The Effect of Manganese Palmitate as Pro-Oxidant Additive on Mechanical Properties of Polypropylene

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Abstract. Polypropylene (PP) is one of the most widely used polymer materials, such as in textile, automotive spare part, furniture, household appliances, and packaging. However, PP is very difficult to degrade naturally. When the product from PP is not reused and discharged into the environment, this plastic can cause problems to the environment. One of the solution to improve degradability of PP is by adding pro-oxidant additives. The addition of pro-oxidant additives can make polypropylene to easily oxidize and degrade into shorter chains by producing carbonyl groups. The pro-oxidant additive used in this research is manganese palmitate. The additive was synthesized by reacting palmitic acid with sodium hydroxide and followed by reaction with manganese chloride tetrahydrate. The purpose of this research was to study the effect of manganese palmitate as a pro-oxidant additive to the structure and mechanical properties of PP before and after thermal treatment. The thermal treatment was carried out by providing heating in PP at various temperatures (25, 60, and 90°C) for 2, 4, 6, 8, and 10 days. The structure and mechanical properties of PP was characterized by functional group analysis (FTIR) and mechanical properties (Tensile tester). FTIR spectra of PP film after thermal treatment at temperature 60 and 90°C showed the presence of carbonyl group in 1700-1720 cm\(^{-1}\) region. After thermal treatment at 90°C, PP film could not be analyzed by mechanical properties because it was damaged and destroyed. The peak intensity of the carbonyl group increased with the increasing temperature of heating. PP films with the addition of manganese palmitate both before and after thermal treatment have a lower tensile strength and elongation compared to the pure PP, but their modulus young are higher, so that the films of PP with addition of pro-oxidant became more fragile and rigid. In addition, the PP film with heating treatment at 90°C cannot be analysed due to it was damaged and destroyed.

Keywords: manganese palmitate, polymer oxo-biodegradable, polypropylene, thermal degradation

1. Introduction
Polymer materials have been widely used in various fields such as packaging for food and electronics. Plastic is one of the most commonly used packaging materials in industry, from home industry to large industry. Plastic is a material that has properties such as flexibility, toughness, and another properties that support the product, and often used as packaging materials. The process of making plastic is easy and low cost than the other materials. Plastic is preferred as a packaging material\(^1\). Polypropylene (PP) is...
one of polymers the most widely used as packaging material. However, PP is difficult to decomposed in nature.

The use of many plastics can cause plastic waste to pollute the environment. Approximately 100 million tons of synthetic plastics are produced worldwide each year, and due to plastic can not be biodegraded by microorganisms, so it will continue to exist until hundreds of years.

One of the solutions to solve environmental pollution caused by plastic buildup is by making polymers that has oxo-degradation properties. The oxo-degradation polymer is formed by adding a pro-oxidant additive to the polymer. The addition of pro-oxidant additives is a promising solution to solve the environmental pollution problems caused by plastic waste. The process of oxo-biodegradation occurs in two stages. The first stage is to break the main chain of polymers into smaller fragments through the process of oxidation-reduction and the second stage is the fragment was attacked by microorganisms in environment. These additives are transition metal ion complexes of carboxylic acids. The transition metal salt which have been widely used are stearate salts of iron, cobalt and manganese.

Previous study done by Maryudi, that using manganese carboxilic acid could increasing the degradation process of High Density Polyethylene (HDPE) films. The effect of using Manganese palmitate (MnP) additive on the degradation of Polypropylene (PP) has not been investigated. In this work has been made to evaluate the effect of the addition of MnP on physical and mechanical properties of PP before and after thermal treatment.

2. Experimental

2.1. Materials
Manganese chloride tetrahydrate (MnCl$_2$·4H$_2$O), palmitic acid (C$_{15}$H$_{31}$COOH), sodium hydroxide (NaOH), aqua dim, ethanol (C$_2$H$_5$OH), xylene, were obtained commercially from Aldrich Chemical Co., and polypropylene was obtained from Polymer Industry (PT. Tripolyta).

2.2. Methods

2.2.1. Synthesis of manganese palmitate. Manganese palmitate was synthesized by reacting sodium hydroxide and palmitic acid with ethanol as a solvent to produce sodium palmitic. Manganese chloride tetrahydrate was heated at a temperature of 90 °C under nitrogen atmosphere and sodium palmitic was added into a solution of manganese chloride, then refluxed for 1.5 hours. After that the solution was left for 24 hours at room temperature until it occurs to precipitate. Manganese palmitic was filtered and washed with hot water, and ethanol, and then dried in a vacuum oven at 40 °C for 4 hours.

