

Catalytic Oxidation of Polyethylene with Oxygen in Aqueous Dispersion

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ABSTRACT: The oxidative degradation of polyethylene in aqueous dispersion was studied. The influences of different parameters as well as additives on polyethylene oxidation were investigated. The products obtained in noncatalytic and catalyzed by transition metal salts oxidation processes were compared and characterized by the determination of acid number as well as by means of ICP-OES, GPC analysis, and FTIR spectroscopy. The obtained results have shown that the catalytic processes using manganese(II) or cobalt(II) acetylacetonate proceeded with two to three times higher rate than process without catalysts. Moreover, the FTIR spectroscopy and GPC analysis confirmed similar properties of final product obtained both in noncatalytic and catalytic processes. Another advantage of this process is a very low content of catalyst in product ~ 0.001 – 0.003% of metal used. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Polyethylene, with the biggest share in commodity production of polymers next to polypropylene and PVC, is used for obtaining a broad selection of products applied in numerous industrial brands.

One of the applications of polyethylene is its use as a material in the process of oxidative degradation. The obtained product with an acid number (AN) of 25–30 mg KOH/g, containing ~ 3 – 4% of oxygen, has new properties and may form water emulsions of broad application in the paper, textile, and construction industries, in the production of floor care products, as well as directly as an additive in the production of polymers (PVC) and polymer resin.¹

The hydrophilic nature of the oxidized polyethylene is the result of introducing the following oxygen groups into its structure: carboxylic, hydroxyl, carbonyl, aldehyde, and ester. The process of oxidation occurs in accordance with the known free radical mechanism, which constitutes the subject of numerous studies, especially by Gugumus^{2–8} and Denisov.⁹

The process of polyethylene oxidative degradation, as it stands from patent literature, may be carried out in different systems. Depending on the type of material used, we distinguish oxidation in liquid phase in melt (waxes and LDPE),^{10–13} oxidation in water dispersion (LDPE, HDPE, and UHMWPE),^{14,15} and

oxidation in solid phase (HDPE and UHMWPE).^{16,17} Air, oxygen, and oxygen-enriched air are used as oxidizing agents, while free radical initiators are the main additives.

In the previous work,¹⁸ we presented the studies on the influence of process parameters and selected transition metal compounds on the oxidation process of powdered HDPE in the solid phase using air. In this system, use of oxygen that leads to increase the reaction rate is limited by the possibility of explosion of powdered polyethylene-oxygen mixture. Product with AN about 28 was obtained at 120°C after 40 h in noncatalytic oxidation process and after 4 h in process catalyzed by Co(acac)₂. On one hand, the lack of a necessity to use a solvent argues for selecting this manner of polyethylene oxidation because of economic and ecologic reasons. On the other hand, the faults of this process were the low-reaction rate of noncatalytic process and acceleration of the undesirable crosslinking reactions and, in some cases, also the dark color of the final product in case of catalytic process, which may limit its application.

That discussed in this paper process of polyethylene oxidation in aqueous dispersion has not these disadvantages. The presence of aqueous environment limited the unfavorable crosslinking reactions and improved the process safety, and oxygen can be used as an oxidizing agent. Therefore, it can find application in industry despite high-energy consumption (water heating up), an expensive pressure apparatus, and low volume productivity.

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This work examines the influence of process parameters and transition metal compounds on HDPE oxidation in aqueous dispersion, below the melting point, under pressure, in a three-phase solid–liquid–gas system.

The elevated pressure allows the process to be performed at temperature higher than 100°C and facilitates the dissolution of oxygen in water from which it diffuses to the polymer surface and then to its amorphous phase, which undergoes oxidation. The beneficial way of using elevated pressure is presented by Henry's law. Henry's coefficient k_H is low for water and equals to $k_{H(298K)} = 1.18 \times 10^{-8}$ (mol L⁻¹ Pa⁻¹), while for cumene, dodecane, and polyethylene (amorphous phase), it is high and equals to 9.77×10^{-8} , 8.14×10^{-8} , and 3.00×10^{-8} (mol L⁻¹ Pa⁻¹), respectively.⁹

The aim of the studies was to determine the influence of the selected parameters and additives (especially transition metal compounds) on the course of the process and the quality of the obtained products. Moreover, the possibility of recycling of postreaction water containing a catalyst was checked. Apart from the AN and the melting temperature range, also the ICP–OES, GPC, and FTIR analysis were used to characterize the products.

