Catalytic Oxidation of Polyethylene with Oxygen Under Solid-State Conditions

Jan Zawadiak, Adam A. Marek, Beata Orlinska, Zbigniew Stec

Silesian University of Technology, Department of Chemical Organic Technology and Petrochemistry, Gliwice 44-100, Poland

Received 10 December 2009; accepted 6 March 2010
DOI 10.1002/app.32387

ABSTRACT: The catalytic oxidative degradation of polyethylene in the solid phase was studied. Cobalt(II), manganese(II), or iron(III) acetylacetonates were used as catalysts. The influences of type and amount of catalyst, temperature, and type of oxidizing agent on polyethylene oxidation were investigated. The obtained products were characterized by determination of acid and ester numbers as well as by means of FTIR spectroscopy. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 1414–1420, 2010

Key words: oxidative degradation; polyethylene (PE); metal–organic catalysts; FTIR

INTRODUCTION

Polyethylene (PE) is one of the most important polymers produced on a large scale. In 2007, worldwide production of PE was about 70 million tonnes.[1] Polyethylene has a wide variety of applications, including use as a raw material in oxidation processes. Surface modifications in oxidation processes are combined with partial polymer degradation and introduction of polar groups such as carboxyl, hydroxyl, carbonyl, aldehyde, and ester groups. Oxidized polyethylene with an acid number (AN) of about 25–30 mg KOH/g, containing about 3–4% oxygen, displays special hydrophilic properties resulting in formation of stable aqueous emulsions widely used as floor polishes, water-dispersible coatings, inks, and as additives for textile applications. The oxidized polyethylene is also used as a lubricant for polymer and resin processing.[2]

It is known that polyethylene can be oxidized by a variety of methods such as using fuming nitric acid,[3,4] discharge plasma treatment in oxygen,[5–9] UV irradiation combined with ozone formation,[10] and using corona discharge in air.[11,12] However, in industrial settings, oxidation with air or oxygen is strongly preferred. The specific method of polymer oxidation with air or oxygen depends on the type of polyethylene used. Polyethylene–waxes and LDPE are oxidized in a melt.[13–18] HDPE and UHMWPE are typically oxidized in an aqueous dispersion[19,20] or in the solid phase.[21–24]

The oxidation of polyethylene in the gas–solid phase is the most environmentally friendly and economically preferred method. The most important advantages of the polyethylene oxidation in solid phase are no necessity to use any solvents and relatively uncomplicated reactor system. In comparison to dispersion process, operations of water preheating during the process, water evaporating from product and his drying are unnecessary. As a result of these, the amount of waste water is reduced, less energy is needed, the running cost are decreased, and the product can be used directly.[21–24]

Air, oxygen, and their mixtures (also with ozone) can be used as the oxidizing agents. Reactions are performed with polyethylene in powdered form, a few degrees below the softening point, in the presence of radical initiators. Because reactions are conducted at a relatively low temperature (below 130°C), the oxidation period is relatively long. To achieve a product with an AN of about 25–30, 30–40 h of reaction is required.

The polyethylene is oxidized[25–36] according to the widely known free-radical chain mechanism.[37,38] Polyethylene is a semicrystalline polymer containing crystalline and amorphous phases. The oxygen can diffuse only in the amorphous phase, which is where oxidation occurs.[29] Gugumus[32–36] has discussed the probable mechanisms of hydroperoxide formation and decomposition, as well as carbonyl, hydroxyl, and carboxyl group formation in the polyethylene oxidation process.

Transition metal complexes can be used as catalysts of polyethylene oxidative degradation. They mainly operate by lowering the activation energy of the decomposition reaction of the formed hydroperoxide groups, thereby resulting in significant increases in reaction rate.[39,40]

Correspondence to: A. A. Marek (adam.a.marek@polsl.pl).

