Thermal properties of polyethylene reinforced with recycled–poly (ethylene terephthalate) flakes.

Nik Ruqiyah Nik Hassan¹, Noor Mazni Ismail¹, Suriati Ghazali² and Dewan Muhammad Nuruzzaman¹

¹Faculty of Manufacturing Engineering, Universiti Malaysia Pahang, 26600 Pekan, Malaysia
²Faculty of Chemical and Nature Resources Engineering, University Malaysia Pahang, Lebuhraya Tun Razak, 26300 Gambang Kuantan, Pahang, Malaysia.

E-mail: nikruqiyah77@gmail.com

Abstract In this study, recycled plastic bottles (RPET) were used as a filler in high density polyethylene (HDPE) thermoplastic. The plastic sheet of RPET/HDPE was prepared by using hot and cold press machine. The effects of RPET addition and hot press process to the thermal properties of the composite RPET/HDPE were investigated using differential scanning calorimetry (DSC) and thermogravimetric (TGA). Results from DSC analysis show that the melting point of HDPE slightly shifted to a higher temperature for about 2°C to 4°C with the addition of RPET as a filler. The starting degradation temperature of RPET/HDPE composite examined from TGA analysis also seen to be slightly increased. It was observed that the incorporation of recycled PET flakes into HDPE is achievable using hot press process with slight improvement seen in both melting point and thermal stability of the composite compared to the neat HDPE.

1. Introduction
Nowadays, plastics are getting more popular among the industry of fabrication container compared to other type of materials because of their properties that are light weight, high wear resistance and easy to fabricate. Most important characteristic of the plastic is a low production cost and this make plastic become more valuable. Because of this, the waste from the plastic also increase day by day. The waste of the plastic bottle in Malaysia and plastic industry increase progressively every year, as thus remanufacture of plastic bottle waste can help to reduce the waste and save the environment.

Among many popular thermoplastic polymers, Polyethylene terephthalate (PET) is one of the thermoplastic polymers that has been widely used in manufacturing of fiber, bottles, film and others engineering plastic part. PET has good mechanical properties, chemical resistance, clarity, thermal stability and low cost of production, as well as its process ability and recyclability [1].
PET bottles are normally made from co-polymer PET because of its lower crystallinity, high ductility, better process ability and clarity [2]. The large production of PET plastic bottles nowadays has exponentially increase waste of PET. PET is a non-degradable plastic in normal conditions as there is no known organism that can consume its relatively large molecules.

Thus, recycled is a choice to deal with a problem to manage the plastic waste and in order to reduce the environmental problems, and to reduce oil usage, carbon dioxide emission and PET waste [3].

Normally, there are two types of recycling process, mechanically and chemically. Mechanical recycling is a physical method also known as material method, the process usually consists of separation of waste, wash for contaminants removal, grinding into flakes size, re-extrusion, and reprocessing for production of new PET goods. The plastic will be formed into flakes, granulated, or pallet, and it will be melt through the process of extrusion, injection moulding or blow moulding [4]. Chemical recycling is a process of the polymers chemically convert into monomers through chemical reaction. The monomers were then can be used for new polymerization to reproduce the original or any related product [5]. Comparing both methods, mechanical recycled and fiber reinforced polymer composites are more attractive because of their ease of fabrication and economic (low manufacturing cost with lots of quality of product produced) [7]. In the present study, sheet samples of RPET/HDPE composite were prepared mechanically by hot compressing method using hot and cold press machine. DSC and TGA analysis were then carried out to investigate the thermal formability behavior of the RPET/HDPE composite as in plastic sheet form.

