CHAPTER FIVE: GENERAL DISCUSSION

Biodegradation of EDP is a two steps reaction. The first step is abiotic polymer degradation. Most synthetic carbon-based polymers are inert towards microorganism in the form in which they are originally produced. In order to make the carbon nutrients available to microorganisms, polymers must be transformed by a variety of physical or chemical reactions to low molecular weight metabolites.

Abiotic actions can be divided into two: chemical or physical degradation mechanisms. Hydrolysis and oxidation are examples of chemical degradation mechanisms. The first two experiments done in this project were to determine the optimal chemical degradation mechanism of the given samples. Oxidation was the preferred chemical degradation as proven especially by sample LL. The oxidation of polymers depends on the chemical structure and morphology. According to Scott (1994), HDPE should degrade faster than LLDPE as HDPE undergo chemicrystalisation, which is breaking of tie-bonds between crystallites faster than LLDPE. However, in this study, samples LL, which is made from LLDPE degrades faster. This points to one difference between LL samples and other samples, that is, the amount of TDPA^{TM}. In LL sample used here it was 7% whereas other samples contained only 3% of TDPA^{TM}. TDPA^{TM} is an additive that contains a certain amount of prooxidant that acts like a catalyst (Khabbaz, 1999) that helps to initiate the chemical degradation process. The oxidation initiation rate for LL sample is assumed to be faster since the amount of TDPA^{TM} in sample LL was twice higher than in other samples. Another reason could be because LLDPE has higher amorphous regions than HDPE.

Temperature also played a role in oxidative degradation. In this study 60°C was chosen as this is the typical composting temperature in an active composting system (Day, 1997). Khabbaz et al found that at a higher temperature of 100°C the average molecular weight of samples LDPE-PO (LDPE mix with prooxidant additive similar to TDPA™) was lower than the same samples exposed to 60°C within the same exposure duration. In addition to that, the changes in carbonyl index for 14 days at different temperatures was higher for samples exposed to 100°C than samples exposed to 60°C. This means that at a higher temperature, the sample degraded faster. However this depends on the thermal behaviour of EDP. As explained by Day et al (1997), some EDP have low melting temperature. Thus, for these EDP when they are exposed to a temperature higher than the melting temperature any changes are attributed to physical rearrangements of molecule of the samples rather than chemical oxidative actions. Khabbaz (1999) also reported that there are other factors that influenced the rate of thermal and thermooxidative degradation such oxygen pressure and sample thickness.

On the other hand, all the samples in this project did not show any reaction when exposed to hydrolytic treatment. The hydrolysis of polymers also depends on the chemical structure and morphology of polymers. Polyethylene has higher crystalline regions than amorphous regions; therefore, there is less access for hydrolytic actions. This makes polyethylene hydrophobic. Day (1997) obtained similar results, where polyethylene-based samples did not show any hydrolytic degradation.

Since the degradation path of the samples is oxidative, composting is the suitable waste management option. Landfill is not suitable because the chemical reactions inside landfills are mostly anaerobic.

Through a report written by Dr. Benhard Raninger (2000), it was established that EPI's EDP can be composted. The latest test done in composting containers in Germany showed complete degradation after 84 days. In this present study the composting trial was done for 45 days with no significant change in weight loss or additional functional groups from oxidation. However there was a 20% decrease in percentage elongation at break point for all samples. Perhaps this was a sign that there were some molecular rearrangements within the polymer structure. The slight increase in weight of all samples at the beginning of the exposure was probably due the same reason stated before. Day et al (1997) showed that nonpolyethylene-based samples could be composted within 12 days while polyethylene-based polymers were not affected. By analysing both reports from Day et al (1997) and Raninger (2000), nonpolyethylene-based polymers can degrade faster than polyethylene-based polymers.

Other factors also influenced the rate of degradation of plastic films in composting environment such as surface area. For example Raninger (2000) shredded the plastic samples together with waste and the results was after 2 weeks of intensive composting approximately 25% of the EPI TDPA^{TM} plastics degraded. Therefore, the higher the surface area, the higher the rate of degradation. Other factor is the carbon to nitrogen ratio of compost mixture as recorded by Gross et al (1994). The rate of degradation differs when different carbon to nitrogen ratio was used. For example Gross et al (1994) exposed same type of samples in five different C:N ratio compost mixture. The rate of degradation of the sample was highest for compost mixture C, where its C:N ratio was 31.2 followed by mixture B, where its C:N ratio was 61.4. The former C:N ratio was the optimum value for composting. In this study moisture content did not affect the rate of degradation, as the samples were hydrophobic as proven in the thermal hydrolytic exposure experiment. For EDP that is not hydrophobic, moisture

content does play a role. In addition to that, moisture content is an important factor for composting process itself where moisture content between 50 to 60% is the optimum value for maintaining a highly biological system for the decomposition of organic matter (Agamuthu, 2001).