Journal of Applied Polymer Science, Vol. 118, 1414–1420 (2010)

Metal ions can also participate in other free-radical reactions such as free-radical formation in the initiation step.[39]

To date, the influence of transition metal complexes on polyethylene oxidation has only been partly investigated.[41–43] Previous research was concerned with oxidation of molten PE with metals salts (Cu, Pb, Au, Al, Zn, and Ag)[41] as well as solid-phase oxidation and crosslinking of PE in the presence of Mn, Cu, and Al salts.[42,43] Moreover, the surface oxidation of polyethylene under solid-state conditions with potassium permanganate and microwave irradiation has been investigated.[44]

Although the rate of oxidation in the presence of transition metal catalysts is high, the large amount of heat formed can cause unwanted local overheating and melting of product. These effects can be intensified by exothermic crosslinking reactions of alkyl radicals that proceed under conditions of oxygen insufficiency. As a result, the obtained product can have improper qualities (such as darker color). The higher degree of crosslinking can also limit the application of the product as a component of aqueous emulsions because of formation of insoluble residue. For these reasons, efficient stirring and heat removal, as well as process parameters selection (mainly temperature and type and amount of catalyst), are important for the quality of the product.

EXPERIMENTAL

Materials

The polymer used in this work was nonstabilized high-molecular-weight polyethylene Braskem Idealis 500 with distinct properties such as: intrinsic viscosity of 4.7 dL/g, 5.5×10^5 g/mol, density of 0.951 g cm^{-3}, melting point 136°C, and average particle size of 170 μm.

Acetone 99.5% and catalysts were purchased from Merck Schuchardt and used as received.

Methods

Preparation of polyethylene for oxidation

First, 50–170 g of powdered PE was introduced into a ca. 750-cm^3 round-bottom flask with additives-like initiators or transition metal salts. To the mixture, 70–250 cm^3 of acetone was introduced as a solvent. The contents of the flask were mixed for 10 min to provide a homogeneous solution of constituents. Next, the acetone was evaporated. The resulting dry, powdered polyethylene with additives was transferred into the oxidation reactor.

Catalytic solid-phase oxidation of polyethylene in glass reactor

Dry, powdered polyethylene (50 g) with additives was oxidized in a 500-cm^3 glass round-bottom flask with a long neck. The flask was installed in a rotary evaporator drive at an angle of about 30° to enable flask rotation and mixing of PE. The flask was immersed in an oil bath at the set temperature. Air or oxygen from a gas cylinder was supplied over the surface of PE through the flowmeter with a rate of 7.5 dm^3/h.

Catalytic solid-phase oxidation of polyethylene in metal reactor

Dry, powdered polyethylene (170 g) with additives was oxidized in a metal stainless steel (acid-resistant) reactor. The reactor was equipped with a slow-speed paddle stirrer, cooling-heating jacket, and temperature sensor, as well as an air (oxygen) inlet and outgas outlet. The air or oxygen from the cylinder was supplied into the reactor at a rate of about 15 dm^3/h.

Analytical methods

The reaction rate was controlled by determination of the AN.[45] The final products were characterized by AN and ester number (EN)[46] as well as by FTIR spectroscopy.

The structural characterization was followed by using a Philips PU9800 FTIR Spectrometer. Spectra of oxidized PE were carried out using KBr pellets and were taken as an average of 20 scans at a resolution of 2 cm^{-1} in the wavenumber range of 4000–400 cm^{-1}. To minimize errors from sample amount, the 2020 cm^{-1} peak was selected as an internal reference in this study.

RESULTS AND DISCUSSION

The catalytic oxidative degradation of high-molecular-weight polyethylene in the solid phase, at temperatures below the melting point of raw material, in the presence of transition metal compounds as catalysts was studied. The possibility of reaction time reduction without changes in product quality was checked.

