**ENVIRONMENTAL COMPETENT FOR POLYMERIC BLENDS AND COMPOSITES BASED ON BIODEGRADABLE POLYETHYLENE**

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**Abstract**

The expansion of environment-friendly materials based on natural sources increases dramatically in terms of biodegradable, recyclable, and environmental disputes throughout the world. Plant-based natural fibre; a high potential field of the reinforced polymer composite material is considered as lightweight and economical products as they possess lower density, significant material characteristics, and extraordinary molding flexibility. The usage of plant-fibers on the core structure of composite materials have drawn significant interest by the manufacturers to meet the increasing demand of the consumers for sustainable features with enhanced mechanical performances and functionalities. The plant-fiber-based composites have widespread usage in construction, automotive, packaging, sports, biomedical, and defence sectors for their superior characteristics. Therefore, this critical review would demonstrate an overview regarding the background of natural fibre composites, factors influencing the composite properties, chemical interaction between the fiber and matrices, future potentiality, and marketing perspectives for triggering new research works in the field of biocomposite (BC) materials.

**Keywords:** Biopolymer, Polymeric blends, Bio-composites, Sustainable, Biodegradable polyethylene,

**CONTENTS**

**ENVIRONMENTAL COMPETENT FOR POLYMERIC BLENDS AND COMPOSITES BASED ON BIODEGRADABLE POLYETHYLENE**

1. The importance of polyethylene in packaging
2. Disposal of polyethylene
3. Environmentally degradable plastics (EDP)
4. Oxo-degradable polyolefins
5. Degradation after the useful life-time
6. PE-Starch Based Composites

**Environmental competent for polymeric blends and composites based on biodegradable polyethylene**

The growing amount of synthetic polymeric materials is a great environmental problem that has to be solved as soon as possible1. The main factor aggravating this problem is the abundance of products made from traditional synthetic polymer, such as packaging materials, cases, containers and other equipment with a short period of use, which quickly turns into polymer waste that pollutes the ecosystem for decades. One of the problems contributing to this is that of waste disposal2. Their amount naturally is rising constantly, not only due to the increasing of the world population but additionally due to its features: urbanization increasing; rising standards of living and consequent changing patterns of social behaviour and habits (higher consumption); and changes in waste composition patterns (more consumer product packaging). These social changes and the waste generation are independent of the status of the countries: industrialized or in developing. Besides, the mode of waste disposal still predominantly remains through land filling, a conventional and unhygienic method. Alternative modes like composting and other scientific approaches are scarcely used. Consequently, land and water are polluted and degraded besides the fact of being a health hazard. Polyolefins are the largest family of polymer used in packaging applications arriving up to 61% of total material used in packaging market3-5. Among polyolefins, polyethylene presents a constant increasing demand. Although this polymer is characterized by an excellent cost-benefit ratio, it represents a big problem for the environment. An attempt to overcome this drawback, different approaches has been used to improve the PE degradability. One of them is based on the addition of biodegradable polymers obtained from renewable resources. The aim of this chapter is to discuss the polyethylene oxo-biodegradability through the blending of PE with prodegradants and biodegradable polymers of biosynthetic origin. This chapter is focused on materials based on polyethylene (PE), which remains as the largest polymer used in the field of packaging. This polymer is not biodegradable and its waste represents a serious problem to the environment. A proposal of eco-compatible PE based materials will be presented. This is bound to the enhancement of the polyethylene oxo biodegradability through the blending with biodegradable polymers of biosynthetic origin, starch poly(hydroxybutyrate) (PHB) and commercial prodegradant additives6.

***1. The importance of polyethylene in packaging***

Polyethylene, the first commodity plastic used on packaging, came into general use in the 1950s. Polyethylene (PE) is a family of polymers including for example the following: low-density polyethylene (LDPE), linear lowdensity polyethylene (LLDPE) and high-density polyethylene (HDPE). These PE differ principally in their density, which is related with their degree of crystallinity. Consequently, this property will influence their melting point ranges. Some typical properties values ranges for PEs are illustrated in Table 1.3.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Type of PE | Density (g/cm3) | Crystallinity (%) | Tm (°C) | MW (KDa) |
| LDPE | 0.913-0.939 | 44-53 | 101-114 | 10-50 |
| LLDPE | 0.914-0.921 | 29-43 | 110-123 | 50-200 |
| HDPE | 0.939-0.969 | 69-89 | 119-129 | up to 250 |

Tm is melting temperature; MW is average molecular weight

The dominance of PEs on packaging products is principally due to its low cost. The range of packaging forms for which PE is used extends from simple plastic film bags to combinations with other plastics or materials, such as paperboard and aluminium, to provide sealable packaging ensuring that the quality of the packaged foodstuff is effectively maintained.

