

Full Length Research Paper

Plastics: The good, the bad and the ugly

Kamweru Paul K.^{1*} and Tindibale Edward L.²

¹Department of Physical Sciences, Chuka University, P. O. Box 109-60400, Chuka, Kenya.

²Physics Department, Egerton University, P. O. Box 536-20115, Egerton, Kenya.

Received 29 August, 2016; Accepted 23 September, 2016

Plastics' demand and consumption is on the increase since 1950s due to their unique properties. Their high use coupled with challenges in end-of-use handling and their inherent resistance to degradation has led to their accumulation in the environment, which is a matter of grave concern. This review presents a general overview of the state of knowledge of the diverse faces of plastics with special reference to polyethylene. This includes an outline of the polyethylene blends and grades put into most use, disposal methods, polyethylene degradation and its effects on the environment. The Current state of knowledge suggests that future trends and policies should be directed towards increased efforts to recycling and minimizing the introduction of virgin materials into the cycle.

Key words: Polyethylene, degradation, polymers, plastics, environment.

INTRODUCTION

Plastics otherwise referred to as Polymer Based Materials (PBMs) are macromolecules, formed by polymerization and having the ability to be shaped by the application of reasonable amount of heat and pressure or any other form of forces. There is a wide range of applications of PBMs, ranging from their use in aerospace industries to a simple shopping bag. Almost all aspects of daily life involve PBMs in some form or the other. PBMs outclass all other materials such as metals and ceramics in their low density, strength to weight ratio, low corrosion rate, ease of processing and excellent barrier and surface properties. Consequently, there has been a worldwide increase in demand of PBMs since 1950s (Figure 1).

Chemically, PBMS are the most non-biodegradable materials man has ever produced. They are beyond any sort of biodegradation, though weathering and ultraviolet

light can fragment large chunks. The extreme durability of plastic defies the natural recycling process of the biosphere. This in turn causes a major pollution menace, obscuring the benefits of PBMs. Most PBMs as finished products are non-toxic, but in plastic products there may be non-bound residual monomers, polymerization chemicals, degradation products, and additives which have toxic properties (Lithner et al., 2009; DeMatteo, 2011). Although the advocates of plastics consider it as the most eco-friendly material saving natural resources such as timber, the growing mountains of plastic garbage is now assuming dreadful proportions in many developed societies.

Polyethylene is the most demanded and produced plastic in the world (Plastics Europe, 2012). This is because Polyethylene is strong, it is safe and it is

*Corresponding author. Email: pkamweru@gmail.com or pkkamweru@chuka.ac.ke.

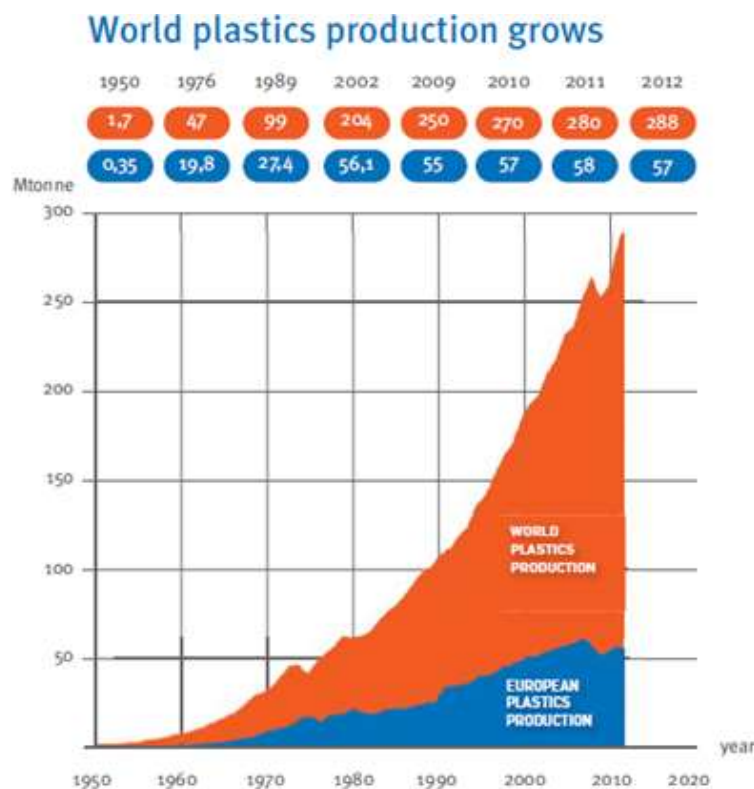


Figure 1. World Plastics Production 1950-2012. This figure has been obtained and adopted from Plastics Europe (2013).

Table 1. Global and European plastic demand by resin type for the year 2011 (Plastics Europe 2012; Rappaport, 2011).

Resin type	Europe % demand (2011) of total 57 million metric tonnes	Global % demand (2010) of total 190 million metric tonnes
Others	20.0	6
Polypropylene	19.0	25
Polyethylene		
Low density/linear low density (LDPE/LLDPE)	17.0	21
Polyethylene-High density (HDPE)	12.0	17
Polyvinyl Chloride	11.0	18
Polystyrene solid/expandable	7.5	6
PolyurEthene	7.0	-
Poly(ethylene terephthalate)	6.5	7

versatile (Hayden et al., 2013). In this review paper, we discuss the good, the bad and the ugly sides of PBMs with special reference to Polyethylene.

POLYETHYLENE GRADES, BLENDS AND CONSUMPTION

Polyethylene is a polymer of Ethene/ethylene, $(C_2H_4)_n$, whose demand and production is approximately 30% (Table 1) of all plastics in Europe in 2011 and

approximately 38% of all plastics worldwide in 2010.

By making polyethylene more or less "dense" (Table 2) in the factory, there is a suitable type of material available for every application (Vasile and Pascu, 2005). In practice one of the following types/forms is used in 90% of the applications, low density (LDPE), linear low density (LLDPE) and high density (HDPE) (Table 1). Other forms of polyethylene include medium density (MDPE), ultra-high molecular weight polyethylene (UHMwPE).

Polyethylenes are frequently modified with other polyethylenes to improve processability, mechanical

Table 2. Density of various polyethylene (PE) grades.

