

Review

# Oxo-Additives for Polyolefin Degradation: Kinetics and Mechanism

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**Abstract:** This review considers the recent investigations in the scope of biodegradability of synthetic polymers, spanning polyethylene (PE), polypropylene (PP), and their corresponding composites, with a focus on the influence of oxo-additives (mostly transition metal salts). The types of oxo-additives and the mechanisms of oxidation acceleration are discussed. Furthermore, the influence of oxo-additives on both physicochemical and biological stages of degradation is evaluated (laboratory and field experiments with microorganisms/fungi action) with recent standards suggested for degradation estimation. Comparisons of the metal salts are given with respect to catalysis, as well as the synergetic influence of additives. The additives presented on the commercial market are also discussed.

**Keywords:** polyolefin; oxidation; oxo-additives; biodegradation



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## 1. Introduction

The demand for plastic materials has risen considerably over the last few decades. The main reasons for this are low price, long operational period, and adaptability. According to The Economist, in the period 1950–2015, the world’s plastic production was approximately equal to 8.3 billion tons of different kinds of plastic. Currently, about 25% of the plastic produced is being used, whereas 9% is converted or reprocessed, 12% is burned, and 79% is spread in the environment [1]. In other words, there is a problem of plastic waste accumulation, which is of harm to ecosystems. The reason for the existence of such a large mass of nonutilized plastic waste is its inability to decay, which in turn can be attributed to the following factors:

- (1) The highly hydrophobic character of PE and many other polymers.
- (2) The high density of macromolecule chain packing such that a product’s physical properties are close to a crystal.
- (3) Absence of water diffusion and oxygen in the crystal domain of the polymer.
- (4) The presence of antioxidants added during molding in some cases (to reduce oxidation at high processing temperature) and to reduce external factor influence during the exploitation period [2].
- (5) High molecular mass and long chain length are retarding factors concerning destruction, whereby terminal groups are mostly situated deeply in the volume of material and introduce steric hindrance [3].
- (6) Embrittlement to microparticles (microplastic) and, as a consequence, the complexity of investigation and monitoring, as well as the inability to influence its destruction.

Biodegradation of PE is debatable; many experts state that biodegradation of PE is impossible. Numerous investigations of film biodegradation revealed that oxidation by molecular oxygen induces carbon chain rupture and the formation of corresponding products, whereas more short chains are consumed by bacteria [4,5]. Elaboration of materials

that are efficient to decay in the presence of atmospheric oxygen (i.e., oxodegradation) by the end of the exploitation period has been intensively conducted. As a consequence, these materials have become more prone to biodegradation.

There are now certain industrial approaches to polymer waste utilization problems. One of the approaches of how to accelerate biodegradation is the search for optimal conditions of oxodegradation and additives, which are the overall process catalyzers (mostly pro-oxidants) applied. The oxodegradation stage is, however, nontrivial concerning its kinetics: the chain radical reaction, which is influenced by UV light, and autocatalysis, which is brought about by metal ions. Many empirical data have been obtained during the elaboration of polymer/additive pairs and laboratory or field testing. However, there is a lack of a systematic kinetic approach to (1) oxidation mechanism, (2) plastic decay, and (3) microplastic generation and its further transformation. In this review, recent research in the area of metal activators of polyolefin (mostly PP and PE) degradation is discussed.

In a prior review [6], the nanoscale particle additives were considered, in addition to their perspectives; this question is beyond the scope of the present work.

## 2. Definitions

*Polymer degradation* is a process when mostly the physical properties (tensile strength, other mechanical characteristics, color, length, shape, etc.) change due to environmental factors such as heat, light, or chemicals [7].

*Polymer degradation* implies the process in which a chemical change takes place [8]. It is analogous to *biodegradable polymers*, which are defined as materials whose chemical and physical characteristics undergo deterioration and completely degrade when exposed to microorganisms and aerobic or anaerobic processes [9].

A *bioabsorbable polymer* is a polymer that can be absorbed by certain biosystems and assimilated by them [8].

*Erosion* means that the polymer dissolves, is washed away, or is worn off from the polymer object's surface [8].

In general, it is accepted that biodegradation is divided into three stages:

- (1) *Biodeterioration* described the decomposition of the material when subjected to microbes/fungi. At this stage, the action of nonbiological factors is also important (e.g., hydrolysis, chemicals, the character of media in which the sample is immersed, and swelling). It takes place with the action of bacteria (in recent investigations, the gut biota was intensively discussed [10,11]) and micromycetes enzymes. However, their actions are efficient when the sample has been exposed to light and heat, whereby lower molecular mass and new functional groups appear.
- (2) *Bioassimilation* is the incorporation of carbon from the initial polymer mass when the biomass grows, whereby *biomineralization* (carbon and hydrogen to CO<sub>2</sub> and H<sub>2</sub>O) describes aerobic processes [12,13] and *methanization* (carbon and hydrogen to CH<sub>4</sub>) describes anaerobic processes. Oxo-additives can considerably help to increase the degree of degradation.

## 3. Abiotic and Biotic Treatment

In general, it is accepted that the investigation of polymer degradation includes abiotic pretreatment. The latter often consists of UV and/or thermal oxidation. Following that, biotic treatment (in soil, water, and laboratory respirometry device) is applied. In this case, the material has some structural defects and cavities, and the molecular mass decreases along with the length of molecular chains, which are then more prone to the action of biotics enzymes. In addition, it is important to highlight that functional groups (especially with oxygen) can considerably stimulate enzymatic reactions. Here, another series of investigations for biologically treated samples has been conducted. In the most recent work, the analysis, which included several stages, was carried out after the abiotic stage and biodegradation stage.

- (1) Investigations of physico-mechanical properties (tensile strength, Young modulus, etc.)

- (2) Molecular mass distribution and mass loss with chromatographic methods are intended to determine how the average molecular mass (using, for instance, gel-penetrating chromatography, GPC) and dispersity change.
- (3) Infrared spectroscopy (to estimate the number of functional groups); shortwave infrared hyperspectral imaging (SWIR-HIS); Fourier-transform infrared spectroscopy (FTIR); attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR).
- (4) Scanning electron microscopy (SEM) for morphology of sample; X-ray diffraction analysis (XRD) for structure determination; transmission electron microscopy (TEM).
- (5) Mass loss.
- (6) Thermal properties (crystallinity and temperature of melting) by differential scanning calorimetry (DSC); successive self-nucleation and annealing (SSA).
- (7) Nuclear magnetic resonance (NMR) to characterize the products of the degradation of polymers and microplastic [14]. Such approaches can provide kinetic data to help reveal the mechanism of the process.
- (8) Thermal gravimetric analysis (TGA) to estimate mass loss and find kinetic curves of mass altering.
- (9) Isotope method for direct monitoring of carbon transfer from polymer to other substances (seldom used and expensive).
- (10) Respirometry, oxygen uptake, and CO<sub>2</sub> emission.
- (11) Electron spectroscopy for chemical analysis (ESCA).
- (12) Principal component analysis (PCA).

According to the results of these investigations, one can conclude the efficiency of the abiotic stage and the biotic stage. Such a two-step approach allows separating the effects of UV light, oxygen, and other natural factors. The results of certain studies are discussed later, such as those including the oxodegradation of polyolefins, mechanism of oxodegradation in the presence or absence of UV light, the synergetic or antagonistic influence of different metal compounds, susceptibility to oxidation of different polyolefins, and the biotic stage of degradation.

#### 4. Abiotic Stage: Oxodegradation of Polyolefins

Degradation in the presence of oxygen takes place according to the radical chain mechanism. This first stage has been intensively discussed in the scientific literature [15]; there are different ways to initiate the first radical species and the subsequent oxygen addition reactions:

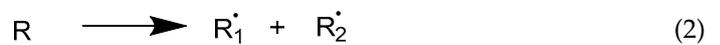
- (1) Direct oxidation of C–H by molecular or atomic oxygen, which has quite a high activation energy.
- (2) thermal rupture of C–C or C–H bonds, which also has quite a high activation energy
- (3) Mechanochemical rupture of C–H bond, which could take place at the extrusion stage during the manufacturing of polymer or composite [16]. Once radicals are generated, another oxidation reaction takes place.
- (4) Oxidation by molecular oxygen
- (5) Reaction of O<sub>2</sub> with unsaturated carbon–carbon bonds (impurities).

Some variations of chain radical reactions take place depending on the presence of light and higher temperatures. The light-induced mechanism differs from that of autocatalytic “dark” stages. The products of these are hydrocarbons with functional groups (aldehydes, ketones, carboxylic acids, alcohols, lactones, esters, etc. with lower molecular mass), as discussed in the next section.