2.2.2. Preparation of polypropylene films. PP films were prepared by addition pro-oxidant additive with concentration from 0.2%, 0.6% and 1.0% (w/w) of the total mass, then it was dissolved in xylene. The mixture was placed in petri dish, its solvent was evaporated, and then pressed by using hot press at 150 °C for 5 minutes to form films.

2.2.3. Thermal degradation. PP films were heated for various days from 0, 2, 4, 6, 8 and 10 days at 60 °C and 90 °C. PP films before and after thermal treatment were characterization by using FTIR Bruker Alpha and Tensil tester faviraph Textechno41066.

3. Results and discussion
The most used parameter to evaluate the extent of thermal degradation of PP film is carbonyl index. This was due the presence of autooxidation reaction mechanism of the transition metal to catalysis the degradation of the PP films. The presence of heat and oxygen, hydroperoxides (ROOH) as an impurity in polymer chains can be formed and further this hydroperoxides were decomposed by reduction-oxidation reaction to produce radicals by the presence of pro-oxidant additive in polymers. These
radicals then attack to other polymer chains to produce carbonyl group in polymer chains. Figure 1 show the carbonyl group that was formed after thermal treatment at 60 and 90 °C for 10 days.

![ATR spectrum of oxo-biodegradable PP films contains 1% MnP with various temperature for 10 days.](image1)

**Figure 1.** ATR spectrum of oxo-biodegradable PP films contains 1% MnP with various temperature for 10 days.

![Carbonyl index of oxo-biodegradable PP films contains 1% of MnP with various temperature for 10 days.](image2)

**Figure 2.** Carbonyl index of oxo-biodegradable PP films contains 1% of MnP with various temperature for 10 days.

Carbonyl index was calculated by comparing the absorbance of carbonyl group to absorbance of reference group. The increasing of carbonyl index at higher temperature treatment indicates that the degradation of PP film was higher occurred at higher temperature. The carbonyl index was smallest observed at room temperature, so this degradation of the PP films is slower than that of at higher temperature. This clearly indicates that the contribution of manganese palmitate (MnP) to accelerate the thermal degradation of the PP films at higher temperature. The increasing of temperature would effect the mobility of free radical to react with oxygen and polymer chain to produce new hydroperoxides. The physical change of the PP films show that heating treatment at 60 ºC and 90 ºC, the PP films become more brittle than heating treatment at room temperature. In addition, the PP films with heating treatment at 90 ºC was very brittle and can not be analyzed further. The previous work indicated that pro-oxidant additive will increase degradation process with using thermal treatment. 

Figure 3 shows that with the various duration of thermal treatment could increase the degradation process showed with the increasing of carbonyl index value. This indicates that the presence of MnP could make the PP easier to degradate than pure PP. PP Oxo-biodegradation films was tested using tensile tester before and after thermal treatment to know the mechanical properties of the PP films.

![Carbonyl index of oxo-biodegradable PP films contains 1% of MnP with thermal treatment at 60 ºC for various days.](image3)

**Figure 3.** Carbonyl index of oxo-biodegradable PP films contains 1% of MnP with thermal treatment at 60 ºC for various days.
The sample used for mechanical test were the pure PP films and the PP films with 1% MnP additive before and after thermal treatment at 60 ºC for 10 days. The PP film with 1% MnP additive after thermal treatment at 90 ºC for 10 days could not be analyzed the mechanical properties because the physically of film has been broken. This indicates that the PP film with 1% of MnP after thermal treatment at 90 ºC for 10 days had been thermally degraded. The results of tensile strength and elongation can be seen in Figure 4 and Figure 5.

The tensile strength and the elongation of the PP films containing 1% of MnP decrease after thermal treatment (Figure 4 and 5). This behaviour is explained due to phenomenon of the polymer chain reorganization with a lower degree of orientation. This is attributed by the presence of MnP. After thermal treatment, the MnP could accelerate to produce of free radical to produce macroradical and further react with oxygen and other PP chain to become smaller chain fragments and this is related with the increasing carbonyl index results. The increase in Modulus young indicates the brittleness of film PP increases (Figure 6), and so physically the PP films after thermal treatment is more brittle than pure PP.

4. Conclusion
The intensity of the carbonyl group peak increased with the increasing temperature of thermal treatment. The PP films with addition of manganese palmitate (MnP) both before and after thermal treatment have a lower tensile strength and elongation compared to the pure PP, but their modulus young are higher, so that the PP films with addition of pro-oxidant became more fragile and rigid. This result indicate that the presence of MnP and thermal treatment could make the PP easier to degrade than pure PP.
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