

COMPARISON OF MANGANESE LAURATE, MANGANESE PALMITATE AND MANGANESE STEARATE ON ACCELERATING DEGRADATION OF HDPE DURING NATURAL WEATHERING

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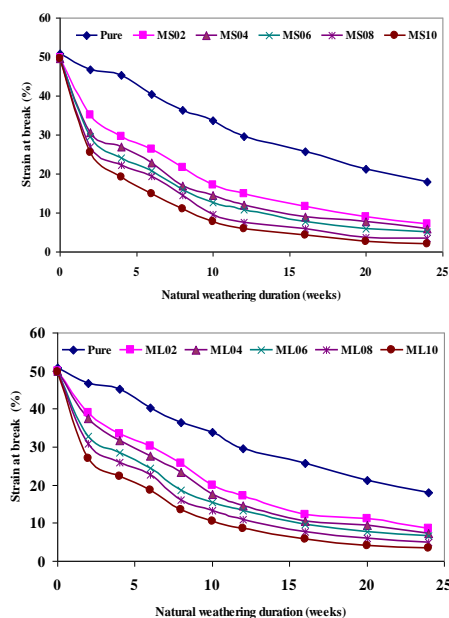
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Graphical abstract



Abstract

High density polyethylene (HDPE) degradation has been studied. In this study, HDPE was incorporated with manganese laurate, manganese palmitate and manganese stearate as pro-oxidant additives. Preparation of samples were conducted by adding the HDPE resin with pro-oxidant additives in the range of 0-1.0 wt %. A twin screw extruder was employed prior to the injection molding technique. Samples were subjected to natural weathering for the maximum duration of 24 weeks. Assessments on the change of the properties of samples after natural weathering treatment were conducted by FTIR analysis, tensile testing and average molecular weight analysis. In term of their capabilities to accelerate degradation of HDPE, manganese stearate exhibited more influence than manganese laurate and manganese palmitate. The carbonyl group's peak arises as a result of oxidation during the treatment as revealed by FTIR traces. Samples with pro-oxidant additives shows a loss of their strain at break. The amount of pro-oxidant additives increases the degradation of samples.

Keywords: HDPE degradation, natural weathering, manganese laurate, manganese palmitate, manganese stearate

Abstrak

Degradasi polietilena berketumpatan tinggi (HDPE) yang diperbadankan dengan bahan pro-oksidan iaitu mangan laurat, mangan stearat dan mangan palmitat di bawah cuaca semula jadi telah disiasat. Sampel telah disediakan dengan memuatkan bahan tambahan pro-oksidan dalam julat 0 – 1.0% berat dalam resin HDPE menggunakan ekstruder skru berkembar diikuti oleh teknik pengacuan suntikan. Rawatan cuaca semula jadi dilakukan untuk tempoh maksimum 24 minggu. Penilaian terhadap perubahan sifat-sifat sampel selepas rawatan cuaca semula jadi telah dijalankan oleh analisis FTIR, ujian tegangan

dan purata analisis berat molekul. Tambahan pro-oksidaan mempamerkan keupayaan untuk mempercepatkan degradasi HDPE, di mana mangan stearat mempengaruhi lebih daripada mangan laurat dan mangan palmitate. Kesan FTIR telah mendedahkan bahawa puncak kumpulan karbonil timbul akibat daripada pengoksidaan. Sampel dengan bahan pro-oksidaan menunjukkan kehilangan ketegangan mereka pada patahan. Degradasi meningkat dengan peningkatan jumlah bahan tambahan pro-oksidaan.

Kata kunci: Degradasi HDPE, rawatan cuaca semula jadi, mangan laurat, mangan palmitat, mangan stearat

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1.0 INTRODUCTION

In the modern day, plastics become the materials that can be found easily anywhere. Plastics materials provide various products with wide range of strength, durability, and flexibility that can be utilized for many purposes. Utilization of plastics include their applications in the packaging, automobile, construction, electrical and electronics industries [1]. In the same time, increasing of plastic products utilization leads to enormous waste generation, which can rise environmental concern. In Malaysia, plastic wastes contribute up to 11.2% form total 1.2 million tons of solid wastes generated annually. It is estimated at about 15% of the total weight of landfill [2]. Plastic waste has poor degradability properties. The degradation of plastics, particularly for PE, is very slow under environmental conditions, and it takes place to a certain extent [3], [4]. For the reasons, many studies on degradation of plastics have been conducted, particularly for thermoplastics such as PP, LDPE and LDPE. The studies involved additives containing trans-metals to accelerate the degradation process under artificial treatment or weathering [5]–[7]. Additives are incorporated with plastic resins for the purpose of accelerate the degradation process. Some pro-oxidants additives are transition metal ion complexes in the form of either stearates or other organic ligand complexes. The most commonly used pro-oxidants are Fe^{3+} , Mn^{2+} , and Co^{2+} stearates [7], [8].