EXPERIMENTAL

Materials

The material used was HDPE IDEALIS 500 of the Braskem Company of the following properties: viscosity 4.7 dL/g; average molecular mass 5.5×10^5 ; density 0.951 g/cm³; m.p. 136°C; average crystallite size 170 μm.

Initiators and catalysts of a 99.9% purity were purchased from Merck; Rokanol NL6, Rokanol L10 (ethoxylated fatty alcohols), and ABS (sodium dodecyl benzene sulfonate) from PCC Rokita SA, while Pluronic 6800 (block-copolymers based on ethylenoxide and propylenoxide) from BASF. All the additives were used without further purification.

Methods

Oxidation of Polyethylene in a Pressure Autoclave. The oxidation processes were carried out in a 100-cm³ miniautoclave (Autoclave Engineers), made of Hastelloy C-276 steel and supplied with a magnetic Dispersimax-type agitator, a heating jacket, and temperature sensor.

Powdered PE, additives (DCP–dicumyl peroxide as initiator, catalyst, and surfactant), and water were introduced to the autoclave. Next, the autoclave was filled with oxygen to the adequate pressure, and the agitator was started. The reagents were heated up with the rate of 3°C/min to process temperature.

Analytical Methods. In the final products, the AN¹⁹ and the melting temperature range (m.p.)²⁰ were determined. Moreover, for selected products, metal content analyses by means of the ICP–OES method (Optima 5300 V emission spectrometer, Perkin Elmer), the FTIR analyses (Philips spectrometer, PU9800 model with a resolution of 2 cm⁻¹ in KBr), and GPC analyses (Alliance GPCV 2000 apparatus, Waters) were performed.

RESULT AND DISCUSSION

The Influence of Basic Parameters and Surfactants

Initial studies including the determination of the effects of agitation (500–2200 rpm), temperature (100–125°C), oxygen pressure (3.5–14 bar), polymer/water ratio (1/1–1/4), and reaction time (5–25 h) as well as the influence of an addition of selected surfactants on the HDPE oxidation in aqueous dispersion were carried out. The results of the initial studies were gathered in Table I.

To eliminate the induction period, dicumyl peroxide was added as an initiator. This compound showed the best initiating properties from studied initiators as presented in Table II.

The carried-out studies showed that together with the increase of agitator speed in the range of 500–1800 rpm (Item no. 1–4), the obtained product has a higher oxidation level, which is the result of a better diffusion of the oxidation agent into the polymer in a three-phase system. Higher agitation speed (2200 rpm) probably caused that HDPE was splattered on the wall of reactor above liquid level, and product with lower AN was obtained. For this reason, agitation with a velocity of 1800 rpm was used in subsequent studies.

The increase of temperature in the range of 100–125°C (Item no. 5–8) influences favorably the rate of the process. However, the best effects were obtained at 120°C, while above this temperature, a partial melting of polymer particles was observed. The product obtained at 125°C was melted and useless. Together with the increase of temperature, also degradation processes of the polyethylene chain are intensified, which is confirmed by the decrease of the product's melting point values.

To provide sufficient amount of oxygen, it is necessary to use elevated pressure in studied process (Item no. 9–12). The presented results showed that it is enough to use pressure of 6 bar; a further increase of pressure does not impact the oxidation rate.

Water present in the system facilitates the mixing of reagents and the removal of the reaction heat. On the other hand, it results in a lower volume productivity. Because of economical reasons, it was important to check whether the decrease in the amount of water would impact the process of PE oxidation. Based on the obtained results (Item no. 13–14), it was stated that it is possible to conduct the process with a PE/water ratio of 1/2. With a lower amount of water (PE/water = 1/1), there are considerable agitation difficulties, and the process cannot be carried out.

To facilitate the contact between polyethylene, oxygen, water, and other additives, selected emulsifiers were added to the reaction mixture (Item no. 15–19). Nonionic emulsifiers with the structure of ethoxylated fatty alcohols (Rokanol NL6, Rokanol L10), block-copolymers based on ethylenoxide, and propylenoxide (Pluronic 6800) as well as anionic ones such as sodium dodecyl benzene sulfonate (ABS) were used. Thanks to the addition of the aforementioned emulsifiers, hydrophobic polyethylene was well moistened and formed a water slurry easily, which increased the effectiveness of mixing materials with water and provided slightly higher ANs of the obtained products.