#### 5. Mechanism of Oxodegradation in the Presence or Absence of UV Light

Previous reviews [17,18] indicated that the impurities of unsaturation are a major initiation factor causing the further formation of allylic hydroperoxides. The major reactions of polymer chain RH (1) and (2) are presented below. These can initiate the primary radical reaction and take place when the sample is exposed to heat (vinyl, vinylene, or vinylidene

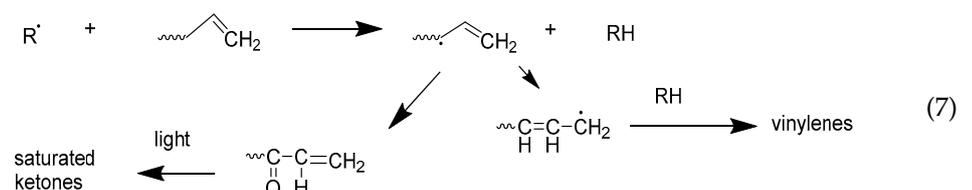
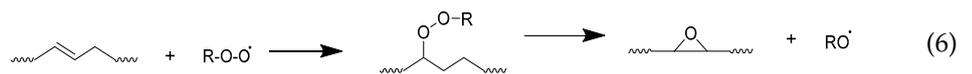
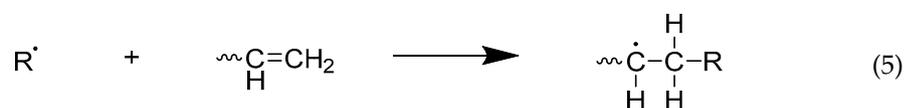
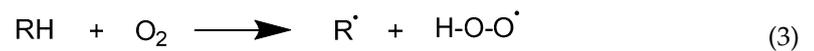
impurities are thermolabile groups), UV light, high-energy photons, X-rays, electrons, or mechanical force (e.g., tension from shear forces during extrusion).



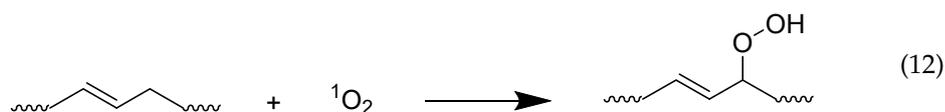
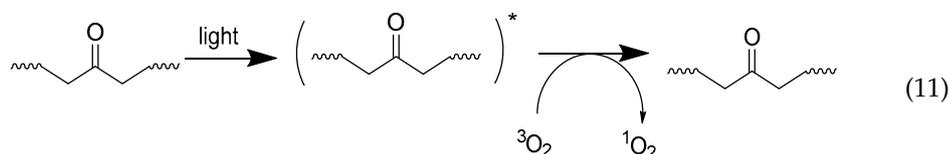
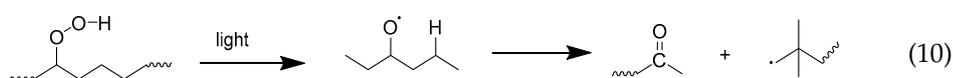
The latter case is less considered; however, comprehensive work has been conducted on the reactivity of stressed molecules [19]. Shear forces act, for example, when the polymer is being (re)extruded. Reprocessed polymers generally have lower mechanical properties. This influence is, however, quite ambiguous, as proven in [20], where six successive reformations of thermoplastic polyurethane did not change the mechanical properties. Thus, mechanical forces which are applied during reprocessing extrusion need thorough consideration.

The schemes of oxidation stages presented below were adapted from [15,16,21–23] and earlier fundamental works [24]. The existing schemes are presented below. These schemes can be classified as initiation reactions (1), (2), reactions where unsaturated compounds participate (5), (6), (7), (27), (28), recombination reactions (18)–(22), (30), Norrish I and II reactions (15, 16), propagation reactions (4), (8), (10), (23), (25), (26), (29), (31)–(33), branching reactions (9), (17), (24), reactions with singlet oxygen (11), (12), and metal autocatalysis reactions where the metal ion is oxidized (13) or where metal ion reduction takes place (14).

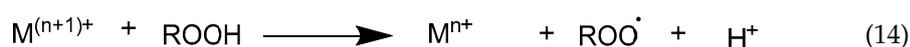
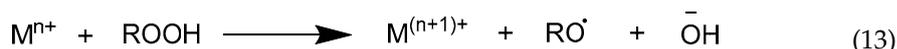
Along with (1) and (2), (3) provides two radicals:  $\text{R}^\bullet$  and  $\text{HOO}^\bullet$ ; the direct reaction has high activation energy (and highly endothermic) and is neglected as a rule. However, it can proceed through a charge transfer complex, which absorbs UV photons and then decays to  $\text{R}^\bullet$  and  $\text{HOO}^\bullet$ . The polymer alkyl radical ( $\text{R}^\bullet$ ) reacts easily with an oxygen molecule to give a polymer peroxy radical  $\text{RO}_2^\bullet$  (4). It is well known that peroxy radicals can react with unsaturated  $\text{C}=\text{C}$  bonds, which may stem from an impurity in the polymer chain (vinyl, vinylene, or vinylidene). The reaction of an unsaturated alkyl radical  $\text{R}^\bullet$  (5) with a new macroradical as a product is thermodynamically feasible. The macroradical can abstract hydrogen from another  $\text{RH}$  polymeric chain. The peroxy radical can react with a double  $\text{C}=\text{C}$  bond, giving an epoxide and alkoxy radical (6). The alkyl radical  $\text{R}^\bullet$  can also abstract hydrogen from a chain with a vinyl group (7), where another unsaturated bond is formed, i.e., a more complex pathway to saturated ketone products.



The peroxy radical can abstract hydrogen from the PE chain and (8), where ROOH and a new alkyl radical  $R^\bullet$  forms. The fate of key intermediate ROOH can vary: decaying to  $\bullet\text{OH}$  and  $\text{RO}^\bullet$  (9) or decaying to ketone and macroradical (10). ROOH can also play a role in autooxidation in the presence of metals (13), (14); the scheme is considered below). Ketone, e.g., as a product of (10), can absorb a UV photon and be a source of highly reactive singlet oxygen (11). The latter can readily react by shifting an unsaturated C=C bond (12), which is the main reaction of singlet oxygen in such systems.



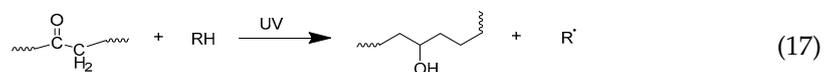
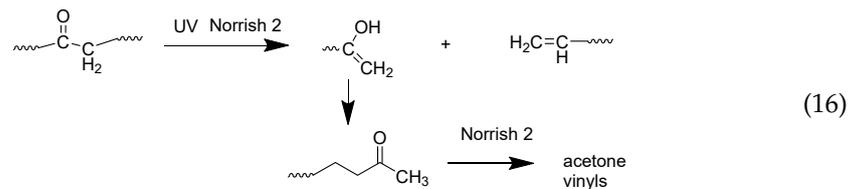
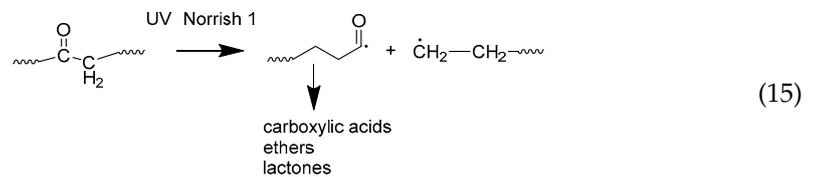
In [25], different compounds, metal salts, and others were considered concerning their ability to accelerate or retard the oxidation of polymers. At the same time, some metallic compounds can be an accelerator for certain polymers and a retardant for others.



The kinetics of the overall rate and the oxidation mechanisms including (13) and (14) were considered in [24]. Different mechanisms of acceleration were also considered [25] (hydroperoxide decomposition; direct reaction Me + substrate; oxygen activation; metallic compound decomposition; photosensitization and subsequent generation of singlet oxygen; inhibition; scavenging of hydroperoxides; free-radical scavenging; screening or absorption of radiation; quenching of excited-state energy; quenching of singlet oxygen). Some metals can be inhibitors for one polymer and accelerators for another [26,27].

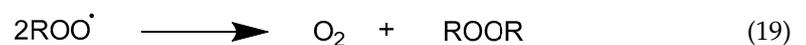
Recent research [28] revealed that, in the order HDPE < LDPE < LLDPE < itPP, the overall photo-oxidation degradation rate increases when oxo-biodegradable additives are applied. The authors suggested that this trend toward photo-oxidation is due to the molecular structures of the considered polymers, mostly the difference in the number of tertiary carbons. The schemes used to rationalize the dynamics of photodegradation and its peculiarities include the Norrish I and II mechanisms, which do not take place in "dark" conditions. The intramolecular reactions of abstraction of the hydrogen atom represent a well-known characteristic of carbonyl compounds with sufficiently long (more than two carbon atoms) substituents. The intermediate diradical decomposes into two unsaturated fragments—an olefin and an enol, with the latter then isomerizing into a ketone. This reaction is called Norrish type II, in contrast to Norrish type I, which consists

of photodissociation (pre-dissociation) along the bonds adjacent to the carbonyl group. The intermediate diradical formed in the Norrish type II mechanism can not only decompose, but also cyclize.