Although PE plastics were first produced over 50 years ago, manufacturing and processing developments continue to improve its properties, performance, and packaging applications7. One well-known example is concerned with the oxidation stability of PE. Olefin polymers are prone to oxidative degradation, particularly at the elevated temperatures used in their processing. The reaction of PE oxidation results in the formation of long-chain branches and cross-linking. Therefore, the formulations of all commercial PE plastics contain antioxidants8,9. Besides, other additives must be incorporated in order to maintain and provide the desired physical properties and to ensure the efficient processing and handling of the finished products10. Additives such as colorants, whitening agents, slip additives, and antistatic agents are often conveniently incorporated into the basic polymer before processing into the final product (films, containers, etc.) by means of master batches. Master batches are concentrates of the additive(s) dispersed in the same or similar polymer types. Both HDPE and LDPE plastics are used to produce a wide variety of caps and covers for bottles and containers. The use as films for container labels is also growing. To make PE films, the particular properties of slip (friction) and blocking (film layers sticking together) must be enhanced for effective and efficient handling during manufacture and processing into the finished packaging. Enhancement of these properties is achieved by the addition of slip agents and suitable fine particulate fillers to the polymer. Typical slip agents are the fatty acid amides oleamide and erucamide, which “bloom” (exudates) to the film surface after manufacture. Titanium dioxide and calcium carbonate are typically used to produce white plastics. The inclusion of calcium carbonate in the polymer also improves the properties of hardness, stiffness, and printability as well as permeability to oxygen and to water vapour. Shrinkage and elongation are reduced11. To improve adhesive properties of PE its structure was modified forming a class of polymer called ionomer. This new family of material is a polyolefinic copolymer containing a small amount of ionic comonomer, which contain sulphonic or carboxylic acid groups neutralized with a metal cation. Aggregation of these metal salt groups induces heterogeneity with a length scale of a few nanometers. The best-known (and commercially most important) ionomer are derived from ethylene-methacrylic acid copolymers, by neutralizing some or all of the methacrylic acid units with a metal cation (e.g., Na+ or Zn2+). Materials in this category are marketed by DuPont under the trade-mark Surlyn®. This polymer can be used in packaging seals, films, cosmetic goods and personal care sports, recreation foam sheet and encapsulants12.

In multi-layers films PE is combined with a variety of polymer types, such as polyethylene terephthalate (PET), polypropylene (PP), poly(vinylidene chloride) (PVdC), and ethylene-vinyl alcohol copolymer (EVOH). The polymer used in each layer is selected to provide a required properties and performance characteristics. When good oxygen barrier property is essential, an aluminium foil layer is incorporated. Such flexible packaging is used for coffee, where the structure also acts as gas barrier in reverse, ensuring that the coffee aromas are retained. In special multi-layer packaging materials, PE is combined with paperboard and aluminium by extrusion coating. A typical example is the container for packaging long-life fruit juices and milk (Tetra Pak)13. The PE allows the container to be easily heat-sealed and also provides water barrier. The paperboard provides rigidity, and the aluminium acts as oxygen barrier, which ensures that the safety and quality of the packaged product are maintained during its shelf life. For foodstuffs with a short shelf life, it is not used the aluminium layer. Paperboard coated on both surfaces with PE is extensively used for boxed containers for milk products, take-away high-moisture and fatty foods, and for disposable beverage cups. Polyethylene-coated paperboard is widely used as external cartons for many foods, over a wide temperature range (frozen to ambient). Such cartons are easily heat sealed in food packaging line processes by spot contact heating.

Polyethylene-coated aluminium foil is extensively used as lidding material for pots and other containers. The PE coating that melts under heat and bonds the aluminium to the substructure provides the sealability of these foils14. Many of the PE films and containers used to package are printed to provide product identification, information on use, and decoration. Because PE has low surface energy, surface treatments are necessary to enable printing inks to achieve adequate adhesion. Corona discharge, flame, and ozone treatments are commonly used to increase the surface energy by imparting a degree of oxidation to the PE surface.

***2. Disposal of polyethylene***

In the 1970s, all the technical advantages, which made hydrocarbon polymers so useful in the past (as biologically inert and resistant to peroxidation) become disadvantages. This was a consequence of the discarded polymer-based products at the end of their useful life, particularly when they appeared as litter in the environment. As the concentration of the PE used in packaging sectors such as in the manufacturing of shopping bags, bottles and containers is very large, the amount of problems relating the final disposal in landfills increases. Hence, the degradation and disposal options, or possibly the biodegradation of the used PE represent a very important subject from the point of view of both economic and environmental aspects. As aforementioned, in an attempt to reduce the visible environmental pollution caused by post-consumer plastic materials, the members of EU States brought together to find a solution to plastic pollution. One of the objectives is the reduction of the waste through the recovery and recycling of these materials. However, recycling presents a great number of limitations. The most important is related to the technological problems, once this type of material often are disposed with organic products such as food, making recycling hard and sometimes impossible. Moreover, the costs of collecting, cleaning and sorting all these post-consumer plastics are high and the market for mechanically recycled plastics is limited, partly for this reason. Proper incineration of waste plastics would enable the recovery of most of the energy stored in them (polyolefins are excellent fuels) but modern incinerators are expensive. Considering the aspects above, one possible solution for the problem of the PE disposal can be the partial or total replacement of PE for the named “Environmentally Degradable Plastics” (EDP). EDP can be considered to include a wide group of natural and synthetic polymeric materials or blends of both, that undergo chemical change under the influence of environmental factors15. The chemical changes must be followed by complete microbial assimilation of degradation products resulting in carbon dioxide and water16. The process of EDP degradation comprises two phases, disintegration and mineralization. During the first phase, disintegration is associated with the deterioration in physical properties, such as discoloration, embrittlement and fragmentation. In the second phase is assumed that a complete conversion of plastic fragments, after being broken down to low molecular weights should occurs17.

