtained by the FTIR analysis. Besides, it is found that the rate laws for the carbonyl index and [POOH] increases seem more complicated, instead of an exponential-type increase in the early stage of the oxidation. When they are fitted by polynomial equations, the greater the rate of degradation, the more the number and content of the high-power members in the polynomial. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 523–527, 2000

Key words: polyethylene; metal ion; compost; degradation

INTRODUCTION

The main intermediate compounds for PE during the oxidation and degradation at simulated composting temperatures are products containing hydroperoxide groups, whose decomposition and branching, are the key reactions during the degradation of PE. The degradation mechanism for PE can be known by tracing the changes in hydroperoxide concentration ([POOH]) in the PE/additives systems during the degradation. Determination of [POOH] has been reported many times in the literature. Infrared spectrometry (IR) is powerful to analyze the structures of POOH in polymers,^{1,2} but cannot be used in quantitative

determination of [POOH]. However, it can be well quantified by using modified iodometry.^{3,4} In this work, [POOH] in PE/additives films during the degradation was measured by using iodometric potentiometric titration, compared with Fourier transform infrared spectrometry (FTIR).

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°C. The polymers used were LDPE(1F7B) acquired from the Beijing Yan-Shan Petrochemical Co.(China), and LLDPE

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(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 that were introduced into the PE matrix [LDPE:LLDPE = 1 : 1 (w/w)] in the form of a masterbatch in the amount of 10%. The additives mainly consisted 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+} made in our lab.

Degradation Environments

The samples were all aged in an oven at a simulated composting temperature, for example, 70°C , with a humidity of 60%. Half of them were directly exposed to air in the oven, while the other were buried under soil in a box about $50 \times 50 \times 20$ cm. The aged samples were taken out and examined at regular intervals.

Molecular Weight Measurement

The viscosity-average molecular weight (M_η) of samples was calculated by measuring the viscosity of its tetrahydronaphthalene solution at $80 \pm 0.05^\circ\text{C}$ ($K = 0.088 \text{ mL/g}$ and $\alpha = 0.635$).⁵ All the values were achieved by using linear regression.

Degradation Products Analyses

Hydroperoxide and carbonyl groups in samples were analyzed by using iodometric potentiometric titration (IPT),⁴ and NICOLET FTIR-170SX Fourier Transform Infrared (FTIR) Spectrometry. In the IR spectra, special interest was focused on the carbonyl and hydroperoxide regions. Carbonyl absorbance at 1718 cm^{-1} and a hydroperoxide absorbance at 3560 and 3410 cm^{-1} were measured relative to the CH_2 scissoring peak at 1463 cm^{-1} .⁶ All the measurements were performed with three or four samples.

RESULTS AND DISCUSSION

Change in Molecular Weight

The change in M_η for the samples during the degradation is shown in Figure 1. It can be seen that the samples with Fe^{2+} or Fe^{3+} show almost immediate reductions in M_η within 2 months. Samples with only OA or OE also demonstrate reductions in M_η , but not as evident as for the

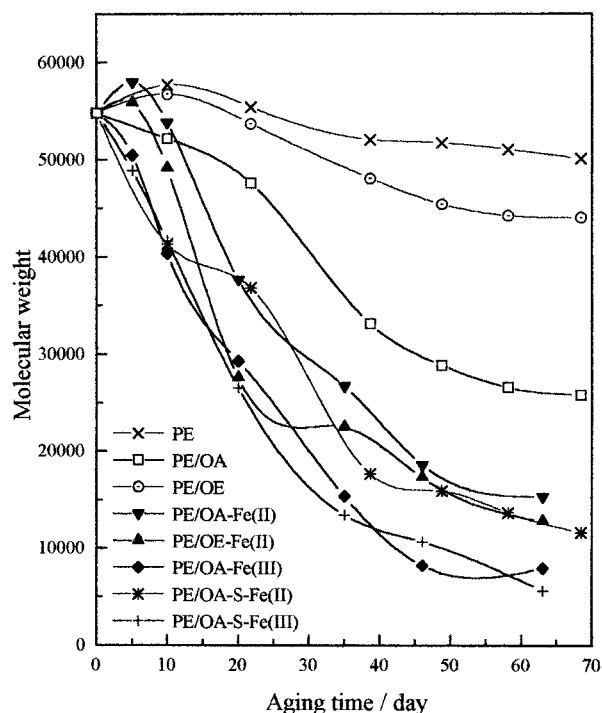


Figure 1 Viscosity-average molecular weight changes with time for samples.

samples with Fe^{2+} or Fe^{3+} , while the pure PE stays very stable. 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 thus accelerates the degradation of PE matrix, which has been studied in other areas,⁷⁻¹¹ but not reported in our system.

