

Degradability Studies of Photodegradable Plastic Film

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Abstract—Polypropylene blended with natural oil and pigment additives has been studied. Different formulations for each compound were made into polybag used for cultivation of oil palm seedlings for strength and mechanical properties studies. One group of sample was exposed under normal sunlight to initiate degradation and another group of sample was placed under shaded area for five months. All samples were tested for tensile strength to determine the degradation effects. The tensile strength of directly exposed sunlight samples and shaded area showed up to 50% and 25% degradation respectively. However, similar reduction of Young's modulus for all samples was found for both exposures. Structural investigations were done using FTIR to detect deformation. The natural additives that were used in the studies were all natural and environmental friendly

Keywords—Agriculture, mechanical strength, photodegradable polymer.

I. INTRODUCTION

THESE days, the use of plastic polybag in oil palm cultivation is not uncommon. Carbon black filled plastic polybag provide sufficient strength for seeds to grow and conditional environment for develop into fully competent seedlings to be transferred into plantation field. International plantation organization [1] reported that Malaysia is accommodating 13.9% of its total land for oil palm plantation covering 32.855 million hectares. Optimum amount of seedlings to be planted per hectare is 163; possibly causing vast quantity of 15"x18" (36cm x 42cm) sized polybag wasted per hectare. Considering the huge oil palm plantation size in Malaysia, it is estimated that 5.3 billion polybag were already wasted and ended up anywhere on the soil. Leftover polybag could disrupt soil fertility as it is only be fully degraded after hundreds of years. Conventional polybag are considered non-degradable thus its fate is often dumped on site or collected to be dumped outside the planting area. Even though plastic products such as polybag can be recycled, however the dirt and soils that come together with the polybag make it inconvenience for the process. Cleaning process before recycling will cost much higher cost thus make it not economically viable for recovery [2].

As the demand for plastics products is increasing by 5% in consequent years [3], it is imperative to discover the best way

to pull over the pollution and environmental issues caused by plastics products especially in agricultural sector where it consumes indefinite amount of plastics products. Degradable plastics are genuinely a solution for adverse effect by non-degradable plastics or polymer. In order to overcome pollution issue caused by non-degradable polybag, the use of degradable polybag is currently being studied. Degradation of photodegradable polybag is aim to emulate the life cycle of natural biomass [2]. Biodegradable plastic is a degradable plastic in which the degradation results from the action of naturally occurring microorganisms such as bacteria, fungi, and/or algae. There are two primary differences between 'degradable' and 'biodegradable'. Heat, moisture and/or UV exposure most often causes the degradation of a degradable product, whereas micro organisms degrade a biodegradable product. Degradable products tend to take much longer to break down into carbon dioxide, biomass and water [4]. According to [5], there are three types of plastics materials, namely (i) conventional materials, (ii) partially degradable materials; and (iii) completely degradable materials.

When degradable plastics break down into smaller molecules, eventually they will be small enough to be consumed by microorganisms and so biodegradation occurs. In essence then, all degradable films will eventually biodegrade but at different speeds. Photodegradable polybag can be used to protect seeds and seedlings but rapidly degrades so that it does not interfere with ripening, harvesting or replanting [6]. This polybag can be degraded in variety of ways through reacting with sunlight (photo oxidation), bacteria (microorganisms), chemicals and macro organisms (invertebrates and insects) [7]. A novel photodegradable film plastic developed by [8] based on polypropylene (PP) has been proposed to be analyzed weather suitable for cultivation of oil palm. Most degradable bags either degrade too fast or too slow. The use of degradable bag based PP can solve the problems compared to using starch based films which has low strength after few weeks used. Degradable polybag employing starch has poor mechanical strength than additive based example – filling a starch bag with wet leaves and placing curbside can result in the bottom falling out when a hauler picks it up.

