

Degradable Polyethylene: Fantasy or Reality

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S Supporting Information

ABSTRACT: Plastic waste disposal is one of the serious environmental issues being tackled by our society today. Polyethylene, particularly in packaging films, has received criticism as it tends to accumulate over a period of time, leaving behind an undesirable visual footprint. Degradable polyethylene, which would enter the eco-cycle harmlessly through biodegradation would be a desirable solution to this problem. However, the “degradable polyethylene” which is presently being promoted as an environmentally friendly alternative to the nondegradable counterpart, does not seem to meet this criterion. This article reviews the state of the art on the aspect of degradability of polyethylene containing pro-oxidants, and more importantly the effect these polymers could have on the environment in the long run. On exposure to heat, light, and oxygen, these polymers disintegrate into small fragments, thereby reducing or increasing the visual presence. However, these fragments can remain in the environment for prolonged time periods. This article also outlines important questions, particularly in terms of time scale of complete degradation, environmental fate of the polymer residues, and possible accumulation of toxins, the answers to which need to be established prior to accepting these polymers as environmentally benign alternatives to their nondegradable equivalents. It appears from the existing literature that our search for biodegradable polyethylene has not yet been realized.



INTRODUCTION

Polyethylene, particularly as blown films, has found widespread use as a packaging material primarily because of its excellent mechanical properties, chemical and biological inertness, low cost, and high energy effectiveness. The extensive use of this plastic led to an era popularly known as the age of “throw away living”. However, this also led to accumulation of plastic waste, which has caused much criticism.¹ Several strategies have evolved for managing plastic wastes, the most common being primary/secondary recycling and incineration. Recycling of waste into new products after processing requires prior collection and segregation, which adds to the cost of the process and the recycled products. In addition, even after proper stabilization, the recycled products tend to have inferior long-term properties, thereby having limited markets. Quaternary recycling, incineration for recovering energy, although an environmentally benign process, is only practiced in a few countries, while in most countries, a large fraction of plastic wastes end up in landfills.

Detailed degradation studies on polyethylene in the early 1970s clearly revealed that the biodegradation process is extremely slow.^{2–4} These plastic wastes could, thus, stay around for quite extensive time periods and become ubiquitous environmental contaminants. Parallel scientific activity saw the emergence of so-called “degradable polyethylene”, which was primarily introduced to reduce the visual presence of plastic waste. At that point of time, it was thought of as the most effective

tool to deal with the plastic accumulation problem.⁵ These polymers, when disposed of, broke into small pieces thereby satisfying this criterion of reduced visibility.

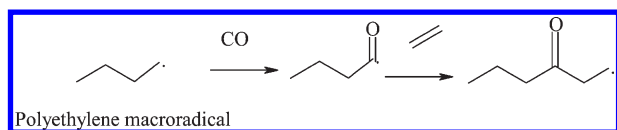
However, the use of these polymers can lead to several problems which need to be deliberated upon. One of the important concerns is regarding the formation and release of persistent polymer fragments, additives, and degradation products into the soil when these polymers are used or disposed. The fate of these fragments is currently unknown. To be a practical and environmentally benign solution for prevention of waste accumulation, the whole material should degrade to low molecular weight products and these products should within a reasonable time frame be completely consumed by micro-organisms. The entire process of biodegradation may require extended time periods, but the time scale needs to be specified and the nontoxic nature of the intermediates and the final degradation products has to be established. Mere visual disappearance is a temporary solution, and in the long run it may create a new set of problems. There have been claims that “enhanced environmentally degradable” polymers are completely “biodegradable”.⁶ This article

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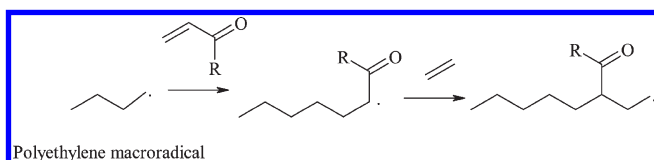
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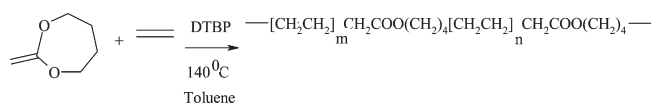
Scheme 1.1. Copolymerization of Ethylene and Carbon Monoxide



Scheme 1.2. Copolymerization of Ethylene and Ketonic Comonomers



Scheme 1.3. Copolymerization of Ethylene with 2-Methylene-1,3-Oxepane



reviews the current state of these polymers and the potential impact these polymers could have on the environment.

