Thermo-oxidative Degradation of High Density Polyethylene Containing Manganese Laurate

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ABSTRACT

This paper reports the study of utilization of manganese laurate for accelerating the degradation process of high density polyethylene (HDPE). Specimens were prepared by loading manganese laurate from 0 to 1 %(w/w) in HDPE resins using twin screw extruder followed by injection molding. Thermal treatment was performed at 70°C, for maximum duration of 1000 hours to examine the thermo-oxidative degradation of HDPE blends. Tensile testing, FTIR analysis, molecular weight analysis, melt flow index (MFI) analysis, differential scanning calorimetry (DSC) test, thermogravimetric analyzer (TGA) test, were carried out to assess the changes during treatment. The results reveal that sample containing manganese laurate are readily to undergo thermo-oxidative degradation under temperature condition of 70 °C. Tensile strength and elongation at break decreased during treatment. Pure and HDPE containing 1 % of manganese laurate (ML10) samples have lost about 11.74 and 43.33% of tensile strength, and about 16.21 and 55.85 % of elongation at break respectively. FTIR traces exhibited that carbonyl group's peak in the region 1700-1800 cm^{-1} arise during thermal treatment as the result of oxidation. Average molecular weights were found to decrease about 16.12 and 67.51% from their initial value for pure and ML10 samples respectively, and consequently MFI increased significantly. Thermal stability and melting temperature were found to shift to lower temperature, while crystallinity generally increased. The degradation rate of HDPE increased by increasing the amount of manganese laurate incorporated.

Keywords: manganese laurate, pro-oxidant additives, HDPE, thermo-oxidative degradation.

1. INTRODUCTION

Nowadays the utilization of plastic material has grown tremendously. In 1999, The principal thermoplastic polymers (LDPE/HDPE, PP, PVC, PS, and PET) consumptions exceeded 28 millions tones in Western Europe, 79% of the plastic markets [1]. Locally in Malaysia, total resin consumption increased by 8% from 1.6 million MT in 2004 to 1.72 million MT in 2005, of which about 65% were polyolefins (PE & PP) [2] and the total consumption still remained at level of 1.7 million MT in 2009 [3]. The utilization of plastics has led to growth of plastic waste amount [4]. The municipal solid waste stream in the U.S. totals nearly 160 metric tons per year and consists of about 7% by weight of post-consumer plastics [5]. The growing environmental concern has made plastics a target of much criticism due to their lack of degradability [6]. Recycling, as alternative to reduce plastic waste, only covers 25-30% of polymer waste. The other products eventually find their way to landfills or incinerator [7]. The large amount of plastics ending up in the waste stream has resulted in a trend towards manufacture and development of plastics with accelerated degradation [8].

The additions of transition metal pro-oxidants is one of methods used to accelerate the degradation process which is designed to catalyze photo degradation and thermal degradation periods [8]. There are several transition metals which have been reported to be alternatives as pro-degradant additives [9]. Many studies were mostly utilized cobalt-salt-based additives for LDPE or LLDPE [10-15]. The other studies applied other transition metals, such as iron and calcium stearate [16], manganese stearate [17-19] for LDPE.

The polymer with incorporated pro-degradant additives, undergo accelerated oxidative degradation initiated by natural daylight, heat and/or mechanical stress, and embrittle in the environment and erode under the influence of weathering [20]. The artificial treatments have been widely applied to simulate natural weathering, e.g. outdoor sunlight exposure weathering, soil burial or composting, aquatic environment. If instead composting, thermal treatment is commonly used to simulate composting temperatures [6,19].

Mechanical properties are the most sensitive changes, occurring during degradation [8]. The initiation of the degradation process is accompanied by loss of useful tensile properties [5]. Accordingly, mechanical properties, i.e. tensile

strength and elongation at break, are commonly used to monitor degradation process.

Degradation of polyethylene under thermal condition has been widely studied. However there are only a few studies on degradation of HDPE even though HDPE is also type of polyethylene which is widely applied in daily life beside LDPE. The utilization of manganese as pro-degradant additives was also very few, although manganese is sufficiently available in nature and relatively cheap. Moreover, manganese laurate has not been utilized yet as pro-degradant additive. The purpose of this study was to investigate effect of manganese laurate on enhancing degradation of HDPE under thermal treatment.

2. EXPERIMENTAL
2.1 Materials

Manganese chloride tetrahydrate (Systerm), sodium hydroxide, lauric acid (Merck), ethanol (industrial grade), acetone, n-hexane (R&M Chemicals), cyclohexane, benzene (Merck), and toluene (Systerm) were used without any treatments. High density polyethylene, Etilinas HD5301AA, manufactured by Polyethylene Malaysia Sdn. Bhd., was used to prepare samples. The HDPE had a density of 0.951 g/cm^3 and melt flow index (MFI) 0.081 g/10 min at temperature of 190°C and load of 2.16 kg.

2.2 Methods
2.2.1 Synthesis of characterization manganese laurate

Manganese laurate was synthesized by reacting sodium hydroxide and lauric acid to produce sodium laurate, and followed by reaction of sodium laurate and manganese chloride as reported previously. The characteristics of manganese laurate have also been reported in the previous work [21].

2.2.2 Sample preparation

The compounding of HDPE with manganese laurate was carried out using co-rotating twin screw extruder (MODEL: Lab Tech Engineering with L/D 40) at setup temperature of 200°C. Prior to extrusion, HDPE and manganese laurate were dried in the oven at 80°C for 6 hours. Following extrusion, the material was pelletized and injection molded into specimens for tensile testing using a Nissei NS20-2A injection molder at setup temperature of 200°C. Pellet was also dried in the oven at 80°C for 2 hours before molded. Finally, the samples were labeled in accordance with loading percentage of manganese laurate as listed in Table 1.

