

The degradation of high density polyethylene containing manganese stearate under accelerated weathering

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Abstract: The utilization of polyethylene particularly high density polyethylene (HDPE) has led to growth of amount of plastic waste. The study on utilization of manganese stearate as pro-oxidant additive for HDPE has been conducted. Specimens were prepared by incorporating manganese stearate from 0 to 1.0 wt% in HDPE resin using twin screw extruder followed by injection molding. Accelerated weathering was carried out by combining UV exposure, condensation and water spray for maximum duration of 1000 hours. FTIR analysis, tensile testing, average molecular weight analysis, and thermogravimetric analyzer (TGA) test were carried out to assess the changes during accelerated weathering. FTIR traces revealed that carbonyl groups arose during accelerated weathering as the result of oxidation. Strain at break of samples decreased more significantly by incorporation of manganese stearate. Thermal stability and molecular weight has decreased significantly by the present of manganese stearate. The results show that manganese stearate is able to enhance degradation of HDPE. The degradation rate of HDPE depends on the amount of manganese stearate loaded.

Keywords: *manganese stearate, pro-oxidant additives, HDPE, degradation, accelerated, weathering.*

1 Introduction

The utilization of thermoplastic, particularly PE has led to environmental issues. Plastic waste amount has grown significantly as the increase of resin consumption. In 1999, The principal thermoplastic polymers (LDPE/HDPE, PP, PVC, PS, and PET) consumptions exceeded 28 millions tones in Western Europe, 79% of total plastic markets [1]. Polyethylene is by far the most widely used polymeric material, accounting for 41% of the US plastic production [2]. Consumption of HDPE in United States was predicted that it would increase significantly [3].

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[4,5] to accelerate the degradation process under artificial treatment. Artificial treatments are commonly used to simulate natural conditions or natural weathering.

Some studies of photo-degradation of polyethylene utilized artificial UV light instead of solar UV light. Roy et al.[6] studied 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. The other

studies utilized 40 W sunlamps generating energy between 280 and 350 nm for photo-degradation of LDPE [7,8]. The studies showed that LDPE degraded at different stages according to compositions under UV exposure.

Studies of degradation of thermoplastics under thermal treatment have been conducted. Saccani et al. [9] have studied ageing of LDPE and coated-LDPE in air-circulated oven at 95°C. LDPE was found to be more brittle than LDPE with coating after ageing process. Bikiaris et al. [10] studied the effect of methyl methacrylate-butadiene-styrene copolymer on the thermo-oxidation of LDPE/plasticized starch blends. In other study, Sharma et al. [11] conducted a study on the effect of pro-oxidant, i.e. manganese stearate, on the thermo-oxidative degradation of sago starch filled polyethylene.

However, individual treatment such as thermal treatment, UV treatment alone could not simulate natural weathering conditions precisely. Natural weather condition comprises temperature, sunlight exposure, rain, humidity etc. Integrated treatments that combine those factors are needed to closely simulate the natural weather conditions. Accelerated weathering has designed to fulfill that requirement by combining UV exposure, thermal conditioning, condensation and water spray.

The study on the degradation of HDPE containing manganese stearate as pro-oxidant additive under natural weathering has not existed yet. The purpose of this study is to investigate effect of manganese stearate on the degradation of HDPE under accelerated weathering.

2 Materials and Methods

2.1 Materials

Manganese chloride tetrahydrate (System), sodium hydroxide, stearic acid (Merck), ethanol (industrial grade), acetone, n-hexane (R&M Chemicals), cyclohexane, benzene (Merck), and toluene (System) 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 kg/m³ and melt flow index (MFI) 0.081 g/10 min at temperature 190°C and load 2.16 kg.

2.2 Methods

2.2.1 Synthesis of manganese stearate

Manganese stearate was synthesized by following the methods of synthesis of cobalt (II) linolenat, cobalt (II) oleat as reported in literature [12]. The synthesis comprised of two steps; (i) reaction between stearic acid and sodium hydroxide (in stoichiometric ratio and liquid phase) to produce sodium stearate at 80-85°C and (ii) reaction between manganese chloride and sodium stearate at 80-85°C. Manganese stearate was filtered and washed with hot water to separate sodium chloride and then dried in the oven at 60 °C for 2 hours.