The effect of catalysts

The oxidation of polyethylene was performed without additives as well as using dicumyl peroxide (DCP) as radical initiator and transition metal compounds as catalysts. The reactions were carried out in glass reactors. It has been shown that among the metal acetylacetonates of Mn(II), Co(II), Fe(III),

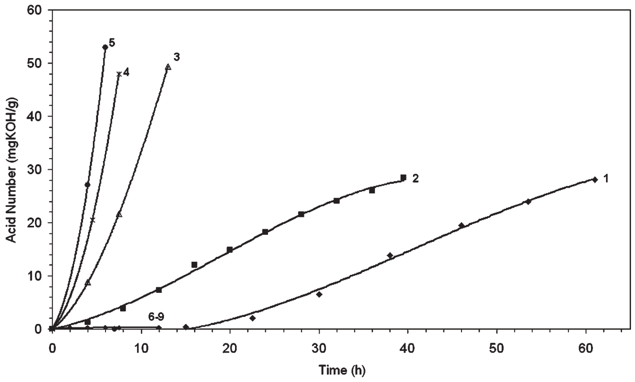

Figure 1 The effect of metal ions on the formation of carboxyl groups in PE oxidation catalyzed by metal acetylacetonates: (1) without additives; (2) with DCP; with acetylacetonates: (3) Fe(III); (4) Mn(II); (5) Co(II); (6) V(III); (7) Cu(II); (8) Ni(II); and (9) Al(III). PE: 50 g; DCP: 1 wt %; metal acetylacetonate: 0.294 mmol (0.15 wt %); air: 7.5 dm^3/h; 120°C.

V(III), Cu(II), Ni(II), and Al(III), only the first three have given positive results and have increased the rate of oxidation processes. The courses of the PE oxidation at 120°C are depicted in Figure 1 as a dependence of AN versus time of reaction.

The oxidation without initiator demonstrated a 16-h induction period after which the oxidation reaction occurred (after 62 h a product with AN = 28 was obtained). When oxidation was performed in the presence of initiator (DCP) or catalysts, the induction period was not observed. In the presence of 0.294 mmol (about 0.15 wt %) of Co(II), Mn(II), or Fe(III) acetylacetonates at 120°C, a period of 4, 6, or 9 h, respectively, was required to obtain products with AN = 28. When the DCP was used as initiator, the process had to be carried out for 40 h. Acetylacetonates of V(III), Cu(II), Ni(II), and Al(III) did not catalyze the oxidation process, and after 12 h the ANs of products were about zero.

Table I presents the results of the oxidation of polyethylene at 110°C in the presence of the chosen catalysts. ANs and ENs of final products as well as standard electrode potentials of metals used are given.

The obtained data showed that the catalytic activity of the studied metals on PE oxidative degradation can be placed in the following order: Co > Mn > Fe $\gg$ $V \approx 0$. The order of metal activities may be a result of their different reduction potentials together with varying influences of the metals on the rate of hydroperoxide group decomposition. Notably, the activities of the metals correlate with increasing potential.

The effect of the amount of catalysts

The influence of the amount of Co(II), Mn(II), and Fe(III) acetylacetonates on the oxidation of PE with air at 110°C has been investigated. In Table II, the obtained results are shown.

According to the obtained results, it was found that the application of larger amounts of catalysts led to an increased rate of reaction and content of oxygen-containing groups such as carboxyls and esters. A threefold increase in the amount of Co(II), Mn(II), and Fe(III) acetylacetonates caused respective increases in AN of ~1.7, 3.6, and 2.3 times and an increase in EN of 1.1, 1.3, and 1.8 times.

The effect of temperature

The influence of temperature on the process of PE oxidation in the presence of Fe(III), Mn(II), and Co(II) acetylacetonates (0.196 mmol) was tested at 110, 115, and 120°C, respectively. The results obtained after 7.5 h have been compiled in Table III.

An increase in temperature from 110 to 120°C induced—as might have been expected—an increase in the reaction rate and content of oxygen-containing groups such as carboxyl and ester groups. When the manganese acetylacetonate was used at a temperature of 120°C, the product was partially melted. At the same temperature, cobalt acetylacetonate caused complete melting of the product, and the PE

TABLE I
Catalytic Oxidation of Polyethylene with Air in the Presence of Selected Transition Metal Acetylacetonates

	The results of the oxidation			Standard electrode potential[47]	
Catalysts	AN (mg KOH/g)	SN (mg KOH/g)	V_{ox} (AN/h)	Metals	$E°$ (V)
Co(II) acetylacetonate	20.6	19.8	2.75	Co^{2+}/Co^{3+}	+1.84
Mn(II) acetylacetonate	6.9	13.8	0.92	Mn^{2+}/Mn^{3+}	+1.51
Fe(III) acetylacetonate	4.7	5.8	0.63	Fe^{2+}/Fe^{3+}	+0.77
V(III) acetylacetonate	0.8	6.5	0.10	V^{2+}/V^{3+}	−0.26

110°C, PE: 50 g; air: 7.5 dm^3/h; acetylacetonates: Co(II), Mn(II), Fe(III), and V(III): 0.098 mmol; reaction time: 7.5 h.