2.2.3 Sample Properties Evaluation

Tensile testing: Tensile testing was carried according to ASTM D638-08: Standard Test Method for Tensile Properties of Plastics. Test specimens were conditioned at 23±3°C for 40 hours prior to tensile testing according to ASTM D618-99: Standard Practice for Conditioning Plastics for Testing. Following the conditioning process, specimens were tested using a universal testing machine (MODEL: Shimadzu AG-X) with a 5 kN load cell operated at a crosshead speed of 10 mm/min and gauge length (grip-to-grip) 25.4 mm. Five samples were tested under each batch and the average value was reported. All the tests were carried out at 25°C.

Table 1 Sample labeling

Sample label	Manganese laurate loaded (%)
Pure	0
ML02	0.2
ML04	0.4
ML06	0.6
ML08	0.8
ML10	1.0

Fourier Transforms Infrared spectroscopy: Functional group analysis was performed using Fourier Transforms Infrared (FTIR) spectroscopy (MODEL: Thermo Nicolet Avatar 370). ATR technique was applied with 64 scans and resolution of 4 cm^{-1}. Smart performer part was used to collect background and samples spectra. The thin slices of samples surface were taken and analyzed under the smart performer accessories of FTIR. The tests were repeated three times for each sample. The interest was focused on the carbonyl group region at the band of 1700-1740 cm^{-1} [18]. Carbonyl indices of samples were monitored. Carbonyl index was defined as the ratio of area around band of 1718 cm^{-1}, attributed to carbonyl groups, and area of band at 1375 cm^{-1}, attributed to CH$_3$ [22].

Molecular weight: Average molecular weight of HDPE was determined from viscosity measurement. Sample was dissolved in xylene at temperature of 135°C. The viscosity was measured using Ostwald Capillary Viscometer. The average molecular weight was obtained by using intrinsic viscosity-average molecular weight relationship or known as The Mark-Houwink-Sakurada equation as shown below [10,23].

$$[\eta] = 16.5 \times 10^{-3} \overline{M_v}^{0.83} \qquad (1)$$

where $[\eta]$ = intrinsic viscosity and $\overline{M_v}$ = average molecular weight. The tests were done for selected samples at 0, 600 and 1000 hours of thermal treatment.

Melt Flow Index (MFI): MFI was measured according to ASTM D1238-94a: Standard Test Method for Melt Flow Rates of Thermoplastics by Extrusion Plastometer using melt indexer (MODEL: Dynisco LMI 4000) at temperature of 190°C and using an applied load of 2.16 kg. Three

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measurements were carried out under each batch. The selected samples at 0, 200, 600 and 1000 hours were tested.

Degradation temperature: Evaluation of degradation temperatures were performed using thermogravimetric analyzer (TGA) (MODEL: TA Instruments Q500). The applied heating rate was 20°C/min from room temperature up to 800°C under nitrogen atmosphere. The tests were carried out using platinum pan. The test were only performed for pure and ML10 samples, before and after 1000 hours of thermal treatment.

Melting point: Melting point tests were carried out using DSC (MODEL: TA Instruments Q1000), where the applied heating rate of 10°C/min in nitrogen atmosphere, at gas flow rate of 50 mL/min, and temperature range of 35-170°C. The three consecutive (heating-cooling-heating) steps have been applied during test. The test were only performed for pure and ML10 samples, before and after 1000 hours of thermal treatment. The crystallinity degree was determined by calculating the ratio of heat of fusion (ΔH_f) of sample and heat of fusion of fully crystalline HDPE, 293 J/g [24,25].

$$Crystallinity, I_{DSC} = \frac{\Delta H_f\, samples}{\Delta H_f\, fully\, crystalline} \quad (2)$$

2.2.4 Thermal Treatment
Thermal treatment was carried out using oven (MODEL: Memmert). Samples were incubated with circulated air at temperature 70°C [11,14,17] for the maximum duration of 1000 hours. Five samples were taken at 100, 200, 400, 600, 800 and 1000 hours for tensile testing. Another five samples were taken at selected periods for other tests e.g. FTIR, molecular weight, MFI, thermal properties, and SEM.

3. RESULTS AND DISCUSSION
3.1 Mechanical properties
There was no effect of loading of manganese laurate on the tensile strength of HDPE before thermal treatment. Fig. 1 represents the changes in tensile strength during thermal treatment. Tensile strength of pure sample increased in the early period of thermal treatment and followed by slowly decreased after 200 hours treatment. In the early period, crosslinking of HDPE might have occurred [26], resulting the higher tensile strength observed [10]. The crosslinking might have partially occurred on HDPE, and thereafter chain scissions might occur dominantly as oxidation started. Chain scission due to thermal treatment lead to the decrease of tensile strength and elongation at break. Pure samples lost about 11.74% of their tensile strength after 1000 hours of thermal incubation. On the other hand, the tensile strength of ML02 samples slightly increased in the first hundred hours and

thereafter decreased gradually. Meanwhile the tensile strengths of ML10 samples were relatively constant until a hundred hours and then decreased. On the early hours of incubation, the crosslinking phenomenon probably took place, while the oxidation might have not occurred yet or occurred at a slow rate, so that tensile strength appeared to rise with a minor scale. At the initial stage, if the higher concentrations of manganese laurate were loaded, then increasing of tensile strength did not obviously occur.
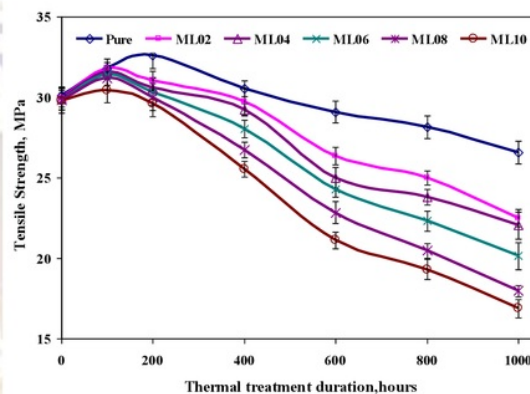

Figure 1 Changes of tensile strength of samples during thermal treatments

After 200 hours of thermal treatment, tensile strength of samples containing manganese laurate started to decrease. It suggested oxidation was initiating to take place on the polyethylene and then resulting in the chain scissions of polyethylene. With the increasing of amount of manganese laurate, decreasing the tensile strength observed. After 1000 hours of thermal treatment, tensile strength decreased for ML02 and ML10 samples about 24.80% and 43.33% respectively. This result indicates that the manganese laurate plays a role for increasing the rate of degradation of HDPE. Simply, the degree of tensile strength decreasing is in accordance with manganese laurate loading.