DEGRADABLE POLYETHYLENE

As a result of extensive research in the area of lifetime programmable polyethylene, several strategies have evolved, most of which deal with either the introduction of certain weak sites, e.g., carbonyl groups in the hydrocarbon backbone/side chain, olefinic bonds, or addition of biodegradable polymer (e.g., starch), pro-oxidants, or photoinitiators.

Introduction of Weak Sites during Polymerization. Carbonyl groups have been introduced by copolymerization of ethylene with CO, e.g., ethylene-carbon monoxide copolymers (ECO polymers) where the carbonyl group becomes a part of the polymer main chain (Scheme 1.1).^{7–9}

The carbonyl groups have also been introduced in the side chain by copolymerization of ethylene with vinyl ketone monomers (Guillet process, Scheme 1.2). Here, the carbonyl group is introduced in the α -position of short branches.^{10,11}

Introduction of Unsaturation in the Polymer. A new generation of Ziegler–Natta catalysts has been developed for the synthesis of photodegradable compositions based on polyethylene containing unsaturation.¹² The rate of degradation is greatly influenced by the diene content in the copolymer.¹³

Introduction of Hydrolyzable Linkages. Bailey prepared hydrolyzable polyethylene by introducing ester groups into the polyethylene chain by copolymerization of ethylene with 2-methylene-1,3-dioxepane (Scheme 1.3).¹⁴

Austin followed Bailey's idea and patented a tercopolymer by introducing carboxy ester groups into the polyethylene chain by copolymerization of ethylene with 2-methylene-1,3-dioxepane and CO in the presence of a free radical initiator.¹⁵

Introduction of Pro-Oxidants in PE Formulations. This approach involves introduction of pro-oxidants which can promote the oxidation of the polyolefins when they are exposed to heat/light in the presence of oxygen. These pro-oxidants are usually based on transition metals added in the form of long-chain carboxylates or as acetylacetonates.^{16–18} The major areas where these polymers are finding usage are in the field of agriculture and packaging. The compositions used in the packaging sector generally contain Mn,^{19–21} Fe,^{22–24} and Co^{25–30} as the active component, while those used as mulching films (in agriculture) contain Ni.^{31,32} Other transition metals like Ce have also been reported to exhibit strong pro-oxidative effect.³³

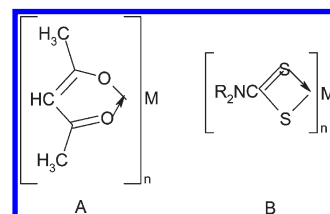
In the early 1970s, Griffin introduced the idea of increasing biodegradability by adding granular starch in its natural form along with pro-oxidants, in the presence of compatibilizers.^{34–36} In such formulations, the biodegradable additive may be utilized by micro-organisms, thereby leaving a polymer with increased surface area.³⁷ Detailed studies revealed that starch, alone, does not accelerate the oxidative degradation of polyethylene.¹⁹ In fact, in many cases the presence of natural antioxidants in starch caused stabilization of the polymer. In the technology developed by Griffin the combined action of the pro-oxidants and the unsaturated compatibilizers results in hydroperoxidation of the polymer chain, which subsequently leads to physical breakdown of the polymer.^{38,39}

Several organic photoinitiators such as hindered aralkylketones, allyl esters and ethers, and thioxanthone, have been reported to accelerate the oxidative degradation process. In this context, aromatic ketones, typical of the efficient triplet activators such as benzophenone and its derivatives have been studied extensively.¹⁶ However their effectiveness is lower than that of transition metal complexes, thereby limiting their commercial success.²⁴

Combination of Additives for Time-Controlled Environmental Disintegration. In certain applications, particularly in the agricultural field, the requirement of mechanical property retention until near harvest time is very important. To achieve this, the aim is to control the onset of pro-oxidant activity for peroxidation by the use of appropriate antioxidants. In addition to the transition metal based pro-oxidants, preventive antioxidants, particularly metal deactivators are added.⁴⁰

Another formulation used to control the degradation is an optimized mixture of a photosensitizing/photoactivator and antioxidant additive (Scott–Gilead process). It is based on variations of the following compositions:^{13,41–43}

- An activating complex consisting of iron or cobalt complexed with acetylacetone, which is a photo/thermal degradation promoter (A).
- A thermal stabilizing complex consisting of nickel or cobalt complexed with dialkyldithiocarbamate (B)/ dialkyldithiophosphate/alkylxanthate/mercaptobenzothiazole.