TABLE II
The Effect of Catalyst Amount on the Oxidation of PE with Air Catalyzed by Selected Transition Metal Acetylacetonates

Catalysts amount (mmol)	Co(II) acetylacetonate			Mn(II) acetylacetonate			Fe(III) acetylacetonate		
	AN (mg KOH/g)	SN (mg KOH/g)	V_{ox} (AN/h)	AN (mg KOH/g)	SN (mg KOH/g)	V_{ox} (AN/h)	AN (mg KOH/g)	EN (mg KOH/g)	V_{ox} (AN/h)
0.098	20.6	19.8	2.74	6.9	13.8	0.90	4.7	5.8	0.63
0.196	26.8	25.9	3.58	21.4	26.8	2.86	6.6	13.1	0.88
0.294	34.9	22.3	4.65	25.0	18.2	3.34	10.7	10.5	1.43

110°C, PE: 50 g; air: 7.5 dm^3/h; reaction time: 7.5 h.

oxidation had to be stopped after 2 h. Consequently, there are no results reported at 120°C for the cobalt catalyst. The product melting may be an effect of insufficient removal of the huge amount of heat of the exothermic accelerated oxidation and crosslinking reactions.

The effect of the type of oxidizing agent

The influence of the type of oxidizing agent (air or oxygen) on the process of catalytic oxidation of PE was tested at 110°C. Cobalt, manganese, and iron acetylacetonates (in amounts of 0.098 and 0.294 mmol) were used as catalysts. The results obtained after 7.5 h are listed in Table IV.

The obtained data showed that the application of oxygen has led to an increase of PE oxidation rate. When the cobalt acetylacetonate (0.294 mmol) was used as catalyst and oxidation was carried out with oxygen, the product was completely melted, and the process was stopped. The product was also partially melted when the manganese catalyst was used with oxygen. To avoid PE melting, the amount of catalyst was lowered by a factor of three. This decrease allowed powdered product to be obtained and the effect of type of oxidizing agent on the catalytic oxidation process to be observed.

Despite the positive influence on the reaction kinetics and reduction of the amount of catalyst required, application of oxygen in PE oxidation has some disadvantages, including the explosion hazard of the powdered polyethylene–oxygen mixture as well as the higher price of oxygen.

The effect of the amount of raw material

In another experiment, we studied the effect of increasing the amount of raw material. The previously shown processes were carried out in glass reactors with 50 g of PE. When the amounts of PE and catalyst were doubled (PE = 100 g and Fe = 0.588 mmol), the obtained product had a similar degree of oxidation. Unfortunately, it was melted, especially in the inner part of the reactor. The reason was probably poor mixing resulting in insufficient removal of heat of exothermic reactions as well as a deficiency of oxygen leading to an increase in the extent of chain crosslinking reactions. These disadvantages have been eliminated by using a metal reactor equipped with a slow-speed paddle stirrer. Even when the amount of raw material was increased to 150 g (0.882 mmol of Fe(III) acetylacetonate), the obtained product was in powder form and

TABLE III
The Effect of Temperature on the Oxidation of PE with Air Catalyzed by Selected Transition Metal Acetylacetonates

Catalyst	Temperature (°C)	AN (mg KOH/g)	EN (mg KOH/g)	V_{ox} (AN/h)
Fe(III) acetylacetonate	110	6.6	5.1	0.88
	115	13.0	4.8	1.73
	120	15.0	13.3	1.87
Mn(II) acetylacetonate	110	21.4	26.8	2.86
	115	34.3	32.5	4.57
	120	36.8	25.5	4.91
Co(II) acetylacetonate	110	20.6	19.8	2.74
	115	40.3	24.4	5.37
	120[a]	–	–	–

PE: 50 g; air: 7.5 dm^3/h; acetylacetonates: Fe(III), Mn(II), and Co(II): 0.196 mmol; reaction time: 7.5 h.