Experimental Kinetics of Functional Groups Formation

Compounds containing hydroperoxides and carbonyl groups are usual degradation products of PE, specifically in thermo-oxidation. The amounts of hydroperoxides and carbonyl groups have been quantified by both IPT and FTIR. Formations of hydroperoxides in the samples exposed directly to air or buried under soil (measured by IPT) are shown in Figures 2 and 3, respectively, and formations of carbonyl groups tested by FTIR are plotted in Figure 4. It can be seen that the increase of the [POOH] with aging time proceeds according to S-shaped curves, and carbonyl index with aging time shows an obvious increase. However, the curves for samples with different additives show varying behavior, the rates of increase

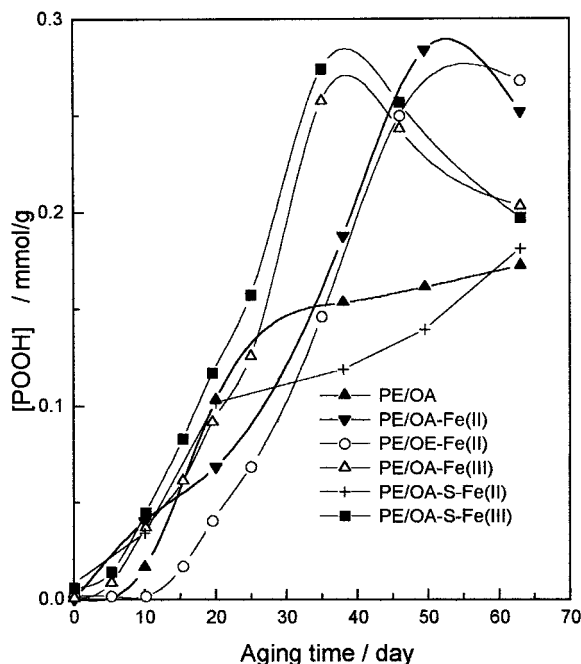


Figure 2 Formation of hydroperoxides in samples during the degradation directly exposed to air in the oven (measured by IPT).

in both hydroperoxides and carbonyl groups in samples with Fe^{3+} are faster than those in samples with Fe^{2+} . Meanwhile, the fitted curves for

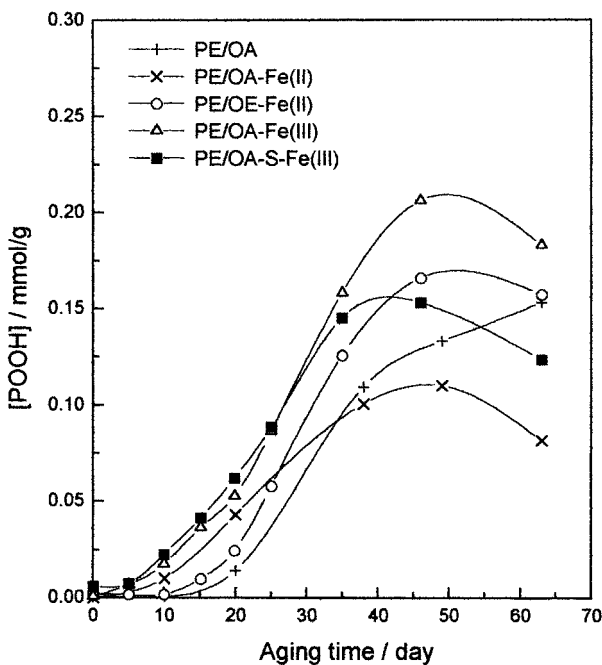


Figure 3 Formation of hydroperoxides in samples during the degradation buried under soil (measured by IPT).

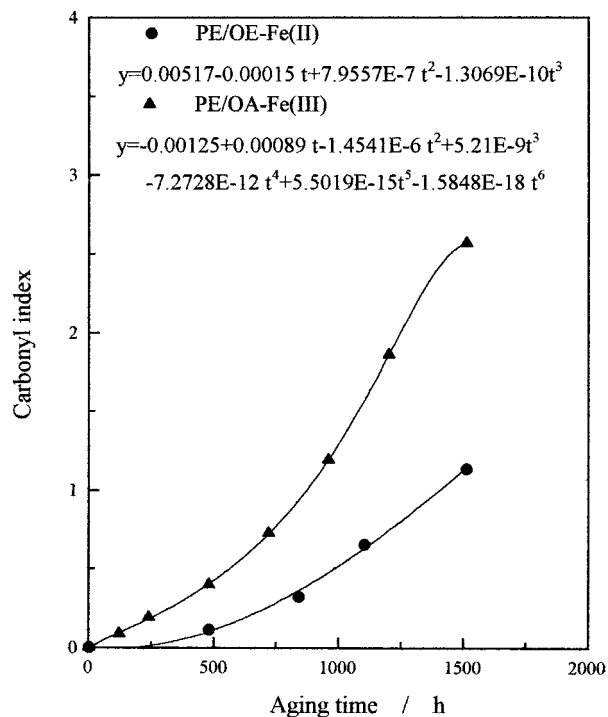


Figure 4 Formation of carbonyl groups in samples during the degradation directly exposed to air in the oven (measured by FTIR).

