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Standard and Processing of Photodegradable Polyethylene

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***Abstract*—**The introduction of degradable plastic materials into agricultural sectors has represented a promising alternative to promote green agriculture and environmental friendly of modern farming practices. Major challenges of developing degradable agricultural films are to identify the most feasible types of degradation mechanisms, composition of degradable polymers and related processing techniques. The incorrect choice of degradable mechanisms to be applied during the degradation process will cause premature losses of mechanical performance and strength. In order to achieve controlled process of agricultural film degradation, the compositions of degradable agricultural film also important in order to stimulate degradation reaction at required interval of time and to achieve sustainability of the modern agricultural practices. A set of photodegradable polyethylene based agricultural film was developed and produced, following the selective optimization of processing parameters of the agricultural film manufacturing system. Example of agricultural films application for oil palm seedlings cultivation is presented.

***Keywords*—**Photodegradable polyethylene, plasticulture, processing schemes.

I. Introduction

THE application of photodegradable polymers in agriculture (plasticulture) has increasing spectacularly in the last two decades [1] and becoming a better option for a sustainable agricultural practices [2]. The introduction of plasticulture in the last five decades was initially begun in developed countries [2] and was later commenced to the developing countries such as India and Thailand [1]. Application of plasticulture can be seen in the soil mulching system, construction of greenhouses [1], drip irrigation system [3] and composts and seedling bags [4] and other agricultural plastics. The use of polyethylene in many sectors is driven by its bioinert property where it is less likely to be degraded easily in nature without degradative additive or blended with other degradable polymers such as poly(lactic acid) or PLA and starch.

It is known that polymeric material itself is considered non-degradable due to its slow degradation rate process [5]. Polymeric material such as polyethylene is highly stable due to its long chain of ethylene monomer that is highly hydrophobic, which means the component is less likely to react with water molecule in order to induce biodegradability. The compound is recalcitrant and remains inert in natural environment thus causing to its accumulation and there creating detrimental environmental problem [6]. However, due to its high availability and low prices, polymeric materials such as linear low density polyethylene (LLDPE), low density polyethylene (LDPE), high density polyethylene (HDPE) and polypropylene (PP) are used widely in many sectors such as agriculture, product packaging and also medical equipment.

The advancement of polymer degradation has brought researchers to develop degradable plastic additive to promote degradation reaction of conventional thermoplastics that is not readily degradable in nature. There are different types of polymer additives which can be processed together with selected polyolefin depending on suitability and purposed of product, in order to induce degradation. The commonly used degradative additive is metal complexes and co-polymerisation of conventional thermoplastic with readily degradable polymeric material such as starch and polyvinyl alcohol (PVA) [7]. There are enormous benefits of plastic additives such as to provide easiness during processing stages, to make the plastic product looks good for end market, making the plastic product works longer and to produce a safer and cleaner plastic manufactured goods in the market.

In the last decade, metal complexes additive is widely studied [7] and already being commercialized into commercial application of plastic products and bags. However, metal complex additive has potential to be leached out into environment when the plastic is starting to degrade, hence causing harm to the flora and fauna of the nature. Though, heavy metal complexes are widely used due to its availability and cheaper cost [4].

The leaching of metal complex additives from commercial plastics into the environment can cause harm effect to the soil condition. The accumulation of metal complexes can retard nutrient absorption by plant root and when leached into water channel, can affect the marine food source quality. The accumulated metal complexes in marine food source can be transferred to human when it is consumed and it can cause health problem to human.

The addition of foreign substances into virgin polymeric material can cause changes on its process ability. It is known that commercially used polymeric material, such as polyethylene has distinguished processing method and easily replicated either in laboratory or manufacturing facilities. However, there is an arising issue when foreign component is compounded together with polyethylene in normal setting,

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temperature and condition. The addition of photodegradant into polyethylene resin and the extrusion of the materials are problematic due to different melting index and melting temperature. Thus, this paper is aimed to present the processing setting of polyethylene supplemented with photodegradant developed by Green Polymer Research Group [7]. This paper is also aim to depict related standards and application of photodegradable polyethylene in today's world.

II. Literature Review

A. Degradable Polyethylene

Polyethylene is considered non degradable due to its inert properties to nature. Although in theory, all kind of polymer is subject to degradation in nature, however the rate is too slow to be considered fully safe and not harmful to nature. The application of polyethylene in many sectors, especially agriculture has made degradability aspect of it becomes more prominent and important. In the last decade, the intensive and semi-intensive agricultural practices in the Europe used large amount of plastics materials for soil mulches, pipes for irrigation systems and fertilizer sacks [4]. However, the extensive use of non-degradable polyethylene had caused harmful wastes accumulation in rural areas and also in agricultural lands. Most of agricultural polyethylene are non-degradable and is categorized as generally low-recyclability because in most condition, the plastic materials are consist of thin plastic films and commonly heavily contaminated with dirt and soil.

