Degradable Polymers - The Future for Environmental Management in Nigeria: A Review

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ABSTRACT
Disposal of plastic wastes poses serious environmental challenges in the country and several environmentally friendly methods have been proposed to effectively manage the plastic wastes. Biodegradable polymers present an effective eco-friendly way of managing plastic wastes, however biodegradation of polymers have its own challenges and may not meet all the requirements for a desirable eco-friendly polymer. This manuscript tries to review various stages and aspects of degradation and their effect on the environment with emphasis on polyethylene films. The effects on heat, light and oxygen on the polymer was discussed. In addition, the mechanical degradation of polymers produces small fragments which remain in the environment over a long period of time. This article also tries to address the problem of incomplete degradation, time scale, and environmental impact of the polymer residues particularly in accumulation of toxins. Polymers that can be accepted as environmentally friendly compared to the non-degradable ones still commonly utilized today is yet to be realized.

(Keywords: degradation, eco-friendly composite, biodegradation, plastic wastes, environment)

INTRODUCTION
Polyethylenes are used as blown films in the packaging of materials due to its excellent mechanical properties. The extensive use of these plastics has led to accumulation of plastic wastes. However, several methods have been developed for managing plastic wastes, the primary method being recycling and incineration.

Recycling of wastes into new products after processing requires prior collection and separation which leads to higher costs. More so, the qualities of the recycled plastics are much more inferior properties than the virgin ones reducing its market value. In most developing countries like Nigeria most of the plastic waste ends up in landfills (Thompson et al., 2004).

Detailed studies (Albertsson, 1977) of degradation of polyethylene have showed that the degradation process is very slow and over time become prime environmental pollutants. This has given rise to the emergence of degradable polymers whose primary aim was to reduce the effect of conventional plastics in the environment. At some point in time it was considered as the most effective way of dealing with the environmental impact of waste plastics. Biodegradable polymers on disposal breaks down satisfying the criterion of reduced visibility.

Biodegradable polymers may lead to the release of harmful additives and degradation products in the environment. To have a more practical and workable approach to this problem in prevention of waste plastics accumulation, the waste plastics should degrade to a very low molecular weight products and these products low molecular weight products should be completely consumed by micro-organisms within a short period of time. The entire process of biodegradation may require extended periods of time. The time scale for the degradation may need to be specified, the degradation products and intermediates would have to be established. Mere visual disappearance is a temporal solution but may create a new set of problems in the long term.
The quest for enhanced environmentally friendly degradable polymers that are completely degradable is highly desirable. This article reviews the current state of these polymers and the potential impact these polymers could have on the environment (Thomas et al., 2010).

**Degradable Polyethylene**

Extensive research in the areas of lifetime programmable polyethylene, several methods have been developed to make polymers more degradable and environmentally friendly, one of which includes the introduction of weak sites (e.g., carbonyl groups in the hydrocarbon backbone/side chain, olefinic bonds, pro-oxidants and photo-initiators).

**Introduction of Weak Sites During Polymerization**

Carbonyl groups can be introduced by the process of copolymerization of ethylene with carbonmonoxide (e.g., ethylene-carbon monoxide copolymer) (ECO polymers) where the carbonyl group is part of the polymer main chain as shown in Figure 1 (a).

The carbonyl groups can also be introduced in the side chain by copolymerization of ethylene with vinyl ketone monomers “Guillet process” (Guillet, 1973). Here the carbonyl group is introduced in the α-position of short branches (Harlan and Kmiec, 1995).

**Introduction of Hydrolyzable Linkages**

This can be achieved by the introduction of ester groups in the polymer backbone by copolymerization of and ester groups with 2-methylene-1,3-dioxepane shown in Figure 1[c] (Bailey et al., 1990).

**Introduction of Unsaturation in the Polymers**

Photodegradable polymers can be produced can be produced by polyethylene polymers that contain unsaturation in their backbone. The rate of biodegradation is greatly influenced by the diene content in the copolymer as shown in Figure 1[b] (Bremer, 1982).

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**Figure 1:** Introduction of Biodegradability in Polymers.
Introduction of Pro-Oxidants in PE Formulations

This involves the introduction of pro-oxidants which promotes the oxidation of polyolefins when they are exposed heat/light in the presence of oxygen. The pro-oxidants are transition metals added in the form of long-chain carboxylates or as acetylacetones. These polymers are finding increasing usage in agriculture and packaging. Transition metals such as manganese (Mn), iron (Fe), cobalt (Co), Nickel (Ni) and cesium (Ce) have been reported to exhibit strong pro-oxidative effect (Albertsson and Karlsson, 1993).