2.2.2 Characterization of manganese stearate

The characterization comprises bulk density, solubility, melting point, and degradation temperature. Bulk density test was performed using volumetric cylinder. The cylinder with volume of 25 ml was filled with the sample. The excess material on top of the measuring cylinder was scraped off. The bulk density was determined by dividing the net weight of sample by volume of cylinder. The solubility was tested

in water with various solvents e.g. ethanol, n-hexane, cyclohexane, acetone, benzene, and toluene. Water content test was performed in an oven operated at 105°C.

Degradation temperatures were evaluated by thermogravimetric analysis (TGA) (MODEL: TA Instruments Q500). The applied heating rate was 20°C/min from room temperature up to 1000°C under nitrogen atmosphere. Melting points were measured by differential scanning calorimetry (DSC) (MODEL: TA Instruments Q1000), where the heating rate was 10°C/min in temperature range 30-200°C under nitrogen atmosphere.

2.2.3 Sample preparation

The compounding of HDPE with manganese stearate was carried out using co-rotating twin screw extruder (MODEL: Lab Tech Engineering with L/D 40) at temperature 200-210°C. Prior to extrusion, HDPE and manganese stearate 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 temperature 195-200°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 stearate as listed in Table 1.

Table 1. Sample labeling

Sample label	Manganese stearate incorporated (%)
Pure	0
MS02	0.2
MS04	0.4
MS06	0.6
MS08	0.8
MS10	1.0

2.2.4 Sample Properties Evaluation

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. Carbonyl groups at around 1700-1800 cm⁻¹ became the interest since they were the major products in degradation [13].

Tensile testing: Tensile testing was carried out 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.

Molecular weight: Average molecular weight of HDPE was determined from viscosity measurement. Sample was dissolved in xylene at temperature of 105°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 [6,14].

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

where $[\eta]$ = intrinsic viscosity and \overline{M}_v = average molecular weight.

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.

2.2.5 Accelerated Weathering Treatment

Accelerated weathering treatments was carried out using an accelerated weathering tester (MODEL: Q-LAB QUV/spray with solar eye irradiance control) following ASTM G154-06: Standard Practice for Operating Fluorescent Light Apparatus for UV Exposure of Nonmetallic Materials, using UVA 340 lamps at an irradiance of 0.68 W/m² [15,16]. Every cycle comprises 3 steps: 8 hours UV exposure 0.68 W/m² at 60°C, 0.25 hour water spray and 3.75 hours condensation at 50°C. The samples were submitted to the aging process for durations of 100, 200, 400, 600, 800 and 1000 hours. The samples positions were turned every 50 hours to ensure UV light reaching both sides of sample's surfaces. Five samples were taken for tensile testing and five additional samples at certain periods for other tests e.g. FTIR, molecular weight, and TGA.

3 Results and Discussion

3.1 Characterization of manganese stearate

Characterization of manganese stearate was performed in order to observe the essential properties to be a polymer additive. Thermal properties are most important since polymer processing take place at a relatively high temperature. It was found that manganese stearate possessed properties which could be summarized in Table 2. Manganese stearate possesses adequate thermal stability to mix with HDPE resin in compounding process. It was also found that manganese stearate was insoluble in water, ethanol, n-hexane, cyclohexane, acetone, benzene, and toluene.

Table 2. Properties of manganese stearate

Property	Value
Bulk density, g/cm ³	0.201
Water content, %	2.39
Ash content, %	14.34
Degradation temperature, °C	

T_{onset}	287.98
T_{maximum}	347.72
T_{final}	411.73
Melting temperature, °C	
T_{onset}	114.69
$T_{\text{m (peak)}}$	117.66