Further studies (Item no. 20–23) have proven that in order to obtain a product with an AN about 20 mg KOH/g, the process should be conducted for at least 15 h at 120°C. Together, with

Table I. The Influence of Process Parameters and Surfactants on HDPE Oxidation in Aqueous Dispersion

No	Agitation (rpm)	Temp. (°C)	Pressure ^a (bar)	PE/H ₂ O	Surfactant	Time (h)	AN of PE (mg KOH/g)	m.p. (°C)
1.	2200	120	8	1/4	Rokanol L10	5	4.9	130-131
2.	1800	120	8	1/4	Rokanol L10	5	7.7	130-133
3.	1000	120	8	1/4	Rokanol L10	5	6.2	131-133
4.	500	120	8	1/4	Rokanol L10	5	3.3	131-134
5.	1800	100	8	1/4	Rokanol L10	10	1.5	134-137
6.	1800	110	8	1/4	Rokanol L10	10	4.9	130-133
7.	1800	120	8	1/4	Rokanol L10	10	14.3	130-133
8.	1800	125 ^b	8	1/4	Rokanol L10	10	18.7	128-129
9.	1800	120	3.5	1/4	Rokanol L10	10	9.6	130-133
10.	1800	120	6	1/4	Rokanol L10	10	15.1	130-133
11.	1800	120	8	1/4	Rokanol L10	10	14.3	130-133
12.	1800	120	14	1/4	Rokanol L10	10	14.5	131-133
13.	1800	120	8	1/4	Rokanol L10	10	14.3	130-133
14.	1800	120	8	1/2	Rokanol L10	10	14.2	130-133
15.	1800	120	8	1/4	Rokanol NL6	5	6.9	130-132
16.	1800	120	8	1/4	Rokanol L10	5	7.7	130-133
17.	1800	120	8	1/4	Pluronic 6800	5	6.6	129-132
18.	1800	120	8	1/4	ABS	5	6.7	131-133
19.	1800	120	8	1/4	-	5	5.6	130-133
20.	1800	120	8	1/4	Rokanol L10	5	7.7	130-133
21.	1800	120	8	1/4	Rokanol L10	10	14.3	130-133
22.	1800	120	8	1/4	Rokanol L10	15	19.5	130-132
23.	1800	120	8	1/4	Rokanol L10	25	26.8	129-131

PE = 2.5 g, DCP = 1 wt %, surfactant = 2 wt % (Rokanol-ethoxylated fatty alcohols, Pluronic-block-copolymers based on ethylenoxide and propylenoxide, ABS, sodium dodecyl benzene sulfonate).

^aPressure at reaction temperature, ^bMelted during reaction.

the further process time extension, a decrease of the product's melting point is observed, which proves the occurring of polymer degradation, just like with the increase of temperature.

These studies showed that it is possible to obtain oxidized HDPE with AN about 20 in oxidation process carried out in aqueous dispersion (120°C, 15–20 h, 6–8 bar). The obtained products were powdered and could be easily separated from the aqueous phase. The rate of the studied noncatalytic oxidation processes in aqueous media was much higher in comparison with the rate of previously described oxidation process in the solid phase using air.

The Influence of the Type of Catalyst

Studies on the catalytic HDPE oxidation in aqueous dispersion were carried out using selected variable valence metal compounds. Cobalt(II), manganese(II), iron(III), and copper(II) acetylacetonates and acetates were used as catalysts. The obtained results are presented in Table III.

The previous studies on polyethylene oxidation in solid phase have proven that compounds such as Co(II), Mn(II), and Fe(III) acetylacetonates increase the rate of the oxidation process, while Cu(II) acetylacetonate presented inert properties. Similar results were obtained in the process carried out in aqueous

dispersion. The activity of applied metals may be grouped in the following way: Co > Mn > Fe > Cu. The direction of the decreasing activity is coherent with the decrease of redox potentials of the metals used.²¹

The best results were obtained when Co(II) acetylacetonate was used as the catalyst; the reaction rate was about three times