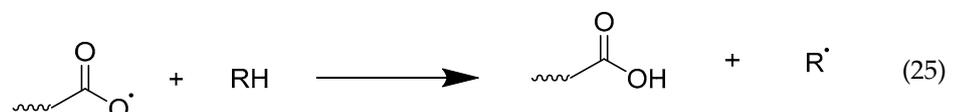
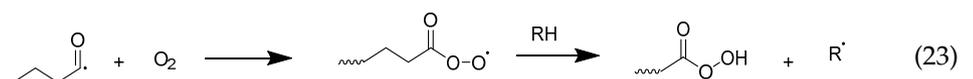


Once a C=O group is generated, the corresponding reaction can take place in the presence of light (15) and (16). The products of these stages are new chromophore and unsaturated groups. Another branching reaction with hydrogen abstraction is (17), which can take place in the presence of light, where a new macroradical forms.

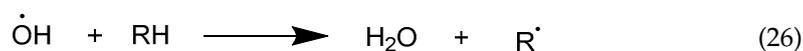
Reactions of radical recombination (18)–(22) are easily proceed during polyolefin oxidation.



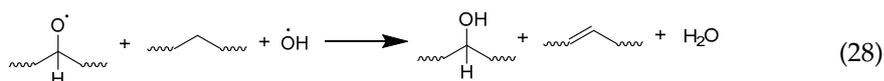
Other important chain propagation reactions are (23), (25) and branching (24), in which the highly reactive product of the Norrish I reaction interacts with molecular oxygen. In these reactions, hydroxyl and macroradicals form.



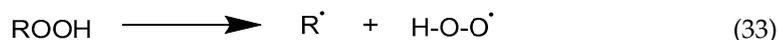
The hydroxyl radical plays a role in reactions with the RH chain (26) and the alkoxy radical (27).



The alkoxy radical which forms, for example, in (6), (9), and (13) plays a role in the following interactions:



Other propagation reactions include the rupture of O–O and R–O bonds of ROOR (31) and (33) and hydrogen abstraction of ROO from RH polyolefin chain (32).



Abundant studies are devoted to the influence of oxo-additives (at first, metal salts) on polyolefins oxidation. In the work by La Mantia et al. [29], a comparison of some antioxidants and hindered amine light stabilizers (HALS) was presented. The antioxidants (AO) were found to only partially reduce the oxodegradation of crosslinked ethylene-vinyl acetate (EVA) as they reduce the oxidative reaction, but not the scission reaction, which is crucial for the whole process. A comprehensive theoretical investigation (PBE function in terms of generalised gradient approximation (GGA)) into the crystallinity phase of PE oxidation was conducted by Olewoye et al. [30], considering the following elementary reactions: scission of C–C, molecular oxygen, elimination of hydrogen, and others. Intramolecular hydrogen transfer occurs from the C-branch to the peroxide radical of another C-branch. Accordingly, direct H abstraction by O<sub>2</sub> has an activation energy of 212.6 kJ·mol<sup>-1</sup>.

In the work by Scott [16], the mechanism of primary initiation of the thermos-oxidative radical mechanism was discussed. Scott stated that C–C and C–H homolysis or the direct O<sub>2</sub> reaction are unlikely to proceed due to the high activation energy in standard conditions. Mechanochemical scission is the most probable mechanism that leads to alkyl macroradicals, taking place at high shear stress when extruded. Alkyl traps (nitroso compounds) prevent further macroradicals from subsequent reactions that inhibit mechano-oxidation. In the work by Carlson et al. [31], the important role of radical formation during the extrusion of PP was also indicated. In the work by O'Toole et al. [32], the mechanism of polystyrene degradation under UV light was studied using the time-of-flight secondary ion mass spectrometry (ToF-SIMS) technique. The authors concluded that the degradation mechanism includes charge transfer complexes of phenyl substituents and oxygen or energy transfer to phenyl from another excited state.

Holland and Rae [33] presented a model experiment to prove that rupture of the C–C bond is a crucial process for thermal oxidation. Here, the model compound (tetramethyl 2,4,5,7-tetramethyloctane-2,4,5,7-tetracarboxylate) was heated in a sealed tube under vacuum at ~200 °C for hours, and the degradation products were analyzed by GPC. In the work by Zha et al. [34], an elevated temperature test was conducted for PE service time estimation (PE-pipes). The authors considered diffusion-limited oxidation and discussed the degradation mechanism of heterogeneous processes at lower temperatures (which are close to service conditions and do not change morphology unless at higher temperatures).

The difference in reactivity of radicals generated when PP is oxidized was thoroughly discussed by Bertin et al. [35], who considered different elementary stages. The authors used the quantum-chemical method for estimation of the effectiveness of radical reactions for H abstraction from different macromolecular C–H bonds.

Detailed information on key elementary reactions helps to understand the degradation mechanisms. In the study of PP, the crucial role of formaldehyde in photodegradation was investigated using TD-DFT [36] by Meng et al. Such information (activation energy and enthalpy) can provide additional quantitative information to experimental data. New insight into the mechanism of oxidation of high-molecular-mass PE was given in [37], where radicals were generated by gamma irradiation, and the fate of oxidation intermediates was investigated.

In the work by Portillo et al. [38], a sigmoidal curve was established representing the degree of degradation vs. the exposure time of neat PE and PE + additive to UV. Interestingly, at an equal whole dose, the degradation was more intensive when the intensity was lower (and, correspondingly, when the time of exposure to UV was larger). The sigmoidal curves of feature vs. time had approximately one plateau. The additive exhibited an effect at the early stages of degradation (rapid molecular mass decay). The model for PE degradation process prediction was proposed by Barr-Kumarakuisinghe et al. [39] (dependence of the percentage elongation on time) taking oxo-additives into account.

## 6. Comparison of Metals as Oxidation Catalysts: UV Acceleration

Metal carboxylates, especially stearates of Ce, Co, and Fe, are accelerators of peroxide formation during polymer oxidation. Iron has photo-initiating activity with a delayed effect, whereas Cr (IV), Ni, and Cu catalyze thermal reactions [40–43].

Eyheraguibel et al. [44] discussed a new approach to estimate products of oxodegradation (HDPE with Fe and Mn stearates as photocatalysts) at consecutive stages. The products of degradation were extracted in three solvents: water, acetone, and chloroform. This allowed identifying the most precise information about oligomer formation during the process. In addition, element analysis was performed in terms of MS and <sup>1</sup>H-NMR. Table 1 presents the overall relative reactivity of different metal compounds in different media, phases, and conditions (light or the absence of light).

**Table 1.** Comparison of the action of different metals. Role of metals as activators or retarders.

System	Condition/Method	Result	Ref
Thermo-oxidation of polyolefin			
aPP + Mn stearates	Liquid/oxygen uptake	Mn has an optimal concentration; Mn stearate is an efficient catalyst	[24]
LDPE + Co, Mn, Fe stearates	UV, thermal degradation	Efficiency as prodegradant: Co > Mn > Fe	[45]
itPP + different ionic and covalently bounded Co salts	Solid/oxygen uptake	Diethyldiselenocarbamatocobalt(III)—strong inhibitor; acetylacetonatocobalt(III)—strong accelerator	[46]

Table 1. Cont.

System	Condition/Method	Result	Ref
PP, metal stearates	Solid (powder)/oxygen uptake	Catalyst efficiency: Co > Cr > Mn > Cu > Fe > V > Ni > Ti ≈ Pb ≈ Ca ≈ Ag ≈ Zn > Al > Mg ≈ Cd > control	[25,47]
PP, metal stearates	Liquid/trichlorobenzene solution	Catalyst efficiency: Cu > Mn > Fe > Cr > Co > Ni > Ti > control > Al >> Zn >> V; Cu and Fe oxygen uptake decreases after a certain time	[26]
iPP + Zn, Ni, Pd, Cu, Cr, Co N,N-diethylselenocarbamates	Solid/(powder)/oxygen uptake	Inhibitor efficiency: Zn > Ni > Co.Pd > Cu > Cr in both the presence and the absence of Cu stearates; a decrease in hydroperoxide concentration was observed	[48]
iPP + different Co compounds	Solid (powder)/oxygen uptake	Acceleration of degradation of iPP: Acetylacetonatocobalt (III) > potassium trioxalatocobaltate(III) > trisethylenediammincobalt(III) chloride > sodium hexanitrocobaltate > potassium hexacyanocobaltate(III) > diethylselenocarbamatocobalt (III) > acetylacetonatocobalt(II) cupric stearate	[46]
PE+ the deactivatedchromium catalyst	Solid/TGA	The deactivated chromium catalyst behaves as a pro-oxidant at low concentrations (1–6 ppm) and suppresses oxidative pyrolysis at high concentrations (100 ppm).	[49]
Photodegradation of polyolefines			
PE, PP + stearates	Solid	Catalyst efficiency: V > Ti > Co ≈ Mn ≈ Ni ≈ Zn ≈ Cr > pure >> Cu (retardation); Cu acts as a radical scavenger and UV adsorber	[50,51]
PP + metal diethylselenocarbamates	Solid/IR, luminescence	Co > Ni > Pure > Cr > Zn phr at ~1 phr; Zn and Cr could be a retarder (0.5–1.0 phr) or accelerator (0.01–0.1 phr)	[27]
			[25,52,53]
PP, PE + Cu, Fe stearates	HDPE, PP; films/FTIR, XRD	Less than 5 wt.% Cu stearate accelerates UV degradation; more than 5 wt.% Cu stearate reduces UV degradation	[54]
PP, LDPE + 2,4-pentadione complexes	HDPE, PP films/FTIR	PE activity: Ti > Al > Zr > VO >> Cu; PP activity: Fe > Ti > Zr > Mg > V > Cu > Ca > Al	[55]

It is worth noting that, as revealed by Kiryakova et al. [56], PE has the highest extent of photo-oxidation corresponding to manganese(II) and cobalt(III) acetylacetonates, whereas, for PP, vanady(II) and iron(III) acetylacetonates had the most pronounced effect.