formation of carbonyl groups during the degradation and the hydroperoxides in the initial stage are shown in Figures 4 and 5. It can be observed that when they are fitted to polynomial equations, the greater the rate of degradation, the more the number and content of high-power members in the polynomial. On the other hand, formations of hydroperoxides in the PE/OE-Fe(II) sample measured by both IPT and FTIR represent a dramatic correspondence, which indicates that hydroperoxides in PE/ additives systems can be well quantified by using the IPT, as shown in Figure 6.

Formal Kinetics for PE/additives with Metal Ions

A simplified system of reactions envisaged for thermal oxidation of PE/additives is shown in Scheme 1 (as an example of samples with Fe^{3+}).

It follows the usual line of chain reactions with chain initiation, propagation, branching, and termination. Before the scheme was put forward, assumptions were taken into account as follows: (1) oleic acid or ester only participates in the initiation of free radicals, (2) metal ions participates in the initiation of free radicals and the branching reactions of hydroperoxides, (3) in the initial stage, the PE concentration ($[\text{PH}]$) and ad-

ditives concentration [RH] are constants, (4) unimolecular and bimolecular hydroperoxide decomposition reactions are neglected for the extremely low [POOH], (5) $\{P\cdot\}/[POO\cdot] \ll 1$, and $[P\cdot]/[POO\cdot] \ll 1$,¹² and (6) the rates of initiation (r_i) and termination are equal. The usual steady-state approximation applied to the reactions in Scheme 1 yields the following set of equations:

$$\frac{d[P\cdot]}{dt} = 0 = r_i + k_6[PO\cdot] + k_7[PO\cdot] + k_3[PO_2\cdot] - k_2[P\cdot][O_2] \quad (1)$$

$$\frac{d[PO\cdot]}{dt} = 0 = r_i + k_4[PO_2\cdot] - k_6[PO\cdot] - k_7[PO\cdot] \quad (2)$$

$$\frac{d[PO_2\cdot]}{dt} = 0 = k_2[P\cdot][O_2] - k_3[PO_2\cdot] - k_4[PO_2\cdot] - k_8[PO_2\cdot]^2 \quad (3)$$

$$\frac{d[POOH]}{dt} = k_3[PO_2\cdot] - r_i \quad (4)$$

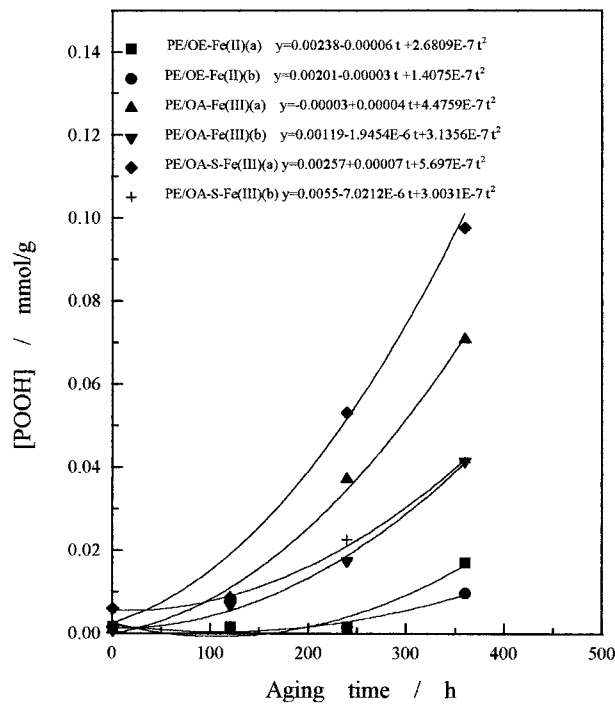


Figure 5 Formation of hydroperoxides in samples in the initial stage of the degradation (a) directly exposed to air in the oven, and (b) buried under soil (measured by IPT).