The significant decrease in mechanical properties occurs during the course of thermal incubation. The reason is that the concentration of high-molecular-weight chains, which contribute to the most of the mechanical properties, is decreasing during the oxidation and as a result of chain scission [11]. During thermo-oxidative aging, heat and oxygen will initiate free radical reactions to degrade polyethylene [27,28]. Thermal degradation of polymers may follow either chain end degradation or random degradation route. The chain end degradation initiates from the end of the chain and successively releases the monomer units [29,30]. Random degradation occurs at any random point along the polymer chain. This is reverse to

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condensation process where the polymer degrades to lower molecular weight fragments [30].

Fig. 2 reveals the changes in elongation at break of samples during treatment. The elongation at break of pure sample was about 50% which was not similar with common value of elongation at break of HDPE. It was due to different sample type and different processing method. There was no significant decrease of elongation at break for pure samples; however, the significant lowering was observed for the manganese laurate-containing samples.
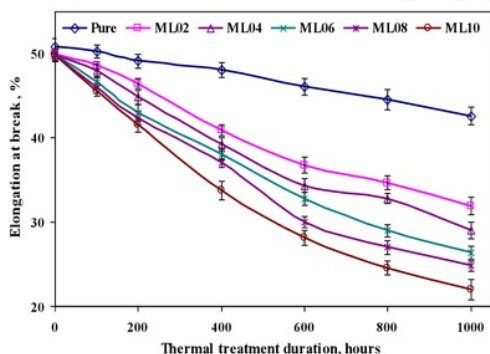

Figure 2 Changes of elongation at break of samples during thermal treatment

Despite the increase in tensile strength of all samples with different levels, at the first hours of thermal treatment, elongation at break tended to decrease from the beginning of treatment. When crosslinking underwent, specimens grew to be harder and more brittle, so that the elongation at break decreased. Elongation at break proceeded to decrease more rapidly when the chain scissions took place in the oxidation stage of degradation. Fig. 2 shows the decrease of elongations at break is rising by increasing the amount of manganese laurate loading in HDPE. For comparison, pure samples lost 16.21% of the initial elongation at the break, while 36.07% for ML02 samples and 55.85% for ML10 samples, after 1000 hours of treatment.

In the previous study, Sharma *et al.* [17] conducted thermo-oxidative aging of LDPE containing manganese stearates. They found that the manganese stearate improved the degradation process of LDPE resulting in the dramatic loss of elongation and tensile properties during thermal exposure. However, HDPE samples containing manganese laurate showed lesser amount of loss of tensile and elongation at break compared with LDPE containing manganese stearate. This is probably due to the stability against aging of HDPE is higher than LDPE as reported in literature [31] and may be also different length of carboxylic chain of manganese salt. Winslow [32] and Iring *et al.* [33] have also

reported that branched polyethylene is more readily oxidized than the linear analogues due to the presence of tertiary C-H site at each branch point.

3.2 FTIR study

The initiation of the thermo-oxidative process of polyethylene may follow the ways of the formation of alkyl free radicals from the polymer (RH) [34] or direct formation of hydroperoxide groups [35]. Once the alkyl radicals are formed, they may react rapidly with oxygen and generate alkylperoxy free radicals (ROO$^\bullet$). The peroxy free radicals may then abstract hydrogen from the polymer substrate to form hydroperoxides(ROOH) [34]. The formation of alkyl radicals can be presented in the following scheme 1 [30].

$$\wedge\!\!\!\!\wedge R\!\!-\!\!(R)_n\!\!-\!\!R\wedge\!\!\!\!\wedge \xrightarrow{\Delta} \wedge\!\!\!\!\wedge R\!\!-\!\!(R)_n\!\!-\!\!R^\bullet$$
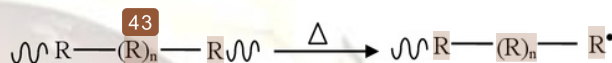
Scheme 1 Formation of alkyl radicals

On the other hand, Scheme 2 shows the direct formation of hydroperoxide groups (ROOH) attached to carbon atom in the polymer backbone under the effect of heat and air i.e. oxygen. The hydroperoxide groups are readily cleave and forming radicals [35].

$$RH(heat, O_2) \rightarrow ROOH$$

$$ROOH(heat\ and/or\ UV\ light) \rightarrow RO^\bullet + {}^\bullet OH$$
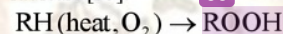
Scheme 2 Reaction of hydroperoxides formation and cleavage

At the elevated temperatures, hydroperoxides rapidly cleave to form alkoxy and hydroxyl radicals. These compounds may in turn rapidly abstract hydrogen from the polymer substrate to form more alkyl radicals [34]. The alkoxy radical (RO$^\bullet$) is exceedingly unstable. It will decompose spontaneously to form ketones and aldehydes (depending on the structure of the 'parent' hydroperoxide group) and these carbonyl compounds will undergo further oxidation to produce acids and esters [35]
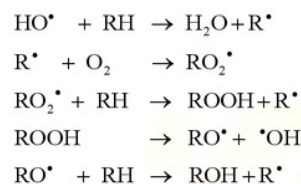
The mechanism of the transition metal-catalyzed degradation of PE has been described as a free radical mechanism proceeding from the formation of hydro-peroxides along the polymer back bone through reaction of the polymer with molecular oxygen [17]. The presence of metal compound will catalyze the hydroperoxide decomposition step of the oxidation mechanism [11,17,28]. In analogy, the manganese compound catalyzes oxidation by following the mechanism shown in Scheme 3