Recently a patent was filed claiming to increase the rate of oxidative degradation of the carbon-containing polymer without

to this scheme the carbonyl groups formed as a result of oxidation are attacked by the microorganisms which degrade the polymer chain to its final end products, CO_2 and H_2O .

■ STANDARDS FOR TESTING BIODEGRADABILITY

For a material to be claimed as “biodegradable”, enough evidence has to be generated regarding the complete consumption of the material by micro-organisms. As per ISO/CD 16929, “biodegradation” has been defined as “degradation that is caused by biological activity, especially by enzymatic action”. However, interestingly, no time frame has been specified, rendering all carbonaceous materials theoretically “biodegradable” as they can be consumed by micro-organisms over an indefinite time period. On the other hand, mineralization is defined as the conversion of materials or biomass to gases (like CO_2 , CH_4 , and nitrogenous compounds), water, salts and minerals, and residual biomass. Complete mineralization symbolize the rendering of all chemical elements into natural biogeochemical cycles.⁷⁴

All studies on enhanced degradable polymers reveal that abiotic oxidation of pro-oxidant containing polymers leads to loss of mechanical properties, evolution of functional groups, increase in melt flow index (MFI), and decrease in molecular mass. Most of these parameters, like decrease in mechanical properties, indicate loss of usefulness of the polymer. However, these changes are not related to the biodegradability of the material. Similarly the increase in MFI, which is a measure of increased ease of flow of the polymer melt, results from lowering of molecular mass and viscosity, and is not indicative of biodegradation.

■ BIODEGRADATION TESTS

Aerobic Tests. The material is exposed to a microbial consortium under aerobic conditions (presence of air). The microbes feed on the substrate thereby converting the polymer to biomass and CO_2 . Most of the standards in this area specify methods, either for determination of oxygen demand in a closed respirometer or that of the amount of released CO_2 . The percent biodegradation is determined by comparing the amount of released CO_2 with the theoretical amount (Th_{CO_2}). Alternatively, biodegradation can be quantified in terms of consumption of oxygen (BOD), where it is calculated as the ratio of the BOD to the theoretical oxygen demand (TOD).

Anaerobic Tests. These tests are performed in the absence of oxygen as a result of which, the polymeric carbon ends up as a mixture of CH_4 and CO_2 , which are quantified and used for the calculation of percent biodegradation. However, plastics usually do not end up in sewage/water treatment plants for which the above tests were designed. Instead, they find their way to landfill and composting sites for which the following tests are more appropriate. A list of standards which are used as the basis of certification for environmentally degradable plastics is presented elsewhere.^{66,75}

Composting. During these tests, the material is exposed to a compost medium, either at a constant temperature or a temperature program and the extent of mineralization is measured by the conversion to CO_2 . The standards most commonly referred to include ASTM-D6400, D6868, D7021, EN13432, and ISO17088. According to the European standard, EN13432, a biodegradation level of at least 90% must be achieved in less than 180 days for a plastic to be labeled as “compostable”. According

to ASTM-D6400 standard, the criteria for compostability is 60% mineralization for homopolymers and 90% for copolymers, blends, and materials containing low molecular mass additives or plasticizers. By specifying the time period in these tests, the term “compostable” is more precisely defined than “biodegradable”. It has been argued that the criteria for complete conversion of the polymer to CO_2 and H_2O in a short duration of time should not be considered a mandatory requirement for a material to be termed biodegradable, as many ligno-cellulosics do not evolve CO_2 in a short time scale and hence do not classify as compostable materials either. The degradation of such materials takes a long time, but the materials are undoubtedly mineralized, if left under proper conditions for extended time periods.