Polyethylene grade	Density (kg/m ³)
Linear low density (LLDPE)	920-930
Low density (LDPE)	910-935
Medium density (MDPE)	940
High density (HDPE)	955-977

performance and other material properties. Depending on miscibility, such combinations can produce extremely complex rheological results with behaviors and concentrations spanning a range from those normally considered characteristic only of solutions, to those normally considered characteristic only of blends (Utracki, 2003). In a detailed review of the miscibility of polyethylene blends, Zhao and Choi (2006) points out that primarily it's the branch content and not the differences in molecular weight averages, molecular weight distribution, and branch length of the two polyethylenes that governs their miscibility.

Though immiscible under flow, an LLDPE/LDPE blend nevertheless behaves as a compatible combination. (Utracki and Schlund, 1987) The assertion of immiscibility of LLDPE/LDPE is supported by previous thermal studies of the combination under differential scanning calorimetry (DSC), generating the melting and recrystallization temperatures and creating the associated enthalpies, and degrees and types of crystallinity (Neway and Gedde, 2004). These studies have yielded distinct phase diagrams of the upper critical system temperature (UCST) form (Hill et al., 1992) Indeed, UCST proved the applicable phase diagram type for all PE/PE blends. Additional studies examined the blends' steady-state and dynamic tensile mechanical properties in the solid state. (Luyt and Hato, 2005)

Similarly to LLDPE/LDPE blends, LLDPE/HDPE and LDPE/HDPE blends have been studied in melt under conditions of oscillatory shear flow (Yamaguchi, 2006), elongation flow (Valenza et al., 1986), and steady state tensile elongation in the solid state. HDPE/HDPE (a like/like combination) blends have been examined, specifically targeting the effects of different molecular weights and the use of m-HDPE, using oscillatory shear flow, DSC and solid-state mechanical testing (Bai et al., 2010). The significance of this blend type is that it is considered miscible by all characterization techniques across all compositions and conditions used.

A blend type of particular interest under the purview of PE/PE mixtures is of PE with paraffin wax. This far, studies have considered only mixtures wherein each component possesses a molecular weight substantially above the critical molecular weight for entanglement of linear polyethylene ($M_c = 3660-3800$ g/mol) (Zang and Carreau, 1991). However, the molecular weights of paraffin oils and waxes are significantly below this value. Indeed, in order to examine any PE/PE mixture as if it

were a solution, at least one of the components must have a molecular weight below this M_c . Wax has been combined with or used as a modifier for LLDPE, LDPE, and HDPE, with studies performed targeting the rheological (Yang et al., 2004), thermal (Hato and Luyt, 2007), and solid-state mechanical properties (Lee et al., 2010). Additionally, wide angle x-ray diffraction (WAXD) has been employed to examine the crystallization of wax/wax blends, with the intensity pattern used to estimate the apparent degree of wax crystallinity (Lee et al., 2010). Small angle x-ray scattering (SAXS) has been used to study the phase structures in elongated HDPE/wax blends. (Ogino et al., 2006) Both WAXD and SAXS (in-situ) have been employed to study shear-induced crystallization precursors in model PE blends under flow conditions (Yang et al., 2004).

Polyethylene, its grades and blends mentioned, have contributed much to society wellbeing. The LDPE or LLDPE form is preferred for film packaging/shopping bags and for electrical insulation. HDPE is blow-moulded to make containers for household chemicals such as washing-up liquids and drums for industrial packaging. It is also extruded as piping. Other uses of Polyethylene blends include medical implants, cable and marine ropes, sail cloth, sport equipment, fish nets, concrete reinforcements, protective clothing, ponds lining material especially that contains industrial wastes, geotextile applications, making pipes for nuclear plants applications (Krishnaswamy, 2007) etc. However the good use of polyethylene is almost obscured by its potential harm arising from challenges in handling the products after use, and its strength against degradation as discussed in the following sections.

POLYETHYLENE DISPOSAL METHODS, RECYCLING AND ENERGY RECOVERY

Worldwide most polyethylene products after use, ends up in landfills, incinerated or in a recycling plant with higher percentages in landfills. Each method of disposal has its own limitations.

Landfills

The versatility and simplicity of landfills in terms of technical requirements, environmental and socio-

economic aspects makes it popular than other known techniques, for examples incinerate and biological composting (Malek and Shaaban, 2008). There are also other major deficiencies of "dry tomb" landfilling as reviewed by Lee and Jones-Lee (1996). A major drawback associated with landfill method is that the landfill facilities occupy space that could be put into other uses such as for agriculture or human settlement (Zhang et al., 2004). With slow degradability of Polyethylene for example, landfill waste have been shown to persist for more than 20 years (Tansel and Yildiz, 2011) meaning that the landfill space is unavailable for other uses for much longer time. The slow degradability is attributed to the inherent nature of polymer degradation and compounded by limited availability of oxygen in landfills; the surrounding environment is essentially anaerobic (Andrady, 2011; Massardier-Nageotte et al., 2006; Tollner et al., 2011). Plastic debris in landfill also acts as a source for a number of secondary environmental pollutants and these includes volatile organics, such as benzene, toluene, xylenes, ethyl benzenes and trimethyl benzenes, released both as gases and contained in leachate (Urase et al., 2008) and endocrine disrupting compounds, in particular BPA (Xu et al., 2011; Zhang et al., 2004). High concentrations of hydrogen sulphide are potentially lethal (Tsuchida et al., 2011). In addition, a major drawback to landfills from a sustainability aspect is that none of the material resources used to produce the plastic is recovered—the material flow is linear rather than cyclic (Hopewell et al., 2009).

Recycling and reuse

Polyethylene can easily be recycled and reintroduced into the production chain once more or reused e.g. waste polyethylene has been tested for reuse in road construction (Raju et al., 2007). However, low recycling and reuse rates are often observed in conventional centralized recycling plants due to the challenge of collection and transportation for high-volume low-weight polymers. The recycling rates decline further when low population density, rural and relatively isolated communities are investigated because of the distance to recycling centers makes recycling difficult and both economically and energetically inefficient (Kreiger et al., 2013). Consequently the traded volume of waste plastic globally is very minimal for example, less than 5% of the new plastics produced in 2012 (Velis, 2014).