[a] Process was stopped after 2 h, because of PE melting.

TABLE IV
The Effect of Oxidizing Agents on the Catalytic Oxidation of PE with Air in the Presence of Selected Transition Metal Acetylacetonates

Catalyst	Amount of catalyst	Oxidizing agent	AN (mg KOH/g)	EN (mg KOH/g)	V_{ox} (AN/h)
Co(II) acetylacetonate	0.294	Oxygen[a]	–	–	–
		Air	34.9	22.3	4.65
	0.098	Oxygen	38.3	24.0	5.11
		Air	20.6	19.8	2.74
Mn(II) acetylacetonate	0.294	Oxygen	31.1	23.0	4.15
		Air	25.0	18.2	3.34
	0.098	Oxygen	8.8	4.9	1.17
		Air	7.2	4.0	0.95
Fe(III) acetylacetonate	0.294	Oxygen	12.7	6.0	1.69
		Air	10.7	3.2	1.43

110°C, PE: 50 g; air, oxygen: 7.5 dm^3/h; reaction time: 7.5 h.

[a] Process was stopped after 2 h, because of PE melting.

had a similar degree of oxidation after the same reaction time.

FTIR analysis of oxidized polyethylene

To identify the presence of carbonyl groups in the oxidation reaction product, FTIR analysis was performed. The carbonyl group absorption intensity, as well as the total band area (region of 1650–1800 cm^{-1}), was determined in the spectra of oxidized PE samples. The peak at 2020 cm^{-1} was used as the internal standard.

Figures 2 and 3 present the FTIR spectra of polyethylene oxidized at 110°C with air in the presence of iron(III) acetylacetonate. The region of 1700–1800 cm^{-1} shows the carbonyl group absorption intensity. The peaks of functional groups containing C=O groups such as peroxycarboxyl, ester, carboxyl, and ketones can be observed by extension of this region as shown in Figure 3.

The application of mathematical separation of the carbonyl group band allowed calculation of the relative contents of peroxycarboxyl, ester, and carboxyl as well as ketone groups in oxidized polyethylene. The peak at 2020 cm^{-1} was used as the internal standard. Based on the calculations, the increased amounts of groups containing C=O groups are depicted in Figure 4 as dependence of relative peaks areas (functional group peak area/peak area at 2020 cm^{-1}) versus time of reaction.

Based on the obtained results (Fig. 4), it has been found that the greatest increase in the carbonyl groups belongs to the ester groups. The lower increase in carboxyl groups can be caused by their reaction with low-molecular-weight alcohols leading to esters.

Similar FTIR tests have been performed for products of polyethylene oxidation in the presence of different amounts of iron(III) acetylacetonate. Figures 5 and 6 present spectra of raw PE and oxidation products having similar ANs (about 26 mg KOH/g). The

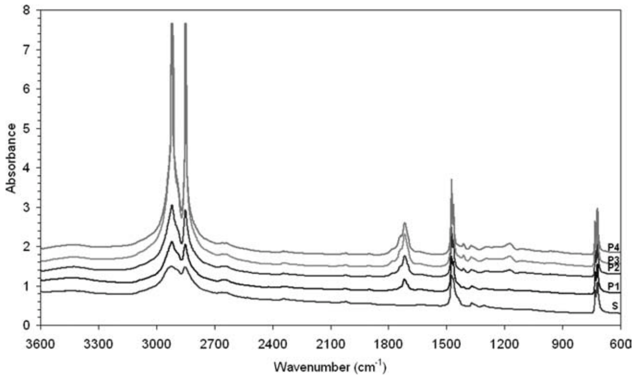

Figure 2 FTIR spectra of: raw PE (S) and oxidized PE catalyzed by Fe(III) acetylacetonate (0.098 mmol) after 3.5 h (P1); 14.5 h (P2); 20.5 h (P3); and 37 h (P4). PE: 50 g; air: 7.5 dm^3/h; 110°C.