***3. Environmentally degradable plastics (EDP)***

The worldwide consumption of biodegradable polymers has increased from 14 million kg in 1996 to 68 million kg in 2001. Mainly markets for biodegradable polymers include packaging materials as shopping bags and food containers, hygiene products, consumer goods as fast-food tableware and toys, containers and agricultural materials as mulch films18. Several definitions are useful in understanding the complexity of the topic of biodegradable polymers. These begin with the concept of plastic waste following with that of natural polymers, degradable, biodegradable, hydrolytically degradable, and oxidatively degradable materials. Natural polymers are by definition those biosynthesized by various routes in the biosphere. Proteins, polysaccharides, nucleic acids, lipids, natural rubber, and lignin, among others, are all biodegradable polymers. Moreover, the rate of the biodegradation may vary from hours to years depending on the nature of the functional group and degree of complexity of the macromolecule19. Degradation is a process where the deterioration in the polymer properties takes place due to different factors like light, heat, shear, etc20. As a consequence, the resulting smaller fragments do not contribute effectively to the mechanical properties and the material becomes brittle. Besides, the life of the material becomes limited21. The degradation of polymers may proceed by one or more mechanisms, including biodegradation, chemical degradation, photo and thermal oxidation, etc., depending on the polymer environment and desired application22. Environmentally biodegradable polymers are designed to degrade upon disposal by the action of living organisms23. Biodegradation is defined as the conversion of a material to CO2, H2O and traces of inorganic chemicals under aerobic conditions or to CH4, CO2 and inorganic chemicals under anaerobic conditions by the action of Microorganisms (MO). So, biodegradation in aerobic (Eq. 1.1) and anaerobic (Eq. 1.2) environments may be described by the following chemical equations taking into account a hydrocarbon polymer24:

Polymer + MO + O2 → CO2 + H2O + biomass + residue

Polymer + MO → CH4 + CO2 + H2O + biomass + residue

Biomass represents an important part of the organic carbon cycle, which has been assimilated by microorganisms. It should be pointed out that though fragmentability of the polymer and loss of elongation (95% is defined as the embrittlement point) should constitute inherent characteristics of degradable polymers, several additional features are required if the polymers are to be acceptable from the ecological point of view: (i) a predetermined service time (induction time) during which no properties change whatever; (ii) the end of induction period should be followed by an accelerated fragmentation stage; (iii) a final, total and innocuous assimilation of the fragmentary products by the ecosystem25. At the present time, there are three main classes of biodegradable polymers. In the first one, it is found the synthetic polymers. These polymers contain groups susceptible to hydrolysis attack by microbes such as polyesters, polyanhydrides, polyamides, polycarbonates, polyurethanes, polyureas and polyacetals26-30. The second class of materials is composed of bacterial polymers as poly(3-hydroxybutyrate) (PHB) and poly(3hydroxybutyrate-co-valerate) (PHBV)31. Finally, it is considered the polymeric blends and bio-based composites as the third series of materials that are readily consumed by microorganisms. A classic example is the blends of PE with starch32-35. In this CHAPTER, special attention will be given to the third class of EDP. In particular, it will be reviewed the literature related to materials based on oxo-biodegradable polyolefins, their preparation, its blends with natural polymers, the thermo and/or biodegradation mechanisms, the main applications, advantages and inconvenient of this family of materials.

***4. Oxo-degradable polyolefins***

There are two mainly applications for oxo-degradable polymers. The first is where biodegradability is part of the function of the product as for example in the biomedical or agriculture fields, and the second application is when degradability is desired at the end of the use of the product, as for packaging. An essential feature for both applications is a variable and controllable induction time to the beginning of peroxidation, which is the rate-controlling step in the overall biodegradation process36,37. Carbon-chain polymers vary remarkably in their ability to resist peroxidation. The following sequence shows some common commercial hydrocarbon polymers in order of decreasing oxidative stability: Polyvinyl chloride (PVC) > Polyethylene (PE) > Polypropylene (PP)38. What is needed, is a way of controlling the time during which the polyolefin retains its normal, useful properties as well as a way of having it undergo subsequent oxo-biodegradation at a much higher than normal rate that is commensurate with the application and with the disposal environment39. The key to this control requirement is a sound understanding of the peroxidation mechanisms and kinetics. In the environmental degradation of oxo-degradable polymers, the total degradation will be a synergistic effect of several agents40. The main degrading agents are UVradiation, heat and oxidizing agents leaving to a brittle material with a higher susceptibility to biodegradation41,42. The final end products of the total mineralization will be carbon dioxide and water. Before that stage is reached, many low molecular weight degradation products will be evolved, which in turn can increase or decrease the degradation43.