Incineration

Incineration of waste offers a number of advantages including volume reduction of wastes and destruction of pathogens. However, the discharge of air pollutants may reduce the overall usefulness of incineration. Plastic

incineration overcomes some of the limitations placed on landfill in that it does not require any significant space, and there is even the capability for energy recovery in the form of heat (Sinha et al., 2010). However, there is a significant trade-off in that incineration of plastics leads to the formation of numerous harmful compounds, most of which are released to the atmosphere.

Heavy metals, toxic carbon- and oxygen-based free radicals, not to mention significant quantities of greenhouse gases, especially carbon dioxide, are all produced and released when plastics are incinerated (Shen et al., 2010). The significant environmental drawbacks of plastic disposal via both landfill and incineration were the driving force behind the development of plastic recycling processes.

POLYETHYLENE IMPACTS TO THE ENVIRONMENT

Among all the plastic debris collected on several debris studies on Oceans, Polyethylene, mostly HDPE and LDPE is among the plastics that constitutes the highest percentage (Thompson et al., 2004). This may infer that Polyethylene products are the highest plastic environmental pollutants. Next to Polyethylene in use and pollution quantities is Polypropylene (PP) (Morét-Ferguson et al., 2010; Corcoran et al., 2009; Barnes et al., 2009). Such high levels of plastic debris in the environment can be attributed to the high availability, high use of plastic products and its ability to persist in the environment (Frost and Cullen, 1997; Ivar do Sul and Costa, 2007). Polyethylene films from packaging and green houses for example cause hazardous and economically damaging effect to both marine and dry land environments (Webb et al., 2013). They poses threats to wildlife such as marine birds (Azzarello and Van Vleet, 1987), turtles (Barreiros and Barcelos, 2011), cetaceans (Baird and Hooker, 2000), fur seals (Pemberton et al., 1992), sharks (Sazima et al., 2002) and filter feeders (Moore et al., 2001; Wright et al., 2013). The main dangers associated with the plastic objects are ingestion (Denuncio et al., 2011; Laist, 1997; Lazar and Gracan, 2011; van Franeker et al., 2011; Yamashita et al., 2011) leading to internal and/or external abrasions, ulcers and choking and animals entanglement restricting movements (Webb et al., 2013). Plastic particles in the ocean have been shown to contain quite high levels of organic pollutants. Some of these compounds are added to plastics during manufacture while others adsorb to plastic debris from the environment (Thompson et al., 2009; Teuten et al., 2009). Toxic chemicals, such as polychlorinated biphenyls (PCBs), nonylphenol (NP), organic pesticides, such as dichlorodiphenyl-trichloroEthene (DDT), polycyclic aromatic hydrocarbons (PAHs), polybrominated diphenyl ethers (PBDEs) and bisphenol A (BPA) have been consistently found throughout oceanic plastic debris (Mato et al., 2001; Rios

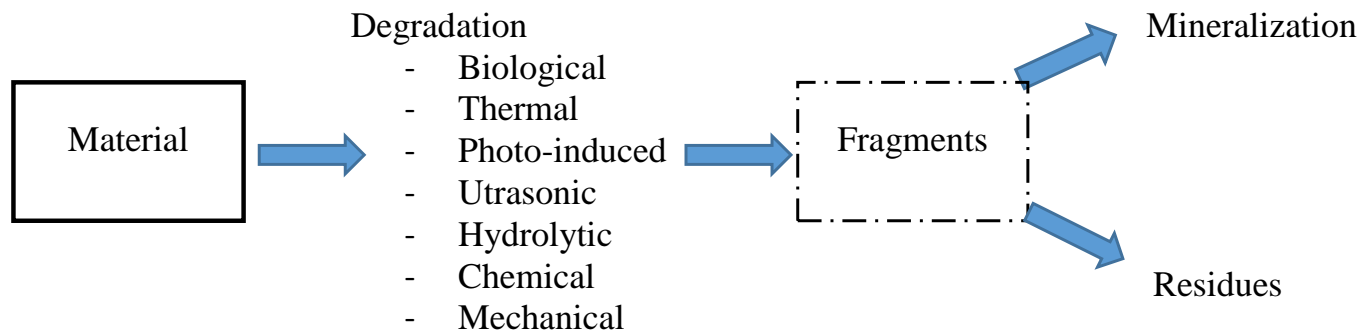


Figure 2. Schematic steps in polyethylene degradation process.

et al., 2007; Hirai et al., 2011). As mentioned earlier, most polyethylene products in their pure form are not toxic. However, when the material interacts with the environment, degradation occurs which may lead to formation of toxic and irritant Acrolein, Aldehydes and acids (Hakkarainen and Albertsson, 2004).

DEGRADATION OF POLYETHYLENE

Ultimate degradation of synthetic polymers may take several hundred years (Vasile, 1993; Matsumura, 2005; Gu, 2003; Gilan et al., 2004). Generally degradation is the irreversible process, that affects directly, or indirectly, several properties of the material related to its functional characteristics as a result of environmental factors (such as light, heat and moisture etc.), chemical condition or biological activity (Pospisil and Nespurek, 1997; Dilara and Briassoulis, 2000). Ultimately, degradation makes the materials susceptible to mechanical failure, leading to fragmentation and formation of residues or mineralization (Figure 2). It is the susceptibility to mechanical failure that scientists normally rely upon when monitoring the degree of degradation e.g. tensile strength, elongation at break (expressed as a %) stress at yield or the modulus of elasticity (Randy and Rabek, 1983). As mentioned above, degradation of polymers is induced by different external factors and mechanisms. Corresponding to the various environmental induction, the various polymer degradation types are;

- i) Thermal occurs- due to exposure to high temperatures (Singh et al., 2008),
- ii) photo-induced - on exposure to the UV radiation or any other high energy radiation, the polymer or its morphological defects or impurities within the polymer absorb the radiation, inducing degradative chemical chain reactions (Singh et al., 2008),
- iii) Mechanical- due to an application of mechanical stress /strain (Caruso et al., 2009).
- iv) Ultrasonic-due to the application of sound at certain

frequencies inducing vibrations and eventually breaking of the chains (Suslick and Price, 1999),

- v) hydrolytic –occurs in polymers containing functional groups which are sensitive to the effects of water (Gewert et al., 2015),
- vi) chemical-corrosive chemicals, such as ozone or the sulphur in agrochemicals, may attack the polymer chain causing bond breaking or oxidation (Gaca et al., 2008) and
- vii) Biological-specific to polymer with functional groups that can be attacked by microorganisms e.g. bacterial, fungi and algae (Restrepo-Flórez et al., 2014; Shah et al., 2008; Leja and Lewandowicz, 2010).