The UV wavelength dependency of photodestruction was described by Bourgoigne et al. [57], where the authors revealed the 300–350 nm part of the UV spectrum dramatically influences the mechanism and is crucial for modeling natural solar conditions.

## 7. Synergetic or Antagonistic Influence of Different Metal Compounds

In some cases, the stearates of different metals act simultaneously with each other and with the antioxidant added to the same polymer. In these cases, synergetic or antagonistic effects can take place. Allen et al. [58] found an synergetic and antagonistic influence on antioxidants in PP: Irgastab 2002, Cyasorb UV 1084, and Irganox 1425. CaSt had an antagonistic action on the photostabilizing features of Irgastab 2002 and increased the action of Cyasorb UV 1084. NiSt had a synergetic (antagonistic) action on nickel chelate Irganox 1425 in unprocessed (processed) polymer. Allen et.al [59], considered a wider range of metal stearates was investigated with respect to their ability to enhance the stabilization

of the polymer; the authors accounted for such synergetic/antagonistic effects in terms of metal atom exchange. In the case of Cyasorb UV 1084, SrSt gave synergism, while Zn, Na, Mg, and Co stearates gave antagonism; in the case of Irgastab 2002, all Na, Co, Zn, Sr, and Mg stearates gave an antagonistic effect.

The synergetic or antagonistic effects of pro-oxidants (namely, metal stearates) have been evidenced in several studies. The investigation by K erouani et al. [60] proved that effective PE degradation is enhanced by the synergetic effect of iron and cobalt stearate combined at the same concentration subjected to accelerated aging (thermal and photo-oxidation). This synergetic effect was found to be more pronounced in the thermal than UV degradation effect in these films.

In Fa et al. [61], both TiO<sub>2</sub> and Fe stearates were introduced into LDPE for 30 days of thermodestruction, which brought about a decrease of 60% in tensile strength. Interestingly, Co and Fe stearates acted with TiO<sub>2</sub> nanoparticles in a different way, with CoSt and FeSt bringing about an antagonistic effect in the photo-oxidation experiment, which was not observed in dark thermos-oxidation [62]. The CoSt + TiO<sub>2</sub> system had about a 90% longer embrittlement time compared to surface-compatibilized nano-TiO<sub>2</sub> LLDPE.

The mechanism of thermal degradation of PVC is profoundly different and does not directly fall within the scope of the present work. It worth noting that, in this case, synergetic effects of different stearates take place. A Ca/Zn stearate mixture was considered in [63], Ca/Ba/Zn stearates were considered in [64], and Be/Mg/Ca/Ba stearates were considered in [65] with nonoxidizing conditions.

## 8. Susceptibility to Oxidation of Different Polyolefins

Clark [66] used the ESCA of cyclically UV-exposed PS to atmospheric air to characterize the degradation peculiarities and compared it to continuous irradiation. In this study, the natural (day/night) UV action was modeled, and it was found that the dark phase distinctly influences the oxidation rate.

However, the rate of degradation of polyolefins, which have saturated C–C bonds, is influenced by chain defects, e.g., unsaturation and branching points, which are more easily oxidized, resulting in hydroperoxide and cleavage reactions [67]. In general, it was proven that reactivity toward oxidation follows the order iPP > LDPE > LLDPE > HDPE, where high-density polyethylene is the most stable [68,69].

Iring [70] presented a serious kinetic study of photo- and thermo-oxidation of PE with unsaturated groups (vinyl, vinylene, and vinylidene). It was found that these groups induce more intensive thermos-oxidation, and that their concentration does not affect the photo-oxidation rate. The results of time-dependent density functional theory (TD-DFT) computations by Khatri [71] proved that the impurities of polymers, i.e., side groups, caused their susceptibility to photodegradation. The relative stability of the polymer hydroperoxide derivatives was studied (polyethylene, polypropylene, polybutene, polyhexene, and polydecene), and the least stable were found to be PE and PP.

According to the results of Winslow et al. [68], one could state that UV screens and absorbers both influence photooxidation rate but in quite different ways. Light screens greatly affect the product quantity of the whole process, whereas absorbers only diminish the intensity of light, i.e., the rate of initiation reaction. A synergetic effect can be found in screens and ROOH decomposers.

Photosensitizers induce hydroperoxide formation, e.g., via singlet oxygen. Then, hydroperoxides decay to form different species with free valence. Lastly, Norrish I and II reactions proceed, which are C–C skeleton rupture processes.

Iring et al. [69] studied LLDPE and HDPE in a torque rheometer, oxidized at elevated temperatures. These data proved that unsaturation changed the rate of oxidation (the induction period crucially leveled off), whereas branching points increased the maximum oxygen uptake rate, indicating a higher reactivity of the tertiary C–H bond.

In Khatri et al. [72], UV photodegradation of PS was conducted in terms of the FTIR GPS and XPC. Here, the authors underlined two stages of deterioration—surface stage (the

total number of chemical changes can be very small) and bulk degradation, where great mechanical fragility takes place. There are differences in LLDPE and LDPE concerning long-time degradation; the linear sequences of LLDPE are more prone to destruction [73]. In this study, accelerated and environment aging was performed and discussed.

A novel technique was used by Watanabe et al. [74], where two traces with two-dimensional correlation mapping were used to estimate the dynamics of UV degradation and the depth of photodegradation. The latter was about  $1.3 \times 10^{-6}$  m after 1 h and did not change during the next dozens of hours. In a recent investigation [75], UV aging of PE, PP, and PS was studied in terms of spectroscopy (SWIR-HSI) and principal component analysis (PCA), along with chemometric models for prediction to estimate the extent and dynamics of marine degradation of each type of plastic. The novel approach by Julienne et al. [76] is intended to estimate microplastic generation from ultrathin LDPE films and to examine the products of accelerated weathering. They also found that spherulite size did not influence the rate of photo-oxidation.

In the study by Julienne et al. [77], an increase in Mn stearate concentration brought about the degradation of HDPE, which slightly depends on concentration, reaching the maximum value. In Antunes et al. [78] thermomechanical degradation of HDPE was considered, along with a viscosity investigation on a torque rheometer. Mn stearate served both as a prodegradant additive and a lubricant. Increasing the MnSt weight percentage was found to increase the auto-oxidation reaction product yield at later stages (increasing the amount of HDPE gel). It also served as a lubricant at early stages, as proven by the decreasing torque.

### 9. Biotic Stage: Recent Biodegradation Studies

The review by Liu et al. [79] considered the additive influence on degradation of the system polyolefin/biopolymer and composites, as well as the investigation methods. The factors taken into account when designing the material were indicated: (1) type of polyolefin (thermal stability changes in the order HDPE > m-PE > linear-LDPE, while photo-oxidation occurs in the order m-PE > HDPE > linear-LDPE, as there in degradation in real conditions); (2) type of metal of pro-oxidant. The most active pro-oxidants are transition metal complexes in the form of stearates, in which two ionic states are of approximate or equal stability, with the oxidation degree difference being equal to 1 (e.g., Fe<sup>2+</sup> and Fe<sup>3+</sup>). Different complexes were described by Liu et al. [80].

In Ammala et al. [81] a review of the degradation mechanism of polyesters, polyamides, polycarbonates, polyurethanes, and polyacetals in aerobic or anaerobic conditions was given in the presence of light, bacteria, and micromycetes.

In a thorough review by Liu et al. [80] the standard oxo-additives were considered including those that are available on the market. Mechanisms of degradation and biodegradation, testing methods, and toxicity of the products were discussed. The following stages of degradation were outlined:

- (1) Interaction with atmospheric oxygen and the formation of oxo-groups at polymer chains change the characteristics from hydrophobic to hydrophilic. More short fragments appear. This stage can be accelerated by heating and UV exposure-induced decay (the latter includes keto-groups, which are stable to heating) via the Norrish mechanism (I, II, and III).
- (2) Biodegradation takes place when bacteria, mucoromycetes, and algae convert fragments with functional groups (=O, -OH, etc.) into carbon dioxide, water, and biomass. The number of carbonyl groups diminishes, and the microbiota assimilates small fragments, which have a molecular mass lower than 5000 Da [82].

Table 2 summarizes the data from some recent studies on biodegradation, including abiotic and biotic treatment.