The most common practices for waste disposal are to either burn them or bury in the soil [4]. Burying the plastic waste is less expensive and time saving compared to collecting them, clean and prepared for recycling. Especially for thin films, they are not readily collectable and the foreign contaminant is common which can get up to 80% of the total weight of the waste itself. The cost to recovering used agricultural films are much higher and hence if not left in the soil, the waste is commonly buried in the landfills, which does not either solve or lessen the pollution issue. Burying agricultural films to dispose them can cause negative effect to the soil condition and eventually environment.

The growing use of plasticulture has enabled farmers to increase their productivity and systematically upgraded their production schemes. Crop technology and advancement of plasticulture have made the use of degradable plastic materials to be more important. The use of degradable plastic material is expanding in the agricultural sectors especially for soil mulching system where the plastic materials are often left in the soil after usage. In order for farmer to reuse the soil, they will roto-tilled it [8] and hence fragmenting the mulching materials. The degradable plastic or polyethylene films will eventually continue breaking down into smaller pieces and degraded by the microorganisms in the soils. This technique of applying plasticulture is much easier and practical. Although the application of degradable polyethylene or other degradable polymeric materials such as polypropylene in agriculture is not fully practiced, especially for pots and clips, the benefits are obvious and proven worthy. This in return can be a powerful marketing tool because it is not only environmental friendly, which is later translated into green agricultural technology; it is also save farmers' time and money.

Degradable polymers are consisted of materials that are [8]:

i. When exposed to nature environment, the polymer chains will break down into smaller fragments by microorganisms such as fungi and bacteria.
ii. The monomer is totally mineralized into carbon dioxide (CO_2), water molecule (H_2O) and inorganic biomass under aerobic conditions.
iii. The rate of mineralization is high and compatible with composting process.

The current use of degradable plastics in Europe, which is mainly bio-based is very limited, which is only about 2000 tons/year in 2006 [4]. However, the amount is increasing for a specific application in agriculture especially for soil mulching systems, plant pots, nets and bags. In Malaysia, the use of non-degradable polyethylene bags is everywhere, especially in plantation land. 13.9% of total land in Malaysia is covered with oil palm plantation, which means millions of oil palm seedlings being transplanted in every interval year. The conventional polyethylene bags are left on the soil after transplanting seedling into plantation field and the number of leftover waste are increasing by year. Thus, the application of degradable polyethylene bags to for seedlings cultivation is helpful [9] and can reduce the soil infertility problem caused by the plastic wastes.

B. Types of Degradation

There are few different types of degradation processes either with help of additive or naturally occurred. The four degradation conditions which differ according to their degradation reactions are [10]:

i. Thermal degradation: this degradation condition is classified into two subcategories, namely thermal degradation in the absence of oxygen (thermal decomposition) and thermal degradation in the presence of oxygen (thermal oxidation).
ii. Chemical degradation: this degradation condition can be happened with the help of chemical factors such as oxidation and hydrolysis of the polymer and acidic/basic condition of the materials.
iii. Biological degradation: this degradation condition is the most common degradation reaction especially for the bio-based polymer such as starch based plastics. This kind of degradation can occur either indoor or outdoor, as the rate of degradation is increased with the number of microorganisms, moisture and heat.
iv. Photodegradation: photodegradation is an ordinary degradation reaction mostly occurred to UV light sensitive material such as polypropylene. The reaction is induced by UV irradiation. The reaction is subcategorized into two classification, namely photodegradation with the absence of oxygen (photodecomposition) and photodegradation with the presence of oxygen (photooxidation). However, photooxidation is much more

relevant for researches due to its natural condition and relevancy.

Initiation

$$R\text{-}H \longrightarrow R\bullet + H\bullet$$

Propagation

$$R\bullet + O_2 \longrightarrow R-O-O\bullet$$

$$R-O-O\bullet + R\text{-}H \longrightarrow R-O-O-H + R\bullet$$

Termination

$$2R\bullet \longrightarrow R\text{-}R$$

$$R-O-O\bullet + R\bullet \longrightarrow R-O-O-R$$

$$2R-O-O\bullet \longrightarrow 2R-O\bullet + O_2$$

R: Polymer substituent

Fig. 1 Photooxidation mechanism of polymer materials in the presence of oxygen [10]

Degradation reaction of conventional polymer can be induced with additives that are sourced either chemical or natural based. Some of aromatic hydrocarbon and metallic compound can act as sensitizer of the photooxidation such as ferum and titanium. When the photooxidation is triggered, the oxidized layer can be appeared up to 20µm depth from the surface [10]. Upon degradation by UV irradiation, the mechanical strength of the polyethylene or any other polymer will reduce and this process is irreversible.