Just like for general polymers, polyethylene degradation initiation depends on where the material is being used and the type of environmental exposures it is prone to. For example, degradation of LDPE films used as greenhouse covering materials is governed mainly by thermal, radiation, mechanical and chemical mechanisms and not the other mentioned mechanisms (Dilara and Briassoulis, 2000).

Thermal-oxidative degradation of polyethylene

Most polymeric molecules are only stable below 100 - 200°C. Above some critical temperature, bond scission may occur with high frequency leading to quick deterioration of the polymer structure and properties. This critical temperature is usually higher than 400-600°C, and beyond which, the temperatures are able to provide sufficient energy for bonds scission. Typical bonds have a dissociation energy around 150-400 kJ per mole at 25°C. Polyethylene is practically stable up to 100°C in inert atmosphere (Schnabel, 1981) with a very low glass transition temperature of below 125K (Fakirov and Krasteva, 2000). Practically most polyethylene is used at ambient temperatures, the most extreme cases being in green houses that do not exceed 80°C. This means that degradation by chain scission due to thermos processes is rare and given little attention. However, elevated

temperatures can significantly increase the rate of various chemical reactions, such as oxidation, and therefore lead in an indirect way to degradation of the polymer. This effect is discussed further in the course of this research on photo-degradation.

Biodegradation of polyethylene

For degradation to be termed biodegradation and to occur, the following elements are indispensable.

1) Existences of microorganisms and their attachment to the surface of the polymer. These microorganisms should be able to grow utilizing the polymer as the source of carbon, that is, have an appropriate metabolic pathway to synthesize enzymes specific for the target substance to initiate depolymerization and mineralization of monomers and oligomers.

2) The environmental conditions such as oxygen, temperature, moisture, salts and pH should render the biodegradation processes possible.

3) The material structure also influences the degradation process. Therefore, chemical bonds, degree and type of branching, degree of polymerization (DP), degree of hydrophobicity, stereochemistry, molecular weight distribution (MWD), crystallinity and morphological aspects.

As a first step of biodegradation, cleavages of side chains or backbone lead to an increasing contact interface between microorganisms and polymers. Microorganisms can attach to the surface, if the polymer surface is hydrophilic. Since Polyethylene has only CH₂ groups, its surface is hydrophobic. The initial degradation (e.g. mechanical or photo-induced) that cleaves the side chains or backbones therefore, it is necessary to allow the insertion of hydrophilic groups on the polymer surface making it more hydrophilic (insertion of hydrophilic groups also decreases the surface energy). The second step in biodegradation, which often is referred as the primary biodegradation, involves fragmentation of the material, aided by extra cellular enzymes (endo-enzymes) secreted by the organism. The resultant low molecular weight compounds are further utilized by the microbes as carbon and energy sources. The last step, mineralization, occurs after the sufficiently small oligomeric fragments are bio assimilated by the microbes, resulting to the final products CO₂, CH₄, H₂O, N₂, H₂, salts, minerals and new biomass (BM). Under sulfidogenic conditions, the end products could also be H₂S, CO₂ and H₂O. The environmental conditions decide the group of microorganisms and the degradative pathway involved. Additives, antioxidants and other stabilizers added to commercial polyethylene may be toxic to the organisms or may slow down the rate of biodegradation. The following strategies are used to assess and monitor the

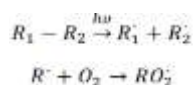
biodegradation of the polymers (Andrady, 1994, 2000; Arutchelvi et al., 2008; Zaikov and Gumargalieva, 2010).

- a) Accumulation of biomass (experimentally determine the growth rate of microorganisms with the polymer as the sole carbon source)
- b) Oxygen uptake rate
- c) Carbon dioxide evolution rate
- d) Products of reaction using chemical analysis
- e) Surface changes
- f) Changes in the mechanical and physical properties of the polymer.

Photodegradation

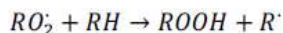
Mechanical properties of many plastic materials/polymers degrade upon exposure to high energy radiation (Amin et al., 1995; Hamid et al., 1992; Hollander and Behnisch, 1998). When the energetic UV radiation, 290-400 nm (Khan and Hamid, 1995) is absorbed by the polymer, direct photolysis could occur i.e. bond cleavages and depolymerization. On the other hand, the free radicals produced in this way may then react with the atmospheric oxygen and lead to further degradation of the plastic, which is called photo-oxidation (Dilara and Briassoulis, 2000). Generally, initiation and progression of photo degradative processes depends on the types of bonds present in the material (Dyson, 1992), radiation energy available at the earth's surface, presence of absorptive chromophores (mainly as impurities) in the polymer (Kroschwitz, 1990; Global, 2008; Dilara and Briassoulis, 2000; Schnabel, 1981), thickness of the material (Yakuphanoglu et al., 2005) etc. Light absorbed by chromophores especially the carbonyl groups can induce bond scission by either Norrish type I and type II processes. Whenever the carbonyl groups are on the polymer backbone both Norrish I and Norrish II processes cause main chain ruptures (Schnabel, 1981).

Therefore the mechanism of photodegradation in PE is one of thermo oxidative or photo oxidative degradation rather than of direct photolysis. The photo oxidative degradation of macromolecules is initiated by the absorption of light quanta by chromophoric groups and the products of thermo oxidative transformations of macromolecules (Goldade et al., 2004). The photo oxidative mechanism proceeds when free radicals that are formed by photo illumination react with molecular oxygen, the chemical quantum yield in presence of oxygen being rather high. Peroxides are formed according to the conventional mechanisms of autoxidation



Electronspin Resonance (ESR) measurements in a study

of long-lived free radicals in gamma – irradiated UHMWPE, PE showed changes from alkyl to peroxy radicals in air due to oxygen reaction, which did not change in vacuum (Choon et al., 2004). The auto oxidative process has three important steps namely, initiation, propagation and termination. Initiation in this case is by photo irradiation and there is formation of radicals. Propagation step can be divided into six steps and leads to the scission process of polymer alkoxy radicals with the formation of aldehyde end groups and end polymer alkyl radicals (Rabek, 1987).