**Table 2.** Summary of recent studies of oxodegradation of polymers.

Matrix	Additive	Treatment 1	Result After Treatment with Thermo- and/or Photo-Oxidation before Biodegrading	Treatment 2	Result After Biodegrading	Methods of Investigation/Analysis	Ref.
LDPE, LDPE + LLDPE	Co acetylacetonates	Thermal oxidation PE (40–70 °C); thermal oxidation in compost	$M_w$ was obtained as a function of time; crystallinity decreased.	Biodegradation in solid agar in presence of 4 fungi agar suspensions, with respirometry in liquid phase	Bioassimilation was seen with micromycetes and in compost. Micromycetes cover increased, PE molar mass decreased by 40% (initial was 1500 g·mol <sup>-1</sup> ). A high-molecular-mass fraction emerged. Crystallinity increased. Oxygen uptake was determined.	Respirometry, scanning electron microscopy (SEM) (erosion), FTIR, DSC, GPC	[83]
EVA with VA 9%	Stearates Fe, Ca	Photodegradation (432 h, Xe lamp, sun filter)	Molecular mass decreased; carbonyl groups accumulated; number of ester bonds decreased; long-chain alkane and alcohol concentrations increased (GC–MS).	Biodegradation after photodestruction in 3 bacterial species + control (45 °C + 90 days)	Mineralization of EVA 15% and mineralization of EVA + stearates ~25%, regardless of the kind of colony.	ATR-FTIR (ester and carbonyl groups), GPC, DSC/TGA, chemiluminescence (activity of stearates), induction time (OIT, by DSC), GC–MS (molecular mass), indirect impedance (mineralization)	[84]
PE	Stearates Fe, Ca	Photooxidation (500 h, Xe lamp)	Molecular mass decreased; carbonyl groups accumulated; number of ester bonds decreased; long-chain alkane and alcohol concentrations increased (GC–MS).	Biodegradation after photodestruction in 3 bacterial species + control (45 °C + 90 days)	Low-molecular-weight oxidation products were found. Biodegradation in colonies for PE was weak at 1%; in the presence of stearates, it was 10% ( <i>Bacillus</i> ) and 11.5% ( <i>B. borstelensis</i> ).	ATR-FTIR, GPC, DSC/TGA, chemiluminescence, GC–MS, mineralization measured by CO <sub>2</sub> emissions (impedance)	[85]

Table 2. Cont.

Matrix	Additive	Treatment 1	Result After Treatment with Thermo- and/or Photo-Oxidation before Biodegrading	Treatment 2	Result After Biodegrading	Methods of Investigation/Analysis	Ref.
LDPE	Stearates Fe, Co, Mn	Thermal oxidation at 45, 55, 60, and 70 °C for 216 h Photooxidation (500 h LDPE and LDPE-Fe), (LDPE-Co and LDPE-Mn) for 240 h	Molecular mass decreased; carbonyl groups increased.	Biodegradation after photodestruction in 3 bacterial species + control (45° C + 90 days)	LDPE films in <i>B. borstelensis</i> and <i>Bacillus MIX</i> efficiency decreased in the order LDPE-Co > LDPE-Mn > LDPE-Fe. Mineralization was ~10–60%. LDP/Fe-stearate film had no thermocatalytic effect.	ATR-FTIR, GPC, DSC/TGA, chemiluminescence, GC-MS.	[86]
LDPE	D2W oxo-degradable d2w additive 5 wt.% prodegradant	Xenon arc chamber for 300 h	Carbonyl index increased	The percentage of degraded material (1, 5, 10, 20, and 50 wt.%) was included in the neat LDPE matrix; test for estimating of ability to recycling and melt flow index	Strength to rupture decreased while Young's modulus increased. With low concentration, the features were close to those of neat LDPE. Melting temperature (Endset Temperature) and crystallinity were measured during the second cycle of melting. The maximum content of oxodegradable LDPE which could be added to a neat polymer to withstand three cycles of treatment without losing features was 10%.	FTIR to assess the carbonyl index and the hydroperoxide band, mechanical features, melt flow index, thermal features, crystallinity	[87]
PE (LLDPE, HDPE)	CaCO <sub>3</sub>	—	—	Biodegradation in the selected soil KUVEIT in terms of ASTM D 5988; measurement of CO <sub>2</sub> emitted	Carbon content was measured in three samples; it did not depend on the rate of carbon evolution. Pro-oxidants strongly influenced carbon emissions.	TGA (heating to 900 °C), GC-MS, ICP-OES for identification of additives; CHNS-O for measurement of carbon content	[88]

Table 2. Cont.

Matrix	Additive	Treatment 1	Result After Treatment with Thermo- and/or Photo-Oxidation before Biodegrading	Treatment 2	Result After Biodegrading	Methods of Investigation/Analysis	Ref.
HIPS	0%, 1.5%, and 3% mass of D2W	Degradation in convection oven at 50, 55, 60, and 65 °C	Neat HIPS did not change; HIPS with 1.5% oxo-additive degraded faster than with 3% ( $t = 50/55$ °C). When $t = 60/65$ °, no difference was seen.	–	–	FTIR analysis during processing, DSC, thermogravimetric analysis (TGA), durability tests, and stretching to rupture	[89]
LLDPE, LDPE	A compound named Oxo (0%, 1%, 2% w/w), unknown	Air oven/60 °C 260 days,	Mechanical properties were lost.	After 260 days of environment weathering, mechanical properties were lost.	Mechanical properties were lost.	FTIR, DSC, SSA, thermal test, GPC	[73]
LDPE	3% Ca stearate, vitamin E, ferulic acid	–	Reology, mechanical and thermal analysis	Q-UV chamber, 480 min irradiation/ 55 °C + 240 min condensation/ 35 °C	Plastifying action on PE and his strength and rigidity and crystallinity (decreasing) with certain increasing of ductility. Vitamin E and ferulic acid 2 and 3% considered as prodegradant for LDPE.	Rheological (strain-controlled rheometer), DSC (N <sub>2</sub> ), mechanical tests (ASTM method D882), FTIR	[90]
PE	TiO <sub>2</sub> –FeSt <sub>3</sub> (different content) FPE with stearate TPE with TiO <sub>2</sub> TFPE with both	UV exposure 240 h; in an air oven for 720 h at 70 °C	After 240 h thermo, C=O groups arose; tensile strength loss was ~60%. After 240 h UV irradiation, the weight loss was ~14%; C=O and –OH groups arose. In first 15 h, chain scission of TFPE and chain oxidation occurred.	Residues immersed in aqueous medium for the test	ISO 14852 (1999): titrimetric analysis of evolved carbon. The degree of biodegradation of TFPE sample was 10 times that of the PE sample. The carbonyl index was in the order TFPE (max CI) > FPE > TPE > PE. There was 14% weight loss after 240 h UV.	Mechanical features, SEM, ATR-FTIR	[61]

Table 2. Cont.

Matrix	Additive	Treatment 1	Result After Treatment with Thermo- and/or Photo-Oxidation before Biodegrading	Treatment 2	Result After Biodegrading	Methods of Investigation/Analysis	Ref.
LDPE	Polyaniline + TiO <sub>2</sub> with different mass ratios 1:25/1:100/1:300	Photocatalytic oxidation under UV light irradiation; 40 W 340 nm (light at midday in summer); UV light for 792 h	LDPE + polyaniline + M-TiO <sub>2</sub> (1/300) had ~88% weight loss.	720 h with isolated fungi	Polyaniline improved the dispersity of TiO <sub>2</sub> particles and both enhanced photodegradation and improved the assimilation of small molecular fragments by fungi	XRD, FTIR, spectroscopy, TGA, TEM, UV/visible spectroscopy, HT-GPC, mechanical features	[91]
LDPE	PEG with nano-TiO <sub>2</sub> + HALS: LDPE LDPE/TiO <sub>2</sub> LDPE/PEG/TiO <sub>2</sub> LDPE/PEG/TiO <sub>2</sub> /HALS (0.2–0.5 wt.%)	180 h UV irradiation	LDPE/PEG/TiO <sub>2</sub> films reached ~70% degradation after 180 h UV. LDPE/TiO <sub>2</sub> films reached ~31% degradation after 180 h UV. After 100 h irradiation, elongation at break of LDPE decreased by ~52%, of LDPE/PEG/TiO <sub>2</sub> decreased by ~96%, and of LDPE/TiO <sub>2</sub> decreased by ~85%. The material fit ASTM D6954-04 after ~370 h.	Respirometry testing 58 °C; in compost, fungal mycelia were found	For photo-oxidized TiO <sub>2</sub> /PEG/LDPE, massive growth was observe. For photo-oxidized LDPE or LDPE/TiO <sub>2</sub> , no colonization was observed. According to respirometry at 58 °C for 4800 h, mineralization of TiO <sub>2</sub> /PEG/LDPE was ~17%, and of LDPE, LDPE/TiO <sub>2</sub> was ~12%.	FTIR, HT-GPC, UV/visible light spectra, mass loss, mechanical measurements, SEM, respirometry, biodegradation test in compost and inoculate	[92]
LDPE	No additive	The test was performed in (1) air, (2) double-distilled water (DDW), or (3) salt solutions with ionic strengths of 0.017 M and 0.6 M for 90 days at 30 °C	LDPE mechanical properties were estimated after 30, 60, and 90 days, along with chemical properties. LPDE photodegradation followed the order air > DDW > salt solution.	—	—	SEM, AFM, FTIR, tensile test	[93]

Table 2. Cont.