3.2 Degradation Evaluation of HDPE

3.2.1 FTIR study

During accelerated weathering, thermal and UV light exposure play simultaneous effects on HDPE samples. Thermal exposure leads to thermo-oxidative degradation, whereas UV light exposure leads to photo-degradation. The UV light gives the major contribution on degradation of HDPE. Figure 1 shows the FTIR spectra of MS10 samples before and after accelerated weathering. The absorbance in the region of 1700-1800 cm^{-1} which is the region of carbonyl groups, increases after accelerated weathering. The region of carbonyl groups normally comprises peaks of some compounds. However, they consolidate in one wide peak. A small increase in the region of 3300-3500 cm^{-1} was detected. This region is attributed to hydroxyl groups. This result is consistent with results of previous studies. In the degradation of polyethylene, Bikiaris et al. [10] observed absorbance at 3450 cm^{-1} and 3380 cm^{-1} that are attributed to formation of alcoholic groups and hydroperoxides groups respectively. Albertson and Karlsson [17] reported that in pure LDPE degraded in accelerated environment, alcoholic compounds, i.e. butanol, pentanol, were found in degradation products. Other small increase is also observed in the region of 1000-1300 cm^{-1} . This region is attributed to ether (C-O) bond [18]. An increase in absorbance is also observed at the region between 940 and 970 cm^{-1} , where vinyl groups absorb [10]. During water spray and condensation, some degradation products on the sample surface might be leached as they are water soluble, allowed UV light to penetrate deeper and resulted in further photo-degradation

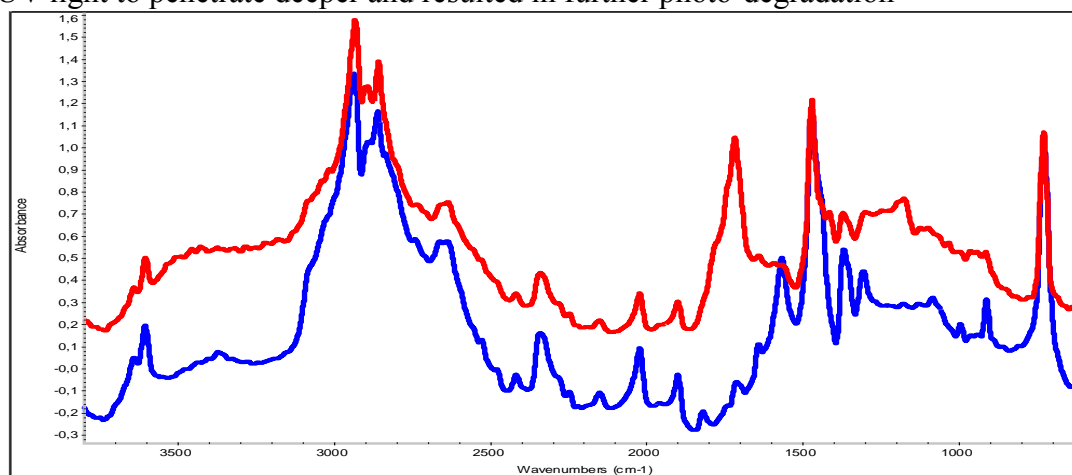


Figure 1 FTIR spectra of MS10 samples, before (lower trace) and after (upper trace) 1000 hours of accelerated weathering

3.2.2 Strain at Break

Strain at break is commonly used to monitor degradation process rather than other mechanical properties. Figure 2 reveals the changes of strain at break of various samples during accelerated weathering. All samples experienced decreasing strain at break systematically during treatment. Pure samples experienced gradual decrease of strain at break since the beginning of accelerated weathering. The crosslinking happened in the beginning of accelerated weathering led samples to be more brittle and lowering strain at break. When accelerated weathering continued, it led to chain scission and decreasing tensile strength continuously. However, all samples containing manganese stearate underwent decrease of strain at break much faster than pure samples. The strain at break decreased rapidly since accelerated weathering started. They demonstrated faster decrease of strain at break in the beginning of accelerated weathering than in the end periods.