Griffin (1980) in his study increased the biodegradability of the polymer by introducing starch in its natural form with a pro-oxidant in the presence of compatibilizers. In this kind of formulation, the starch additive is biodegraded by micro-organisms increasing the surface area of the polymer. Studies have shown that starch on its own does not necessarily accelerate the oxidative degradation of polyethylene 19. The study of Griffin has shown that the combined action of pro-oxidants and the unsaturated compatibilizers results in hydroperoxidation of the polymer chain, which subsequently leads to physical breakdown of the polymer.

Many organic photo-initiators such as hindered aralkylketones, allyl esters, ethers and thioxanthone have been reported to accelerate the oxidative degradation process. In this regard aromatic ketones, typical of the efficient triplet activators such as benzophenone and its derivatives have been studied. However, their effects are lower than the transition metals complexes, thus limiting their commercialization (Wang et al., 2006).

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 (Scott, 2000).

Another formulation used to control the degradations is an optimized mixture of photosensitizing/ photoactivator and antioxidant additive (Scott–Gilead Process). It is based on variations of the following compositions:

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

![Figure 2: Scott-Gilead Process.](image)

Degradation Mechanism and Degradation Products of Polyethylene

Environmental degradation of polyethylene follows a two-step process:

1. Rate Determining Step

This is the abiotic oxidation which is followed by bioassimilation or mineralization of the oxidized products. The major obstacle to the degradation of PE lies in its high molecular weight and the presence of non-polar C–C and C–H bonds. The macromolecular chains are densely aligned forming a semi-crystalline region, which creates additional hindrance to degradation of the polymer due to little or no diffusion of water or oxygen into these regions. A combination of these factors leads to the inertness of polyethylene. In addition, antioxidant package is usually added to the polymer to prevent degradation during processing, which further decreases the susceptibility toward degradation (Albertsson, 1980).
2. Other Physical Factors

These factors that affect the degradation rate are morphology, and surface area of the material. In general the degradation of polyethylene is initiated in weak sites and proceeds via the formation of hydroperoxides intermediates to form carbonyl compounds. These can undergo Norrish I and II type reactions, which lead to chain scission resulting in the loss of mechanical properties. Pro-degradants on exposure to light/heat decompose to form free radicals, which further generate polyethylene macro radicals. This reacts with oxygen to produce hydro peroxides, which leads to decomposition of the polymer. In the final stage of the reaction, the auto-oxidation and chain cleavage of polyethylene occurs via classical free radical chain reactions (Karlsson and Albertsson, 1998).

Transition metals possess a unique ability to switch between two oxidation states differing by a single unit, which can result in the catalytic decomposition of hydroperoxides, thereby pushing forward the entire reaction (Lemaire, et al., 1996). The oxidative degradation, once initiated by light, continues even under dark thermal conditions as shown in Figure 3 (a). The crystalline regions due to their inaccessibility to oxygen however remain practically unaffected.

The oxidative degradation of polyethylene leads to formation of low molecular weight products shown in Figure 3 (b) which could be identified by chromatographic analysis. The following degradation products have been identified; alkanes, alkenes, aldehydes, ketones, alcohols, mono- and dicarboxylic acids, lactones, keto acids and esters. Dicarboxylic acids are the most abundant in oxidized samples.

Earlier studies on aliphatic paraffins have shown that only alkanes with low molecular weight (<620) can be biodegraded. The oxidative degradation can drastically reduce the molecular weight of polyethylene as low as 5000 Da especially when accelerated oven aging is applied. Polar solvents with higher molecular weight can be biodegraded, a large fraction of polyethylene degradation products could still have very large molecular weights to be easily broken down by microorganisms (Koutny et al., 2006).

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\begin{align*}
\left( R_1R_2\text{OO} \right)_{3M} + \left( R_1R_2\text{OO} \right)_{2M} & \rightarrow R_1R_2\text{O} + R_1R_2\text{O} + \text{R}_1\text{H} \\
R_1R_2\text{O} + \text{O}_2 & \rightarrow R_1\text{C} = \text{O} + \text{R}_2\text{C} = \text{O} \\
\text{Acids, Esters, Ketones} & \rightarrow \text{M}^{(n+1)+} + \text{H}_2\text{O} \\
\text{Note: } R_1 = \text{CH}_3, R = \text{C}
\end{align*}
\]

a. Transition Metal Catalyzed Degradation of Polyethylene
The large molecules, which cannot pass through the cell wall, need to be first oxidized by the extracellular or cell wall associated enzymes, which at times can act indirectly via production of diffusible radicals.

The biosurfactants improve the adhesion of cells to the materials and mobilize the water insoluble degradation products to pass through the cell wall and be acted upon by enzymes and transformed into smaller products in the cytoplasmic and/or periplasmic space. Molecules with smaller size may be transported across the cytoplasmic membrane and be utilized completely by β-oxidation pathway (Bonhomme et al., 2003).

Mineralization can be defined as conversion of materials to gas such as CO₂, CH₄ and nitrogenous compounds. Other includes waster, salts, and minerals.