Artificial treatments are commonly used to simulate natural conditions or natural weathering. Studies of degradation of thermoplastics under thermal treatment have been conducted to simulate the natural condition. Study of LDPE and coated-LDPE ageing in air-circulated oven at 95 °C found that LDPE was more brittle than coated-LDPE after ageing process. Bikiaris *et al.* [9] studied the effect of methyl methacrylate-butadiene-styrene copolymer on the thermo-oxidation of LDPE/plasticized starch blends. It was found that the oxidation rate increases with increasing amount of pro-oxidant in the blends. Some studies of photo-degradation of polyethylene utilized artificial UV light instead of solar UV light, included effect of cobalt carboxylates on the photo-oxidative degradation of low-density polyethylene by using 40W UV-B lamps generating energy between 280 and 370 nm with

maxima at 313 nm [10]. However, artificial treatments could not exactly represent natural weathering conditions.

Furthermore, some natural weathering treatment of PE products have been conducted to study the degradability of the materials. However, the condition of the weather is closely related with the geographical, or the location where the study is conducted. Recent studies on natural weathering of PP or PE, whether incorporated with pro-oxidant or without pro-oxidant have been conducted in several locations. Study of natural weathering on degradation of polyethylene in Tehran, Iran, indicated that the overall rate of degradation process is clearly dependent on the polyethylene composition, season of the year, and the duration of the weathering of the samples [11]. Addition of commercial pro-oxidant in HDPE and LLDPE increased the degradation process rapidly under natural weathering conducted in Porto Alegre, Brazil [12]. Natural weathering treatment was also conducted to assess the degradability of acetylated bamboo plastic composites in Taiwan [13]. Local climate in Wuhan, China was also employed to perform study of degradation of wood composite consisted from rice straw and HDPE [14]. However, there was no pro-oxidant loaded into the composites. Effect of cobalt stearate on natural weathering of LLDPE/soya powder was also studied under local climate in Penang, Malaysia [15]. The natural weather treatment had affected the crystallinity, weight loss and molecular weight of the composites with the presence of cobalt stearate. To the best of our knowledge, the study on the degradation of HDPE containing manganese laurate (ML), manganese palmitate (MP) and manganese stearate (MS) under natural weathering has not existed yet. The purpose of this study is to investigate effect of manganese laurate, manganese palmitate and manganese stearate on enhancing degradation of HDPE during natural weathering under weather conditions of Gambang, Malaysia.

2.0 METHODOLOGY

2.1 Materials

Manganese laurate, manganese palmitate and manganese stearate that have been synthesized and characterized previously [16] were used as pro-oxidant additive. The high density polyethylene (HDPE) resin used was Etilinas HD5301AA, product of Polyethylene Malaysia Sdn. Bhd. The properties of HDPE resin were density of 0.951 kg/m³ and melt flow index (MFI) 0.081 g/10 min at temperature 190 °C and load of 2.16 kg. Xylene (purchased from Merck) was used for molecular weight determination.

2.2 Methods

2.2.1 Preparation

Compounding and injection molding were carried out to prepare samples. Resin and additive (manganese laurate or manganese palmitate or manganese stearate) were blended and dried in the oven at temperature of 80 °C for 6 hours. Co-rotating twin screw extruder (MODEL: Lab Tech Engineering with L/D 40) was used to perform the compounding process of HDPE separately with manganese laurate, manganese palmitate, manganese stearate at the temperature of 200 °C. The pellet of compounding process was dried at temperature of 80 °C for 2 hours, before injection molding process in a Nissei NS20-2A injection molder at temperature of 200 °C [17]. Pellet was molded into standard shape and dimension according to ASTM D638-08, specimen of type V. Samples were labeled based on the amount of pro-oxidant loaded as listed in Table 1.