It is accepted that polyolefins are bioinert44, which means that they are highly resistant to assimilation by microorganisms such as fungi and bacteria. This is expected, since the surfaces of materials and articles made from polyolefins are hydrophobic, which inhibit the growth of microflora on them. Besides, there are common mechanisms of biodegradation that involve bioassimilation from the ‘‘ends’’ of substrate molecules. Since commercial polyolefins have relatively high molar mass values, there are very few ends of molecules accessible on or near the surfaces of materials made from these resins. Different approaches to render synthetic plastics degradable have been considered. It is generally found that photo and thermal-oxidation increases the biodegradation of polymers45. Photo and thermal-oxidation increase the amount of low molecular weight material by breaking bonds, increasing the surface area, through embrittlement and increasing the hydrophilicity by the introduction of carbonyl groups and all these effects promote biodegradation46. Although the family of polyolefins is considered to be not eco-friendly, it has been observed that its oxidation products are biodegradable47,48. Such products have molar mass values that are significantly reduced, and they incorporate polar, oxygen-containing groups such as acid, alcohol and ketone. This is the basis for the term oxobiodegradable polyolefins. This concept is used to distinguish polymers that biodegrade by a hydrolysis mechanism from those that are inert to hydrolysis but undergo oxidation. Oxo-biodegradation then denotes a two-stage process involving, in sequence, oxidative degradation, which is normally abiotic in the first instance, followed by the biodegradation of the oxidation products49. Oxo-degradable polymers can be produced by the addition of sensitizer additives that will promote the formation of free radicals in the presence of heat. Hence, peroxides will be generated and auto-oxidation will be consequently enhanced50. Oxo-degradable polymers can also be prepared by changing the polymer structure by introducing chromophores51. In this class of materials, the carbonyl groups can be introduced, for example, through the copolymerization of PE with a small amount of monomer such as carbon monoxide producing a degradable copolymer. Jones et al.52 has formulated a copolymer of vinyl ketones and styrene or ethylene where the ketone groups are part of the main polymer chain. These materials were shown to biodegrade and the degradation was monitored using respirometry. Albertsson and Karlsson present different means of modifying otherwise relatively inert polymers (in particular PE) in order to obtain environmentally degradable polymers53. They concluded that the incorporation of transition metal complexes facilitates the photo-oxidation of inert LDPE, and that was also possible to induce early photo-oxidation by polymerization of ethylene with carbon monoxide or by the addition of other ketonic groups to PE. LDPE samples containing (1) iron dimethyldithiocarbamate, (2) iron dimethyldithiocarbamate and (3) 0.8% carbon black and iron dimethyldithiocarbamate and nickel dibutyldithiocarbamate were aging in a weatherometer where the temperature increased during ageing, achieving a mean value of about 50°C. The dithiocarbamates are effective processing stabilizers and heat stabilizers for polyolefins. Their photo-antioxidant activity depends on the metal ion, where iron and manganese complexes are the least stables54. These metal complexes show a well-characterized induction period, which increases with their concentration in the polymer. The sulphur ligand iron complexes combine a high level of antioxidant activity during processing, storage and in the early stages of exposure to light. After this initiation, a very fast photo-oxidation occurs54. Polyolefins with enhanced degradability have been available commercially for more than three decades and have been successful used in agricultural products for most of this time. They can be obtained through the mixture of inert polymers with others from renewable resources as starch. Starch is the lowest priced and most abundant worldwide commodity, it is the major form in which carbohydrates are stored by plants in the form of granules (mainly from potatoes, corn, and rice). Among other features, it is inexpensive and annually renewable. Starch granules vary from plant to plant but are in general composed of a linear polymer, amylase (in most cases up about 20 wt-% of the granule), and a branched polymer, amylopectin. It is produced in most countries and is available at low cost in all countries. In Europe, it is industrially produced with a volume of almost 7 million tones/year. Nearly 50 % of the starch produced is already used for non-food applications and about 30 % of the starch production is industrially precipitated from aqueous solutions because of its very good film-forming properties55. Animals, plants and microorganisms are able to utilize starch as a source of energy. Microorganisms produce various starch hydrolyzing enzymes such as amylase and their wide distribution assures the biodegradation of starch in nature. The first attempts to increase degradation of hydrocarbon chain polymers as PE, regards to the incorporation of natural polymers, in particular starch and transition metal pro-oxidants. Microorganisms initially attack this biopolymer leaving a brittle material with a greater surface/volume ratio. Hence, the sunlight, heat, oxygen, etc. promote auto-oxidation of the chemically unstable pro-oxidant, generating free radicals, which attack the molecular structure of the PE. With time, the molecular weight will have decreased so much that biodegradation of the PE can take place These materials are useful in applications such as mulching films56,57. However, this type of blends usually leads a phase separation and reduction in mechanical properties due to the lack of compatibility between hydrophilic biopolymer and generally hydrophobic thermoplastic58. The idea of using starch inside synthetic polymer matrix was proposed by Griffin. His study was based on introducing starch in its natural form into the synthetic matrix at amounts lower than 10 % while keeping the granular structure intact. In this case, starch is only a filler susceptible to enzymatic degradation but unable to affect the mechanical properties of the final material (20-30 MPa tensile strength and 700-900 % elongation at break point for a 90:10 PE:starch blend). The original concept has been improved also by the addition of unsaturated polymer, a thermal stabilizer and together with the formulation containing starch, a transition metal salt. The starch and other additives are mixed in a master batch (MB), which can be included in polymers in different concentrations. However, blends of LDPE with high amounts of starch exhibits poor mechanical properties owing to their inherent differences in polarity that results in immiscible blends59. The main areas of research concentrate on determining compatibility or coupling agents and repeatable processing parameters. Different ways has been proposed to incorporate functionalized PE in LDPE-starch blends60. In these studies, either dry granular starch or starch plasticized with water and glycerol has been used. Nevertheless, poor water resistance is a major limitation in their use. An alternative approach is to bring about some compatibility in starch and synthetic polymer by blending starch with polymers containing polar functional groups that can interact with starch improving the adhesion and hence the mechanical properties of these biodegradable blends. Another method of producing compatible thermoplastic blends is via reactive blending, which relies on the in situ formation of copolymers or interacting polymers. This differs from other compatibilization routes where the addition of a separate compatibilizer is required. In reactive blending, the blend components themselves are either chosen or modified so that reaction occurs during melt blending, which improves the compatibility and interfacial adhesion of the two immiscible polymers. The small amount of graft or block copolymers formed during the blending process, due to reaction between the two components, is generally enough to stabilize the morphology and improve the properties of the blends. Sailaja et al.61studied blends consisting of LDPE and esterified starches, starch acetate (Stac) and starch phthalate (Stph). Starch