The initiation process reactions are independent of temperature and cease when irradiation is removed. The secondary reactions, which includes oxidations are temperature dependent and can proceed without further irradiation (Birley et al, 1992). It's therefore hypothesized that initiation can be done pre- consumer use (for example during manufacture) of these short term use products. Once they are exposed to sunlight, propagation of the photodegradation take place with consequent degradation.

Mechanical degradation

PBMs respond to mechanical forces on the molecular level by changing conformation, chain slippage, segmental alignment, disentanglement, and ultimately bond scission. These molecular scale events evolve to the macroscale, resulting in the formation of crazes and cracks, ending in catastrophic failure (Caruso et al., 2009). PBMs, because of having higher molecular weights, free radicals are produced by chemical bond rupture during mechanical treatment (Stoekel et al., 1978). Smaller molecules are generally free to change positions and accommodate the applied mechanical stress that lead to rupture of chemical bonds are produced in macromolecules which possess lower mobility (Mills, 1993). Although bond scission is a relatively rare event, studies has shown that the rupture of bonds due to mechanical loading depends on the amount of elastic energy that a macromolecule is capable of storing and on the time the macromolecule remains under strain (Dilara and Briassoulis, 2000). Mostly energy is dissipated through non-chemical processes such as slippage of the chains, changes in chain conformation and crystallinity. Those two categories, chemical and non-chemical energy dissipation, compete with each other. In cases where the non-chemical processes are inhibited, such as in stiff polymers, e.g. nylon, the bond scission occurs with higher frequency. In contrast, more supple polymers, such as polyethylene, where strong bonding between macro- molecules does not exist, slippage of chains occurs more frequently and bond

scission less so (Igarashi and De Vries, 1983). However, LDPE still suffers to some extent of de-gradation due to mechanical loading. For linear macro-molecules, such as PE, it has been shown that the probability of scission is higher in the middle of the chain (Schnabel, 1981). In another work (Popov et al., 1983), increased degradation has been observed for LDPE held under tension (from 0 to 34 kg/mm²) in an ozone environment, that could not be explained by changes in the degree of crystallinity, orientation or chain mobility. The rate of oxidation decreased with increasing orientation and a linear relationship was observed between the level of stress and the degradation. Finally, increased reactivity of the stretched macromolecules, especially at the parts of the chains which are held in high tension, was put forth as a plausible explanation of the observed behavior.

Chemical degradation

The effect of a solvent on the structure of the polymer material can be significant at times. Most thermoplastics are soluble in several solvents. Usually, a swelling stage precedes the dissolution. Polymeric materials capable of forming crystallites, such as LDPE, tend to be rather resistant to physical interaction with solvents. Dissolution is impeded by the strong intermolecular interactions between macromolecules. Only when these interactions are overcome by thermal activation will the polymer swell and eventually dissolve. However, apart from the physical action of dissolution, solvents can also chemically attack such polymers. Immersion tests show that while PE had satisfactory resistance at ambient temperature to methanol and only limited resistance to acetone, it exhibits unsatisfactory resistance to other saturated hydrocarbons, benzene, carbon disulphide and carbon tetrachloride (Schnabel, 1981).

Environmental pollution can also be harmful to the structural integrity of the polyethylene due to chemical attack of the polymer bonds. Atmospheric pollutants such as nitrogen oxides, sulphur oxides, hydrocarbons and particulate can enhance the degradation of the polymers (Ranby and Rabek, 1983; Schnabel, 1981; Dilara and Briassoulis, 2000), especially when combined with applied stress (Igarashi and De Vries, 1983) and must also be taken into account. For instance, infrared studies have revealed that polyethylene reacts with NO₂ at elevated temperatures, and that chemical attack is observed even at 25°C, probably due to the presence of impurity olefinic bonds which react readily with NO₂ (Schnabel, 1981). Similarly, SO₂ is rather reactive, especially in the presence of UV irradiation, which it readily absorbs and forms triplet excited sulphur dioxide (3SO₂*). This species is capable of abstracting hydrogen from the polymer chains leading to the formation of macroradicals in the polymer structure, which in turn can undergo further depolymerization (Schnabel, 1981).

Even more severe is the chemical attack brought upon the polymer films by the use of agrochemicals combined with the UV irradiation in greenhouses. The agrochemicals most commonly used are sulphur and halogen containing compounds. Trials have shown that combinations of agrochemicals can severely limit the service life of the LDPE greenhouse coverings (Dilara and Briassoulis, 2000; Desriac, 1991). Sulphur containing pesticides were shown to be particularly harmful and extremely high concentrations of sulphur have been found in LDPE films after pesticide use. In a relevant study (Desriac, 1991), the effect of the daily spray of cyspermethrin on three types of films, long-life PE, Filled PE and EVA, was studied in conjunction with accelerated ageing. All films showed increased degradation, compared to the non-sprayed films, starting at 12-16 days of accelerated ageing depending on the film. The problem of rapid degradation due to pesticide use could not be controlled by increased concentration of stabilizers, but increased thickness seemed to improve the situation. Similar results were reported from studies of natural ageing performed in Spain and Italy (Henninger and Pedrazetti, 1988). In fact, it is clear that the problem depends heavily on the type of pesticide applied, the method and frequency of application, ventilation and the structure of the greenhouse.

CONCLUSION

There is a seemingly increasing demand for the production and use of polyethylene, arising from its important properties that can be summarized as follows; it is *strong*, it is *safe* and it is *versatile*. This continued use, coupled with poor reuse, low recycling and challenging waste disposal strategies is a major threat to both land and marine environments. Many suggestions have been put forward in response to the menace caused by Polyethylene pollution. They include, Increase taxes on single use plastic products, Adoption of biodegradable plastic bottles, improving recycling technologies, and finally, implementing bans on plastic if and only if sufficient alternatives have been accepted and in good supply in the community. However of all the suggested strategies recycling makes economic as well as environmental. Hence more effort should be geared towards enhancement of substantial increase in the rate of recovery and recycling of polyethylene wastes. This could start from tackling the significant challenges that exist from both technological factors and from economic or social behavior issues relating to the collection of recyclable wastes, and substitution for virgin material.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