2.2.2 Sample Properties Evaluation

Fourier Transforms Infrared (FTIR) spectroscopy (MODEL: Thermo Nicolet Avatar 370) was used to investigate the functional group. Attenuated Total Reflectance (ATR) technique was applied with 64 scans and resolution of 4 cm⁻¹ as reported previously [17]. The collections of background and scanning of the spectra of samples were carried out using smart performer part. The investigation was focused on carbonyl group region that laid down at the band of 1700 – 1740 cm⁻¹ [18]. Carbonyl index (CI) was the investigated parameter that defined as the ratio of area around band of 1718 cm⁻¹ and area of band at 1375 cm⁻¹, attributed to carbonyl groups and CH₃, respectively [19].

Tensile testing was performed following ASTM D638-08: Standard Test Method for Tensile Properties of Plastics. The test also followed ASTM D618-99: Standard Practice for Conditioning Plastics for Testing that recommended the conditioning of specimens at 23±3 °C for 40 hours prior to tensile testing. The universal testing machine (MODEL: Shimadzu AG-X) was run at a crosshead speed of 10 mm/min with a load cell of 5 kN

and a gauge length (grip-to-grip) of 25.4 mm. The temperature of tests was maintained at 25 °C.

Average molecular weight of samples were determined by using Mark-Houwink-Sakurada equation [10], [20] as expressed in Eq. (1).

$$[\eta] = 16.5 \times 10^{-3} \bar{M}^{0.83} \quad (1)$$

Where $[\eta]$ = intrinsic viscosity and \bar{M} = average molecular weight. Intrinsic viscosity was obtained by measuring the viscosity of dissolved HDPE in xylene at 105°C. Ostwald capillary viscometer was used for the test.

Table 1 Sample labeling according to the additives loading onto HDPE resin

Sample label	Manganese laurate loaded (wt%)	Manganese palmitate loaded (wt%)	Manganese stearate loaded (wt%)
Pure HDPE	-	-	-
ML02	0.2	-	-
ML04	0.4	-	-
ML06	0.6	-	-
ML08	0.8	-	-
ML10	1.0	-	-
MP02	-	0.2	-
MP04	-	0.4	-
MP06	-	0.6	-
MP08	-	0.8	-
MP10	-	1.0	-
MS02	-	-	0.2
MS04	-	-	0.4
MS06	-	-	0.6
MS08	-	-	0.8
MS10	-	-	1.0

2.2.3 Natural Weathering Treatment

Natural weathering treatment of samples was carried out on the open rack facing at an angle of 450 to south (equator) following method reported in literatures [11], [21]. Samples were mounted on the rack, exposed directly to outdoor natural environment. Natural weathering treatment was conducted Gombang, Malaysia (latitude: 3°43'07"N and longitude: 103°07'16"E). Generally, this site is tropical area with relatively high rainfall, high temperature and high intensity of sunlight. In Peninsular Malaysia, the minimum range of mean relative humidity varying from a low 80% in February to a high of only 88% in November. April and May are the months with the highest average monthly temperature in most places and December and January are the months with the lowest average monthly temperature as reported by Malaysian Meteorological Department [22]. The temperature and rainfall are summarized in Table 2. The samples were submitted to treatment for the duration of 2, 4, 6, 8, 10, 12, 16, 20, and 24 weeks. The samples positions were turned every week to ensure sunlight reaching both

sides of sample's surfaces. Five samples were taken for tensile testing and five additional samples at certain

periods for other tests include FTIR and molecular weight analysis.

Table 2 Gambang (latitude: 3°43'07"N and longitude: 103°07'16"E) average weather throughout the year [22]

Month	Temperature (°C)				Average rainfall (mm)	
	Average		Absolute		Daily	Monthly
	Max	Min	Max	Min		
January	29.5	22.5	36.1	11.5	8.8	274.3
February	30.8	22.5	35.2	18.5	6.1	170.3
March	31.8	23.1	39.4	19.2	5.9	181.7
April	32.9	23.7	38.8	20.3	4.6	138.8
May	33.3	23.9	38.6	13.7	6.2	193.4
June	32.9	23.7	36.4	21.5	5.5	165.4
July	32.6	23.5	37.5	20.6	5.8	180.2
August	32.7	23.4	36.6	13.5	7.3	227.5
September	32.6	23.3	35.0	14.9	6.5	196.0
October	32.0	23.3	35.6	21.0	9.0	279.2
November	30.7	23.2	35.0	14.8	13.2	395.9
December	29.5	22.9	34.2	20.2	21.8	674.5