The use of degradant material predominantly requires an active microbial environment for example municipal compost or functional soil before they will start to degrade. The heat, moisture and aeration will eventually assist degradation processes. In plantation industry practices, degradable polybag or any other plastics based tools might be degraded not in the most suitable period. In the case of oil palm seedlings

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cultivation, at least three months of is required for the primary nursery stage and ten months for secondary nursery stage. The addition of photodegradant in the polybag polymeric formulation will induce photodegradation. However, the degradability of the polybag must be studied so that the exact quality and specification of planting materials can be used by the plantation industry sectors. Hence, this study will assist to predict the period of time where polybag degrade upon direct sunlight and in shaded area (relatively lower light intensity).

Photodegradable film using current degradable additive technology is currently cheaper, stronger, and recyclable compared to starch based film and does offer a reasonable environmental solution to packaging waste. Breakdown of films into fragments of low molecular weight can be controlled via thickness variation and degradable additive content. The commercially available degradant is favorable to many industrial sectors as long as it does not interrupt the processing procedures of the end products.

In agriculture, plastic films play significant role in almost all part of the activities. The uses of plastic material in agriculture normally include soil mulches, seedlings bag, green houses and storage materials. In many cases, most of the plastics film wastes are not economically removable from the point of application such as soil mulches which often left unattended after its single use. To overcome the issue, photodegradable film can be applied as mulch films and polybag customized into the right degradation period and condition. The objectives of this study are to investigate the degradability of plastic polybags that are used in cultivation of palm oil seedlings via FTIR analyses and tensile properties changes.

Previous researches [4] [7] [6] stated that the exposure of degradable materials to sunlight showed highest weight loss (>10%) and samples buried in soil showed the lowest ($\approx 1\%$). Pro-oxidant blended high density polyethylene (HDPE) showed higher weight loss when compared to starch blended (22.7% as against 11%). Scanning electron microscopy revealed surface deterioration and decrease in contact angle indicated reduction in surface hydrophobicity. Increase in the carbonyl and hydroxyl groups in the infra-red spectrum of the exposed samples suggested abiotic degradation. Starch blended polypropylene exposed to sunlight showed the highest thermo gravimetric weight loss (63.8%) followed by the same polymer buried in soil (46.1%) [9].

II. METHODOLOGY

A. Introduction

In preparing the experiment, there were several steps. Ten photodegradable plastic films were divided into two sets, with all samples were used to plant oil palm seedlings aged 4 months. The reason of planting oil palm seedlings using tested samples is because agricultural sector is major user of plastic film and oil palm planting contribute million of hectares for its plantation. Then, the samples were divided into two conditions to study the different effect of exposure in different light intensities. Five samples with oil palm seedlings were exposed

under direct sunlight for degradation initiation and the other samples were placed under shaded area with interrupted sunlight condition to investigate the different effect of sunlight on the tested samples.

TABLE I
PREPARATION OF SAMPLE

Set of Samples	Condition
A	5 samples: sunlight exposure
B	5 samples: under shade area

B. Testing Methods

All the mechanical testing methods that were carried out are in accordance to American Society for testing Materials (ASTM). In this experiment, Films will be tested with, namely Tensile Test (ASTM D602) and analysis of film investigated using Fourier transform infrared spectroscopy (FTIR).

C. Tensile Tests

All Samples were tested according to ASTM (D828), specifically for films. Samples were cut with rectangular dimension of 200mm (length) x 20mm (width) x (in range) 0.003-0.005mm (thickness). The testing were done in standard condition of $24^{\circ}\text{C} \pm 2^{\circ}\text{C}$ and 50 ± 5 percent of relative humidity. The test was done using testometric 500 testers with cross- head speed of 100mm/minute 20kN load. The samples were positioned vertically in the grips of the testing machine. The grips were then tightened evenly and firmly to prevent any slippage with gauge length at 60mm at both side of two grips. After the sample name was keyed in, the testing precedes. And in every testing, all samples were repeated for 5 times and the average was calculated. When each of the sample was tested, the graph and the data obtain will be analyzed. Tensile properties, such as tensile strength, tensile modulus and elongation at break were analyzed.