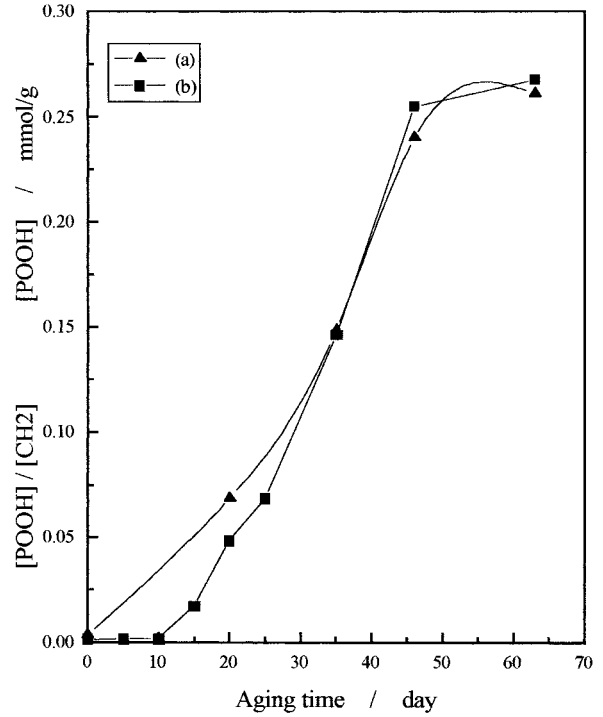


Figure 6 Formations of hydroperoxides in sample PE/OE-Fe(II) measured by (a) IPT, and (b) FTIR.

$$\frac{d[P=O]}{dt} = k_7[PO\cdot] + k_4[PO_2\cdot] + k_8[PO_2\cdot]^2 \quad (5)$$

After arrangement and integration, the solutions are:

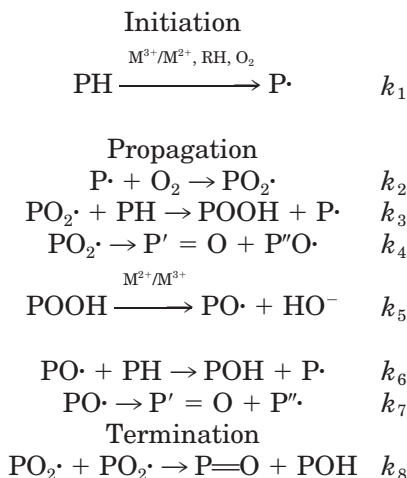
$$[POOH] = \frac{a^2}{b^2} (1 - 2e^{-bt/2} + e^{-bt}) \quad (6)$$

$$\begin{aligned} [P=O] &= c \int_0^t [POOH] dt + d \int_0^t [POOH]^{1/2} dt \\ &= -\left(\frac{3ca^2}{b^3} + \frac{2ad}{b^2}\right) + \left(\frac{ca^2}{b^2} + \frac{ad}{b}\right)t \\ &\quad + \left(\frac{4ca^2}{b^3} + \frac{2ad}{b^2}\right)e^{-bt/2} - \frac{ca^2}{b^3}e^{-bt} \quad (7) \end{aligned}$$

where

$$a = k_3 \left(\frac{2k_1}{k_8}\right)^{1/2} [RH], \quad b = k_1[RH],$$

$$c = \frac{(2k_6 + 3k_7)k_1}{k_6 + k_7} [RH],$$



Scheme 1 Some chemical processes on the degradation of PE/additives systems

and

$$d = \frac{(k_6 + 2k_7)k_4}{k_6 + k_7} \left(\frac{2k_1}{k_8} [RH] \right)^{1/2}$$

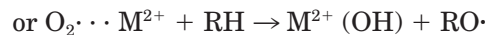
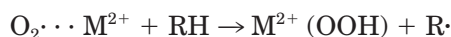
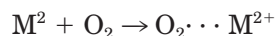
It can be found that the rate laws are different from the polyolefins in the solid state² and seem more complicated instead of simple exponential type increases in the early stages of the degradation, which has been reported in the literature.² When it is fitted by polynomial equations, eqs. (6) and (7) are transformed into:

$$[POOH] = a_0 + a_1t + a_2t^2 + \dots + a_nt^n \quad (8)$$

$$[P=O] = b_0 + b_1t + b_2t^2 + \dots + b_nt^n \quad (9)$$

where $a_i, b_i (i = 0, 1, 2, \dots, n)$ are constants, and t is the aging time.

The r_i varies in different PE/additives systems. For example, the initiation of samples with Fe^{2+} is:



However, an overall equation of r_i can be assumed as follows:

$$r_i = k_1[RH]^\alpha[POOH]^\beta[O_2]^\gamma \quad (10)$$

where α, β , and γ are dependent on PE/additives system and aging environment. Replacing eq. (10) into eqs. (6) and (7), the similar equations to eqs. (8) and (9) are obtained, only $a_i, b_i (i = 0, 1, 2, \dots, n)$ are different. As a result, eqs. (8) and (9) are formal kinetics in the initial stage of degradation for PE/additives with metal ions, which can be used to explain the experimental phenomena.

CONCLUSION

Hydroperoxides in the PE/additives systems during degradation at a simulated composting temperature can be well quantified by using the IPT. [POOH] increases during the early stage of degradation, followed by a more or less flat maximum before it starts to decrease. The carbonyl index and [POOH] shows more complicated, instead of exponential-type increase in the early stage of the oxidation.

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