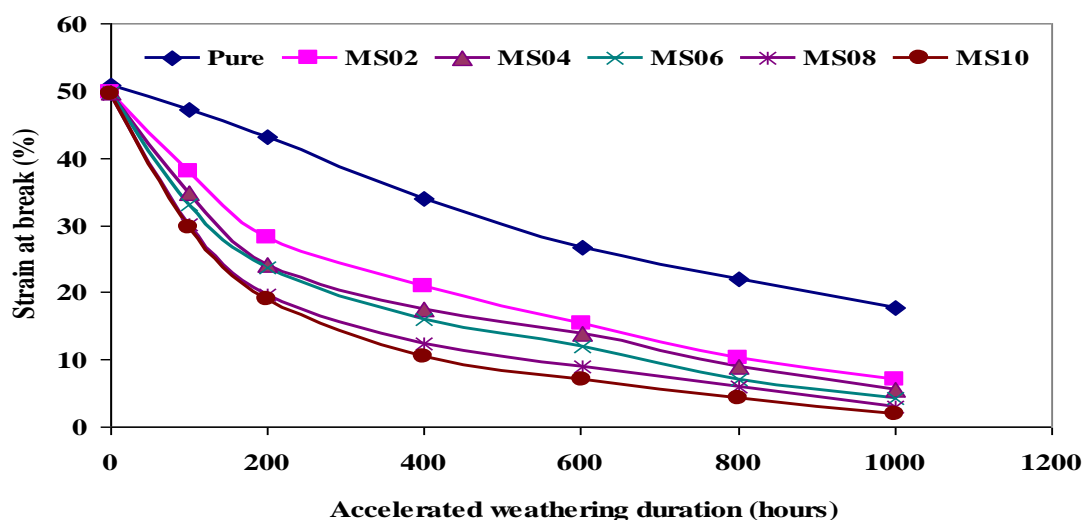


Figure 2 Strain at break of HDPE containing manganese stearate during accelerated weathering treatment

The increasing amount of manganese stearate results in increasing degradation. For example, pure HDPE loses 65.19% of its initial strain at break after 1000 hours of accelerated weathering exposure. Meanwhile, MS 02 and MS10 samples lose 85.79 and 96.33 % of their strain at break, respectively.

After 1000 hours of accelerated weathering, the cross section of samples containing manganese stearate showed that accelerated weathering, which dominated by UV light effect (photo-degradation) rather than thermal effect (thermo-oxidative degradation), mostly affected the surface of samples, while the inner part was still in good condition. It is due to the limited penetration of UV light into the inner part of samples, particularly for thick samples. Water spray also contributes in leaching degradation products and prevents some products to block UV penetration into deeper surface. However, it only affects on thin surface of sample. It is confirmed by the rapid decrease of strain at break of samples in the beginning periods of accelerated weathering, and going slower in the end periods of accelerated weathering. Further effect on strain at break is contributed by thermal effect or thermo-oxidative degradation only.

3.2.3 Molecular Weight

Average molecular weight is a direct measure of degradation. Figure 3 represents the changes of average molecular weight (Mv) of pure sample and various compositions of samples during accelerated weathering. The Mv of pure sample significantly decreased during accelerated weathering. The Mv of pure sample reduced 42.53% of its initial value. On the other hand, the Mv of the samples with manganese stearate decreased dramatically during accelerated weathering. However, this result reveals that HDPE is quite sensitive to UV exposure; moreover it is worsened with the presence of manganese stearate as pro-degradant additive. The greater reduction of Mv occurs by increasing the amount of incorporated manganese stearate. For example, MS02 sample underwent a reduction of 70.32% of its initial value, and 88.49% for MS10 sample,

Generally, the reductions of molecular weight at period of 0 to 600 hours of accelerated weathering are greater than those of period of 600 to 1000 hours. Simply, it suggests a faster degradation in the beginning period of weathering than in the end period. The result is in agreement with that of Roy et al. [6] who studied molecular weight of LDPE containing cobalt-based pro-oxidant additives during UV exposure for maximum duration of 600 hours. Pure LDPE experienced a slower decrease of molecular weight than LDPE containing pro-oxidant additives.