2. Materials and Method

2.1 Materials

The materials used in this experiment were recycled poly (ethylene terephthalate) RPET and HDPE polyethylene. The properties of raw HDPE and RPET are listed in Table 1. The recycled PET was obtained from mineral water bottles.

| Polymer | HDPE | RPET |
|---------|------|------|
| Melting Temperature | 135⁰C | 250⁰C |
| Density | 1.00 g/m³ | 0.96 g/m³ |
| Shape Form | Pallet | Flakes |

2.2 Sample preparation

The sample preparation process start by collecting the empty mineral water bottles from the recycle bins around UMP campus. The bottles were then crushed into flake size using crusher machine [8]. After that, the flakes were washed with water to get rid of dust and dirt, followed by drying in oven for 5 minutes at 80⁰C. Three different percentage of RPET (0% RPET/100% HDPE, 30% RPET/70% HDPE, 50% RPET/50% HDPE) samples were prepared which were then hot-pressed into sheet shape with 1 mm thickness by using hot and cold press machine, Lotus Scientific 25 Ton Hot Cold Molding Press (Model LS22025). The temperature for both the bottom and upper plate compress machine were set at 135⁰C.
2.3 Thermogravimetry (TGA) and Differential Scanning Calorimetry (DSC) analysis
In TGA testing, samples with approximately 3 mg were scanned from room temperature to 600 °C under nitrogen atmosphere with 50 ml/min flow rate and heating rate of 10 °C/min. In DSC testing, samples weighing about less than 3 mg in an aluminum pan were heated up to 200 °C with heating rate of 10 °C/min under nitrogen gas, flow rate of 50ml/min. Nitrogen gas was used to prevent the oxidation of the samples.

3. Results and Discussion
3.1 DSC test results and discussion
The result of DSC test are shown in table 2, it was observed that the melting point of HDPE with increasing the amount of recycled PET in HDPE. If compared the heat HDPE, the melting point of 30% RPET/HDPE and 50% RPET/HDPE increased for about 2°c and 3°c, respectively. A higher melting point observed in the RPET/HDPE samples can be suggested due to the dislocation locking by RPET flakes [9].

DSC analysis for the polyethylene plastic pellets graph change before and after present of RPET shown in Figure 1a, 1b, 1c below. The PE pellet sample shows a peak of melting at 129°c with heat of melting 11.66 J/g. The increased value of recycled PET flakes percentage into the HDPE, the melting temperature increased because due to RPET destruct the repeating structure.

| Polymer        | Melting point (Tm) |
|----------------|--------------------|
| Polyethylene (PE) | 129°c              |
| (PE)+ 30% RPET   | 132°c              |
| (PE)+ 50% RPET   | 133°c              |

3.2 TGA test results and discussion
Thermogravimetric analysis (TGA) is a thermal analysis technique that measure the weight change of a sample under a certain temperature time [10].
Figure 2 shows the decomposition patterns of HDPE and RPET/HDPE samples. As can be seen in figure 2, thermal decomposition of all 3 samples occurred in a single stage pattern, with a maximum decomposition rate occurred between 370°C to 470°C. At 500°C, the HDPE sample undergoes complete degradation. Meanwhile, RPET/HDPE samples show few percentage of residue. The residue seen in RPET/HDPE samples can be assigned to the RPET flake which increased with the increment of RPET content.

As label in Table 3, there are 3 different points were recorded. The points refer to the onset temperature of degradation (Tₒ), the degradation temperature at 5% of mass loss (Tₛ) and the end temperature of degradation (Tₑ). The heat PMMA initially loss about 3% of moisture at 320°C and then it pyrolyzed in a single step between 370°C to 470°C. The heat degradation temperature of HDPE+ 30% RPET and HDPE+50%RPET shown in the table 3, at 5% of mass loss (Tₛ) and end temperature of degradation (Tₑ) are at the same temperature which is 370°C to 460°C.

Addition of RPET into the thermoplastic HDPE degrade thermally at low temperature. Table 3 below show when 30% and 50% of RPET were added the temperature degrade at 460°C. Figure 2 below shows the graph of weight change (%) vs temperature (°C) of heating the sample of polyethylene after added the RPET 30% and 50%. The weight lost probably associate to the join lignin degradation during process of hot press. The orange color of line in graph define as polyethylene (HDPE).The residue weight of sample at different temperature was obtain accordingly. The thermal of HDPE can be divide into 2 stage by refer to the figure 2 below. The first stage, HDPE, HDPE+ 30%RPET and HDPE +50% RPET start to degrade at the same temperature up to 320°C about 3% weight loss is refer to the moisture departure. Thermal degradation of HDPE start at 360°C and continued up to 470°C with weight loss of about 96.7%. The thermal degradation of HDPE with the addition of RPET become more sensitive which are the weight lost become less than HDPE only, for HDPE with 30% RPET about 92.9% weight loss and HDPE with 50%RPET is about 83.6%. The temperature start degrade for this HDPE +30% RPET and HDPE+50%RPET sample are same, as shown in table below.