Photooxidation can also be induced with the blend of polypropylene to the polyethylene compound. Polypropylene is sensitive to UV irradiation and the polymer chain will start to break down upon sunlight exposure. The photon energy from the UV irradiation induced break down mechanism and cause the scissions of polymeric chain. Previous research has proved that polypropylene alone can be degraded when exposed to sunlight [11]. The mechanism of photodegradation as depicted in Fig. 1. It is demonstrated that higher intensity of sunlight reduce the tensile strength of the polypropylene films and hence the overall strength.

Photodegradation of polyethylene can be induced with impurity in the polymer chains. The photodegradant (RM master batch) previously developed [7] has been proved can induce and promote higher rate of photodegradation under tropical climate in Malaysia. The natural based photodegradant promote photodegradation initiation of polyethylene by mean of free radical formation formed from decomposition of chromophoric impurities during the processing procedures [11]. Once the degradation has been initiated with the help of natural based RM master batch photodegradant, the chemical degradation will occur via autocatalytic processes [11]. As a result, formation of carbonyl group products such as ketones, carboxylic acid and ester will be increased over time. The rate of photodegradation can be traced via observing these carbonyl group products formations. Another explanation for photodegradation mechanism is the process is normally induced by the addition of photosensitive polymer additive which when exposed under UV lights, will release free radicals and randomly attack and break polymeric bonds which are susceptible for oxidation under aerobic environmental and produce carbonyl group products [12]. The photodegradation of polyethylene is at the most, with help of RM master batch photodegradant, under terrestrial sunlight at wavelength as short as ~290nm up to the visible through the infrared region [13]. The most energetic, thus most damaging part of this spectrum is in the near UV region, where the energy is consider sufficient to break a chemical bond of a polymer [13]. The excitation of electrons by mean of lower energy process such as photolysis excites the electrons within the specific functional groups presents in the polymer such as carbonyl groups [14].

III. Standards Relevant to Photodegradation of Polyethylene

A. ASTM Norms and Standards for Degradation of Plastics

TABLE I
ASTM Standards and Norms for Degradable and Photodegradable Plastics

ASTM	Title	Specification
D6400-12	Compostable plastic	This specification covers products made from plastic that are designated to be composted under aerobic condition where thermophilic reaction is achieved.
D6954-04(2013)	Oxidation and biodegradation of plastics	The standard provides a framework to rate and compare the controlled laboratory rates of degradation and degree of physical property losses.
D883-12	Terminology	Covers the definition of technical terms used in plastic industry.
D5272-08(2013)	Photodegradable plastic	Outdoor exposure testings of photodegradable plastics. Provides information on characterization of exposure.
D5071-06(2013)	Photodegradable plastic	Specific procedures and test condition that are applicable for xenon arc exposure of photodegradable plastics.
D5208-09	Photodegradable plastics	Covers specific procedures applicable for fluorescence ultraviolet exposure of photodegradable plastics.
D3826-98(2013)	PE and PP tensile test	Determination of degradation point for PE and PP
D4364-13	Outdoor accelerated weathering	This practice covers the use of Fresnel-reflecting concentrators that use the sun as a source of ultraviolet (UV) and longer wavelength radiation.

ASTM D6400-12 covers the specification of acceptable decomposition of plastics and polymeric materials under municipality wastes facilities. The standard sets that the compostable polymer must be satisfactorily disintegrate after twelve weeks of decomposition in a controlled composting test, with no more than 10% of its original weight remains after sieving on 0.2mm sieve. ASTM D6954-04(2013) is the standard guide to expose and test plastic that degrade in the environment by a combination of oxidation and biodegradation. This guide provides framework to compare and rank the degradation process in controlled laboratory tests and the degree of physical losses of the plastics. In this guide, there are three tiers for accelerating and measuring the loss in properties and molecular weight by both thermal and photooxidation process and other abiotic processes (tier 1), measuring biodegradation (tier 2), and assessing ecological impact of the products (tier 3). ASTM D5272-08(2013) defines the test condition pertinent for outdoor exposure of photodegradable plastics. The practice requires characterization of exposure under UV light as a function of exposure location and time of year. ASTM D5071-06(2013) comprises specific procedures and test condition that are applicable to photodegradable plastic testing using an apparatus that simulates sunlight, control temperature and moisture. ASTM D5208-09 covers the standard practice applicable to photodegradation of plastics for fluorescent UV light exposure. The standard practice is for photodegradable plastics that are made for long term use of outdoor application. ASTM D3826-98(2013) outlines the standard practice to determine the degradation end point (a brittle point) for degradable PE and PP using tensile test. This standard works in line with D882 testing procedure. ASTM D4364 -13 covers the standard practice of concentrated UV light exposure of photodegradable polymer using Fresnel – reflecting concentrator, which is located outdoor during experimental. This practice is applicable to wide range of polymers forms, sheets, molded or films.