The radicals formed during initial stage of thermo-oxidation will attack polymer backbone. They initiate the oxidation of polyethylene by

Maryudi, Anwaruddin Hisyam, Rosli Mohd Yunus, Mohammad Dalour Hossen Bag /
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following the mechanism shown in Scheme 4[19]. When oxidation proceeds in the polymeric chains, chain scission predominate[11]

$$ROOH + Mn^{2+} \longrightarrow RO^{\bullet} + Mn^{3+} + OH^{-}$$

$$ROOH + Mn^{3+} \longrightarrow ROO^{\bullet} + Mn^{2+} + H^{+}$$

Scheme 3 Manganese catalyst reaction with hydroperoxides

$$HO^{\bullet} + RH \rightarrow H_2O + R^{\bullet}$$
$$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet}$$
$$RO_2^{\bullet} + RH \rightarrow ROOH + R^{\bullet}$$
$$ROOH \rightarrow RO^{\bullet} + {}^{\bullet}OH$$
$$RO^{\bullet} + RH \rightarrow ROH + R^{\bullet}$$

Scheme 4 Oxidation of polyethylene

The oxidation of polyethylene resulting products with carbonyl groups was monitored by measuring the existence of carbonyl peaks. Fig. 3 shows the FTIR spectra of treated and untreated sample of ML10. As mentioned earlier, the bands of around 1718 and 1375 cm-1 were used as basis of carbonyl index calculation. Nevertheless, the region of 1700-1800 cm^{-1} seems to consolidate and also region of 1350-1400 cm^{-1}. Sometimes it is hard to distinguish certain peaks, since they are overlapped by other peaks[11,18], so they appear to be one peak. However, comparison of traces has obviously exhibited by the presence of absorbance peak at around 1718 cm^{-1}. This peak evidenced the process of oxidation. Before treatment peaks around 1718 cm^{-1} did not obviously appear, but grew during incubation.
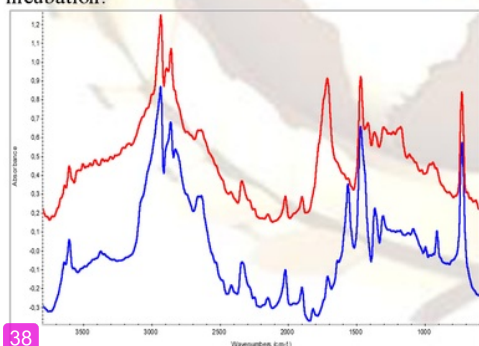

Figure 3 FTIR spectra of ML10 samples, before (lower trace) and after (upper trace) thermal treatment

Polyethylene has main absorptions: CH$_2$ asymmetric stretching (2919 cm^{-1}); CH$_2$ symmetric stretching (2851cm^{-1}); CH$_2$ bending deformation (1473 and 1463 cm^{-1}; CH$_3$ symmetric deformation (1377cm^{-1})[36] or (1375 cm^{-1})[22], wagging deformation (1366 and 1351cm^{-1}); twisting deformation (1306 cm^{-1}); wagging deformation(1176 cm^{-1}); and (rocking deformation (731-720 cm^{-1}) [36].

For polyethylene samples undergo oxidation, the absorption band around 1714 cm^{-1} [51] or 1718 cm^{-1} [22], which can be assigned to the C=O stretching vibration of a ketone group, grows in intensity with extended aging, and at the same time new bands appear. These absorption bands indicate that more than one oxidation product is formed. The carbonyl bands were assigned to C=O stretching vibrations in aldehydes and/or esters (1733 cm^{-1}) carboxylic acid groups (1700 cm^{-1}) and γ-lactone (1780 cm^{-1}) [31] Other study revealed that absorption of carbonyl was composed of different overlapping bands: 1712 cm^{-1} (acids), 1723 cm^{-1} (ketones), 1730 m^{-1}(aldehydes) and 1780 cm^{-1} (lactone)[18].

The peak at around 1560 cm^{-1} appeared for untreated sample and faded during treatment. This peak is assigned to manganese laurate. As reported previous study, the presence of absorbance at 1560 cm^{-1} was due to asymmetric vibration stretching of the carboxylic group coordinated to metal ion [12]. The manganese laurate decomposed when acting as catalyst in decomposing of hydroperoxides.

Fig. 4 shows the carbonyl index (CI) of samples during treatment. In the early periods of treatment, CI slightly increased, after 200 hours of treatment, the CI increased more significantly. Samples containing manganese laurate experienced much more increase of CI than pure sample as the result of higher degradation level. This result is consistent with previous studies which have recorded the increase of CI of polyethylene containing pro-oxidant additives during thermo-oxidative aging [14,18].
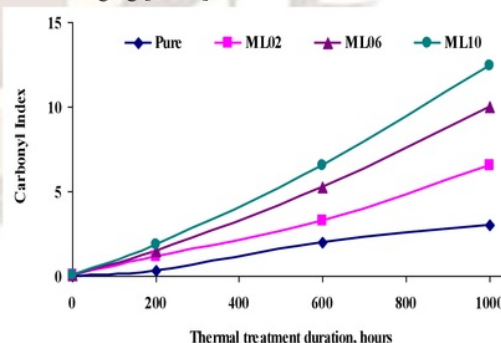
Figure 4 Carbonyl indices of samples during thermal treatment

3.3 Molecular weight
Average molecular weight is a direct measure of chain scissions process resulting lower

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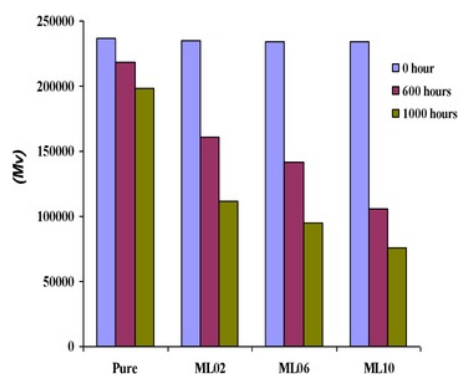chain length of molecules. The average molecular weight $(\overline{Mv})$ obtained by viscometry method and presented in Fig. 5.