3.0 RESULTS AND DISCUSSIONS

3.1 FTIR Study

Figure 1 represents the FTIR trace of MS10 samples due to natural weathering for 24 weeks. It shows the increases of absorbance at 3300 – 3500 cm^{-1} attributed to hydroxyl groups, 1700 – 1800 cm^{-1} attributed to carbonyl groups, and 1000 – 1300 cm^{-1} attributed to ether groups, and 900 – 1000 cm^{-1} attributed to vinyl groups after 24 weeks of natural weathering. However, the absorbance of carbonyl groups that comprise ketonic, ester, carboxylic, aldehyde, and lactone is the most changed. The absorbance of other groups slightly increase. This result is similar to that of Sheikh *et al.* [11] who observed the significant changes in hydroxyl (3200 – 3600 cm^{-1}), carbonyl (1715 – 1720 cm^{-1}) and unsaturated (800 – 1000 cm^{-1}) groups regions as a function of the exposure time under the natural and accelerated conditions.

As carbonyl groups generated during natural weathering, consequently CI rises. Figure 2 shows the change of CI of various samples during natural weathering. It shows the obvious difference between pure HDPE and HDPE with manganese carboxylates. HDPE with additives undergoes more significant increase of CI than pure HDPE. In the first weeks, the increases of CI are larger than those at end period of treatment. It is due to rapid photo-degradation process since the solar radiation in the first weeks is quite high. It leads to rapid formation of carbonyl groups. Andrady *et al.* [19] have reported that the increase in ambient temperatures could play an important role in enhancing the rates of photo-degradation in materials exposed to sunlight. During solar ultraviolet radiation, the greater temperature would contribute higher effect on degradation of plastics than the greater humidity. The degradation takes place slower by the increasing rainfall and the reduced solar radiation. It is shown by

the small increase of CI from the middle to end period of natural weathering. Generally, MS gives the greatest effect on enhancing natural photo-degradation of HDPE, indicated by the greatest increase of CI after 24 weeks of natural weathering.

3.2 Strain at Break

Figures 3 – 5 represent the change of strain at break during natural weathering treatment. Strain at break is presented rather than tensile strength data, since strain at break is more useful measure in oxidative degradation than tensile strength as reported in literature [23]. The changes in strain at break give more obvious indication of degradation than the changes in tensile strength. All samples undergo the decreasing strain at break. However, strain at break of HDPE containing additives decrease more rapidly than pure HDPE. Despite the increase of tensile strength in the first weeks, pure HDPE undergo strain at break decrease during entire period of natural weathering exposure. These figures also obviously show that the strain at break of HDPE with manganese carboxylates decrease rapidly in the first 8 weeks of treatment. That indicates the rapid degradation has occurred. As explained earlier, it is due to high solar radiation that induces rapid photo-degradation supported by effect of high temperature. This result is consistent with that of previous study that comparing the weathering of polyethylene agricultural mulch films under high-UV outdoor exposure conditions at ambient temperature and at 25 °C inside a controlled temperature UV-transparent chamber [19]. Under ambient conditions, in Dhahran (Saudi Arabia), the surface temperature of the plastic rose as high as 60 °C depending on color and thickness, because of the absorption of solar IR wavelengths. The average elongation at break of the polyethylene was periodically measured; this property is particularly sensitive to degradation in this type of material. The rate

of light-induced breakdown of the polyethylene under comparable UV exposure was slower by a factor of four

when the temperature was controlled at the lower temperature of 25 °C.