It has been criticized that the standards for biodegradable plastics are directed and biased toward bioplastics, which are derived from renewable resources. However, when it comes to degradation, nature does not seem to discriminate between the materials based on their origin.⁷⁶ For example, there are many synthetic condensation polymers (e.g., poly(caprolactone), poly(lactide)) which are biodegradable and many biobased materials (e.g., lignin) which do not get converted to CO_2 and H_2O in a short time period. However, as per the fundamental principles, any material which is biodegradable should be able to prove its complete utilization by micro-organisms over a definite time period. If not completely utilized, the degradation should be expressed as percentage biodegradability, which quantifies the fraction of the material which can be converted to CO_2 and CH_4 in a definite time frame, as is the requirement in different standards.

■ STANDARD FOR TESTING OXIDATIVELY DEGRADABLE POLYMERS

In the absence of oxidative degradation step, the subsequent mineralization is not possible for “oxidatively-degradable” materials. Hence, in the year 2004, a standard guide (ASTM-D6954) was developed particularly for such materials, in which the sample is sequentially exposed to a biotic environment after the oxidative step. This oxidative step should be conducted under conditions that are typical for the application. Oxidation should bring about the necessary changes in the polymer structure such as increased hydrophilicity, reduced molecular mass, or accessible chain ends, which enhance its susceptibility toward microbial attack. This guide describes a three-tier methodology in which the material is first tested for its physical degradability in terms of loss in mechanical properties, when exposed to oxidative environment. In the next tier, the fragmented material is exposed to a biotic environment, where the degradation is monitored by measuring the CO_2 evolved. This ensures that the material enters the natural carbon cycle instead of just fragmenting into microscopic particles possibly persevering in the environment.⁷⁵ Finally, the ecotoxicity of the degraded material is studied on seed germination, macro-organism toxicity, and crop yield.

This standard discusses a well-thought-of methodology to assess the biodegradation of carbon-chain polymers and primarily caters to the requirements of the industry. However, to claim “biodegradation”, the test should be performed on substrates containing labeled carbon. In conventional respirometric tests, the carbon content in the respirometer includes the contribution from the organic content in soil and polymeric substrate as well as soil microorganisms. It has been shown that the introduction of sample can significantly influence the background CO_2

production.⁷⁷ It is hence premature to conclude that the observed CO₂ evolution is the result of the degradation of the polymer alone. It is well-known that even in the absence of substrate, a significant amount of CO₂ is liberated from blank experiments. Although the contribution from blank sets is subtracted, to obtain final evidence of mineralization, the experiments should ideally be performed on labeled polymer substrate, which would in turn lead to generation of ¹⁴C-labeled CO₂ proving biodegradability. Considering the commercial aspect of such polymers, it is important that such data are generated for scientific proof of biodegradability, thereby eradicating any skepticism at the consumer end.

Another point concerns the selection criteria of 60% mineralization in ASTM-D6400 standard as against 90% in the EN13432 as the level of biodegradation required for acceptability. It is criticized that the remaining 40% still could remain in the environment. The extent of mineralization of any carbon substrate depends on several factors, one of the important ones being its free energy content. It has been reported that substrates with low ΔG^0 (e.g., cellulose, positive reference material) activate the “zymogenous” species in the compost, which leads to rapid CO₂ production, but negligible carbon assimilation as biomass. However, once the substrate is consumed, these species die, thus causing a fast microbial biomass turnover. The addition of glucosidic materials has also been reported to cause extra mineralization of the soil organic matter, which generates CO₂, which is referred to as the “priming effect”.^{78,79} On the other hand, substrates with a high ΔG^0 (like higher hydrocarbons) activate the “autochthonous” microorganisms, which result in lower mineralization of the substrate, but higher level of carbon bioassimilation.

It is suggested that in the short-term, 50% of the organic carbon gets converted to CO₂ and the rest forms biomass or humus, which mineralizes to CO₂ at a very slow rate. Although there have been studies that show that polymers have a lower tendency to get converted to CO₂, and a higher tendency to get converted into biomass,⁸⁰ the evidence of 50% bioassimilation has not yet been generated. In the absence of this data, the selection of 60% biodegradation as the criteria of acceptance of these materials leaves much to be desired.

■ STUDIES ON BIODEGRADATION OF POLYETHYLENE

The biodegradation of polyethylene^{45,50,66,81–83} and environmentally degradable polyethylene^{31,46,51,53,72,73,80,84–97} in the presence of micro-organisms has been extensively studied and reviewed in the last few decades. Polyethylene, being a long-chain paraffin, could be biodegradable, as it has been shown that low molecular mass paraffins are readily utilized by microorganisms.⁹⁸ However, the tendency toward biodegradation decreases with increasing molecular mass.^{99,100} Although some branched hydrocarbons have been reported to be biodegradable,¹⁰¹ it is the linear analogues that are more susceptible to microbial attack.