REFERENCES

- Andrady AL (1994). Assessment of Environmental Biodegradation of Synthetic Polymers. *Journal of Macromolecular Science, Part C*. 34(1):25-76.
- Andrady AL (2000). *Handbook of Polymer Degradation*, 2nd edn (ed. S.H. Hamid), Marcel Dekker, New York P 441.
- Andrady AL (2011). Micro plastics in the marine environment. *Marine Pollution Bulletin* 62:1596-1605.
- Arutchelvi J, Sudhakar M, Arkatkar A, Doble M, Bhaduri S, Uppara PV (2008). Biodegradation of polyethylene and polypropylene *Indian Journal of Biotechnology* 7:9-22
- Azzarello MY, van Vleet ES (1987). Marine birds and plastic pollution. *Marine Ecology Progress Series* 37:295-303.
- Bai L, Li YM, Yang W, Yang MB (2010). Rheological behavior and mechanical properties of high-density polyethylene blends with different molecular weights. *Journal of Applied Polymer Science* 118:1356-1363.
- Baird RW, Hooker SK (2000). Ingestion of plastic and unusual prey by a juvenile harbour porpoise. *Marine Pollution Bulletin* 40:719-720.
- Barnes DKA, Galgani F, Thompson RC, Barlaz M (2009). Accumulation and fragmentation of plastic debris in global environments. *Philosophical Transactions of the Royal Society B*. B 364:1985-1998.
- Barreiros JP, Barcelos J (2001). Plastic ingestion by a leatherback turtle *Dermochelys coriacea* from the Azores (NE Atlantic). *Marine Pollution Bulletin* 42:1196-1197.
- Caruso MM, Davis DA, Shen Q, Odom SA, Sotto NR, White SR, Moore JS (2009). Mechanically-Induced Chemical Changes in Polymeric Materials. *Chemical Reviews*. 109(11):5755-5798.
- Corcoran PL, Biesinger MC, Grifi M (2009). Marine Pollution Bulletin *Plastics and beaches: A degrading relationship*. *Marine Pollution Bulletin* 58(1):80-84.
- DeMatteo R (2011). Chemical exposure and plastics production: issues for women's health | A Review of literature. National Network on Environments and Women's, Health. Available online, <http://www.nnewh.org/images/upload/attach/2502NNEWH%20Lit%20Review%20-%20Chem%20Exp%20and%20Plastics%20Production.pdf>
- Denuncio P, Bastida R, Dassis M, Giardino G, Gerpe M, Rodriguez D (2011). Plastic ingestion in Franciscana dolphins, *Pontoporia blainvillei* (Gervais and d'Orbigny, 1844), from Argentina. *Marine Pollution Bulletin* 62(8):1836-1841.
- Desriac P (1991). The effect of pesticides on the life of greenhouse films. FAO. <http://agris.fao.org/agris-search/search.do?recordID=FR9202159>
- Dilara PA, Briassoulis D (2000). Degradation and Stabilization of Low-density Polyethylene Films used as Greenhouse Covering Materials. *Journal of Agricultural Engineering* 76(4):309-321.
- Dyson R (1992). *Specialty Polymers*. Blackie Academic and Professional. Willy science publishers. Great Britain P 16.
- Fakirov S, Krasteva B (2000). On the Glass Transition Temperature of Polyethylene as Revealed by Microhardness Measurements. *Journal of Macromolecular Science, Part B-Physics* 39(29):297-301.
- Frost A, Cullen M (1997). Marine debris on northern New South Wales beaches (Australia): Sources and the role of beach usage. *Marine Pollution Bulletin* 34(5):348-352.
- Gaca P, Drzewiecka M, Kaleta W, Kozubek H, Nowińska K (2008). Catalytic Degradation of Polyethylene over Mesoporous Molecular Sieve MCM-41 Modified with Heteropoly Compounds. *Polish Journal of Environmental Studies* 17(1):25-31.
- Gewert B, Plassmann MM, MacLeod M (2015). Pathways for degradation of plastic polymers floating in the marine environment (Critical Review). *Environmental Science: Processes and Impacts*. 17(9):1513-1521.
- Gilan I, Hadar Y, Sivan A (2004). Colonisation and biofilm formation and biodegradation of polyethylene by a strain of *Rhodococcus ruber*. *Applied Microbiology and Biotechnology* 65(1):97-104.
- Global C (2008). www.gcio.org/UNEP1998/UNEP98p62. Accessed 21st July 2008 4.25PM
- Gu JD (2003). Microbiological deterioration and degradation of synthetic polymeric materials: Recent research advances. *International Biodeterioration and Biodegradation* 52(2):69-91.