esters were melted with LDPE using LDPE-co-glycidyl methacrylate copolymer as compatibilizer. The results indicate that, in general, LDPE-Stph blends perform better than LDPE-Stac blends. Esterified starch has better mechanical properties than unmodified starch when incorporated in LDPE. The tensile strength and modulus are close to that of pure LDPE for LDPEStph blends while the impact strength values are 80 % of that of pure LDPE for 20-40 % Stph loading. The elongation at break values were in the range of 60-70 % of that of pure LDPE for LDPE-Stph blends. Jeziorska et al.62 reported results of starch-based blends (5 - 30 wt-%) with LDPE and poly(ethylene-co-acrylic acid) (EAA). During the reactive blending of LDPE/EAA blend with starch, the carboxylic groups in EAA can react with the hydroxyls of the starch to form hydrogen bonds. Results showed that the tensile strength of the blends remained practically unchanged when the starch content increased from 5 to 30 wt-%. Besides, all blends containing starch supported the microbes growth, which was faster for the blends with oxidized potato starch than corresponding samples with corn starch. Moreover, the bigger amount of starch in the samples the higher the rate of microbes growth. Of all the modifying approaches to render starch and PE more compatible, the more efficient is when the compatibilizer is introduced into the blends63. When the starch compatibilized synthetic polymer is placed in a biologically active environment, the microbes show considerable amount of surface growth. The surface growth may not result in the degradation of the body of the polymer if the starch is confined to the surface. For complete degradation of the starch to be notice, the starch fraction should exceed the percolation threshold, so that a number of significant pathways for microbial invasion/enzymatic diffusion are generated. At 1974, a commercial product was released, which the Coloroll Company offered as shopping bags in Europe. Griffin has since then made improvements in the technology and the auto-oxidant, which earlier was food oil, was then replaced by other polymer blends. In these formulations, the auto-oxidation has a more clearly defined induction period after which the molecular weight decreases as does also the physical strength, and the biological breakdown is then said to begin64. In the 1990s, Griffin discloses a degradable polymer composition wherein an antioxidant and pro-oxidant are combined whereby as the antioxidant is stated to be depleted with time. After total depletion of the antioxidant a residual concentration of prooxidant remains and is stated to provide a sharp loss in the physical strength of the degradable polymer composition. The applications discloses use of a stable polymer such as low-density polyethylene, linear low density polyethylene, high density polyethylene, polypropylene, or polystyrene, together with a less stable unsaturated elastomer type compound made from the polymerization of 1:4 dienes, or the copolymerization of such 1:4 dienes with ethenoid comonomers, such as styrene-butadiene elastomer or natural rubber. The invention embodies less stable substances capable of auto oxidation because such substances are more readily initiated by the oxidation process by virtue of their unsaturation. Once the auto-oxidation process is initiated, the process is said to involve more resistant saturated substances such as polyolefins65. In another study, Albertsson et al.66 assessed LDPE containing different amounts of corn-starch without further additives and corn-starch in a pro-oxidant formulation (MB) (10 %, 15 % and 20 % by weight) after irradiation for periods of up to 500 h. The carbonyl and hydroperoxide indexes of samples containing 20 % MB after 500 h irradiation were about 3 times the values obtained in pure LDPE and in LDPE-starch blends. Besides, during the irradiation, the tensile strength decreased to almost the same extent for all three materials. In this study, a material susceptible to photolysis was obtained by the addition of corn-starch and a master batch containing LLDPE, styrene-butadiene copolymer (SBS) and manganese stearate. Incorporating only starch into LDPE did not significantly change the susceptibility of the material to photolysis. LDPE-MB was degraded by an initial photo-oxidation (auto-oxidation) and a subsequent attack by microorganisms (biodegradation). Suominen in his patents describe that a biologically degradable film was prepared consisting of a synthetic polymer and a biologically degradable polymer. The biologically degradable polymer was divided into small particles in an aqueous suspension by means of enzymes that split and release small molecules from the surface of the biopolymer particles. After achieving desired particle size, an emulsion was formed with vegetable oil and the particles coated with enzyme protein become coated with vegetable oil, which at the same time interrupts the degradation of the biopolymer particles by the enzyme. The coated particles with the oil were separated from the suspension to remove small molecules after which the particles were re-dried and then pulverized. The final film was prepared in a film extruder in which the biopolymer was mixed with the synthetic polymer and possibly other additives that are generally used in forming polymer films67. Another attempt to improve PE biodegradability could be through its blending with poly(hydroxybutyrate) (PHB). PHB is a member of a family of natural biodegradable polyesters[58], the poly(hydroxyalkanoates) (PHA). It is produced directly from renewable resources by fermenting a sugar feedstock (glucose is currently being used) with several naturally occurring microorganisms as carbon and energy reserves and can be accumulated to high levels in bacteria, approximately 95% of their dry weight, which can grow in a wide variety of natural environments. PHB can be rapidly hydrolyzed to the monomer by extra cellular depolymerase enzymes secreted by a wide variety of bacteria and fungi that can utilize this compound after it is liberated by the death and lyses of bacteria in which it is stored[60, 61]. Since its discovery in the 1920s, by Maurice Lemoigne, PHB has been extensive studied[62]. PHB is produced commercially by Monsanto and finds applications in different packaging materials, such as thin films and paper coatings. Besides, it is degradable in several environments, including marine water, soil, sewage sludge and compost68-70. PHB has a high melting point, around 180°C and forms highly crystalline solids which crystallize slowly71 and form large spherulitic structures that impart poor mechanical properties in moulded plastics and films, although, addition of nucleating agents and suitable post-treatment after extrusion or casting can lead to much improved properties72. A consequence of this high melting point is that PHB is also susceptible to thermal degradation during melt processing by ester pyrolysis of the aliphatic secondary esters of the repeating units. The pure homopolymer PHB, produced in large quantities, is a brittle material (elongation at break ϒ = 10%, impact strength 3 kJ/mm2) with a large elastic modulus (E =1.7 GPa) and high fracture stress (σ = 35 MPa). Studies of how melt processing influences PHB have shown that the molecular weight is significantly affected by high temperatures and shear forces73. The brittleness of PHB is attributed to: (1) the secondary crystallization of the amorphous phase during storage time at room temperature leading to rapid decrease of elongation at break. As a result of secondary crystallization in the amorphous region, density, crystallinity, stress and modulus increase while the material becomes brittle and hard with much lower elongation at break; (2) the glass transition temperature (Tg) being close to room temperature; (3) the low nucleation density, which results in the development of large spherulites exhibiting inter spherulitic cracks74. Oxo-degradable PE-PHB blends could be a good solution to improve PE degradability resulting in a new material for use in the production of ecocompatible packaging. However, PE and PHB are not compatible due to significant differences in their polarity, so as in the case of starch, to reach a product with good processability and mechanical properties a compatibilizer needs to be used. The literature for this type of blend is very modest, mainly regarding blends of PE-PHB without prodegradants remaining a field still to be explored75.