Matrix	Additive	Treatment 1	Result After Treatment with Thermo- and/or Photo-Oxidation before Biodegrading	Treatment 2	Result After Biodegrading	Methods of Investigation/Analysis	Ref.
LDPE	Components (starch (0–40%); Oxo (0–10%); PLA (0–1.25%)) in different combinations	Six months of exposure in three investigations: (1) open atmosphere, (2) buried underground, and (3) buried underground with regular daily irrigation	In terms of degradability, mechanical features (tensile strength, elongation at breaking point) changed strongly, especially in the sample with all 3 components. In terms of impact, SEM revealed that LDPE + starch changed the most.	–	–	TGA, FTIR, SEM, DSC, XRD	[94]
PE	–	Mixing PE melt with fatty acids	-	<i>Agrocybe aegerita</i> mycelium	Authors reported fourfold larger carbonyl group formation than in analogous systems previously studied.	ATR-FTIR	[95]

## 10. An Overview of Oxo-Additives on the Market

There are numerous additives that have been presented and discussed in the scientific literature, and their behaviors were often thoroughly analyzed. In some cases, additives modify polymeric chains themselves, e.g., C=O group in polystyrene [96], considerably accelerating oxodegradation of the material. This oxodegradation can be applied in mulching films. For example, in Xu et al. [97], a biodegradable superconcentrate was proposed, whereby a mulching film based on PBT and PLA had higher mechanical properties (hardness and impact viscosity). The patent described by Mi et al. [98] presented a fully biodegradable mulching film based on PBAT + PLA; it was ultrahard and ultrathin (4–6 microns), made from biodegradable resin with additives. Its light transmittance was more than 90%, haziness was lower than 13%, mechanical strength was considerable, and tensile strength was lower than 25 MPa, thus meeting the standards for mulching films. Another approach introduced one polymer into another, e.g., starch in PE. The introduction of starch did not help the degradation of the PE matrix, whereas starch itself is a biodegradable substance [99]. However, in most cases, the additive was introduced into the volume of the polymer as a substance that was not covalently bound to the matrix.

1. *Natural fillers.* Special compatibilizers may be added to enhance the adhesion between the polymer matrix and particles of the filler [100]. Biocomposites, based on synthetic polymer matrices filled by biodegradable fillers [101] are very promising materials [102]. In the work by Brebu [103], it was shown that some vegetable fillers (sunflower husk, flax shive, and mixed herb hay) may act as oxo-additives, accelerating the oxidation of polymer matrix in biocomposites. The approach for the elaboration of composites based on pectin and chitosan is evolving [104]; this is also true for cellulose diacetate and starch [105], as well as microcrystal cellulose [106]. However, there are mechanical property drawbacks; thus, the application area is constrained. This approach uses natural fillers that may be wasted; hence, so the utilization problem is taken into account. Another approach uses mostly metal salts or oxides and acts in a more targeted manner than natural filler oxo-additives.
2. *Oxo-additives based on metals salts.* In Ammala et al. [80], a broad range of oxo-additives were presented, as well as the mechanisms of their influence on polymer decay. One of the first patents for oxo-additive usage constituted Mn, Co, Fe, Ni, and Zn acetylacetonates, where it was shown that Mn stearates, oleates, acetates, Co stearate, Cu oleates, and Fe acetates are the most efficient. In the work by Arraez et al. [89], the process of oxodegradation of HIPS with 1.5% and 3% (weight) of D<sub>2</sub>W species as a pro-oxidant was evaluated. As atomic absorption spectrometer investigations revealed, the active components of the additives WERE metal stearates Fe (~56.7 ppm) and Mn (~6500 ppm), as well as stabilizers. D<sub>2</sub>W is a masterbatch for only oxodegradation as it was not developed for anaerobic conditions (compost). It contains metal salts and different stabilizers, and the recommended dose is 1–3 wt.% [80] The tension and DSC testing showed early degradation. In recent work by Yousef et al. [107], D<sub>2</sub>W additive was introduced in LLDPE, and the ASTM D 6954 test was applied to the samples, which showed a considerable decrease in tensile strength. The patent by Gutierrez [108] introduced a two-layer oxo-biodegradable polymer film containing bio-oriented polypropylene (BOPP) in the first layer; the second layer used a PE film with the addition of D<sub>2</sub>W (1 wt.%). Benitez et al. [73] presented the additive PDQ-H (1 and 2% mass percentage; here and below, % denotes the mass percentage) of the Willow Ridge Plastic company. The accelerated decay of LLDPE and LDPE was evidenced. The metal in the additive was 0.8% Mn, as revealed by AAS; the crystallinity obtained from DSC tests changed while accelerated degradation took place, due to annealing and recrystallization after the chain rupture process. Lukanina et al. [109] and Protasov et al. [110] investigated the influence of metal (Co, Fe, and Mn) stearates as pro-oxidants in LDPE film biodegradation. Ojeda et al. [111] considered the influence of D<sub>2</sub>W pro-oxidant additive on abiotic and biotic PE degradation with *Aspergillus* and *Penicillium*. After 1 year of being under the soil, the samples were

incubated in substrates (city solid garbage, perlite, and soil) at 58 °C, 50% humidity. Biodegradation was estimated according to mineralization to CO<sub>2</sub>. The highest mineralization degree was obtained for saturated vaporized conditions as opposed to natural humidity. The growth of *Aspergillus* and *Penicillium* was seen for PE films containing pro-oxidants that were naturally weathered for 1 year or longer. The PE matrix/metal ratio was 4:1. These species appeared to be effective pro-oxidants. Kyrikou et al. [112] presented the analysis of photochemical decay of PE mulching films with pro-oxidants in real soil conditions, as well as in the laboratory. The value of stretching with rupture with respect to chemical content was investigated, including carbonyl group accumulation, increased crystallinity, and reduced melting temperature. In a study by Konduri et al. [113], the authors investigated the influence of pro-oxidants (Fe<sup>3+</sup>, Mn<sup>2+</sup>, and Co<sup>2+</sup>) on the biodegradations of LDPE with *Aspergillus oryzae* and revealed that it acted more efficiently with pro-oxidants and photoinductors with subsequent microbiological treatment. The polyfunctional additive [114] accelerated oxo- and biodegradation, as well as served as a humidity absorber during post-consumer recycling of polyolefins. The species has one or several metal (Fe, Co, Cu, or their combination) stearates (10–30%), with CaO as a filler (70–90 mass%) and polymeric base (PE). In another study by Korchagin et al. [114], additives for controlled exploitation of material over time were presented, including metal (Co, Fe, and Cu) carboxylates (5–15%) or oxides, salts of transition metals, and Na soaps. The polymer base constituted 86–95%. In the work by Suresh et al. [115], the *Biodegradable Masterbatch*<sup>TM</sup> with Co stearates was introduced in LDPE, and mechanical tests, along with FTIR, SEM, and contact-angle measurements, were performed. *AddiFlex* from Green Club Inc and Omya were used for packaging production. LLDPE/*AddiFlex* films were water-degradable. The polymers here were thermally oxidized synergistically with CaCO<sub>3</sub> (the latter increased UV degradation) [80]. The *AddiFlex* additive contains FeSt, MnSt, CaCO<sub>3</sub>, starch, and/or cellulose, as presented in a patent by Forsberg et al. [116] and discussed in Koutný et al. [117]. The *Nor-X* additive consists of FeSt-treated aqueous hydrogen peroxide, which maintains Fe at a 3+ oxidation state. Interestingly, the recommended concentration is only 0.03 wt.% [80]. *TDPA technology* (and additives *DCP540* and *ZSK 1314* based on it) uses a combination of transition metal carboxylates and aliphatic (poly)hydroxy carboxylic acids [118]. In a patent by Petrie [119], a biodegradable package for food containers (and other purposes) was described. The polymer matrix contained PP, LDPE, HDPE, and others with CaO as a filler (35–94.9%), Cd, and other oxo-additive metal salts with 0.01–20 wt.% concentration. In Abed et al. [120], the *OXO-PE* product was studied. It was created by introducing metal (Cu, Ni, and Fe) salts into the PE matrix. Degradation was performed at 2 and 6 m depth in the Persian Gulf. *OXO-PE* has degradable features and degrades further in the benthic zone than in the plankton zone. Protasov et al. [121] showed the destruction of LDPE modified with Cu, Fe, and Co when thermal and UV aging took place for 192 h. PE deformation at rupture was 94% lower at thermal aging, and 46% lower when UV exposure took place; these values were 64%/33% for Cu carboxylates and 35%/40% for Fe carboxylates. The patent by Shtepa and Anisimov et al. [122] describes a plug for protecting pipes from oxodegradable materials (PLA PCL having 2–3% Fe, Mg, and Co salts) and matrices (LDPE, HDPE, PET, and PP). The patent by Ponomarev [123] describes the creation of biodegradable material including three masterbatches in the form of concentrates by mixing powdered polyolefin with certain technological and purpose-oriented additives. The patent by Newland et al. [124] described acetylacetonates of different metals (Mn, Co, Cr, Co, and V), as well as alkyl acetoacetates and alkyl benzoylacetates (of Cu, V, Cr, Mn, Co, Fe, Ni, Zn). The most effective were proven to be salts of Mn (oleates, acetates, and stearates), Co (acetates and stearates), Fe (acetate), and Cu (oleate). In early patents, Fe, Co, and Mn metals were used. The synergic effect of Fe and Zn was demonstrated by Scott [125], where complexes of metals were activated by the light. Co naphthenate is also known

as a photooxidation accelerator of LDPE [126]. Contat-Rodrigo [127] considered PP with additive Envirocare AG1000C (4 and 10 wt.%). After UV irradiation, more severe morphological and thermal changes were evidenced in contrast to clear PP. This higher degree of oxidation proves that abiotic degradation was facilitated by this additive. A masterbatch with fatty acid amides, carboxylic acid, and metal salt was introduced in a patent by Hong [128] (assigned to Gain Mark Technology); the key substances were fatty acid amides.