D. Fourier Transform Infrared (FTIR) Spectroscopy Test

The Fourier transforms infrared spectroscopy (Perkin-Elmer FTIR) was used in the characterizations of unexposed and exposed films. Perkin-Elmer FTIR was used to identify the functional group. Film samples were placed in FTIR instruments and the computer was set to obtain transmission peak and absorbance value evaluated. Carbonyl peak was set at between 1715cm^{-1} and 900cm^{-1} . Carbonyl group indication is an advantageous tool to investigate degradation of samples.

III. RESULTS AND DISCUSSION

Planting project started at the second stage in oil palm seed cultivation whereby 4 months aged of seeds of palm oil had been chosen, then the seed was planted in a tested polybag samples (gauge length:43cm, width: 36cm, thickness: 0.06 mm) for 6 months. The planted oil palm seedlings were placed in exposed area where direct sunlight is achievable. For another set of samples shaded area is where relatively lesser sunlight intensity is observed. This shaded area is closed shelter with minute penetration of sunlight. The cultivation of oil palm started from June 2012 until December 2012.

A. Tensile Test

For modulus after exposure, samples become brittle at the fifth month, and modulus continued to reduce upon longer exposure for more than 2 months; results from the tests indicate that degradation occurred. Some mechanism of dione additive affecting bonding of polypropylene chain had been postulated. Free radical initiation of methyl end group of polypropylene might first occur before being accompanied by oxidation through chain scission. Formation of free radicals from dione have contributed to the degradation; initiation of photo-degradation due to exposure can be attributed to the presence of oxidation products which are formed as a result of heat treatment. Hydroperoxides are commonly the major products of oxidative degradation and are potentially powerful initiators of further degradation. Other functionalities introduced include carbonyl groups, which is a result of hydroperoxides decomposition. The carbonyl groups absorb UV radiation readily and get excited to singlet and triplet states which further decompose via Norrish reactions of type I, II and III [10].

Fig. 1 shows tensile strengths for sunlight aging various samples. First month of samples exposure under direct sunlight showed incremental difference compared to control. The tensile strength decreased to the second month of exposure and did not continually decrease until the fourth month. However, significant decline in tensile strength value was demonstrated on the fifth month which is up to 50%. The instability of tensile strength is observably due to the fluctuating amount of sunlight from the first month until the last day of direct sunlight exposure. The amount of sunlight affected the results significantly since the samples were containing photosensitizer that induce the degradation upon attacked by sunlight. It is also illustrated that the tensile strength for samples exposed under interrupted sunlight showing the similar pattern with the directly exposed samples.

Conversely, the samples exposed under interrupted sunlight still retain its strength at fifth month; the tensile strength reduction is within 25 - 30% only. This indicates that lesser amount of sunlight, regardless its initiation state condition, the degradation of samples still slow due to insufficient sunlight to supply the ultraviolet light in order to sustain the degradation. It proves that, high intensity of sunlight helps in degrading the photodegradable materials by promoting the occurrence of photo radical molecules and eventually enhances the reaction chain in the polymeric films.

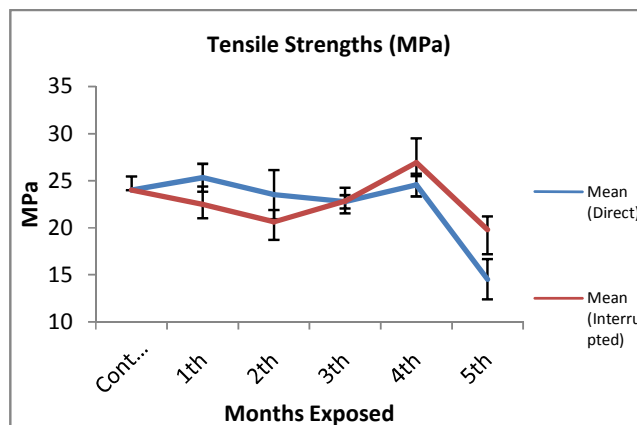


Fig. 1 Tensile Strengths for sunlight aging of samples under direct sunlight and interrupted sunlight condition