Figure 5 Variation of average molecular weight with thermal treatment

As discussed previously, the crosslinking might have occurred in the beginning periods of thermal treatment. In the end periods of treatment, chain scissions have taken place dominantly and generated short chain HDPE that dissolved in solvent during viscosity average molecular weight test. The viscosity average molecular weight of pure samples decreased gradually. In contrary, the molecular weight of samples with manganese laurate decreased significantly during treatment. Increasing the amount of manganese laurate resulted in greater decrease of molecular weight. For example, sample containing 1% manganese laurate experienced the greatest lowering of molecular weight, a decrease of around 67 % of molecular weight after 1000 hours of thermal treatment. The decrease was observed faster at the period of up to 600 hours of treatment, and going slower at the end of period. The samples containing manganese laurate showed the decrease of molecular weight paralleled to the reduction of mechanical properties i.e. tensile strength and elongation at break. This is the evidence of the chain scission took place during treatment. This result is in agreement with that of Erlandsson *et al.* [19] who found that polyethylene containing pro-oxidant experienced a much larger decrease of molecular weight than the pure one during thermal aging.

3.4 Melt Flow Index

Melt flow index (MFI) is indirectly a measure of molecular weight [11]. Molecular weight can be reflected in the mechanical properties. Reduction of mechanical properties reflects reduction of molecular weight [11,37]. Measuring MFI gives supporting evidence on the degradation which has happened.
Loading of manganese laurate resulted in an increase in MFI of the samples during treatment as shown in

Fig. 6. The MFI of samples containing manganese laurate increased slowly at the beginning period, and faster in the end period, while pure samples experienced gradual decrease. With the increase of MFI confirmed the molecular weight decrease as result of chain scission that produced lower molecular weight macromolecules. The MFI increased with increasing the length of thermal treatment also, whereas molecular weight decreased.
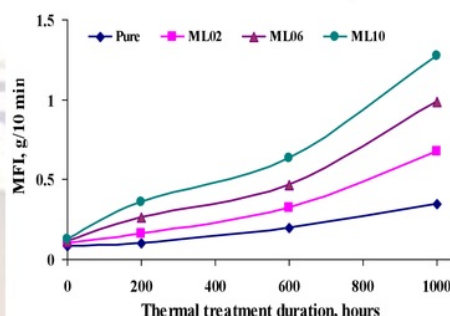

Figure 6 Melt flow indices of samples during thermal treatment

3.5 Thermal stability

Degradation temperature constitutes a measure of thermal stability of samples. The thermogravimetry (TG) traces of ML10 samples are presented in Fig. 7 and the corresponding data are listed in Table 2. The plot showed that TG and its derivative (DTG) traces shifted to lower temperatures after getting thermal treatment for 1000 hours. TG traces of pure HDPE samples were also shifted to lower temperature after 1000 hours of thermal treatment.
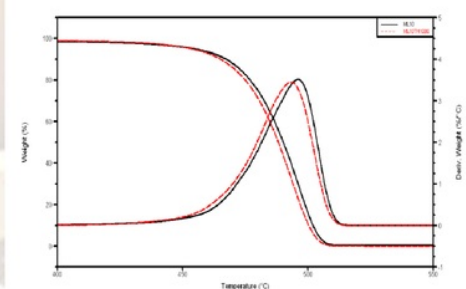

Figure 7. TG and DTG traces of ML10 samples, before (solid line) and after (dashed line) 1000 hours of thermal treatment.

Both pure sample and ML10 sample experienced reduction of thermal stability. It was due to lower molecular weight products of chain scissions, as evidenced by molecular weight measurement. However, ML10 samples underwent a slightly greater reduction than pure one, as a result of manganese laurate played a role in degradation.

Maryudi, Anwaruddin Hisyam, Rosli Mohd Yunus, Mohammad Dalour Hossen Bag /
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Table 2 Degradation temperature of samples, before and after 1000 hours of thermal treatment

Sample	Before treatment				
	T_{onset} °C	$T_{maximum}$ °C	T_{final} °C	Residue %	Ea kJ/mol
Pure	470.15	496.03	518.29	1.04	332.72
ML10	470.02	495.82	518.12	0.44	317.80
	After treatment				
	T_{onset} °C	$T_{maximum}$ °C	T_{final} °C	Residue %	Ea kJ/mol
Pure	464.27	495.16	518.22	0.47	295.97
ML10	463.23	493.26	516.36	0.28	276.00

Activation energy of decomposition process was calculated using Broido equation [38]:

$$\ln\left(\ln\frac{1}{y}\right) = -\frac{E_a}{RT} + \ln\left(\frac{RZ}{E_a\beta}T_{max}^{2}\right) \qquad (3)$$

where y is the fraction of non-volatilized material not yet decomposed, T_{max} is the temperature of maximum reaction rate, β is the heating rate, Z is the frequency factor, and Ea is the activation energy. Initially plots of $\ln(\ln(1/y))$ versus $1/T$ for various stages of decomposition were drawn, such as in Fig. 8 and generally found to be linear, suggesting good agreement with the Broido equation. The activation energies, Ea, determined from the slopes of these plots. The activation energy decreased for both pure and ML10 samples.
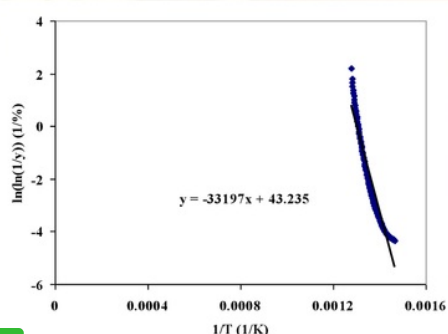
Figure 8: $\ln(\ln(1/y))$ versus $1/T$ for decomposition of ML10 sample after 1000 hours of thermal treatment