IV. Photodegradable Polyethylene Processing

The processing of photodegradable polyethylene based polymer is theoretically not much differs from conventional polyethylene processing settings. However, without sufficient understandings on the characters of the polymer, the processing step can be problematic, especially in large scale production. Modern polyolefin resins and thermoplastic materials are characterized by a narrow molecular weight distribution and advantageous mechanical properties; however they are still subjected to product deterioration during extrusion and processing [15]. Often, the most suitable processing setting is difficult to achieve due to impurities of the polyethylene, because the resin has been compounded with photodegradant in order to produce photodegradable polyethylene. Thus, by providing technical information of the setting of photodegradable polyethylene processing is thought to provide guidance on the processing method and reduce wastes and set up timing.

A. Materials

The photodegradable polyethylene that was developed in this study used industrial grade virgin low density polyethylene (LLDPE) from Polyethylene Malaysia Sdn Bhd code LL0209SA with melting temperature of 100°C. High density polyethylene (HDPE) resin was obtained from Polyethylene Malaysia Sdn Bhd code HD5301AA with melting temperature of 130°C. Carbon black pellet was produced by Plasma Color (KL) Sdn Bhd coded Black MB8605 which is LLDPE based master batch. The photodegradant RM master batch was developed by Green Polymer Scientist from Universiti Teknologi MARA and is polyethylene based. In order to fulfill standard practice of planting practice by Sime Darby Plantation Sdn Bhd, the film was added with 0.5% carbon black. The film was later used for full scale field exposure cultivated with oil palm seedlings by Sime Darby Plantation Sdn Bhd.

B. Processing Method

Melting flow index for photodegradable RM master batch is 1.74g/10min and melting flow index for polyethylene resin is 0.90g/10min and 0.08g/10min for LLDPE and HDPE respectively. Prior compounding, all of the resins which were in pellet forms were mixed to homogenous. This step is crucial in order to avoid inhomogenousity during extrusion.

TABLE II
Formulation of Photodegradable Polyethylene

Polymer	Composition	MFI
LLDPE	12kg	0.90g/10min
HDPE	3kg	0.08g/10min
RM Master batch	0.6kg	1.74g/10min
Carbon black	0.225kg	-

TABLE III
Blowing Machine Setting

Setting	Temperature (°C)	Speed (rpm)
Heater 1	220	-
Heater 2	200	-
Die	220	-
Rotor	-	12.00

Die diameter: 12.7cm

The extrusion of the photodegradable polyethylene was set to produce 31cm x 58cm, 0.06mm thickness at 500 gauge polybag size.

The temperature setting was set to allow vigor mixing process of resins by the twin screw extruder. At heater 2, the temperature is less than heater 1 because at this point, homogeneity is already achieved; higher temperature may cause problematic products. Temperature at die is increased again by 20°C in order to allow smooth flow of materials. The blending of LLDPE and HDPE is to provide extra strength of the aimed product as to be used in the plantation nurseries. Besides, addition of HDPE will allow better manipulation of size and shape of the end product.

Although all resins are having melting temperature less than 150°C, however, in order to allow perfect mixing of materials the temperature of the extruder and blower die were put much higher. In this study, any lesser temperature at the said part of machine will cause low quality of product and may event affect the surface quality of the film.

V. Conclusion

The application of polyethylene in many sectors is becoming more important, especially in the sector where the potential of waste production is high.

Fig. 2 Polybag being blown out from blowing machine die.

As in agriculture, almost all of the used polymeric materials are discarded and often left unattended into soil or being disposed in the landfill. This is due to the high cost of removal and less potential of recycle due to the high percentage of foreign contamination. Thus, the interest of developing degradable polymer is becoming more important and crucial as to counter measure the problem of pollution and soil sterility caused by the polymer wastes. Photodegradable polyethylene has been developed and the processing parameters have been studied in order to produce the desired product for application in the agriculture, product packaging or even medicinal.

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