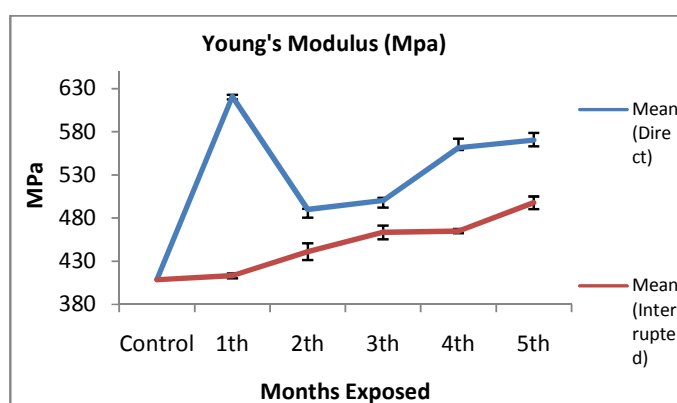


Fig. 2 Young's Modulus for samples exposed under direct sunlight and interrupted sunlight condition

Fig. 2 shows Young's Modulus for samples aging under direct and interrupted sunlight condition. Samples exposed under direct sunlight showed evident change of Young's Modulus value compared to samples exposed under interrupted sunlight where the modulus value were less significantly vary. For samples exposed under direct sunlight, Young's Modulus value for the first month is significantly high. This is due to high sunlight intensity during the exposure. However, the value decline tremendously during the second month. The directly exposed samples' modulus was increased upon longer exposure and the material showed brittleness at fourth and fifth month where the samples were partially started to fragmented when observed with bare eyes. Samples that were placed under interrupted sunlight condition showed similar modulus value as direct sunlight with significantly lesser changes. This indicates that slight degradation occurs during the exposure and minor brittleness was observed. High intensity of sunlight clearly caused the directly exposed samples to show more degradation behaviors and lesser amount of sunlight caused another group of samples to retain its properties and characteristics.

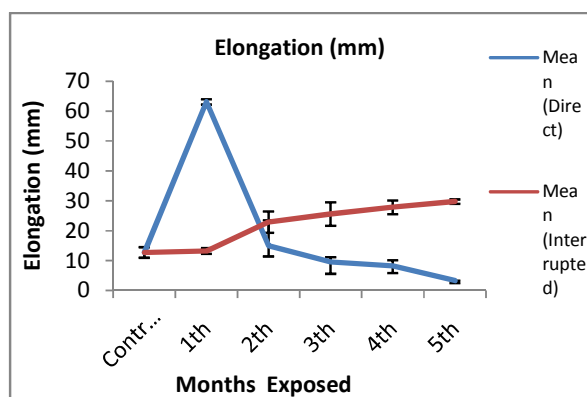


Fig. 3 Elongation for sunlight aging of samples under direct sunlight and interrupted sunlight

Fig. 3 shows elongation of the samples. It shows that there was an effect of degradation after 2 month, where it is found that the elongation persists, whereby chain is not flexible anymore. This is due to the significant degradation that occurred during the first month of exposure. The materials were observably degraded at the first month of direct sunlight renderings and the samples became more brittle as stated. However, samples under interrupted sunlight shows only 2 samples show increment due to different amount sunlight exposed. The difference of elongation values were caused by annealing effect at 50°C, where the polymer chain could have reoriented and restructure for few days exposure before losing its chain alignment at high humidity and temperature. Polypropylene chains could not hold orientation as final degradation started to develop upon free radical attack at its terminal methyl group. Hence, strength was decreased for the entire samples.