Table II. Influence of Initiators on PE Oxidation in Aqueous Dispersion

Initiator	AN of PE (mg KOH/g)	m.p. (°C)
- ^a	4.8	132-135
Dicumyl peroxide	7.7	130-133
Ditert-butyl peroxide	2.5	132-134
Dilauroyl peroxide	3.1	132-134
Potassium persulfate	1.8	133-138
ACHN ^a	8.5	130-134
Dicumyl peroxide ^a	14.3	130-133
H ₂ O ₂ (0.5%) ^b	2.6	132-135

PE = 2.5 g, initiator = 1 wt %, surfactant (Rokanol L10) = 2 wt %, ratio of PE : H₂O = 1 : 4, 120°C, pressure at reaction temperature = 8 bar, 1800 rpm, and reaction time = 5 h.

^aReaction time = 10 h, ^bInitiator = 2 wt %.

Table III. Influence of Catalysts on PE Oxidation in Aqueous Dispersion

Catalyst	AN of PE (mg KOH/g)	m.p. (°C)	AN of H ₂ O (mg KOH/g)
-	7.7	130-133	2.8
Co(OAc) ₂	11.1	130-133	4.9
Mn(OAc) ₂	13.9	129-133	4.7
Co(acac) ₂	26.4	128-131	5.7
Co(acac) ₂ ^a	40.4	129-132	13.2
Mn(acac) ₂	12.9	129-132	3.9
Mn(acac) ₂ ^a	31.8	128-131	11.3
Cu(acac) ₂	8.4	129-133	3.8
Fe(acac) ₃	10.6	131-134	5.6

PE = 2.5 g, DCP = 1 wt %, catalyst = 0.5 wt %, surfactant (Rokanol L10) = 2 wt %, ratio of PE : H₂O = 1 : 4, 120°C, pressure at reaction temperature = 8 bar, 1800 rpm, and reaction time = 5 h.

^aReaction time = 10 h.

higher in comparison with noncatalytic process. From application point of view, the color of oxidized PE as well as amount of metal salts impurities is essential. Fortunately, the products obtained in the presence of Co(acac)₂ and Mn(acac)₂ were bright, slightly creamy-colored. The amount of metal salts in oxidized PE determined by means of the ICP-OES analysis was presented in Table IV.

The amount of Co and Mn constitutes a little over 1–2% of the theoretical amount of the catalyst used in the reaction. This shows that its majority remains in the aqueous phase (thus, it is appropriate to use postreaction water again). This is a significant advantage when compared with products obtained as a result of oxidation in solid phase in which the metal remains.

Postreaction Water Recycling

Tests were performed on the possibility of recycling postreaction water containing the dissolved catalyst Co(acac)₂ or Mn(acac)₂. Two recycles were performed without the addition of further catalyst and surfactant amounts. The obtained results were presented in Table V.

In the case of using cobalt and manganese salts, a significant decrease was observed in the reaction rate at the first attempt of water recycling. The AN at both catalysts dropped twice. With

Table V. Recycling of Postreaction Water

Recycled water	Process	AN of PE (mg KOH/g)	m.p. (°C)	AN of H ₂ O (mg KOH/g)
-	Co(acac) ₂	40.4	129-132	13.2
I	-	20.8	129-132	13.6
II	-	16.2	128-131	15.4
	Mn(acac) ₂	31.8	128-131	11.3
I	-	15.5	130-133	13.1
II	-	11.7	129-131	14.6

PE-2.5 g, DCP-1 wt.%, catalyst-0.5 wt.%, surfactant (Rokanol L10)-2 wt.%, ratio of PE:H₂O-1:4, 120°C, pressure at reaction temperature-8 bar, 1800 rpm, reaction time-10 h

Table IV. ICP-OES Analysis of Oxidized PE

Catalyst	Time (h)	AN of PE (mg KOH/g)	Wt % of metals	
			Mn	Co
- ^a	25	26.8	-	-
Mn(acac) ₂	10	26.9	0.0025	-
Co(acac) ₂	5	22.7	-	0.0014

PE = 12.5 g (^a2.5 g), DCP = 1 wt %, catalyst = 0.5 wt %, surfactant (Rokanol L10) = 2 wt %, ratio of PE : H₂O = 1 : 4, 120°C, pressure at reaction temperature = 8 bar, 1800 rpm.

the next use of the postreaction water, these differences were considerably smaller. The decrease of the oxidation rate may be caused by the catalyst deactivation and byproducts formation, which inhibit the process. Each recycle stage was accompanied by the increase of the postreaction water's AN as a result of polymer degradation and formation of low-molecular acids soluble in water (mainly acetic acid as showed GCMS analysis).