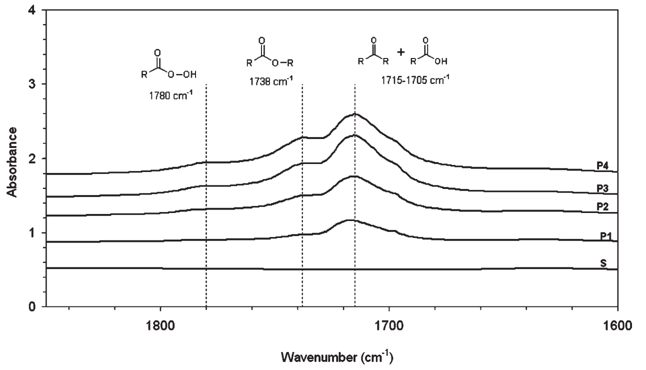

Figure 3 FTIR spectra, expanded region of 1600–1850 cm^{-1}; (S) raw PE and oxidized PE catalyzed by Fe(III) acetylacetonate (0.098 mmol) after 3.5 h (P1); 14.5 h (P2); 20.5 h (P3); and 37 h (P4). PE: 50 g; air: 7.5 dm^3/h; 110°C.

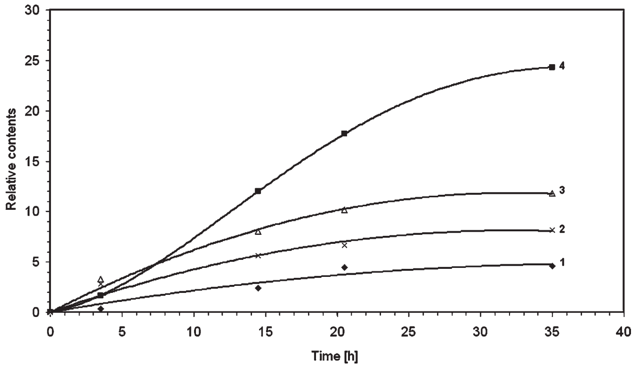

Figure 4 The effect of metal ions on the formation of different groups in the PE oxidation catalyzed by Fe(III) acetylacetonate: (1) peroxycarboxyl groups; (2) associate carboxyl groups; (3) ketone and carboxyl groups; (4) ester groups. PE: 50 g; metal acetylacetonate: 0.098 mmol; air: 7.5 dm^3/h; 120°C.

region of 1700–1800 cm^{-1} representing the carbonyl group absorption intensity is almost identical for both products. This similarity can be clearly seen in Figure 6, where the FTIR expanded region of the peaks of peroxycarboxyl, ester, carboxyl, and ketone group peaks are shown.

The obtained data showed that threefold increase of the catalyst amount led to an increase of the reaction rate but does not influence the relative functional group content.

CONCLUSIONS

The catalytic oxidative degradation of high-molecular-weight polyethylene in the solid phase was studied. It has been shown that use of cobalt, manganese, and iron acetylacetonates as catalysts leads to increase of the oxidation rate. As predicted, an increase in the catalyst amount, temperature, or oxygen concentration in the oxidizing agent also accelerates the oxidation rate.

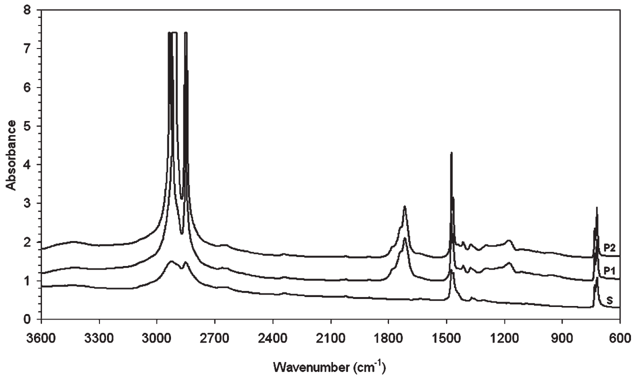

Figure 5 FTIR spectra of samples: raw PE (S) and after oxidation catalyzed by Fe(III) acetylacetonate: (P1) 0.098 mmol (AN = 26.3;10 h); (P2) 0.294 mmol (AN = 26.9; 7.5 h). PE: 50 g; air: 7.5 dm^3/h; 120°C.