B. Fourier Transform Infrared (FTIR) Spectroscopy

In polymer, oxidative degradation plays significant importance. Functional groups such as peroxide, carbonyl and hydroxyl are known to cause breakdown of polymeric chains. Especially carbonyl groups, the double bond between carbon and oxygen C=O provides high electronegativity thus increase the bond's polarity for further radical reactions. The occurrences of carbonyl compounds in samples were detected using FTIR machine to identify the spectra of the carbonyl stretch. Carbonyl stretch can be observed between 1600 and 1760 cm^{-1} wavelength. The spectra that caused by carbonyl stretches were varied due to different carbonyl compound occurred in the samples tested. From FTIR spectra, there were formations of additional peak identified as carbonyl peak caused by C=O bond in either ketone or ester compound at 1714.9 cm^{-1} which were observed in sunlight exposed samples compared to the control sample.

Table II indicates samples for control, 1 month, 4 months, and 5 months exposures. For samples that were exposed under direct sunlight, the occurrence of carbonyl stretch were observed at month one and fourth, attached to amide compounds (1652.6 cm^{-1} and 1645.3 cm^{-1} respectively) and month fifth, where the carbonyl group is attached to ketones

and aldehydes (1714.9 cm^{-1} and 1657.9 cm^{-1} respectively). As shown in Table III, carbonyl groups' stretch only occurred at the fifth months, proving that the intensity of sunlight significantly affected the degradability of the samples added with photodegradant. The non-occurrence of carbonyl groups in control samples was proved with non existence of carbonyl stretches in the FTIR results. The degradation of samples were triggered by the photodegradant which promote the radical molecules formation with aid of ultra violet energy and the degradation processes were accelerated by oxidation reaction of the reactive bond resulted from the radical activities. Lesser intensity of energy gained from sunlight caused the degradation initiation to be delayed. It is known that the initiation of chain breakdown has already started with the occurrence of carbonyl groups as tools of identification; however, longer period of exposure will determine the degradability of the samples with more or lesser intensities of sunlight.

TABLE II
FTIR ABSORBANCE FOR DIRECT EXPOSED SAMPLES

Samples	Absorbance (cm^{-1})	Assignment
Control	1557.6, 1538.2, 1505.4	O-H deformation from degradant additives
	1455.7, 1376.7, 1359.2	C-H deformation of polypropylene chain
	1256.5, 1168.1, 1106.0, 1043.0	C-O stretch from degradant additives
	1652.6	C=O stretch appear from amides
1 st month	1456.3, 1376.8	C-H deformation of CH_2 in polypropylene chain
	1256.2, 1167.7	C-O stretch from degradant additives
	1645.3, 1539.0	C=O stretch appear from amides
4 th month	1456.4, 1376.6	C-H deformation of CH_2 in polypropylene chain
	1100.1, 1031.6**, 1007.7	C-O stretch from degradant additives
	1714.9*	C=O carbonyl stretch from ester/ketones groups
5 th month	1657.9*	C=O carbonyl stretch from aldehyde/ketones groups
	1557.9	O-H deformation from degradant additives
	1455.0, 1376.7	C-H deformation of CH_2 in polypropylene chain
	1167.3, 1099.1, 1031.9**	C-O stretch from photodegradant additives

*Strong absorbance

** Very strong absorbance

TABLE III
FTIR ABSORBANCE FOR INTERRUPTED SUNLIGHT SAMPLES

Samples	Absorbance (cm^{-1})	Assignment
Control	1455.7, 1376.7	C-H bend of polypropylene chain
	1168.1	C-O stretch from degradant photo additives
1 st month	1460.2, 1376.8	C-H bend of polypropylene chain
	1456.0, 1376.7	C-H bend of polypropylene chain
4 th month	1166.8	C-O stretch from photodegradant additives
	1653.6	C=O carbonyl stretch from amide groups
5 th month	1458.4, 1376.7	C-H deformation of polypropylene chain
	1031.2, 1006.9	C-O stretch from degradant additives

The results from FTIR revealed that degradation of samples caused by the exposing the materials under sunlight either direct or indirectly whereby lesser light intensities provide sufficiently proportion of energy to initiate degradation but in slower manner.