- Hakkarainen M, Albertsson AC (2004). Long Term Properties of Polyolefins Chapter; Environmental Degradation of Polyethylene. 169:177-200. Springer Berlin Heidelberg.
- Hato MJ, Luyt AS (2007). Thermal fractionation and properties of different polyethylene/wax blends. *Journal of Applied Polymer Science* 104(4):2225-2236.
- Hayden KW, Jaimys A, Russell JC, Elena PI (2013). Plastic Degradation and Its Environmental Implications with Special Reference to Poly(ethylene terephthalate). *Polymers* 5:1-18
- Henninger F, Pedrazetti E (1988). Aspects of greenhouse film stabilization. *Plasticulture* 80(4):5-24.
- Hill MJ, Barham PJ, Keller A (1992). Phase segregation in blends of linear with branched polyethylene: the effect of varying the molecular weight of the linear polymer. *Polymer* 33(12):2530.
- Hirai H, Takada H, Ogata Y, Yamashita R, Mizukawa K, Saha M, Kwan C, Moore C, Gray H, Laursen D, Zettler ER, Farrington JW, Reddy CM, Peacock EE, Ward MW (2011). Organic micropollutants in marine plastic debris from the open ocean and remote and urban beaches. *Marine Pollution Bulletin* 62(8):1683-1692.
- Hollander A, Behnisch J (1998). Vacuum-ultraviolet photolysis of polymers. *Surface and Coatings Technology* 98(1-3):855-858.
- Hopewell J, Dvorak R, Kosior E (2009). Plastics recycling: challenges and opportunities. *Philosophical Transactions of the Royal Society of London. Series B, Biological Sciences* 364(1526):2115-2126.
- Ivar do Sul JA, Costa MF (2007). Marine debris review for Latin America and the wider Caribbean region: From the 1970s until now, and where do we go from here? *Marine Pollution Bulletin* 54:1087-1104.
- Kreiger M, Anzalone GC, Mulder ML, Glover A, Pearce JM (2013). Distributed Recycling of Post-Consumer Plastic Waste in Rural Areas. *MRS Online Proceedings Library*, 1492. doi:10.1557/opl.2013.258.
- Krishnaswamy P (2007). Report on review of literature on the use of polyethylene (pe) piping in nuclear power plant safety-related class 3 service water systems. A report to the United States nuclear regulatory commission. <http://www.nrc.gov/docs/ml1426/ml14266a208.pdf> accessed online on 27th august 2016
- Laist DW (1997). Impacts of marine debris: entanglement of marine life in marine debris including a comprehensive list of species with entanglement and ingestion records. In: J.M. Coe, D.B. Rogers (Eds.), *Marine Debris—sources, Impacts and Solutions*, Springer-Verlag New York Inc., New York pp. 99-139.
- Lazar B, Gracan R (2011). Ingestion of marine debris by loggerhead sea turtles, *Caretta caretta*, in the Adriatic sea. *Marine Pollution Bulletin* 62(1):43-47.
- Lee EJ, Park JK, Lee YS and Lim KH (2010). Comparison of thermal properties of crude by-product polyolefin wax, fractionated paraffin wax and their blend. *Journal of Chemical Engineering* 27(2):524-530.
- Lee GF, Jones-Lee A (1996). "Dry Tomb Landfills". *MSW Management* 6(1):82-89.
- Leja K, Lewandowicz G (2010). Polymers Biodegradation and Biodegradable Polymers-a Review. *Polish Journal of Environmental Studies* 19(2):255-266.
- Lithner D, Damberg J, Dave G, Larsson K (2009). Leachates from plastic consumer products—screening for toxicity with *Daphnia magna*. *Chemosphere* 74(9):1195-200.
- Luyt AS, Hato MJ (2005). Thermal and mechanical properties of linear low-density polyethylene/low-density polyethylene/wax ternary blends *Journal of Applied Polymer Science* 96(5):1748-1755.
- Malek MI, Shaaban MG (2008). Landfill Common Method and Practices of Solid Wastes Disposal in Malaysia. Conference Paper · November 2008. Conference: ISWA, At Singapore.
- Massardier-Nageotte V, Pestre C, Cruard-Pardet T, Bayard R (2006). Aerobic and anaerobic biodegradability of polymer films and physico-chemical characterization. *Polymer Degradation and Stability* 91(3):620-627.
- Mato Y, Isobe T, Takada H, Kanehiro H, Ohtake C, Kaminuma T (2001). Plastic resin pellets as a transport medium for toxic chemicals in the marine environment. *Environmental Science and Technology* 35(2):318-324.
- Matsumura S (2005). Mechanism of biodegradation, in *Biodegradable polymers for industrial applications*, edited by R Smith (Woodhead, England) pp. 357-409.
- Moore CJ, Moore SL, Leecaster MK, Weisberg SBA (2001). Comparison of plastic and plankton in the north Pacific central gyre. *Marine Pollution Bulletin* 42(12):1297-1300.
- Morét-Ferguson S, Law KL, Proskurowski G, Murphy EK, Peacock EE, Reddy CM (2010). The size, mass, and composition of plastic debris in the western North Atlantic Ocean. *Marine Pollution Bulletin* 60(10):1873-1878.
- Neway B, Gedde UW (2004). Influence of the method of mixing on homogeneity and crystallization kinetics of blends of linear and branched polyethylene. *Journal of Applied Polymer Science* 94(4):1730-1736.
- Ogino Y, Fukushima H, Matsuba G, Takahashi N, Nishida K, Kanaya T (2006). Effects of high molecular weight component on crystallization of polyethylene under shear flow. *Polymer* 47(15):5669-5677.
- Pemberton D, Brothers NP, Kirkwood R (1992). Entanglement of Australian fur seals in man-made debris in Tasmanian waters. *Wildlife Research* 19(2):151-159.
- Plastics Europe (2012). *Plastics-The Facts 2012*. Available online: <http://www.plasticseurope.org/Document/plastics-the-facts-2012.aspx?FoIID=2>
- Plastics Europe (2013). *Plastics – the Facts 2013*. An analysis of European latest plastics production, demand and waste data. Plastics Europe, European Plastics Converters, European Association of Plastics Recycling and Recovery Organizations and European Plastics Recyclers.
- Pospisil J, Nespurek S (1997). Highlights in chemistry and physics of polymer stabilization. *Macromolecular Symposia* 115:143-163.
- Rabek JF (1987). *Mechanism of Photophysical Process and Photochemical Reaction in polymers*. New York: John Wiley and Sons.
- Raju SS, Murali M, Rengaraju VR (2007). Reuse of polyethylene waste in road construction. *Journal of Environmental Science and Engineering* 49(1):67-70.
- Ranby B, Rabek JF (1983). In: *The Effects of Hostile Environments on Coatings and Plastics* (Garner D P; Stahl G A eds), ACS Symposium Series pp. 291-307.
- Rappaport H (2011). *Ethylene and Polyethylene Global Overview*. SPI Film and Bag.
- Restrepo-Flórez J, Bassi A, Thompson MR (2014). Microbial degradation and deterioration of polyethylene. A review. *Int. Biodeterior. Biodegradation* 88:83-90.
- Rios LM, Moore C, Jones PR (2007). Persistent organic pollutants carried by synthetic polymers in the ocean environment. *Marine Pollution Bulletin* 54(8):1230-1237.
- Sazima I, Gadig OBF, Namora RC, Motta FS (2002). Plastic debris collars on juvenile carcharhinid sharks (*Rhizoprionodon lalandii*) in southwest Atlantic. *Marine Pollution Bulletin* 44(10):1147-1149.
- Schnabel W (1981). *Polymer Degradation, Principles and Practical Applications*. Macmillan Publishing Co. New York pp. 95-151.
- Shah AA, Hassan F, Hameed A, Ahmed S (2008). Biological degradation of plastics: A comprehensive review. *Biotechnology Advances* 26(3):246-265.
- Shen C, Tang X, Yao J, Shi D, Fang J, Khan MI, Cheema SA, Chen Y (2010). Levels and patterns of polycyclic aromatic hydrocarbons and polychlorinated biphenyls in municipal waste incinerator bottom ash in Zhejiang province, China. *Journal of Hazardous Materials* 179(1-3):197-202.
- Sinha V, Patel MR, Patel JV (2010). PET waste management by chemical recycling: A review. *Journal of Polymers and the Environment* 18(1):8-25.
- Stoekel TM, Blasius J, Crist B (1978). Chain Rupture and Tensile Deformation of Polymers. *Journal of Polymer Science Part B: Polymer Physics* Ed. 16:485-500.
- Suslick KS, Price GJ (1999). Applications of Ultrasound to Materials Chemistry. *Annual Review of Material Research* 29(1):295-326.
- Tansel B, Yildiz BS (2011). Goal-based waste management strategy to reduce persistence of contaminants in leachate at municipal solid waste landfills. *Environment, Development and Sustainability*. 13(5):821-831.
- Teuten EL, Saquing JM, Knappe DRU, Barlaz MA, Jonsson S, Björn A, Rowland SJ, Thompson RC, Galloway TS, Yamashita R, Ochi D,