In most of the published literature dealing with biodegradation studies of polyethylene, the researchers suggest “biodegradability”, on the basis of observations like biofilm formation and weight loss, when the material is exposed in a biotic medium.^{94,102–105} These observations do not quantify the fraction of the material that can be consumed by the micro-organisms over a definite period of time. For example, weight loss of the polymer can result from additive leaching or fragmentation. Similarly, fragmentation of the polymer may lead to a powdery

mass which cannot be collected for measurement purposes. In this section, we mainly discuss the results from studies where the extent of biodegradation has been quantified by respirometric tests. Some other studies, which have been widely cited as an evidence of biodegradation of polyethylene with pro-oxidants, are also included.

To obtain accurate evidence of biodegradation, the experiments should ideally be performed on ¹⁴C-labeled substrate, which would in turn lead to generation of ¹⁴C-labeled CO₂. A long-term biodegradation study on ¹⁴C-labeled polyethylene that utilized liquid scintillation counting indicated that PE biodegradation requires extremely long periods.^{2,81,82} After 10 years of incubation in soil, <0.5% polymeric carbon (as CO₂) by weight was evolved from a UV-irradiated polyethylene sheet.⁵⁰ The extent of conversion was even lower (0.2% w/w) in the absence of irradiation. These studies demonstrated that photodegradation leads to higher CO₂ evolution compared to when materials are not pre-exposed, an observation which has been pointed out by other researchers later.⁴⁷

The introduction of additives such as *N*-dotriacontane² and UV sensitizers⁸² was found to increase the conversion of the polymeric carbon to CO₂ by as much as 5-fold. Addition of surfactant to the nutrient medium also led to an increase in the rate of degradation.⁷³ Biodegradation of polyethylene in the presence of *Fusarium redolens*,² indicated that the unstabilized polyethylene degraded to a higher extent compared to polyethylene containing antioxidants. There have also been several other studies which confirm that polyethylene films, from which antioxidant had been removed, bioeroded more easily because of their easy oxidizability, while the stabilized compositions were completely inert.^{41,106}

In another study, the photooxidation of polyalkylenes was reported to lead to evolution of volatiles.¹⁰⁷ The nonvolatile fraction was extracted in organic solvent and both fractions were separately exposed to a fungal spore suspensions. The studies indicated that the oligomer fraction supported fungal growth, but the residue was completely inert, which indicated that these may not be completely eliminated even after prolonged exposure in environment.

In a separate study, biofilm formation was observed on the surface of photo-oxidized polyethylene films which had been exposed to definite fungal and bacterial strains.¹⁰⁸ However, “biodegradation” was not monitored by CO₂ evolution, and moreover, the tests were performed on agar, and not on soil, making the situation very different from reality. In the absence of detailed mineralization data, these observations cannot be used to claim biodegradability.

Two different “photo-degradable” samples were exposed to sunlight for a period of 6 or 12 weeks followed by soil incubation.¹⁰⁹ The degradation was monitored by CO₂ evolution, residual mass measurements, and tensile strength reduction. The results showed that percent carbon converted to CO₂ after 6 weeks was 3.5% and 4.5%. Interestingly, samples exposed to 12 weeks of exposure exhibited less conversion to CO₂ (2.9% and 1.5% respectively), which suggested that longer exposure to sunlight had rendered the samples less amenable to microbial consumption, which may be attributed to cross-linking, as previously reported.⁹⁵ Biodegradation studies under both aerobic and anaerobic conditions of commercial polyethylene with pro-oxidants revealed that in the absence of prior oxidation, the amount of CO₂ and CH₄ produced under either kind of biotic exposure was similar to those obtained from blank sets, indicating no significant biodegradation.⁹³

A 65% biodegradation level has been reported for polyethylene films containing manganese stearate pro-oxidants.²⁰ This unusually high level of biodegradation was achieved after rather extensive thermal aging at 70 °C, followed by soil burial for 180 days. Interestingly the evolution of CO₂ from these samples started off without any lag phase and the authors concluded that the material would eventually be biodegraded. In a separate long-term soil burial experiment on LDPE, physical signs of degradation, like whitening and small holes were observed on the surface after 32 years.¹¹⁰