3.6 Melting Temperature
The DSC tests were done in order to investigate melting point and crystallinity. Endothermic curve of DSC scan gives information about melting temperature and degree of crystallinity. The DSC scans of samples containing manganese laurate, for treated and untreated samples, are plotted in Fig. 9, and the related data are summarized in Table 3.
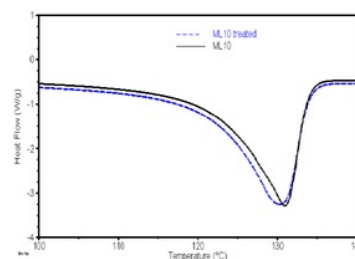

Figure 9. DSC plot of ML10 samples, before (solid line) and after (dash line) 1000 hours of thermal treatment

Fig. 9 showed that the melting temperatures of both pure samples and ML10 samples underwent slight reduction after 1000 hours of thermal treatment. However, samples containing pro-oxidant have lower T_m than pure samples either before or after treatment. The reduction of T_m could be due to the breakdown of HDPE chains and molecular weight reduction. As reported by Colom *et al.* [39] the decrease of the decomposition and melting temperatures is associated with shorter polymeric chains and a lower thermal stability of the material

The crystallinity index obtained from DSC scans and showed the increasing nature during thermal treatment. The crystallinity of pure samples increased around 1%, from 48.04 to 49.03%, whereas ML10 samples underwent a slightly higher increase, about 3%, from 48.86 to 51.86% after 1000 hours of thermal treatment. However, pure sample have initial crystallinity index of 48.04%, and the rest part of material is in amorphous or non crystalline state which allow absorbing oxygen. As reported in literature [40], thermo-oxidative degradation occur with presence of oxygen which is absorbed by the amorphous region of polyethylene. The increase of crystallinity is probably due to chain scission along the amorphous regions. The chain scission allows the freed segments resulted to crystallize [18]. The creation of new intermolecular polar bonds, due to carbonyl groups may also lead to this effect [18,41]. The increase of crystallinity could be contributed by degradation products with shorter chains which possessed the lower Tm than untreated HDPE. Furthermore the increase of crystallinity, particularly ML10 samples, gives supporting evidence on the role of manganese laurate in accelerating degradation process of HDPE during thermal treatment.

Table 3 Melting temperature and crystallinity of samples before and after 1000 hours of thermal treatment

Sample	Before treatment		
	T_m, °C	ΔH_f, J/g	Crystallinity
Pure	131.35	140.8	48.04
ML10	130.95	143.2	48.86
	After treatment		
	T_m, °C	ΔH_f, J/g	Crystallinity
Pure	130.65	143.7	49.03
ML10	130.29	152.0	51.86

T_m: melting point (peak), °C ; ΔH_f: heat of fusion, J/g;
Crystallinity: crystallinity index (%)

4. CONCLUSION
The effect of manganese laurate on enhancing degradation of HDPE during thermal treatment has been investigated. The thermo-oxidative degradation has been confirmed by mechanical properties, FTIR, MFI, viscosity-average molecular weight, TGA, and DSC tests. The mechanical properties were found to be decreased with increasing amount of manganese laurate loading. Samples with 1% of manganese laurate lost 43.33% of their initial strength, whereas pure samples lost 11.74% of their initial strength after 1000 hours of thermal treatment. After thermal treatment, thermal stability and melting temperature were also found to be decreased more significantly for samples with manganese laurate than those of pure samples. The molecular weight of samples with manganese laurate was also found to be decreased significantly and consequently, MFI increased, as proven by MFI measurement. FTIR study also showed that carbonyl groups, as the result of oxidation, grew faster in the sample with manganese laurate than pure samples. The results indicate that manganese laurate accelerates the degradation of HDPE under thermal treatment. It was found that the extent of degradation depended on the amount of additive, i.e. manganese laurate which was added. Manganese laurate has shown the comparable performance with other degradation accelerating agents i.e. cobalt carboxylates.

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REFERENCES
[1] A. Azapagic, A. Emsley and I. Hamerton. *Polymers: The environment and sustainable development.*(Chicester: John Wiley and Sons Ltd.2003.)
[2] MPMA. Performance of the Malaysian Plastics Industry Report. Malaysian Plastics Manufacturers Association (MPMA).Kuala Lumpur,2005.
[3] L. K. Boon. Development of the Malaysian plastic industry and its contribution to the economy. *PRIM Golden Jubilee International Polymer Conference,*, Kuala Lumpur, 2010.
[4] K. Bajer, H. Kaczmarek, J. Dzwonkowski, A. Stasiek and D. Ołdak. Photochemical and thermal stability of degradable PE/paper waste composites obtained by extrusion. *Journal of Applied Polymer Science. 103(4)*: 2007. 2197-2206.
[5] A. L. Andrady, J. E. Pegram and S. Nakatsuka. Studies on enhanced degradable plastics: 1. The geographic variability in outdoor lifetimes of enhanced photodegradable polyethylenes. *Journal of Polymers and the Environment. 1(1)*: 1993. 31-43.
[6] A.-C. Albertsson, C. Barenstedt and S. Karlsson. Susceptibility of enhanced environmentally degradable polyethylene to thermal and photo-oxidation. *Polymer Degradation and Stability. 37(2)*: 1992. 163-171.
[7] E. Lokensgard. *Industrial Plastics: Theory and Applications.* 5th.(New York: Thomson Delmar Learning.2010.)
[8] S. A. Barr-Kumarakuiasinghe. Modelling the thermal oxidative degradation kinetics of polyethylene film containing metal pro-xidants. *Polymer. 35(5)*: 1994. 995-1003.
[9] Z. Osawa, N. Kurisu, K. Nagashima and K. Nakano. The effect of transition metal stearates on the photodegradation of polyethylene. *Journal of Applied Polymer Science. 23(12)*: 1979. 3583-3590.
[10] P. K. Roy, P. Surekha, C. Rajagopal and V. Choudhary. Effect of cobalt carboxylates on the photo-oxidative degradation of low-density polyethylene. Part-I. *Polymer Degradation and Stability. 91(9)*: 2006. 1980-1988.
[11] D. Bikiaris, J. Prinos and C. Panayiotou. Effect of methyl methacrylate-butadiene-styrene copolymer on the thermooxidation and biodegradation of LDPE/plasticized starch blends. *Polymer Degradation and Stability. 58(1-2)*: 1997. 215-228.
[12] P. K. Roy, P. Surekha, C. Rajagopal, S. N. Chatterjee and V. Choudhary. Accelerated aging of LDPE films containing cobalt complexes as prooxidants. *Polymer Degradation and Stability. 91(8)*: 2006. 1791-1799.
[13] P. K. Roy, P. Surekha, C. Rajagopal and V. Choudhary. Thermal degradation studies of