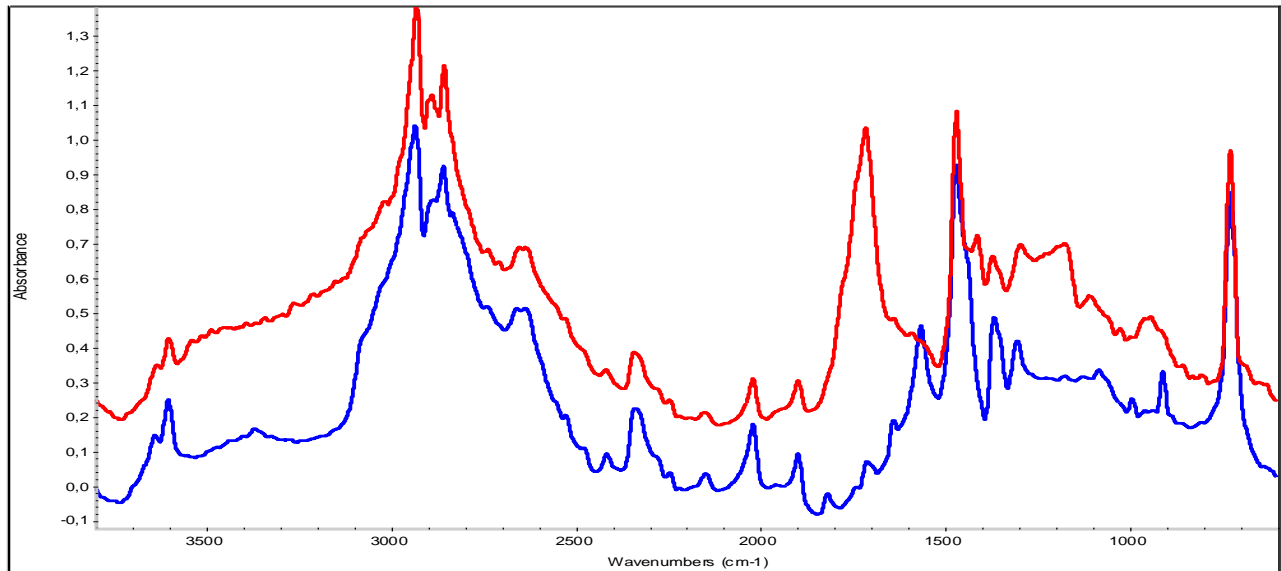


Figure 1 FTIR spectra of MS10 samples before (lower trace) and after (upper trace) natural weathering

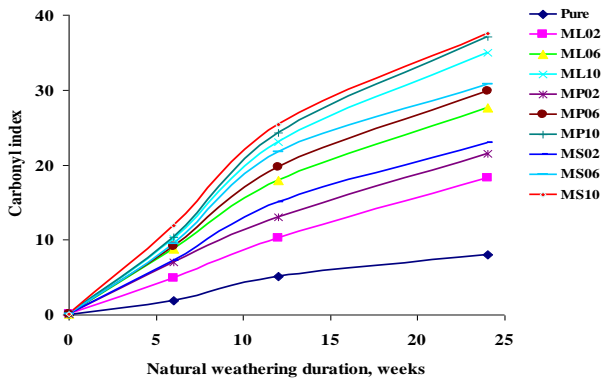


Figure 2 Carbonyl indexes (CI) of various compositions of HDPE samples during natural weathering

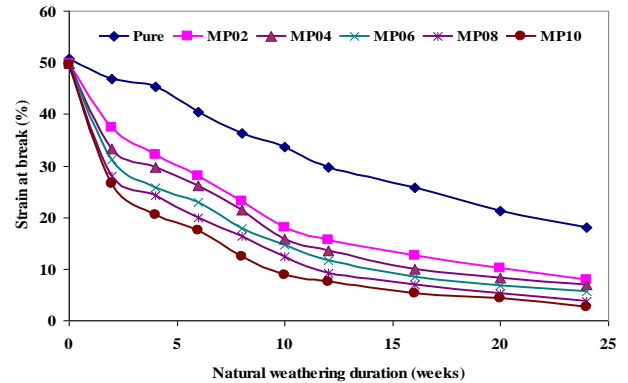


Figure 4 Strain at break of HDPE containing manganese palmitate during natural weathering treatment

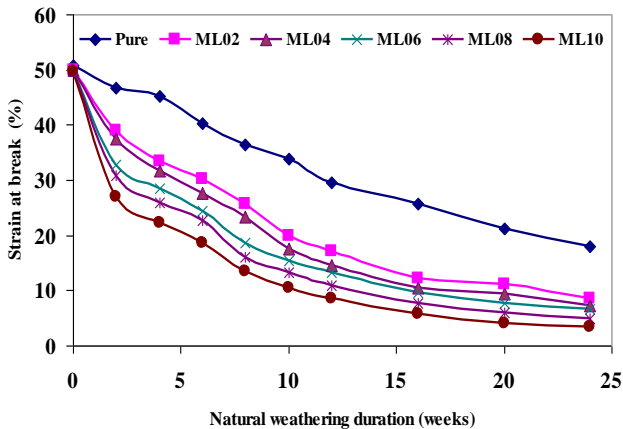


Figure 3 Strain at break of HDPE containing manganese laurate during natural weathering treatment