A test method for studying biodegradability of polymeric materials in soil and mature compost was developed, which involved diluting the substrate with perlite.^{53,96} Studies indicated that CO₂ evolution from commercial degradable LDPE started after a lag phase of >150 days. After 567 days, the highest extent of biodegradation was reported to be 59%. The paper control exhibited 70% degradation at the end of the experiment. In a later study, 60–70% biodegradation of oxidatively degradable polyethylene was reported after 800 days of soil burial, subsequent to a thermal treatment at 55 °C.⁸⁰ In another study, the oxidized products formed as a result of the abiotic oxidation were first extracted with acetone and then subsequently subjected to respirometric tests in medium containing microbes present in river water. Biodegradation of 40–50% was reported under the experimental conditions.⁷² However, from the data presented in the form of graphs, it was observed that the biodegradation (CO₂ evolution) for the entire film (sum of residue and extracted) was less than 10%.

Commercial polyethylene samples containing cobalt reportedly formed biofilms (in the form of dark spots) on their surface when subjected to a year of natural weathering.⁹² The biofilm was absent for the films without pro-oxidants. Subsequently the CO₂ evolution from aged samples was studied for a period of 3 months. Temperature was found to exert a strong influence on the extent of CO₂ evolution, which was found to be 12.4% at 58 °C and 5.4% at 25 °C. In the absence of pro-oxidant but after 12 months of exposure, the corresponding level of biodegradation was reported to be 2.1%. Under similar conditions, in the absence of oxidative attack, the oxidatively degradable compositions exhibited a biodegradation level of 2.9%. The authors also studied the evolution of CO₂ from samples which had been exposed to different periods of natural weathering. An interesting observation was that exposure period longer than 3 months exerted negligible influence on the degradability of films.

A comparative biodegradation study was performed on commercial mulch films,⁹⁵ where polyethylene containing pro-oxidants was reported to be “non-biodegradable” as per the standardized biodegradation tests. However, massive fragmentation under the combined effect of heat and sun under field conditions was observed. On the basis of visual assessment, it was reported that 90% of the films could not be distinguished from other soil constituents after 1 year of field exposure. However, the respiratory tests (at 28 °C) on natural soil revealed only 10–15% degradation as compared to 91% for paper-positive reference material. The degradation experiments were performed in the absence of UV/heat treatment, as the authors argued that 30–50% of the film is buried in the soil and hence is never exposed to UV light/high temperatures.

Recently, other techniques such as monitoring the metabolic activity have been used to understand the behavior of microbes when they are fed with polymers as the sole source of carbon. The degradability of HDPE and LDPE films containing a

combination of photoinducer and thermo-inducer (iron based) was investigated by exposing the films for 120 h in a photoaging chamber followed by 300 h of air oven aging (60 °C), which led to fragmentation of the polymer. The films were subsequently exposed to well-defined strains of bacteria and fungi. The metabolic activity of microbial cells during incubation was determined by the level of adenosine triphosphate (ATP) and adenosine diphosphate (ADP) content in the microorganisms.⁸⁸ In the initial phase, a fast growth was observed, which peaked after 3–4 days. Subsequently, the ATP content dropped, which was attributed to the depletion of easy substrate. A stabilization of the ATP level was, however, observed and it remained at the same level until the end of the experiment (6 months). The results indicated that the microorganisms continued to gain energy from the substrate but at a slower rate. Complementary analysis performed at the end of incubation revealed that the biodegradation processes affected only the surface layer, leaving the core intact.

Subsequently, this technique was used to estimate the biodegradability of three types of polyethylene films (LDPE, LLDPE, and HDPE) containing different pro-oxidants.⁹⁰ The films were first oxidatively aged and then inoculated with *Rhodococcus rhodocrous*. Composting and soil burial experiments were performed and the degradation was evaluated by monitoring the headspace CO₂ concentration. Studies indicated that the *Rhodococcus* strain was able to remain metabolically active on films containing pro-oxidants. However, films containing high amount of cobalt led to reduced metabolic activity. Biodegradation after 317 days of compost incubation was 16% and 24% for LDPE and LLDPE films containing Fe and Mn as pro-oxidant combination, with the biodegradation being lower for HDPE samples. Incubation with soil resulted in lower biodegradation as compared to compost incubation.