Complete mineralization symbolizes the conversion of all chemical elements into natural biodegradable materials (Bonhomme et al., 2003). Studies on enhanced degradable polymers reveal that abiotic oxidation of pro-oxidant containing polymers leads to loss of mechanical properties, evolution of functional groups, and increase in melt flow index and decrease in molecular weight.

Most of these parameters like reduction in mechanical properties may indicate loss of usefulness of the polymer but may not necessarily be a sign of biodegradability of the polymer. Similarly, the increase in MFI, which is a measure of resistance to flow of polymer melt, results from lowering of molecular weight and may not necessarily, be indicative of biodegradation.

**STANDARDS FOR TESTING BIODEGRADABILITY**

For a material to be considered as a biodegradable material it must be totally consumed by micro-organisms. According to ISO/CD 16929, biodegradation can be defined as degradation that is caused by biological activity due enzymatic actions of micro-organisms.

*Figure 3:* Degradation Mechanism and Degradation Products of Polyethylene.
BIODEGRADATION TESTS

**Aerobic Tests**

The material is exposed to microbial condition in the presence of air. The microbes feed on the substrate converting the polymer to biomass and CO₂. This can be determined by calculation of oxygen demand in a closed respirometer or the amount of CO₂ released. The percent biodegradation is calculated by comparing the amount of CO₂ released with the theoretical amount (THCO₂). The rate of biodegradation can also be calculated according to ratio of biological oxygen demand (BOD) to 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 CH₄ and CO₂, which are quantified and used for calculation of percent biodegradation. However, plastics do not end up in sewage or water treatment plants for which the above test were designed. Instead, they find their way to landfill and composting sites for which standards are used as basis for certification for environmental degradable polymers (Hakkarainen et al., 2003).

**Composting**

The plastic is exposed to compost medium at constant or varying temperature and the extent of mineralization is obtained by the conversion to CO₂. According to ASTM-D 6400, a material is compostable at 60% mineralization for homopolymers and 90% for copolymers, blends and materials containing low molecular weight additives and plasticizers. When it comes to degradation, nature does not seem to discriminate between materials based on their origin (e.g., there are many synthetic condensation polymers such as poly(caprolactone), poly-(lactide)) which are biodegradable and many biobased materials (e.g., lignin) which do not get converted to CO₂ and H₂O in a short time period.

Suffice it to say that any material that can be considered as biodegradable must be able to undergo complete utilization by microorganism over a definite period of time. If not completely utilized the degradation should be expressed as a percentage biodegradability, which quantifies the fraction of the material which can be converted to CO₂ and CH₄ in a definite period referring to the utilized standards.

**STANDARDS FOR TESTING OXIDATIVELY DEGRADABLE POLYMERS**

Materials are exposed to biotic environment after the oxidative step. Oxidation should bring about the necessary changes in the polymer structure such as increased hydrophilicity, reduced molecular mass, or accessible chain ends which enhance the susceptibility toward microbial attack. The standard ASTM –D6954 discusses the methodology to assess the biodegradation of carbon-chain polymers and primarily caters for the requirements for the industry.

It is suggested that in the short-term, 50% of the organic carbon gets converted to CO₂ and the rest forms a 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 be converted to CO₂ and higher tendency to get converted to biomass, the evidence of 50% bioassimilation has not yet be generated (Albertsson, 1993).

**STUDIES ON BIODEGRADATION OF POLYETHYLENE**

The biodegradation of polyethylene (Shah et al., 2008) have been studied in the last few years. PE degradation requires very long periods. Long term study on C-labeled polyethylene that utilized liquid scintillation counting indicated that PE biodegradation requires extremely long periods. After 10 years incubation periods in soil, <0.5% polymeric carbon (as CO₂) by weight was evolved from UV–irradiated polyethylene sheet50. 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.

Biodegradation of polyethylene in the presence of Fusariumredolens (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.

A 65% biodegradation level has been reported for polyethylene films containing manganese stearate pro-oxidants (Jakubowicz, 2003). 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 (Thompson et al., 2004).

The composting of commercial polyethylene starch bags filled partially with composted leaves and yard waste was investigated (Greizerstein et al., 1993). 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 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 (Dayet al., 1997) 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" according to ASTM-D6954 and ASTM-D6400 is lacking.

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 (Matthies and Zarfl, 2010).

Concerns have been raised that polymer fragments resulting from polyethylene degradation may act as reservoirs for accumulation of toxins present in the environment (Browne et al., 2007).

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 (Mato et al., 2001).

CONCLUSION

For polymers 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 (Teuten et al., 2007).

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 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 and 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 deal with this problem at the present, provided proper collection and segregation can be done.

CONFLICT OF INTEREST

The authors declared no conflict of interest in this work.

REFERENCES


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