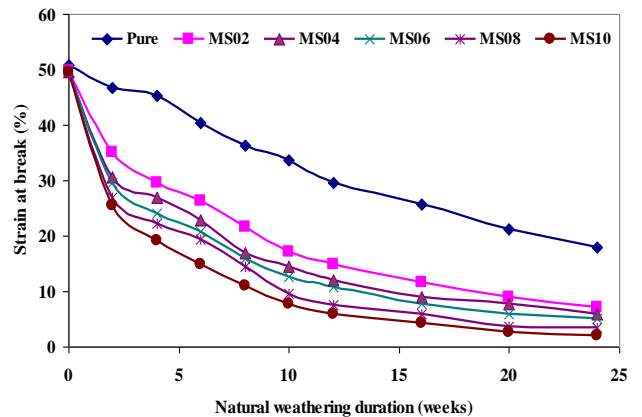


Figure 5 Strain at break of HDPE containing manganese stearate during natural weathering treatment

At around week 10 – 12, the rates of degradation changes dramatically as indicated by extreme deflection of curves, and changes hereafter from high to low slope until end of treatment. Moreover, the end part of curves is found to be flat, indicating very slow degradation. The rain water may leach the degradation products on the surface of sample and lets solar radiation to penetrate deeper. Nevertheless, the lower intensity of solar radiation and lower temperature during high rainfall period lets degradation remaining slow. In the end of treatment, solar radiation increases, as the rainfall decrease. Yet the photo-degradation has been retarded by degradation products on the surface, and thermo-oxidative degradation induced by temperature may play secondary effect that allows the overall degradation keep taking place very slowly. It is also found that the deleterious effect of degradation during natural weathering mostly occurs on the surface of sample. It suggests the photo-degradation, which is stimulated by solar radiation, predominates in the overall degradation.

Figures 3-5 also describe that increasing amount of additives i.e. manganese carboxylates results in increasing degradation. For example, pure HDPE loses 64.54% of its initial strain at break after 24 weeks of natural weathering exposure. Meanwhile, MS 02 and MS10 samples lose 85.56% and 95.74% of their strain at break, respectively. Generally, MS give the most influential effect among other additives i.e. ML and MP as obviously shown in Table 3.

Table 3 Loss of tensile strength and strain at break during natural weathering

Samples	Loss of strain at break, %
Pure	64.54
ML02	82.90
ML10	93.02
MP02	84.04
MP10	94.80
MS02	85.56
MS10	95.74

The result is in agreement with that of Sheikh *et al.* [11] who have compared degradation of commercial LDPE and photosensitized LDPE which contains ferric stearate under weathering condition of Tehran. They have found that photosensitized LDPE films deteriorate more rapidly than commercial LDPE as indicated by the decrease of tensile properties. It has also been reported that polyethylene films exposed to solar UV-B radiation readily lose their extensibility and strength [23], [24]. Ojeda *et al.* [12] have also reported the similar results on natural weathering of PP, HDPE, LLDPE and LLDPE/HDPE blend. All samples experienced decrease of strain at break by increasing exposure time.

3.3 Molecular Weight

Figure 6 represents the changes of average molecular weight of pure HDPE and various compositions of HDPE during natural weathering. All samples exhibit decrease of average molecular weight during natural weathering. HDPE is sensitive to solar radiation, especially solar UV radiation. However, HDPE with additives i.e. ML, MP and MS experience much more significant decrease of molecular weight than pure HDPE. Average molecular weight of pure HDPE decreases about 40 % of its initial value after 24 weeks of natural weathering. The incorporation of manganese carboxylates as pro-degradant additives has enhanced the degradability of HDPE. The average molecular weight decreases more significantly when the amount of incorporated additives increases. For example, MS02 sample undergoes a reduction of 69.02% of its initial value, and 85.82% for MS10 sample after 24 weeks of natural weathering. HDPE containing manganese stearate has demonstrated greatest reduction of molecular weight. This result is in agreement with previous study by Andrady *et al.* [19] who has observed that polyethylene films exposed to solar UV radiation experience decreasing the average molecular weight.

In general, the reductions of molecular weight in the first 12 weeks of natural weathering are greater than those of 12 weeks later. In other words, the degradation takes place faster in the beginning than the end of natural weathering. It parallels to the decrease of strain at break of samples during natural weathering. It has proved that chain scissions occurred during natural weathering consequently result in lowering average molecular weight as well as decrease of mechanical properties i.e. strain at break and tensile strength.