Biodegradation is the bioassimilation of the reduced molecular weight polymers. Degraded EPI TDPA™ polyethylene can be used by bacterium chosen as a carbon source for growth. Therefore it can be concluded that if degraded EPI TDPA™ polyethylene plastics are mixed together other organic waste destined for composting, the plastics will be converted into carbon dioxide, water and inorganic compounds.

The time for EDP to biodegrade into carbon dioxide, water and biomass depends on the rate of abiotic degradation process (Scott, 2000) because the rate of bioassimilation of low molar mass oxidation products is much faster. In comparison between the non-polyethylene based polymers and polyethylene based polymers studied by Day et al (1997) and Yue et al (1996), non-polyethylene based polymers degraded abiotically faster than polyethylene based polymers. Even though the addition of prooxidants helps EPI EDP in accelerating the rate of abiotic degradation rate but so far it has not been able to compete with other EDPs such as PCL or PHB.

Composting or biological recycling is one of the plastic management options. Using EDP in this option has its potentials such as using EDP completes the carbon cycle and divert some wastes from landfills. One of the disadvantage is the cost of EDP, which can be five times more (Agamuthu, 2000). This could discourage people from using it. Perhaps the benefits of using EDP should be imparted to the consumers to encourage them to use EDP.

In this study the compostability of plastic was checked based on loss of weight. According to the American Standard and Testing Method (ASTM) D 6002-96, there are other suggestions in establishing the compostability of environmentally degradable plastic (EDP). Among those, it was suggested that for further study on the compostability of EDP is by doing Sturm Test (ASTM D 5209). This aqueous test method uses a fresh sample of activated sewage sludge that has been aerated, homogenized, and settled. This contains primarily a mixed bacterial population that promotes rapid biodegradation under mesophilic conditions. This metabolism of plastic will produce CO_2, which is trapped in alkali solution and quantify by titration. A more sophisticated method such as CO_2 gas detector can be used. By detecting and quantifying carbon dioxide, this will proof that plastic has degraded as given by Chellini (2000) on the definition of EDP.

The use of biodegradable plastics can be encouraged through the help of the power of economic incentives and environmental awareness. For example in Taipeh the Environmental Protection Bureau is aiming to introduce its "Three-Stage Plan for Ban on Plastics Bags", which aims to replace plastic bags with paper or biodegradable plastics. The first stage is to stop providing plastic bags at government agencies, public and private schools and groceries stores. Second stage is to cover major department stores, supermarkets, fast food chains and chain groceries. Final stage is to ban use of plastic at all retail outlets, dry cleaners and bakeries (The Star, January 2002). Perhaps in the future Malaysia will be able to use this example to reduce the amount of plastic waste.

EDP can be used in many different applications such as single use plastics, in agriculture and in medical applications. Aliphatic polyesters such as PLA which is

more prone to hydrolysis degradation action is more suitable for cosmetics and personal hygiene products (Scott, 2000). The samples used in this study are carbon chain polymers that are more suitable for packaging films or agriculture films. The mechanism of degradation is as stated by Scott (2000) and proven in this study, which is oxidation.

In short, the samples in this project are biodegradable through oxidative degradation and have no adverse impact on the environment (Raninger, 2000) but the time taken to degrade and disintegrate is not competitive with other EDPs. Therefore more progress is required to improve the performance of polyethylene-based EDP.

CHAPTER SIX: CONCLUSION

1. The polyethylene based samples in this study did not show any signs of degradation after being exposed to water at 60°C for 60 days. Therefore the samples did not degrade hydrolytically.

2. The polyethylene based samples in this study showed some sign of degradation after being exposed to free circulating air at 60°C for 60 days especially sample LL. Samples LL were extremely brittle after 60 days and experienced an average weight loss of 8%. FTIR spectrum on LL samples showed that the samples have oxidised with the addition of carbonyl groups as compared to non-exposed samples. This proved that samples LL degraded oxidatively. Other samples showed a lack of mechanical strength and McD samples experienced 23.5% reduction and TDP samples experienced 60% reduction. This proved that McD and TDP samples have started to degrade.

3. In the composting experiments the polyethylene based samples did not show any weight loss and no oxidative actions have taken place based on the FTIR spectrum. However there was a decrease in the elongation percentage on all samples. This means that the samples have started to degrade.

4. The degraded polyethylene based samples were exposed to bacteria *P. aeruginosa* for 28 days and showed degradation potential. There were growths on all inoculated plates where the plastic samples were the only carbon source. Since the bacteria *P. aeruginosa* is widely available in nature and in soil, thus, degraded polyethylene based samples could be biodegraded and can be composted.

5. Quantities of prooxidant additives (in this study TDPA™) also determine the rate of degradation.