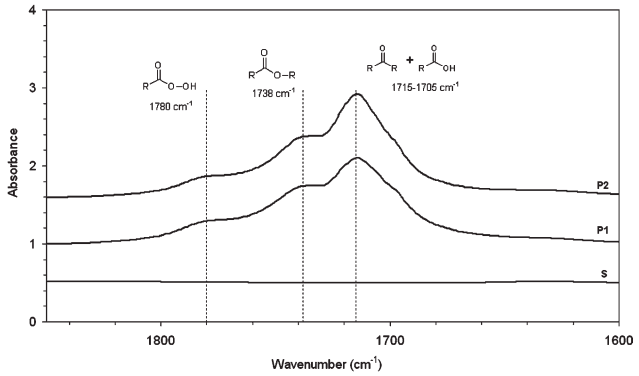

Figure 6 FTIR spectra of samples; expanded region of 1600–1850 cm^{-1}; raw PE (S) and after oxidation catalyzed by Fe(III) acetylacetonate: (P1) 0.098 mmol (10 h); (P2) 0.294 mmol (7.5 h). PE: 50 g; air: 7.5 dm^3/h; 120°C.

The relative activities of the metals in PE oxidative degradation correlate with their redox potential and can be placed in the following order: Co > Mn > Fe ≫ V. However, the use of transition metal complexes in higher contents has some disadvantages. Unfortunately, the catalysts also accelerate side reactions, such as crosslinking reactions, and the products may contain traces of metal impurities and may have a dark color. All of these can limit their applications as components of aqueous emulsions.

This work showed that using the catalysts in adequate amounts and oxidation of polyethylene at lower temperature led to products with good properties, without crosslinking, and after a shorter amount of time than performing oxidation with initiators.

The FTIR spectroscopy showed that products with similar degrees of oxidation obtained under different conditions have similar amounts of carbonyl groups. The FTIR results confirmed also that ester groups are formed from carboxyl groups in secondary reactions.

References

1. http://seminar.unipack.ru/eng/2007/2/.
2. Ullmann's Encyclopedia of Industrial Chemistry, Sixth Editon; Electronic Release; Bailey, J. E.; Bohnet, M.; Brinker, C. J.; Chibata, I.; Cornils, B.; Evans, T.; Greim, H.; Hegedus, L. L.; Heitbaum, J.; Herrmann, W. A.; Keim, W.; Kleemann, A.; Kreysa, G.; Löliger, J.; McClellan, R. O., Eds.; Wiley-VCH, 2002.
3. Bodily, D. M. J Polym Sci Part A-1: Polym Chem 1972, 10, 1709.
4. Takamatsu, T.; Konaga, T. Polym Lett 1969, 7, 27.
5. Hall, J. R.; Westerdahl, C. A. L.; Devine, A. T.; Bodnar, M. J. J Appl Polym Sci 1969, 13, 2085.
6. Clark, D. T.; Dilks, A. J Polym Sci Polym Chem Ed 1977, 15, 2321.
7. Clark, D. T.; Dilks, A. J Polym Sci Polym Chem Ed 1978, 16, 911.
8. Clark, D. T.; Dilks, A. J Polym Sci Polym Chem Ed 1979, 17, 957.