Several studies on the degradation of PE–starch blends (based on the Griffin technology) have also been performed. PE–starch blends containing varying amounts of starch have been exposed to degradation in soil.¹¹¹ Starch removal and FTIR spectroscopy were used to monitor the chemical changes taking place in the polymeric matrix. It was observed that the starch removal was high during the initial period of burial, and reached almost completion in the first 40 days for compositions containing high amount of starch (52% and 67%). For samples containing lower level of starch (29%), the removal was slower and mainly limited to the surface. In another study on PE–starch blend, inoculated with *P. Chrysosporium*, a significant evolution of CO₂ was observed even in the absence of an initial oxidative attack.⁵¹ However, this CO₂ evolution was most probably caused by the biodegradation of the starch in the sample, as the test was not preceded by any oxidative step, which is a mandatory requirement for degradation of polyethylene/pro-oxidants formulations.

The composting of commercial polyethylene–starch bags filled partially with composted leaves and yard waste was investigated.¹¹² Half of the samples were buried inside the pile, with the rest being placed on the surface. The extent of oxidation was higher in films placed on the surface as observed by faster embrittlement, than for the ones buried inside the pile. The biotic and abiotic oxidation of PE-based commercial degradable films in three different degradative environments including lab-scale composting, thermo-hydrolytic, and thermo-oxidative, were studied, which revealed that all films were susceptible to oxidative aging, with the degradation being faster in dry air than in the

hydrolytic environment,¹¹³ which emphasized the role of free access to oxygen.

■ DO POLYETHYLENE PRO-OXIDANT FORMULATIONS MEET THE STANDARD REQUIREMENTS?

It is clear that commercially available degradable polyethylene cannot be classified as compostable due to slow degradation rate and the requirement of a preceding abiotic oxidation step. As these materials are not compostable, the remaining plastic fragments may affect the saleability and quality of the compost, which means that they cannot be allowed to enter the composting stream. What is interesting to note is that even after exposure to accelerated degradation environments, the scientific proof of 60% biodegradation of the resulting polymer fragments in a realistic time frame to be classified as “materials that degrade in the environment by a combination of oxidation and biodegradation” as per ASTM-D6954 and ASTM-D6400 is lacking.

Even if this so-called acceptable mineralization level is achieved, it would still be important to understand whether the results can be extrapolated to actual field conditions. Considering the biodegradation of polyethylene/pro-oxidant formulations can take place only after extensive abiotic oxidation, ensuring the former step is crucial. Because the level of oxidation required for significant biodegradation to take place is not clear and there are large environmental variations, this seems rather difficult. Usually, laboratory experiments for investigating degradation are performed in air ovens, where possibility of cross-linking is reduced. However, the actual field conditions may be completely different, resulting in formation of larger amount of cross-linked polymers. Probably totally new design concepts need to be applied to develop truly biodegradable polyethylene. Keeping the present scenario in mind, the skepticism of the society toward the acceptability of these polyethylene formulations is justified.

Apart from the above, there exists another less highlighted limitation for using masterbatches with relatively high concentrations of pro-oxidants. If these masterbatches are prepared from a polyethylene (e.g., LLDPE), which is rheologically different from the polymer in which it is finally intended to be mixed (e.g., LDPE or HDPE), it may result in processing difficulties thereby resulting in nonuniform distribution of the active ingredient in the product. Moreover, since the concentration of antioxidant in the base polymer varies, the blending of masterbatch may lead to uncontrolled degradation of the final film. However, there are no published studies in this field.