***5. Degradation after the useful life-time***

Since degradation is not desirable during the lifetime of a material, the induction period is a crucial property in that it ensures that the material has a certain shelf life. The lifetime of a polymer is dependent not only on the intrinsic characteristics of the material but also on the surroundings (heat, light, pollutants etc.)76. Even before its use, soon after polymerization, polyolefins are subjected to several processing steps involving extrusions. These processing cycles, which employ temperature and shear cause chemical reactions inside the polymeric matrix. Degradation can be initiated by oxygen, shear, heat, catalyst residues or any combination of these factors. Besides, a variety of environmental factors may affect the polymer: oxygen, temperature, sunlight, water, stress, living organisms and pollutants. The combination of these factors can be cumulative, synergistic or antagonistic77. Oxidation can be defined as the reaction of a polymer with oxygen at temperatures where thermal degradation is negligible. This distinguishes it from pyrolysis, the thermal decomposition of the polymer in the absence of oxygen, and from combustion, the reaction between oxygen and the volatile products of thermal decomposition of the polymer. Model compound studies suggest that most polymers should not oxidise significantly at temperatures of normal use. In fact, oxidation is a major technological problem and few polymers can be used without stabilisation. The reason is the presence of impurities and structural defects in polymers, especially after processing. Oxidation is typically a very slow reaction between a solid, possibly semi-crystalline, polymer and a gas. Oxidative degradation differs from thermal degradation in several important ways: (i) it is slow – reactions over weeks or years; (ii) the production of volatiles may be almost negligible; (iii) diffusion of oxygen into the polymer is required; (iv) polymer is usually solid, and restricted mobility gives complex kinetics; (v) it is possible to stabilize polymers against oxidation, using additives. It was showed that the release of small molecules from the polymer chains during thermal aging change the morphology during the degradation. It is generally known that the amorphous part of a polymer is more easily degradable, in particular this is the case for hydrolysable polymers. This gives a gradual increase in the crystallinity of the remaining polymer because of the rearrangement of the chains78. The thermal oxidation of polyolefins includes initiation, propagation, chain branching and termination steps. Under oxygen deficient conditions not all alkyl radicals (R•) can be transformed to ROO• (Scheme 1).