- Watanuki Y, Moore C, Viet PH, Tana TS, Prudente M, Boonyatumanond R, Zakaria MP, Akkhavong K, Ogata Y, Hirai H, Iwasa S, Mizukawa K, Hagino Y, Imamura A, Saha M, Takada H (2009). Transport and release of chemicals from plastics to the environment and to wildlife. *Philosophical Transactions of the Royal Society B* 364:2027-2045.
- Thompson RC, Moore CJ, vom Saal FS, Swan SH (2009). Plastics, the environment and human health: current consensus and future trends. *Philosophical Transactions of the Royal Society B* 364:2153-2166.
- Thompson RC, Olsen Y, Mitchell RP, Davis A, Rowland SJ, John AW, McGonigle D, Russell AE (2004). Lost at sea: where is all the plastic? *Science* 304(5672):838.
- Tollner EW, Annis PA, Das KC (2011). Evaluation of strength properties of polypropylene-based polymers in simulated landfill and oven conditions. *Journal of Environmental Engineering* 137(4):291-296.
- Tsuchida D, Kajihara Y, Shimidzu N, Hamamura K, Nagase M (2011). Hydrogen sulfide production by sulfate-reducing bacteria utilizing additives eluted from plastic resins. *Waste Management and Research* 29(6):594-601.
- Urase T, Okumura H, Panyosaranya S, Inamura A (2008). Emission of volatile organic compounds from solid waste disposal sites and importance of heat management. *Waste Management and Research* 26(6):34-538.
- Utracki LA (2003). Introduction to Polymer Blends. In: Utracki L.A. (eds) *Polymer Blends Handbook*. Springer, Dordrecht. https://doi.org/10.1007/0-306-48244-4_1
- Utracki LA, Schlund B (1987). Linear low density polyethylenes and their blends: Part 4 shear flow of LLDPE blends with LLDPE and LDPE. *Polymer Engineering and Science* 27:1512-1522.
- Valenza A, LaMantia FP, Acierno DJ (1986). The Rheological Behavior of HDPE/LDPE Blends. V. Isothermal Elongation at Constant Stretching Rate. *Journal of Rheology* 30:1085.
- van Franeker JA, Blaize C, Danielsen J, Fairclough K, Gollan J, Guse N, Hansen PL, Heubeck M, Jensen JK, Guillou GL, Olsen B, Olsen KO, Pedersen J, Stienen EW, Turner DM (2011). Monitoring plastic ingestion by the northern fulmar *Fulmarus glacialis* in the North Sea. *Environmental Pollution* 159(10):2609-2615.
- Vasile C (1993). Degradation and decomposition, in *Handbook of polyolefins synthesis and properties*, edited by Vasile C, Seymour RB (Marcel Dekker Inc, New York) pp. 479-506.
- Vasile C, Pascu M (2005). *Practical Guide to Polyethylene*. Rapra Technology Ltd. Shawbury, UK. 15 p.
- Velis CA (2014). Global recycling markets - plastic waste: A story for one player – China. Report prepared by FUELogy and formatted by D-waste on behalf of International Solid Waste Association - Globalisation and Waste Management Task Force. ISWA, Vienna, September 2014.
- Webb HK, Arnott J, Crawford RJ, Ivanova EP (2013). Plastic Degradation and Its Environmental Implications with Special Reference to Poly (ethylene terephthalate). *Polymers* 5(1):1-18.
- Wright SL, Thompson RC, Galloway TS (2013). The physical impacts of microplastics on marine organisms: A review. *Environmental pollution* 178:483-492.
- Xu SY, Zhang H, He PJ, Shao LM (2011). Leaching behaviour of bisphenol A from municipal solid waste under landfill environment. *Environmental Technology* 32(11):1269-1277.
- Yakuphanoglu F, Sekerci M, Balaban A (2005). The effect of film thickness on the optical absorption edge and optical constants of the Cr (III) organic thin films. *Optical Materials* 27(8):1369-1372.
- Yamaguchi M (2006). Anomalous rheological properties of polyethylene molecular composites. *Polymer Engineering and Science* 46(9):1284-1291.
- Yamashita R, Takada H, Fukuwaka M, Watanuki Y (2011). Physical and chemical effects of ingested plastic debris on short-tailed shearwaters, *Puffinus tenuirostris*, in the North Pacific ocean. *Marine Pollution Bulletin* 62(12):2845-2849.
- Yang L, Somani RH, Sics I, Hsiao BS, Klob R, Fruitwala H, Ong C (2004). Shear-Induced Crystallization Precursor Studies in Model Polyethylene Blends by in-Situ Rheo-SAXS and Rheo-WAXD. *Macromolecules* 37(13):4845-4859.
- Zaikov GE, Gumargalieva KZ (2010). Biodegradation of Polymeric Materials. Generalized Kinetic Data. *Mol. Crystals and Liquid Crystals* 523(1):148/(720)-159/(731).
- Zang YH, Carreau PJ (1991). A correlation between critical end-to-end distance for entanglements and molecular chain diameter of polymers. *Journal of Applied Polymer Science* 42(7):1965-1968.
- Zhang J, Wang X, Gong J, Gu Z (2004). A study on the biodegradability of polyethylene terephthalate fiber and diethylene glycol terephthalate. *Journal of Applied Polymer Science* 93(3):1089-1096.
- Zhao L, Choi P (2006). A Review of the Miscibility of Polyethylene Blends. *Materials and Manufacturing Processes* 21(2):135-142.