■ FATE OF REMAINING FRAGMENTS AND ASSOCIATED TOXICITY

In the absence of scientific evidence that can prove that “oxidatively degradable” polyethylene is completely biodegraded in a realistic time frame, it is important to be aware of the fate of the fragments that linger in the environment. This will be largely decided by the environment in which the polymer finds itself when disposed, most likely being terrestrial, but a lot of plastic waste has been found to end up in the marine environment as well.^{114–117} Concerns have been raised that polymer fragments resulting from polyethylene degradation may act as reservoirs for accumulation of toxins present in the environment.^{118,119} Although polyethylene is reportedly inert, due to its hydrophobic nature, accumulation and transportation of persistent organic pollutants (POPs) by resin pellets and plastic fragments have been observed in the oceanic environments.^{120,121} In another

study, the tendency toward accumulation of a primary pollutant, phenanthrene, onto different kind of plastics was investigated.¹²² This study revealed that the uptake on plastics greatly exceeded the sorption by natural sediments. Furthermore, polyethylene adsorbed an order of magnitude more phenanthrenes. Polyethylene has been reported to exhibit a high tendency to sorb polychlorinated biphenyls as well.¹²³ This property of accumulating hydrophobics is important, because plastics, being buoyant, can travel on the sea surface thereby providing a mechanism for transport of hydrophobic chemical contaminants to remote and pristine locations.¹²⁴ Microscopic plastic fragments have also been reported to be mistaken as food thereby being ingested by invertebrates, seabirds, amphipods, and barnacles, the consequences of which have not yet been established.^{1,125–127} However, it should be noted that the environmental toxicity issue due to adsorption of chemicals is applicable to several plastics, and not restricted to polyethylene alone. Nonetheless, it is very important to understand the fate of the plastic-sorbed pollutants in different environments, a topic which requires immediate attention of researchers.

An additional concern raised is regarding the possible toxic effects of the constituent transition metals being used as the pro-oxidant. To address this issue, Wolfe et al.¹²⁸ performed a study on nickel accumulation in soil after the application of the equivalent of 30 years of continuous annual application of polyethylene mulch films containing nickel dithiocarbamate. The study revealed negligible nickel accumulation. Based on the concentrations of nickel present in pro-oxidants, it has been theoretically predicted that in the “worst case scenario”, it would require 500 years of continuous degradable polyethylene deployment to increase the nickel concentration in the soil by 1 ppm, which contained 300 ppm at the outset.⁸ However, there is still a need to critically examine the retention of transition metals and their ultimate fate in the soil and long-term field application of such materials may lead to other harmful effects, which need to be studied in more detail.

■ CONCLUSIONS

For the polyethylene pro-oxidant formulations to be accepted as environmentally benign materials, the fate of the polymers has to be established. Disintegration of the materials into small pieces which may be visible or invisible to the naked eye has been established, but its final entry into the eco-cycle by bioassimilation or conversion to CO₂ and H₂O in a realistic time frame is a matter of discussion. Moreover, there have been no long-term studies to estimate the actual time frame for which these fragments will persist in the environment. In view of the above, the uncertainty concerning the final fate of these fragmented residues and the time-scale for the material to enter the carbon cycle still exists. If these fragments are not completely mineralized within relatively short periods of time, the potential harmful effects cannot be ignored. Hydrophobic polymers with high surface area have been reported to attract toxins thereby concentrating them to form a reservoir of toxic chemicals in the environment.^{120–122} In the absence of scientific evidence, it is required that protocols are developed to quantify the effect on the environment and the nontoxicity (over a long tenure). Until such protocols are evolved, caution should be exercised over the extensive use of these materials. Moreover, the introduction of these materials into the recycling stream would render the resulting recycled material more susceptible to environmental

degradation. Although, it is theoretically possible to delay the onset of degradation by using proper antioxidant packages, it is practically difficult to estimate the amount of antioxidant required.

In countries where waste management is given due importance, the usage of nondegradable polyethylene for all practical purposes seems to be acceptable from an environmental point of view, as these materials are taken care of once they are discarded. However, in places where waste is not handled effectively and littering is more common, other solutions have to be thought of. This does not necessarily mean that the plastic bags should be banned, a feature which has been imposed in several countries worldwide. The use of hydrolytically biodegradable materials such as aliphatic polyesters, whose biodegradability in a short time period has been well established, may be an alternate solution. The high cost at the present, however, prohibits the widespread use, especially in developing countries. The use of alternate biobased materials like paper and jute bags may in the long term cause more harm than good, as they are derived from wood, and meeting the ever increasing requirements of growing populations would require indiscriminate cutting of trees, which can have far worse consequences. Proper waste management strategy seems to be the most logical strategy to deal with this problem at present, provided proper collection and segregation can be ensured.

■ ASSOCIATED CONTENT

S Supporting Information. Standard terminology dealing with the different degradation processes and definitions of materials undergoing these processes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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