The results showed that probably a partial recycling of the water could be possible after previously enriching with an additional amount of the catalyst.

GPC and FTIR Analyses of Oxidized Polyethylene

Products with a similar AN, obtained as a result of noncatalytic and catalytic oxidation [with Co(II) and Mn(II) acetylacetonate], were subjected to GPC and FTIR analyses.

The GPC analysis results were presented in Table VI, together with the values of the weight-average molecular weight (M_w), the number-average molecular weight (M_n), the viscosity-average molecular weight (M_v), and polydispersity index (PDI).

Comparing the values placed in Table VI, it may be observed that the oxidation products have lower M_w , M_n , and M_v masses than the raw material—on average, ~ 40 times for M_w and ~ 25 times in the case of M_n and M_v , which confirms the presence of occurring polymer degradation reactions. The PDIs of oxidized polyethylene were also lower in comparison with raw material.

Products obtained in a noncatalytic process and catalytic ones using manganese and cobalt salts were compared by means of FTIR spectroscopy. Figures 1 and 2 present the obtained spectra. The first one shows the full scope, while the other one, the carbonyl band scope (1650–1800 cm⁻¹), with the assigning of peaks for specific groups with a carbonyl arrangement.

The obtained results show that the addition of Mn(II) as the catalyst does not influence the content of functional groups. The spectra obtained for products of noncatalytic (AN 26.8) and catalytic oxidation (AN 26.9) with Mn(II) are almost identical. In the case of a product obtained in the presence of Co(II), the carbonyl band is slightly higher, which is the result of a lower oxidation degree (AN 22.7). Generally, no considerable differences between products obtained in noncatalytic and catalytic processes were observed by means of FTIR analysis.

CONCLUSIONS

HDPE oxidation, similar to oxidation of low-molecular weight analogs, proceeds according to free-radical mechanism.²⁻⁸

Table VI. GPC Analysis of Oxidized PE

PE	Catalyst	Time (h)	AN of PE (mg KOH/g)	M_W (10^3 g/mol)	M_N (10^3 g/mol)	M_V (10^3 g/mol)	PDI
Nonoxidized PE	-	-	-	522.2	38.8	183.1	13.45
Oxidized PE ^a	-	25	26.8	13.1	1.4	6.4	9.35
Oxidized PE	Mn(acac) ₂	10	26.9	11.5	1.1	5.5	10.45
Oxidized PE	Co(acac) ₂	5	22.7	15.4	2.1	8.3	7.33

PE = 12.5 g (2.5 g), DCP = 1 wt %, catalyst = 0.5 wt %, surfactant (Rokanol L10) = 2 wt %, ratio of PE : H₂O = 1 : 4, 120°C, pressure at reaction temperature = 8 bar, 1800 rpm.

During the process, macroradicals PE* are formed and rapidly react with oxygen-producing peroxy radicals PEOO* that can abstract hydrogen in intra- or intermolecular reactions. The hydrophilic groups containing oxygen are introduced to polymer in subsequent reactions of hydroperoxyl groups. The presence of these groups was confirmed by FTIR analysis of obtained oxidized HDPE. Additionally, oxidation of HDPE is accompanied by the degradation of macromolecules. The GPC analysis showed that the value of weight-average molecular weight of oxidized polymer was about 40 times lower in comparison with the raw material. The polyethylene degrades mainly through monomolecular destruction of peroxy macroradicals PEOO*.⁹

In this work, the influence of selected parameters and additives on the process of HDPE oxidative degradation in aqueous dispersion below melting point of polymer under pressure of oxygen was studied. It has been showed that to get sufficient diffusion of oxygen in this complex reaction system, the agitation with velocity at least 1800 rpm as well as oxygen pressure at least 6 bar should be applied. Higher rate of agitation and oxygen pressure did not impact the oxidation rate. To improve mixing and removing of heat of exothermic oxidation reaction, the additives of surfactants are recommended as well as a two to four excess of water in relation to the material. The process

should be carried out in the highest possible temperature, however, lower than the melting point of the material and product. The best results were obtained at 120°C.