C. Surface Images of Sunlight Aging Upon Various Samples

Surface morphology was determined by Dulite microscopy with 5000X magnification and was determined to inspect the surface of the film upon different exposure for said period for direct sunlight and interrupted sunlight. Directly exposed sunlight samples were found to start physically degrading at fourth month of exposure. During first month of exposure, discoloration occurred and continued until the texture of the samples were observably rough. At the fourth months, brittleness of the surface can be observed and the roughness was getting more obvious and eventually started to fragment at the fifth month, proving that degradation is already occurred. For samples placed under interrupted sunlight were only discolorations of the samples without brittleness or fragmented. This is due to the lesser and inconsistent sunlight amount during exposure. However, results from analytical analysis shows chemical breakdown activities.

1. Surface Morphology for Directly Sunlight Exposed Samples

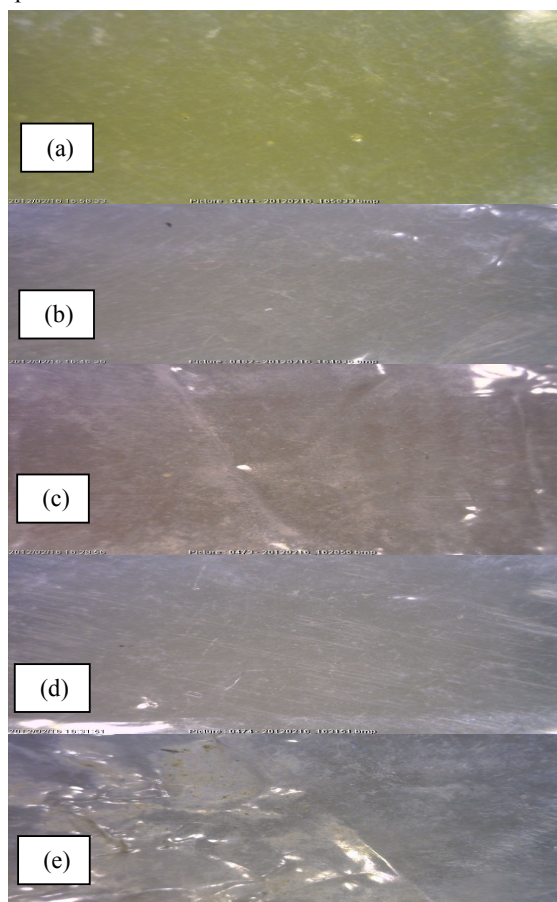


Fig. 4 (a) Control sample (b) Exposed 1st month. (c) Exposed 2nd month (d) Exposed 3rd month. (e) Rougher surface at 4th month exposure (f) Fragmenting started in sample at 5th month

Surface morphology study is important as to identify any changes on the samples' surface upon exposure during the experiment. Embrittlement can be observed with naked eye and laboratory equipment is to confirm the observation.