**Maryudi, Anwaruddin Hisyam, Rosli Mohd Yunus, Mohammad Dalour Hossen Bag /
International Journal of Engineering Research and Applications (IJERA) ISSN: 2248-9622
www.ijera.com Vol. 3, Issue 2, March -April 2013, pp.1156-1165**

LDPE containing cobalt stearate as pro-oxidant. *Express Polymer Letters. 1(4)*: 2007. 208-216.

[14] P. K. Roy, P. Surekha, C. Rajagopal and V. Choudhary. Comparative effects of cobalt carboxylates on the thermo-oxidative degradation of LDPE films. *Journal of Applied Polymer Science. 103(6)*: 2007. 3758-3765.

[15] P. K. Roy, P. Surekha, C. Rajagopal, S. N. Chatterjee and V. Choudhary. Studies on the photo-oxidative degradation of LDPE films in the presence of oxidised polyethylene. *Polymer Degradation and Stability. 92(6)*: 2007. 1151-1160.

[16] J. L. Pablos, C. Abrusci, I. Marín, J. López-Marín, F. Catalina, E. Espí and T. Corrales. Photodegradation of polyethylenes: Comparative effect of Fe and Ca-stearates as pro-oxidant additives. *Polymer Degradation and Stability. 95(10)*: 2010. 2057-2064.

[17] N. Sharma, L. P. Chang, Y. L. Chu, H. Ismail, U. S. Ishiaku and Z. A. Mohd Ishak. A study on the effect of pro-oxidant on the thermo-oxidative degradation behaviour of sago starch filled polyethylene. *Polymer Degradation and Stability. 71(3)*: 2001. 381-393.

[18] F. Khabbaz, A.-C. Albertsson and S. Karlsson. Chemical and morphological changes of environmentally degradable polyethylene films exposed to thermo-oxidation. *Polymer Degradation and Stability. 63(1)*: 1999. 127-138.

[19] B. Erlandsson, S. Karlsson and A.-C. Albertsson. The mode of action of corn starch and a pro-oxidant system in LDPE: influence of thermo-oxidation and UV-irradiation on the molecular weight changes. *Polymer Degradation and Stability. 55(2)*: 1997. 237-245.

[20] Excelplas. The impacts of degradable plastic bags in Australia. Final report to Department of the Environment and Heritage. Excelplas Australia, Nolan-ITU, Center for Design at RMIT.Melbourne,2003.

[21] Maryudi, R. M. Yunus, A. H. Nour and M. H. Abidin. Synthesis and Characterization of Manganese Carboxylates. *Journal of Applied Sciences 9(17)*: 2009. 3156-3160.

[22] A. L. Andrady, J. E. Pegram and Y. Tropsha. Changes in carbonyl index and average molecular weight on embrittlement of enhanced-photodegradable polyethylenes. *Journal of Polymers and the Environment. 1(3)*: 1993. 171-179.

[23] M. Kurata and Y. Tsunashima. Viscosity-Molecular Weight Relationships and Perturbed Dimensions of Linear Chain Molecules. in: J. Bandrup, E.H. Emmergeut and G.A. Grulke (Editors), *Polymer Handbook* (Toronto, John Wiley & Sons.Inc,1999.) pp.

[24] Y. Lei, Q. Wu, F. Yao and Y. Xu. Preparation and properties of recycled HDPE/natural fiber composites. *Composites Part A: Applied Science and Manufacturing. 38(7)*: 2007. 1664-1674.

[25] G. Liang, J. Xu, S. Bao and W. Xu. Polyethylene/maleic anhydride grafted polyethylene/organic-montmorillonite nanocomposites. I. Preparation, microstructure, and mechanical properties. *Journal of Applied Polymer Science. 91(6)*: 2004. 3974-3980.

[26] C. Vasile and M. Pascu. *Practical Guide to Polyethylene.*(Shawbury: Rapra Technology Limited.2005.)

[27] A.-C. Albertsson, S. O. Andersson and S. Karlsson. The mechanism of biodegradation of polyethylene. *Polymer Degradation and Stability. 18(1)*: 1987. 73-87.

[28] A.-C. Albertsson, C. Barenstedt and S. Karlsson. Degradation of enhanced environmentally degradable polyethylene in biological aqueous media: Mechanisms during the first stages. *Journal of Applied Polymer Science. 51(6)*: 1994. 1097-1105.

[29] K. Murata, Y. Hirano, Y. Sakata and M. A. Uddin. Basic study on a continuous flow reactor for thermal degradation of polymers. *Journal of Analytical and Applied Pyrolysis. 65(1)*: 2002. 71-90.