9. Nuzzo, R. J.; Smolinski, G. Macromolecules 1984, 17, 1013.
10. Peeling, J. J Polym Sci Polym Chem Ed 1983, 21, 2047.
11. Blyth, A. R.; Briggs, D. Polymer 1978, 19, 1273.
12. Briggs, D.; Kendal, C. R. Polymer 1979, 20, 1053.
13. (to. Eastman Kodak Company). GB Pat. 1,021,701 (1966).
14. (to. VEB Leuna-Werke). GB Pat. 1,429,012 (1976).
15. Demin, P.; Ebster, K.; Meyer, J.; Kotte, G. (to VEB Leuna-Werke). DD Pat. 125,131 (1977).
16. Hohner, G. (to Clariant GmbH). U.S. Pat. 6,211,303 B1 (2001).
17. Deckers, A.; Brüderle, H.; Sessig, V. (to BASF AG). U.S. Pat. 6,060,565 (2000).
18. (to Sanyo Chemical Industries, LTD.). GB Pat. 1,295,366 (1972).
19. Stetter, K.; Korbanka, H. (to HOECHST AG). U.S. Pat. 3,756,999 (1973).
20. Herrmann, H. F.; Hohner, G. (to Clariant GmbH). U.S. Pat. 6,384,148 (2002).
21. Bush, R. W.; Park, T.; Kehr, C. L. (to Allied Chemical Corporation). U.S. Pat. 3,322,711 (1967).
22. George, L. B.; Su, T. P. (to Allied Chemical Corporation). DE Pat. 1,570,652 (1970).
23. Schuster, L.; Hettche, A.; Liedy, W.; Weiss, S.; Ehemann, L. (to BASF AG). U.S. Pat. 4,889,897 (1989).
24. Schuster, L.; Hettche, A.; Liedy, W.; Weiss, S.; Ehemann, L. (to BASF AG). U.S. Pat. 5,064,908 (1991).
25. Baum, B. J Appl Polym Sci 1959, 2, 281.
26. Iring, M.; Kelen, T.; Tűdős, F. Polym Bull 1986, 15, 531.
27. Sickle, D. E. J Polym Sci Part A: Polym Chem 1972, 10, 275.
28. Bevilacqua, E. M.; English, E. S.; Gall, J. S. J Appl Polym Sci 1964, 8, 1691.
29. Denisov, E. T.; Afanas'ev, J. B. Oxidation and Autoxidation in Organic Chemistry and Biology; CRC Press: Boca Raton, 2005; p 431.
30. Gugumus, F. Polym Degrad Stab 2000, 68, 21.
31. Gugumus, F. Polym Degrad Stab 2000, 67, 35.
32. Gugumus, F. Polym Degrad Stab 1999, 65, 5.
33. Gugumus, F. Polym Degrad Stab 2001, 74, 327.
34. Gugumus, F. Polym Degrad Stab 2002, 76, 329.
35. Gugumus, F. Polym Degrad Stab 2006, 91, 3416.
36. Gugumus, F. Polym Degrad Stab 2006, 91, 3429.
37. Howard, J. A. In Free Radicals; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 2, p 3.
38. Franz, G.; Sheldon, R. A. Ullmann's Encyclopedia of Industrial Chemistry; VCH Verlagsgesellschaft GmbH: Weinheim, 1991; Vol. A18, p 261.
39. Sheldon, R. A.; Kochi, J. K. Metal Catalyzed Oxidations of Organic Compounds; Academic Press: New York, 1981.
40. Russell, G. A. In Peroxide Reaction Mechanism: Peroxide Pathways In Autoxidation; Edwards, J. O., Ed.; John Wiley & Sons: New York, 1962; p 107.
41. Egorenkov, N. I.; Lin, D. G.; Bely, V. A. J Polym Sci Polym Chem Ed 1975, 13, 1493.
42. Alter, H. Ind Eng Chem 1960, 52, 121.
43. Lin, D. G.; Vorobieva, E. V. J Appl Polym Sci 2002, 84, 2776.
44. Mallakpour, S. E.; Hajipour, A. R.; Mahdavian, A. R.; Zadhoush, A.; Hosseini, F. A. Eur Polym J 2001, 37, 1199.
45. DIN EN ISO 2114:2000, Plastics (polyester resins) and paints and varnishes (binders) - Determination of partial acid value and total acid value.
46. DIN EN ISO 3681:1996, Binders for paints and varnishes - Determination of saponification value - Titrimetric method.
47. Dorabialska, A.; Lada, Z.; Michalski, M.; Rodewald, W.; Physico-Chimique Handbook; WNT: Warsaw, 1974, Chapter E, p 297.