2. Surface Morphology for Interruptedly Sunlight Exposed Samples

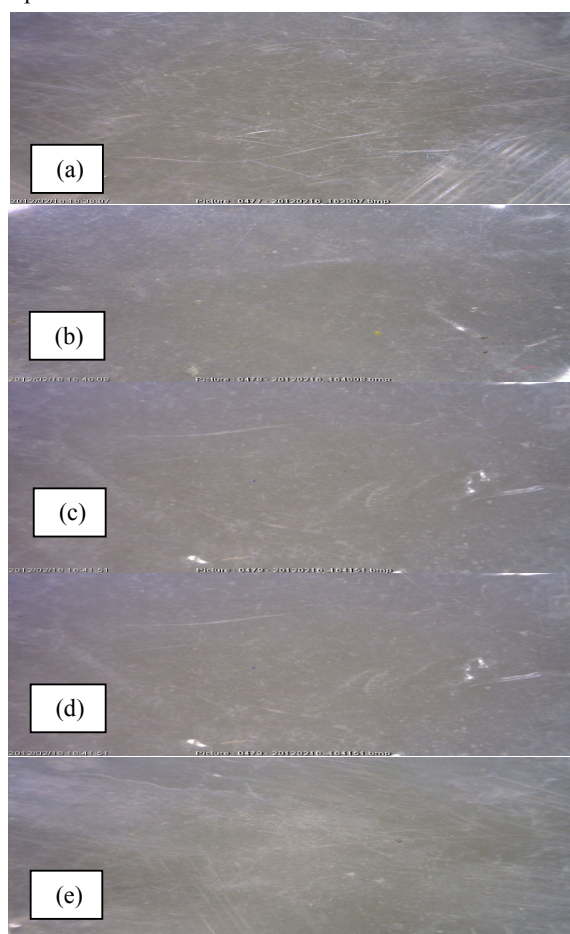


Fig. 5 (a) Discoloration film (1st month) (b) Discoloration film and roughness of film (2nd month) (c) Discoloration film and roughness of film (3rd month). (d) Discoloration film and roughness of film (4th month). (e) Discoloration and roughness of film (5th month)

IV. CONCLUSION

Carbonyl and C-O bond are two functional groups that act as indicator for degradation detection. The additive functioned

as photosensitizer where it triggered and accelerated the degradation process by oxidative degradation of photodegradable plastic and initiated by sunlight and/or heat, before attacking the polymer backbone and this cause embrittlement of sample. Tensile strength of film was consistent up to 4 months for shaded area with interrupted light. Tensile strength of direct sunlight showed reduction of 50% after 5 months and modulus significantly rapidly increase (embrittle). Samples located under shaded area showed similar modulus with slight fluctuation showing some degradation. Signs of degradation shown after 4 months under sunlight shaded with tensile strength reduced from 25% to 30%. The project was successful prove that degradation occurred under sunlight aging.

REFERENCES

- [1] Palm Oil Facts and Figures (2012). Retrieved from <http://www.simedarbyplantation.com/upload/Palm-Oil.pdf>
- [2] Siracusaa, V., Rocculib, P., Romanib, S. and Rosab, M. D., "Biodegradable polymers for food packaging: a review." *Trends Foods Sci Tech* vol. 19, no. 12, pp 634-643, 2008.
- [3] Simonet, B.R.T., Medeiros, P.M., Didyk, B.M., "Combustion products of plastics as indicators for refuse burning in the atmosphere." *Environ Sci Tech*, vol. 39, no. 18, pp. 6961-6970, 2005.
- [4] Ammala, A., Bateman, S., Dean, K., Petinakis, E., Sangwan, P, Wong, S., Yuan, Q., .Yu, L, Patrick, C., and Leong, K.H, "An overview of degradable and biodegradable polyolefins" *Prog Polym Sci*, vol. 36, no. 8, pp 1015-1049, 2011.
- [5] Kolybaba, M., Tabil, L.G., Panigrahi, S., Crerar, W.J., Powell, T. and Wang, B. Biodegradable polymers: past, present and future. *ASAE Annual Intersectional Meeting, North Dakota, USA*, 2001.
- [6] Polyrner, W.R.. *Photodegradable Composition*. Worcestershire, United States Patent, 1993
- [7] Davis, G., "Characterization and characteristics of degradable polymer sacks" *Mat Charact*, vol. 51, no. 2-3, pp .147-157, 2003.
- [8] Mohamed, R, Mohd, A.F., Abdullah, A.F.I., "Effect of Aging on Film Strength and Morphology of Natural Additive Polypropylene Packaging Film. *J Mat Sci Eng*, vol. 5, pp. 555-560, 2010.
- [9] Muthukumar, T., Aravinthan, A., Mukesh, D., "Effect of environment on the degradation of starch and pro-oxidant blended polyolefins." *Polym Degrad Stab*, vol. 95, no. 10, pp. 1988-1993, 2010.
- [10] Roy, P.K., Surekha, P., Rajagopal, C., Chatterjee, S.N., Choudhary, V., "Studies on the photo-oxidative degradation of LDPE films in the presence of oxidized polyethylene." *Polym Degrad Stab*, vol. 92, no. 6, pp. 1151-1160, 2007.