Table 3. The TGA analysis.

| Polymer          | Onset temperature degradation (Tₒ) | Start of Degradation Temperature (Tₛ) | End of degradation temperature (Tₑ) | Weight Loss (%) | Residue after 500°C (%) |
|------------------|------------------------------------|---------------------------------------|-------------------------------------|-----------------|----------------------------|
| HDPE             | 320°C                              | 370°C                                 | 470°C                               | 96.7%           | 0                          |
| HDPE+30%RPET     | 320°C                              | 370°C                                 | 460°C                               | 92.9%           | 1.5                        |
| HDPE+50%RPET     | 320°C                              | 370°C                                 | 460°C                               | 83.6%           | 10.5                       |
It can be observed that addition of RPET to the HDPE prohibits complete degradation of the composite at 500°C and an increase in ash content was noticed with the increase in RPET content.

**Conclusion**

The result shows that the melting temperature were increased in the present of RPET in PE matrix. The increased percentage of RPET into PE increased the value melting temperature. In the future, maleic anhydride will be used as compactibilizer in PE/RPET composite in order to study the effect of compactibilizer in improving the bonding of matrix-reinforcement bonding.

**Acknowledgements**

The authors would like to express gratitude to Universiti Malaysia Pahang for the financial support of this research through RDU130386 grant.

**References**

[1] Ghanbari, A., Heuzey, M. C., Carreau, P. J. and Ton-That, M. T. 2013. A novel approach to control thermal degradation of PET/organoclay nanocomposites and improve clay exfoliation. *Polymer (United Kingdom)*, 54(4), 1361–1369.

[2] Gupta, V. B. and Bashir, Z. 2002 PET Fibres, Films, and Bottles. In: *Handbook of Thermoplastic Polyesters*. Ed. By Fakirov S. Vol. 1, Weinheim, Germany: Wiley-VCH, pp. 317 – 388.

[3] Takoungsakdakun, T. and Pongstabodee, S. 2007. Separation of mixed post-consumer PET–POM–PVC plastic waste using selective flotation. *Separation and Purification Technology*, 54(2), 248-252.

[4] Awaja, F. and Pavel, D. 2005. Injection stretch blow moulding process of reactive extruded recycled PET and virgin PET blends. *European Polymer Journal*, 41(11), 2614-2634.

[5] Braun, D. 2002. Recycling of PVC. *Progress in polymer science*, 27(10), 2171-2195.
[6] Wienaah, M.M. 2007, Sustainable Plastic Waste Management – A Case of Accra, Ghana, in Land and Water Resource Engineering. , Royal Institute of Technology. p38.
[7] Fu, S. Y., Lauke, B., Mäder, E., Yue, C. Y. and Hu, X. 2000. Tensile properties of short-glass-fiber- and short-carbon-fiber-reinforced polypropylene composites. Composites Part A: Applied Science and Manufacturing, 31(10), 1117–1125.
[8] Inada, K., Matsuda, R., Fujiwara, C., Nomura, M., Tamon, T., Nishihara, I. and Fujita, T. 2001 Identification of plastics by infrared absorption using InGaAsP laser diode. Resources, Conservation and Recycling, 33(2), 131–146.
[9] Yu. F. Zabashta. 1974. The dislocation mechanism of polymer deformation: defects of spiral molecules t. G. Shevchenko Kiev State University. merov, No. 4, pp. 579-583, July-August.,June 14, 1973.
[10] Joseph D. Menczel, R. Bruce Prime. 2014 Thermal analysis of polymers: Fundamentals and Applications. John Wiley & Sons; pp 1-50.