Scheme 1.1. Thermal oxidation of polyolefins starting from R•

As shown in the Scheme 1, the carbon radical R• reacts with oxygen to form the ROO• radical. The recombination of two radicals R• is a termination reaction leading to an increase in the molecular weight of the polymer. Another termination reaction is the disproportionation of two R• radicals. The addition of a R• radical to a –C=C– bond is energetically favoured by the formation of a σ-bond at the expense of a π-bond. This reaction leads to chain branching or cross-linking and is related to an increase in the molecular weight of the polymer. The inverse of the addition reaction to a –C=C– bond would be the fragmentation of the R• radical. In the thermal oxidation of polymers, the first oxygen radical formed is the peroxy radical ROO•. After that, occurs the H• radical abstraction from the polymer backbone, which lead to the formation of hydroperoxide ROOH and the carbon radical R•. The life-time of the hydroperoxide ROOH must be considered to be very short under processing conditions and it will decompose immediately to form the alkoxy radical RO• and the hydroxyl radical •OH. Both species will react by abstraction of a H• radical from the polymer backbone. The carbon radical R• reacts with oxygen to form the ROO• radical. With unactivated olefins, ROO• radicals react mainly by abstraction of a H• radical at the allylic position. The reaction of a peroxy radical ROO• with the carbon radical R• causes the formation of ROOR. This species will split into two alkoxy radicals RO• at the processing temperatures. The reaction of two peroxy radicals ROO• is a termination reaction, leading to non-radical products in the case of primary and secondary species79. Hydroperoxide is unstable to both heat and UV light, and its destruction will lead to the formation of several types of oxygen-containing products. One of the few differences between peroxidation initiated by heat and by light is that ketone products are stable to heat but not to UV light. In either case, one is dealing with a branching chain reaction sequence in which the reaction of the hydroperoxide group is the rate-determining step in peroxidation leading to molar mass reduction. Because of its extremely high reactivity, the alkoxy radical RO• reacts by the abstraction of an H• radical from the polymer backbone or by βscission. The β-splitting of alkoxy radicals into molecules with carbonyl groups (ketones and aldehydes, which are subsequently oxidised to form carboxylic acids) and carbon radicals R• leads to a decrease in the molecular weight of the polymer (Scheme 1.2). The reactions of RO• with other radicals as R• and RO• are insignificant80. In the case of oxo-degradable polymers, it is common to use light and/or heat to initiate free radical chain reactions in polymerization and oxidation processes. There are two examples of this process: (i) molecules whose excited states behave as radical initiating species (carbonyl compounds) and (ii) molecules which dissociate to free radicals (peroxides and transition metal ion salts). Using these processes, it is possible to control the oxidative breakdown of polymers.



Scheme 1.2. Thermal oxidation of polyolefins starting with RO•.

Abiotic peroxidation of the polyolefins gives rise to some vicinal hydroperoxides and this process is particularly favoured in the poly-αolefins, such as polypropylene due to the susceptibility of the tertiary carbon atom to hydrogen abstraction via a hydrogen-bonded intermediate. A major proportion of the peroxidic products are hydrogen-bonded vicinal hydroperoxides that break down to small biodegradable molecules81 such as carboxylic acids, alcohols and ketones as well as longer chain oxygenmodified breakdown products, which oxo-biodegrade more slowly. The decomposition of the vicinal hydroperoxides is also facilitated by internal hydrogen bonding and the low molar mass products of this selfinduced degradation are small biodegradable molecules such as acetic and formic acids. In the case of the polyolefins, random chain scission is initially the dominant process. However, some low molar mass oxidation products are formed via vicinal hydroperoxides even in PE. The alkoxyl radicals formed by decomposition of the hydroperoxides contain weak carbon-carbon bonds in the α positions to the hydroperoxide groups, which lead to the formation of low molecular weight aldehydes and alcohols that rapidly oxidise further to carboxylic acids82. Hydroperoxides are important intermediate products in the oxidation scheme and their decomposition rate greatly affects the overall oxidation rate of the polymer matrix. Two examples of reactions of metal catalysts with hydroperoxides are showed in Equations 1.3 and 1.4.

ROOH + Men+ → RO• + Me(n+1)+ + OH−

ROOH + Me(n+1)+ → ROO• + Me n+ + H+

Although biodegradable plastics are required to disintegrate rapidly followed by biodegradation at the end of their use life, it is equally important that their mechanical properties remain essentially unchanged during use. The rate of peroxidation of hydrocarbons, including polyolefins, depends on two primary parameters. The first is the rate of the free radical chain reaction of the polymer with oxygen, which is in turn governed by the rate of reaction of peroxyl radicals with polymers. The second is the presence of initiators that lead to the formation of radicals, of which the most important are the hydroperoxides (ROOH) that are the products of the chain reaction

RH + ROO• → R• + ROOH

The gel content or insoluble fraction (Scheme 1.3) is formed in polyethylene by cross-linking and it is one of the products of PE thermal aging. The thermo-oxidative and thermo-mechanical oxidation can influence polymer molecular weight in two different ways either increasing by crosslinking or decreasing by chain scission and both of these events lead to changes in polymer properties. Cross-linking via an oxidation reaction is due to the recombination of alkyl radicals R• with each other, with RO• or ROO• radicals like is shown in Scheme 1.3. The natural polymers are biodegraded by a range of catabolic metabolisms catalyzed by series of enzymes. This catabolism produces both energy and building blocks for the biosynthesis of new materials. The ultimate degradation products of biopolymers are carbon dioxide, water, and to some extent ammonia. But, it is very important to remember that only a very few amount of the biopolymers ends up as carbon dioxide and water. Series of other called natural metabolites accumulate and are used again and again in nature83.