Stearates are comparably easy to synthesize and are a relatively cheap compound. They dissolve well in polyolefins and can also enable compatibilization, improving the mechanical features of the composite. At the same time, they can serve as pro-oxidants in some cases as they are activated by light, and they can be attenuated to the exploitation of a certain polymer.

3. *Combinations of metal activators and deactivators.* *Renatura* is a patented blend of metal pro-oxidants (iron stearate) and antioxidants/UV absorbers sold as a masterbatch for PP and PE. The use of *Renatura* was exclusively licensed to Diamant Art Corporation in 2007 to produce biodegradable products under the tradename of “BioSmart” by their subsidiary company, Bio-Plastics Film Inc. Their patent [129] discloses the action of metal stearates (cobalt, iron, and zinc) and dithiocarbamates (zinc, calcium, and manganese). This additive is not sensitive to thermal activation. It comprises a hydrocarbon polymer that can biodegrade via an oxidative mechanism, using an antioxidant (zinc, calcium, or magnesium complex of a liquid containing one or more sulfur compounds attached to the metal ion, such as complexes of mercaptobenzothiazoles, mercaptobenzimidazoles, dithiophosphates, and dithiocarbamates) and pro-oxidant that are soluble in the polymer. The pro-oxidant comprises a transition metal compound that is a carboxylate or an oxygen- or nitrogen-coordinated complex. Iron dithiocarbamate is based on *Scott–Gilead* technology on which mulch films are produced. The peculiarity of such technology is that it starts functioning as a catalyzer of thermo-oxidation when exposed to UV. Before that, it functions as an antioxidant. Méndez et al. [130] considered PP + additive (Ca stearate + antioxidant) at concentrations of 1.5 and 3.0 wt.%. The stretching revealed fragility after 5 days in an oven (60 °C) with 3% oxo-additive. Natural examination showed analogous results with a lower rate of degradation. *Reverte* is an oxo-biodegradable additive for PE, PP, PET, and ABS production (bottles, bags, etc.). It is known that *Reverte* includes (1) a photoinhibiting additive system (stabilizers and/or antioxidants), (2) a prodegradant based on metal ions (iron, cobalt, and/or Mn) that accelerates the rupture of chains, and (3) biodegradation promoters (including microcellulose powder) [80]. The additive is activated in the presence of light and thermally, as verified by Barclay et al. [131]. Photosensitizers based on *Scott–Gilead technology* in mulching films are referred to as *Plastor* or *Plastigone*. Here, transition metals serve as both pro-oxidants and antioxidants. When UV-exposed, certain dithiocarbamates (Fe, Mn, and Ce) are activated [132] and then act as pro-oxidants, whereas Cu, Ni, Zn, and Co dithiocarbamates act as antioxidants. Polyolefin material could attain biodegrading features after a certain usage time with the addition of nonorganic components [133]. Here, it contained some metal (Fe, Co, and Ni) stearates as pro-oxidants (15–30%), as well as phenolic antioxidants (10–20 wt.%), CaCO<sub>3</sub> or TiO<sub>2</sub> as a filler, and a polymeric matrix. The additive was introduced at concentrations of 1–5 wt.%. The additive presented in Lukanina et al. [109] initiates the oxidation rupture of polyolefin chains. It includes pro-oxidants (combinations of metal carboxylates, e.g., 2-ethylhexoate of Zn or Zr, 1–3%) set on an inert CaCO<sub>3</sub> (8–10%) plate. In summary, the combination of metal activators and deactivators has great prospects; however, the synergetic actions could be nontrivial, which demands additional investigations.
4. *Combination of dyes and pigments with/without metal oxo-additives.* Dyes and pigments for light absorbance regulation were used by Newland et al. [124], including carbon black and Sterling R. In this case, the dependence of particle size was demonstrated.

In the patent by Nicklajchik et al. [134], a photodegrading composition based on polyolefins comprising a photosensitizing additive (alkyloxysilyl) was described. It functions as a catalyzer for the oxodestruction of polyolefin in the presence of sunlight. In the patent by Taylor et al. [135], the degradation sensitizing reagent was selected from organic peroxides, organic hydroperoxides (e.g., tert-butyl hydroperoxide, and cumene hydroperoxide), organic azo compounds (e.g., 2-azo-bis-isobutyronitrile), metallo-organic compounds, organic materials which undergo facile autoxidation, organic photosensitizers, and organic dyes (Acridine Orange, Acridine Yellow, etc.). In the work by Bailey et al. [136] 2-methylantraquinone, 2-chloroantraquinone, and benzophenone were considered as photosensitizers for polyolefin degradation. A recent patent [137] discussed a natural light/microorganism dual-degradation masterbatch, which included Fischer–Tropsch wax, a photosensitive catalyst, calcium stearate, an antioxidant, and a silane coupling agent. Ammala et al. [80] described ketone copolymers, 1,2-oxo-hydroxy groups, unsaturated alcohols and esters, benzophenones, diketones, polyisobutylene, amines, and peroxides as additives. Thus, degradation acceleration when using dyes with or without metal salts is a perspective that requires future investigations.

5. *TiO<sub>2</sub>-containing additives.* In the work by Nikolić et al. [138], L-LDPE film + 1% nanoTiO<sub>2</sub> was considered. It was shown that UV pre-radiation accelerated strength loss such that the rate of embrittlement was not sufficient for use as a mulching film. In the work by Król-Morkisz et al. [139], different additives were investigated to elucidate their influence on the thermal stability of various polymers: nanoclays montmorillonite, kaolinite, silicon, and silica polyhedral oligosilsesquioxanes hydroxyapatite, metal, and metal oxides (e.g., TiO<sub>2</sub> + PVA). In a recent study by Wójcik-Bania et al. [140], a thorough discussion of the mechanism of certain clay–polymer composites was given. The work by Xu et al. [91] considered additives produced on the basis of mesoporous titan dioxide with polyaniline of different content. These are intended to facilitate photodegradation and biodegradation of LDPE. The influence of these additives on accelerated PE degradation was evidenced after catalytic oxidation under UV radiation and biodegradation with micromycetes action. TiO<sub>2</sub> particles modified with PANI demonstrated light sensitivity at 400–800 nm. Better photocatalytic features were connected to the dispersal and compatibility of the particles with the LDPE matrix. Polymers with TiO<sub>2</sub> (which has anatase and rutile phases) have better properties [141], and the anatase form of TiO<sub>2</sub> is more photoactive than rutile [142] (due to the calcination temperature being higher). The influence of TiO<sub>2</sub> and metals was nontrivial. On one hand, polystyrene TiO<sub>2</sub>-coated particles or TiO<sub>2</sub> with Cr and Mn ions decreased photodegradation, while, on the other hand, TiO<sub>2</sub> with Mo, W, or V ions corresponded to larger rates. Wang et al. [143] considered the systems LDPE and LDPE + TiO<sub>2</sub>. Photocatalytic degradation in air, distilled water, and NaCl solution took place. The carbonyl index and molecular mass were found to be higher in the air after equal exposure time. In the case of NaCl solution, additional C–Cl substances were formed. *Degussa P25* material [144] which contains about 70% rutile, is more photoactive and aggressive than metal-doped pigments (containing rutile and anatase). Janssens and Daponte [145] considered TiO<sub>2</sub> particles with a transition metal oxide layer of iron(III) and manganese, and improved oxodestruction was evidenced by measuring residual tensile elongation. The patents in [146,147] described additives based on TiO<sub>2</sub> combined with metal stearates or ferrocene for plastic packaging films. In [148], additives with TiO<sub>2</sub> and rare-earth metals were presented.
6. *Additives based on metal oxides.* A comparison of the following species in polyolefin film was presented in Garcia [149]: (1) carbonates, (2) nephelinesyenite, (3) talcum, (4) Mg(OH)<sub>2</sub>, (5) aluminum trihydrate, (6) diatomaceous earth, (7) mica, (8) cristobalite, and (9) calcined clay. The best appeared to be CaCO<sub>3</sub>. The surfaces of these compounds were treated with an organic acid to make the filler hydrophobic. The additive was then combined with metal (Cr, Co, and Fe) carboxylates (0.1–15%) and

introduced into polyethylene. Metals also included Al, Sb, Ba, Bi, Mo, Ni, K, Ag, rare earth metals, Cr, Ga, La, Pb, Cd, La, Li, Mg, Hg, Na, K, Sr, W, V, Y, Zn, and Zr. The patent by Forsberg and Mossner [116] presents a polyolefin package (PP and PE) with a salt of one of several metals (Mn, Fe, Cu, Co, and Ni). It is sold with a mineral filler ( $\text{CaCO}_3$ , talcum, granulated marble, chalk and its nanoparticles, calcite,  $\text{SiO}_2$  and its nanoparticles, and natural fibers such as cellulose, wood fibers, wood powder, and starch). The pro-oxidant can be mixed with a polymer base with a concentration of 1–25%. Shtepa and Anisimov [150] made an oxo-additive by introducing the modified Ni salt of benzoic acid (0.3–10 wt.%), RAL dye (0.3–2 wt.%), and stabilizer (Irganox 1076 or Irgafos 168, 0.5–1 wt.%) into a polymeric matrix (LDPE, HDPE, L-LDPE, or PP).