4.0 CONCLUSION

The effect of manganese laurate, manganese palmitate and manganese stearate on enhancing degradation of HDPE during natural weathering treatment under weather conditions of Gombang, Malaysia has been investigated. The natural degradation has been confirmed by FTIR, mechanical properties, and average molecular weight tests. FTIR study has shown that carbonyl groups, as the result of oxidation, grew faster in the sample with additives (i.e. manganese laurate, manganese palmitate and manganese stearate) than pure samples. The reductions of strains at break during natural weathering were found to be greater with increasing amount of additives loading. Pure sample lost 64 % of its initial strain at break, whereas samples with 1% of pro-oxidant additives lost its initial strain at break in the range of 93 – 95. The average molecular weight of samples with additives was also found to be decreased significantly. The results indicate that manganese laurate; manganese palmitate and

manganese stearate accelerate the degradation of HDPE during natural weathering treatment. It was found that manganese stearate had given the greatest effect among the additives. It was also found that the extent of degradation depended on the amount of additives incorporated.

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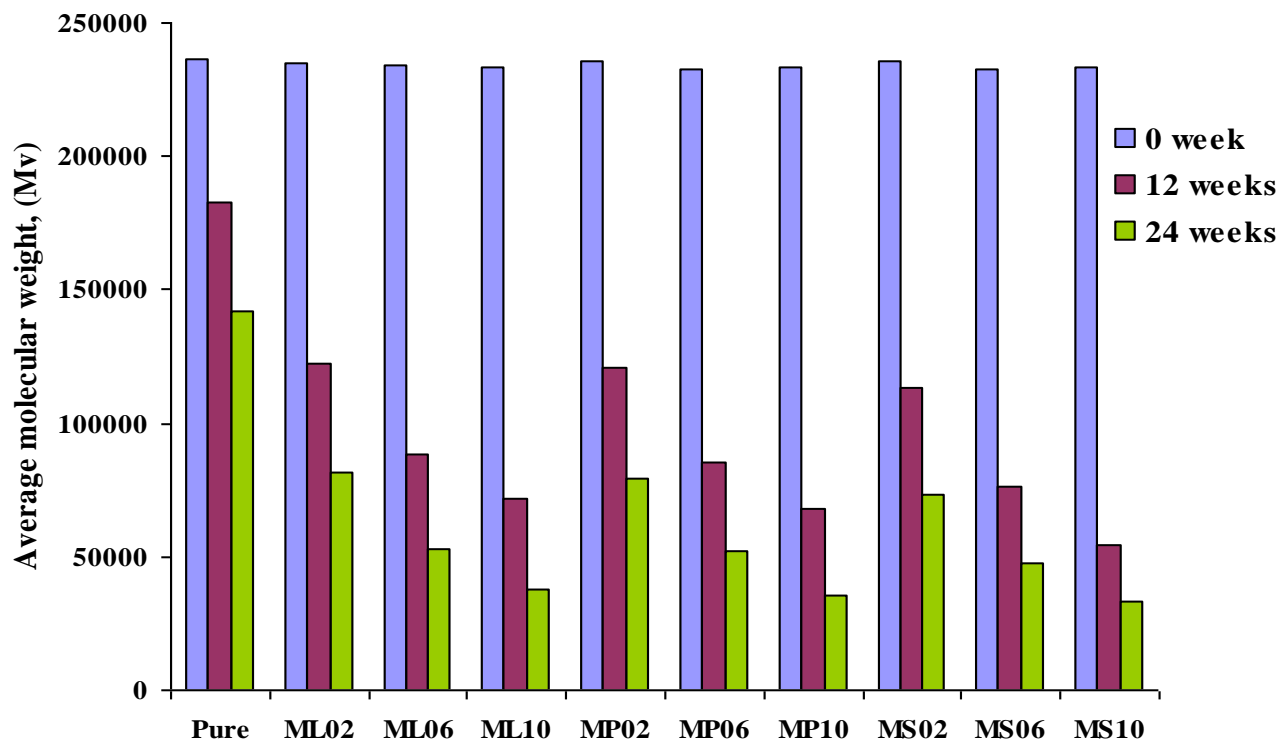


Figure 6 Average molecular weight of samples during natural weathering treatment

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