[30] B. Singh and N. Sharma. Mechanistic implications of plastic degradation. *Polymer Degradation and Stability. 93(3)*: 2008. 561-584.

[31] J. V. Gulmine, P. R. Janissek, H. M. Heise and L. Akcelrud. Degradation profile of polyethylene after artificial accelerated weathering. *Polymer Degradation and Stability. 79(3)*: 2003. 385-397.

[32] F. H. Winslow. Photooxidation of High Polymers. *Pure and Applied Chemistry. 49(4)*: 1977. 495-502.

[33] M. Iring, E. Földes, K. Barabás, T. Kelen, F. Tüdos and L. Ódor. Thermal oxidation of Linear Low Density Polyethylene. *Polymer Degradation and Stability. 14(4)*: 1986. 319-332.

[34] R. T. Johnston and E. J. Morrison. Thermal Scission and Cross-Linking during Polyethylene Melt Processing, *Polymer Durability*. Advances in Chemistry, American Chemical Society,1996.) pp. 651-682.

[35] D. M. Wiles. Oxo-biodegradable polyolefins. in: R. Smith (Editor), *Biodegradable Polymers for Industrial Applications.*(Cambridge, Woodhead Publishing,2005.) pp. 54-75.

[36] J. V. Gulmine, P. R. Janissek, H. M. Heise and L. Akcelrud. Polyethylene characterization by FTIR. *Polymer Testing. 21(5)*: 2002. 557-563.

[37] W. Sung and Z. L. Nikolov. Accelerated degradation studies of starch-filled polyethylene films. *Industrial & Engineering Chemistry Research. 31(10)*: 1992. 2332-2339.

[38] A. Broido. A simple, sensitive graphical method of treating thermogravimetric analysis data. *Journal of Polymer Science Part A-2: Polymer Physics. 7(10)*: 1969. 1761-1773.

[39] X. Colom, J. Cañavate, J. J. Suñol, P. Pagès, J. Saurina and F. Carrasco. Natural and artificial aging of polypropylene–polyethylene copolymers. *Journal of Applied Polymer Science. 87(10)*: 2003. 1685-1692.

[40] ASM-International. *Characterization and failure analysis of plastics.*(USA: ASM International.2003.)

[41] M. Sebaa, C. Servens and J. Pouyet. Natural and artificial weathering of low-density polyethylene (LDPE): Calorimetric analysis. *Journal of Applied Polymer Science. 45(6)*: 1992. 1049-1053.

Thermo-oxidative Degradation of High Density Polyethylene Containing Manganese Laurate

oxidative degradation behaviour of sago starch filled polyethylene", Polymer Degradation and Stability, 2001
Crossref

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7   Anthony L. Andrady. "Studies on enhanced degradable plastics: 1. The geographic variability in outdoor lifetimes of enhanced photodegradable polyethylenes", Journal of Environmental Polymer Degradation, 01/1993
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8   Kadlec, Petr, Michal Cermak, and Radek Polansky. "Influence of Halloysite nanotubes in low-density polyethylene on electric polarization", 2015 16th International Scientific Conference on Electric Power Engineering (EPE), 2015.
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10 L. Boukezzi, A. Boubakeur, C. Laurent, M. Lallouani. "DSC Study of Artificial Thermal Aging of XLPE Insulation Cables", 2007 IEEE International Conference on Solid Dielectrics, 2007
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22 Ann-Christine Albertsson, Camilla Barenstedt, Sigbritt Karlsson. "Susceptibility of enhanced environmentally degradable polyethylene to thermal and photo-oxidation", Polymer Degradation and Stability, 1992
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23 P.K. Roy, P. Surekha, C. Rajagopal, S.N. Chatterjee, V. Choudhary. "Accelerated aging of LDPE films containing cobalt complexes as prooxidants", Polymer Degradation and Stability, 2006
Crossref

15 words — < 1%

24 Chiellini, Emo, Andrea Corti, Salvatore D'Antone, and David McKeen Wiles. "Oxo-Biodegradable Polymers: Present Status and Future Perspectives", Handbook of Biodegradable Polymers Isolation Synthesis Characterization and Applications, 2011.
Crossref

15 words — < 1%

25 Bikiaris, D.. "Effect of methyl methacrylate-butadiene-styrene copolymer on the thermooxidation and biodegradation of LDPE/plasticized starch blends", Polymer Degradation and Stability, 1997
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15 words — < 1%

26 Azapagic. "Feeding the Waste Streams: Sources of Polymers in the Environment", Polymers the Environment and Sustainable Development, 02/14/2003
Crossref

15 words — < 1%

27 Santhoskumar, A. U.. "Improvement of photo- and biodegradation of LLDPE/LDPE with a novel cobalt (II) 11-(9Z, 12Z-octadeca-9, 12-dihydroxy)-10, 13-dihydroxyactadecaneate cinnamic dextrose additives", Polymer Bulletin, 2015.
Crossref

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28 Khan, I., and B. Poh. "Statistical analysis on the effect of the molecular weight and testing rate on peel strength of epoxidized natural rubber (ENR 25)-based adhesives", Journal of Elastomers and Plastics, 2012.
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30   Hanifi, Saeed, Abdulrasoul Oromiehie, Shervin Ahmadi, and Hassan Farhadnejad. "(Corn Starch and Montmorillonite Nanocomposite)-Reinforced Polypropylene: Preparation, Properties, and Biodegradability", Journal of Vinyl and Additive Technology, 2014.   10 words — < 1%
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38 P. K. Roy. "Comparative effects of cobalt carboxylates on the thermo-oxidative degradation of LDPE films", Journal of Applied Polymer Science, 03/15/2007
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42 Roy, P.K.. "Effect of benzil and cobalt stearate on the aging of low-density polyethylene films", Polymer Degradation and Stability, 200512
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