7. *Combination of ZnO and TiO<sub>2</sub>*. Zinc oxide absorbs below 350 nm, which has a protective function; however, it can induce a photocatalytic heterogeneous reaction of polymer oxidation. The latter was used for PVC waste degradation [151]. These opposite effects prevent predicting the lifetime of a polymer. Because of the opposing effects of UV screening and photocatalysis on film degradation, the influence of  $\text{TiO}_2$  and ZnO on polymer lifetime cannot be strictly predicted. An analogous conclusion could be made from Yang et al. [152], where ZnO + PE and  $\text{TiO}_2$  + PE systems were considered under UV exposure; the additive promoted carbonyl group (with  $\text{TiO}_2$  being greater) and  $\text{CO}_2$  generation (with ZnO being greater). This mechanism requires a separate discussion.
8. *Aggressive species as prodegradants*. In the work by Briassoulis [153], a two-factor approach to polyethylene degradation was applied: prestress and aggressive chemical action on UV LDPE photodegradation. The model was elaborated and proven to successfully predict the change in tensile strength upon UV exposure time. Tensile strength was taken as the criteria of degradation. In the recent work by Pinsuwan et al. [154], the conversion of HPDE to low-molecular-weight products and dicarboxylic acids in the presence of nitric acid was presented with quite a high yield (up to 70%). In a study by Chowdhury et al. [155], acids (hydrochloric, nitric, and sulfuric acid) were used to degrade microplastics, and corresponding ab initio modeling was performed.
9. *Ferrocene*. Several patents use *ferrocene* as a base element for an additive [146,156–162]. This photosensitizing additive has been less systematically studied than others [163,164].
10. *Mineral fillers*. Valadez-Gonzalez et al. [165] proved that  $\text{CaCO}_3$  could act as a UV protector, as well as lactone and hydroperoxide formation inhibitor, for HPDE. In a subsequent study, Valadez-Gonzalez et al. [166] presented a comparison of HDPE and HDPE- $\text{CaCO}_3$  photodegradation in different natural environments (rural–urban and marine–coastal). The mineral filler changed the mechanism of degradation, whereas humidity and temperature changed the rate of degradation.

In summary, the plethora of data suggest the prospects of an additive approach. Nevertheless, more precise kinetic data could be of use, along with a deeper understanding of the reaction mechanism. This could provide opportunities for the introduction of oxo-additives in a more targeted manner.

## 11. Standards

There are different standards defining biodegradation. As a rule, they are based on the investigation of processes in compost, soil, respirometry apparatus, etc.; they model different situations.

One of the first standards on biodegradation was EN 13432:2000 [167]. It describes composting and biodegradation tests for packaging materials. According to this standard, a material is compostable if, after 85 days of composting, 90 wt.% of the sample can be filtered through a sieve with a mesh size of 2 mm. Polyolefins with oxo-additives degrade to microplastics after exposure to ultraviolet light and easily go through a sieve. This is why the manufacturers of plastic bags with oxo-additives usually highlight this standard.

Another standard, ASTM D3826 [168], describes the method of determining the changes of strength characteristics for assessing biodegradability; it is also fit for plastics with oxo-additives.

According to ASTM D6954-18 [169], polymeric materials should be exposed to two stages of degradation: physicochemical and biological. In the first stage, the material undergoes oxidative degradation under the influence of ultraviolet radiation, humidity, and high temperature in a climatic chamber according to ASTM D 5071-06 [170] or ISO 4892-2 [171]. In the second stage, the previously destroyed material is placed in glass flasks with liquid medium containing soil microorganisms, and the biodegradability is determined by the amount of carbon dioxide released (Sturm method). When studying the material at the second stage, ASTM D5338 [172] is recommended; it is also harmonized with ISO 14855 [173] and GOST R 57224-2016 [174]. The method of two-stage degradation applies to plastics with oxo-additives.

The standard ISO 18830 [175] describes how to estimate biodegradation in marine water for non-floating plastics using respirometry equipment (oxygen demand). The analogous standard uses the evolving CO<sub>2</sub> measurement [176]. The accelerated conditions for the estimation of such situations are described in ISO/WD 18957 [177] (standard under development). The aerobic degradation test in mesophilic conditions is partially described in standard ISO 5148 [178] (disappearance time determination). There is ultimate biodegradation estimation in mesophilic conditions, as described in ISO 22403 [179]. Another test describes the conditions of seawater/seafloor sediments to model the degradation under aerobic conditions [180] (standard under development). In summary, no standard currently deals with the estimation of microplastics being emitted from polymer waste, and there are no standard laboratory test approaches to estimate their further evolution at the time of writing. Nevertheless, in several recent studies, the “synthesis” of plastic microparticles using a cryomilling-based method was reviewed [181]. The evaluation of the generation and further evolution of PP microplastic from pre-irradiated (UV) material was considered by Cui et al. [182]. Here, the authors performed a simulation of real degradation conditions to evaluate secondary microplastic behavior, where the size of MPs depended on the type of crystallinity of PP ( $\alpha$  or  $\beta$ ).

As indicated in Hann et al. [183], there are no tests evidencing how harmless oxo-additives are (there is a danger to marine animals, which is not considered in the standards), the release of toxic heavy metals (the fact is not considered in many standards), and microplastic production. There is no algorithm for how to transfer the results of industrial compost degradation to the process in real conditions. This is very important for the light phase of degradation when dealing with buried samples (deeply buried samples almost have a complete absence of light and oxygen absorption).

The introduction of a standard that can bind the conditions and parameters of degradation to the quantity of microplastic and its properties (e.g., mass per 1 g of polymer, and dispersity) and the future fate of MPs is needed. This, however, is an extremely complicated task and includes different levels of investigation (modeling, field and laboratory experiments, bacterial and fungal selection, additive and composite elaboration, reaction kinetics, and mechanisms for present polymer/additive/media systems).

## 12. Discussion

The data available in the literature on investigations of polymers with oxo-additives are promising and ambiguous at the same time. In most cases, oxo-additives play a crucial role in acceleration photodegradation and the overall process of deterioration of the polymer product. This can be seen through molecular mass distribution changes, GPC results, and other techniques (see Table 2 and references herein). Nevertheless, the following issues require additional attention: What is the most “optimal” additive for a certain polymer/composite? What is the optimal concentration of an additive (considering the nontrivial dependence of the kinetics of oxidation on the metal selection, ligand, and concentration; see Table 1)? How can the synergistic effects of additives be used? How

do the kinetics of degradation change depending on the medium in which the sample is immersed? How large is the MP mass generated per 1 g of polymer? How does the washout of additives during the deterioration influence the overall process? What is the dispersity of MPs and how does it influence their further fate? It is important to elaborate standards for oxodegradable waste that take these issues into account.

### 13. Conclusions

Despite the large success in improving the processes of oxodegradation and biodegradation, which achieve more than 50% mineralization (Table 2) for PE in certain cases, one should keep the problem of MP generation in mind. Oxodegradable plastics require further accurate investigation and more quantitative approaches, especially to predict the extent of MP generation.

### 14. Future Directions

Some future directions are the following:

- (1) Find the functional dependence of additive type and initial concentration on the kinetics of oxodegradation, using modern techniques (NMR, GPS, mass spectrometry, and theoretical study of elementary acts of oxidation). This will provide comprehensive information and will be a strong basis for choosing additives.
- (2) Find out how additives influence MP generation and its characteristics, as well as the further fate of MPs in the medium (soil, water, etc.).
- (3) Find out how the morphology, size, and dispersal of MPs depend on their interaction with the biota, and whether there is a way to optimally establish these factors.
- (4) Synthesize the optimal additives for each polymer type.
- (5) Introduce standards for industrial polymer production and polymer waste disposal.

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### Abbreviation

MPs—microparticles, GPC—gel-penetrating chromatography, NMR—nuclear magnetic resonance, LDPE—low-density polyethylene, HDPE—high-density polyethylene, PET—polyethylene terephthalate, PP—polypropylene, iPP— isotactic polypropylene, MeSt—metal stearate, HALS—hindered amine light stabilizers, PEG—poly(ethylene glycol), PS—polystyrene, Me(OAc)<sub>m</sub>—metal oxaloacetate, AO—antioxidant, HIPS—high-impact polystyrene, ESCA—electron spectroscopy for chemical analysis, AAS—atomic absorption spectroscopy.

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