Scheme 1.3. General mechanism of polyethylene cross-linking

Biodegradation of oxidable polymers is generally slower than biodegradation of hydrolysable ones. Even polyethylene, which is rather inert to direct biodegradation, has been shown to biodegrade after initial photooxidation. Many inert polymers are, however, more susceptible also to biodegradation if modifications are done. Low molecular weight compounds present in polymers render the polymer more susceptible to biodegradation because they become inherently more accessible to chemical reactions. An oxidized polymer is more brittle and hydrophilic than a non-oxidize polymer, which also usually gives a material with increased biodegradability84. As aforementioned, a very used way to increase the biodegradability of LDPE is the introduction of a natural polymer in the inert matrix. For this purpose, the most commonly used natural polymer is starch. However, the use of starch alone in polyethylene, requires rather large amounts in order to really create an increase in the biodegradation rate85. Certainly, the filler that is biodegradable always gives a matrix that is more easily accessible to abiotic degradation. Albertsson and co-workers studying the degradation of LDPE films containing biodegradable starch filler and a pro-oxidant formulations in aqueous media inoculated with bacteria or fungi demonstrated the greater susceptibility to degradation of the LDPE matrix of the samples containing the pro-oxidant and starch than of samples containing only starch or of pure LDPE samples. In its investigations, authors found that the mechanisms responsible for initiating degradation of the LDPE matrix were hydroperoxyde-catalyzed auto-oxidation of the pro-oxidant in synergistic combination with biodegradation of the starch particles. The biodegradation mechanism of polyethylene showed that initial oxidation is followed by the removal of two-carbon fragments from the chain. This mechanism is confirmed by analysis of carbonyl group formation in the PE surface, which decreases with time in biotic environments86. Thus, microorganisms assimilate the degradation products of PE at the same time as the polymer chains gradually biodegrade.

***6. PE-Starch Based Composites***

The first’s approaches to increase PE biodegradability were based on the replacement of 40 % of PE matrix by biodegradable fillers, especially starch. Even though this type of filler can be relatively rapid to degrade, it is now well accepted that it does not accelerate the biodegradation of the PE matrix itself87. One method to improve the biodegradability of PE materials is to add together with starch some other additives, as prodegradants, which can increase the rate of oxidation by air oxygen and cleavage PE chains under the influence of light and/or heat. Starch is the lowest priced and most abundant worldwide commodity. It is the major form in which carbohydrates are stored. Moreover, it is a well-known polymer, naturally produced by plants in the form of granules (mainly from potatoes, corn, and rice)88. Among other features, it is inexpensive and annually renewable89. Starch granules vary from plant to plant but are in general composed of a linear polymer, amylase (in most cases up about 20 wt-% of the granule), and a branched polymer, amylopectin. It is produced in most countries and is available at low cost in all countries. Starch based products are an option for the replacement of oil based materials. However, the production of starch based materials without other additives presents some difficult such as the poor mechanical properties presented by the films90. Starch materials are fragile and their ability to develop large deformation are rather limited91. Starch films can be made from the native starch or its components, amylose and amylopectin, by various techniques such as thermoplastic processing and solution casting92. Films rich in amylose or amylopectin are reported to have different properties. Preponderance of amylose in starches gives stronger films, stable in water, while the branched structure of amylopectin generally leads to films that disperse quickly in water and with different mechanical properties, such as lower tensile stress. Starch can also be used as the main polymer in macromolecular compositions, which can be processed as thermoplastics such as PE. In this case, the granular structure of starch is completely disrupted by the use of plasticizers under heating, giving rise to a continuous phase in the form of a viscous melt, which can be processed following conventional plastic processing techniques such as injection moulding or extrusion. These types of starch compositions are commonly known as thermoplastic starches (TPS). Starch based biodegradable polymers can also be produced by blending or mixing them with synthetic polymers93. The first attempt to obtain starch based materials concerned the utilisation of starch granules as fillers for synthetic polymer as PE. By varying the PE amount, its miscibility with starch, the morphology and hence the properties of the films can be regulated. Of all the modifying approaches to render starch and PE more compatible, the more efficient is when a compatibilizer is introduced into the blends. Although the literature of PE-starch films is abundant, the results show that the PE-starch films had good biodegradability but very poor compatibility94, which will affect specially the mechanical performance of these materials. In order to improve PE-starch compatibilization, several studies report the properties of PE-starch materials compatibilized with copolymers as for instance the ethylene-acrylic acid copolymer (EAA)95 or ethylene-vinyl acetate (EVA). In addition, very little quantity of studies was dedicated to PE-starch containing prodegradants. Kim et al. 96 prepared PE based blends containing hydroxypropylated starches (HPS) with different degrees of substitution (DS). They studied the effect of HPS DS on thermal and bio-degradation of blends in the period of 12 and 4 weeks, respectively. Thermal degradation in an oven at 70°C began after 7 weeks for PE/HPS blends with higher DS (0.18 and 0.4). The same was observed on biodegradation. This means that PE/HPS blends with higher HPS DS biodegraded faster than the PE blended with not modified starch. Bikiaris *et al*.97 prepared three families of PE based blends containing plasticized starch (PLST) and/or ethylene-acrylic acid copolymer (EAA). For all blends it was added 0.01 wt-% of Cobalt stearate prodegradant (Co). It was observed that the effect of EAA is of acceleration of thermal oxidation whereas that of PLST is of inhibition. Besides, some commercial additives based on thermoplastic starch such as Mater-Bi are available. Mater-Bi is a trademark of Novamont and comprises four classes of biodegradable materials based on starch, which differ in synthetic components98. Mater-Bi products made basically of thermoplastic starch in combination with polymers such as poly(vinyl alcohol) or aliphatic polyesters present a biodegradation rate similar to that of cellulose and their mechanical properties similar to those of PE99.

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