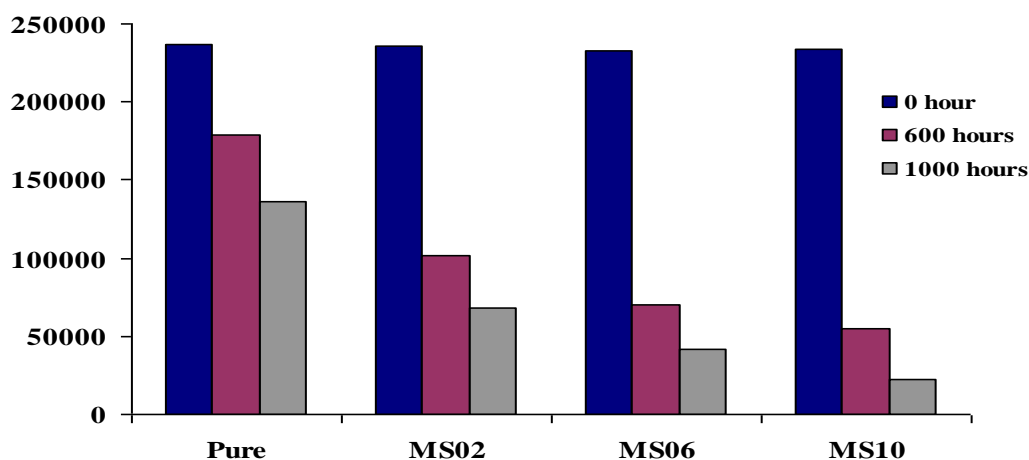


Figure 3 Average molecular weight of samples during accelerated weathering treatment

3.2.4 Thermal Stability

Pure and MS10 samples were analyzed using TGA, since MS10 sample has shown the greatest reductions of properties i.e. strain at break and average molecular weight (Mv). Figure 4 and 5 represent thermogravimetry (TG) and derivative thermogravimetry (DTG) traces of pure sample and MS10 sample, before and after accelerated weathering. The TG and DTG traces shifted to lower temperatures for both pure sample and MS10 sample after 1000 hours of accelerated weathering. All samples demonstrated a single stage of decomposition process. Thermal stabilities of samples which are indicated by degradation temperature are summarized in Table 3.

After getting accelerated weathering, the decrease of degradation temperature of MS10 sample was found to be greater than that of pure sample. The lower degradation temperature of sample indicates the lower average molecular weight. It confirms to the decrease of average molecular weight during accelerated weathering which has been presented earlier.

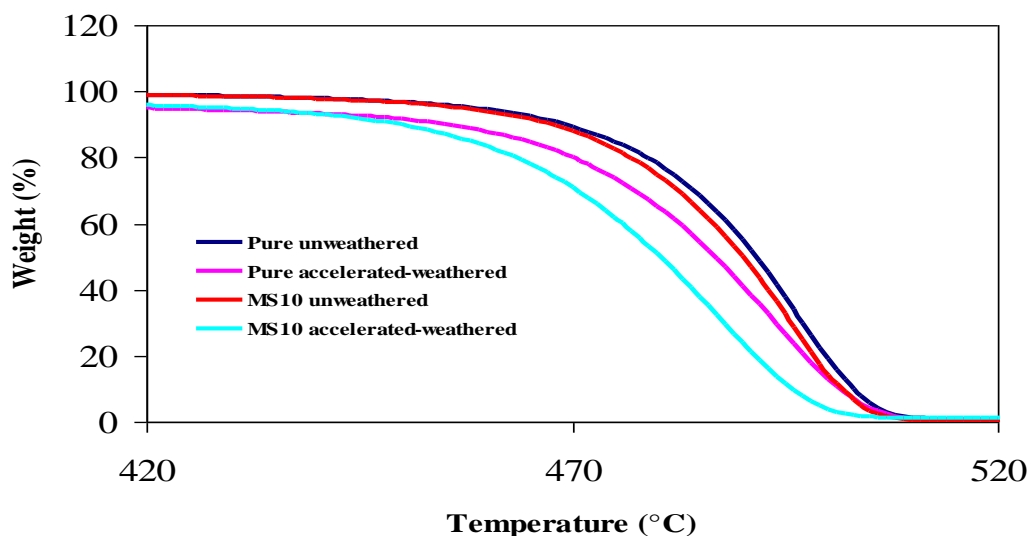


Figure 4 TG traces of pure and MS10 samples, before and after 1000 hours of accelerated weathering treatment