Using established process parameters, significantly, reduction of reaction time was obtained in comparison with the previously described process of HDPE oxidation in the two-phase system using air.¹⁸ A product with an AN about 20 mg KOH/g was obtained in the process carried out in aqueous dispersion at 120°C under 8 bars of oxygen pressure after 15 h of reaction (in solid phase about 35 h was needed). In comparison with the HDPE oxidation carried out in two-phase solid-gas system, the process safety was improved.¹⁸ The aqueous media limit the possibility of dust explosion, and oxygen can be used as oxidizing agent.

The studies showed that transition metals, especially Co(II) and Mn(II) acetylacetonate, catalyzed the oxidative degradation of HDPE very effectively, and the reaction time was shortened two to three times when compared with a noncatalytic process. It is known that variable valence metals increase the rate of oxidation processes by lowering the activation energy of hydroperoxide groups decomposition.⁹ In case of polymer oxidation, the metals can also increase the rate of degradation and unfavorable crosslinking reactions. However, the tests with the use of GPC and FTIR as well as melting ranges did not show considerable

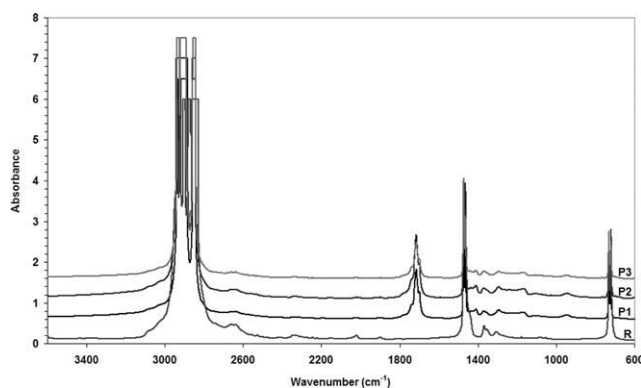


Figure 1. FTIR spectra of raw PE (Rokanol L10) = 2 wt %, ratio of (R) and oxidized PE without additive: PE : H₂O = 1 : 4, 120°C, pressure at reaction temperature = 8 bar, 1800 rpm, reaction time = 25 h (P1), 10 h (P2), and 5 h (P3). PE = 12.5 g, DCP = 1 wt %, catalyst = 0.5 wt %, surfactant

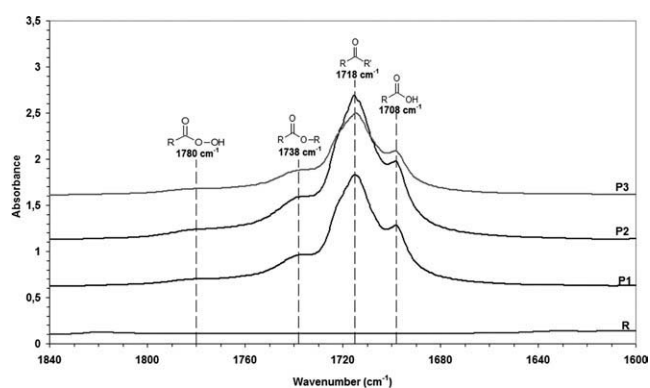


Figure 2. FTIR spectra, expanded region of 1600–1850 cm⁻¹: raw PE (Rokanol L10) = 2.23 wt %, ratio of (R) and oxidized PE without additive: PE : H₂O = 1 : 4, 120°C, pressure at reaction temperature = 8 bar, 1800 rpm, reaction time = 25 h (P1), 10 h (P2), and 5 h (P3). PE = 12.5 g, DCP = 1 wt %, catalyst = 0.5 wt %, surfactant

differences between products obtained in processes of noncatalytic polyethylene oxidation and catalytic oxidation. The obtained products in the presence of $\text{Co}(\text{acac})_2$ and $\text{Mn}(\text{acac})_2$ products were bright, slightly creamy-colored, and contained only 0.001–0.003% of metal used. This is a significant advantage when compared with products obtained as a result of catalytic oxidation in solid phase in which the metal remains, and acceleration of crosslinking processes was observed.

In the described HDPE-oxidative degradation process in aqueous dispersion, at 120°C, the products remained in the form of powder and could be easily separated. We believe that this system can find application in industry.²²

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