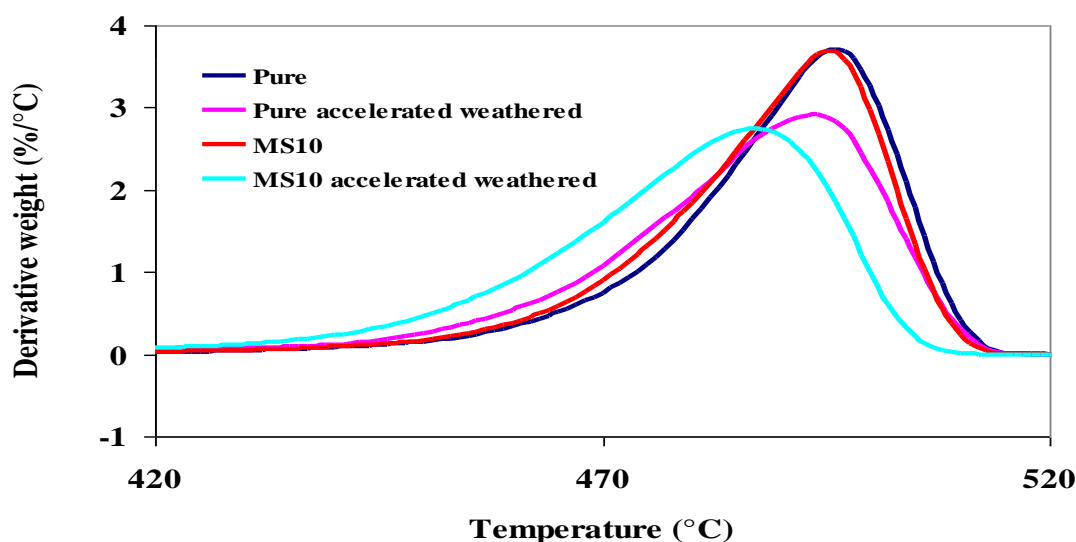


Figure 5 DTG traces of pure and MS10 samples, before and after 1000 hours of accelerated weathering treatment

The activation energy was calculated by using Broido equation [19] as shown below.

$$\ln(\ln(1/y)) = -(E/R)(1/T) + const. \quad (2)$$

The activation energy was also found to be decreased after 1000 hours of accelerated weathering. Yet there was no change in residue. The results are similar with that of Beg and Pickering [16] who observed effect of accelerated weathering on pure polypropylene (PP) and PP composite. They found that pure PP experienced a reduction of thermal stability indicated by decrease of degradation temperature and activation energy after 1000 hours of accelerated weathering.

Table 3 Degradation temperature of HDPE samples before and after 1000 hours of accelerated weathering treatment

Sample	Before accelerated weathering					After accelerated weathering				
	T _{onset} °C	T _{maximum} °C	T _{final} °C	Residue %	Ea kJ/mol	T _{onset} °C	T _{maximum} °C	T _{final} °C	Residue %	Ea kJ/mol
Pure	470.15	496.03	518.29	1.04	332.72	462.00	493.80	516.36	0.78	253.37
MS10	469.15	495.33	517.32	0.55	311.04	451.94	486.90	511.53	0.45	233.42

4 Conclusions

The effect of manganese stearate on degradation of HDPE under accelerated weathering has been investigated. The degradation has been confirmed by FTIR, tensile, average molecular weight, and TGA tests. FTIR study also showed that carbonyl groups, as the result of oxidation, arose significantly in the samples with manganese stearate. The strain at break was found to be decreased with increasing amount of manganese stearate loading. Sample with 1% of manganese stearate lost 96.33% of its initial strain at break, whereas pure sample lost 65.19% of its strain at break. The average molecular weight of samples with manganese stearate was also found to be decreased significantly. After accelerated weathering treatment, thermal stability was also found to be decreased more significantly for sample with manganese stearate than that of pure sample. The results have indicated that manganese stearate accelerates the degradation of HDPE under accelerated weathering treatment. It was found that the extent of degradation depended on the amount of manganese stearate incorporated.

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