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Title	: <u>30 MAY 1992</u>	
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	OF rPET/HDPE BY USING HOT PRESSING	
Academic Session	: <u>SEM II 2019/2020</u>	
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MECHANICAL PROPERTIES AND THERMAL STABILITY OF rPET/HDPE PLASTIC COMPOSITE PREPARED BY HOT PRESSING





Master of Science

Faculty of Manufacturing and Mechatronic Engineering Technology

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AUGUST 2020

UNIVERSITI MALAYSIA PAHANG

ACKNOWLEDGEMENTS

First of all thank you Allah, for this opportunity and always give me direction in any solution to complete this study. I would like to express my appreciation to myself, for stay strong, patient, and do not give up easy toward this research and completing this thesis.

This journey would be impossible without the support of my beloved family, my parents and sibling who never wavering support and encouragement helped me beyond measure in completing this study. Special thanks to my parents who support me emotionally and financially. My sincere indebted and appreciation for their sacrifices and prayer through my life.

I would like to thanks to my supervisor, Ir. Ts. Dr. Noor Mazni bt Ismai for her valuable advices, and ideas and not forget to my co-supervisor, Dr Suriati bt Ghazali on part of my research during my lab at Faculty of Chemistry Engineering and Natural Resources, UMP in any way towards the complication of these works.

I also would like to extend my thanks to all technical staffs in Materials and Machining Laboratory, Faculty of Manufacturing Engineering (FKP), all technical staffs in Chemistry Laboratory in Faculty of Chemistry Engineering and Natural resources, UMP Gambang for their help that made an invaluable contribution to this research.

Finally, I am also grateful to my best friends Nurizzathanis and Mohd Syafiq who always with me through ups and down, and thank you to my colleagues for their encouragement, help and invaluable friendship.

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ABSTRAK

Pada masa kini, sebilangan besar botol plastik sampah di tapak perlupusan telah menjadi isu utama alam sekitar global. Isu ini berlaku disebabkan industri pengeluaran plastik mengeluarkan produk plastik secara berterusan. Seperti yang umum ketahui, salah satu kaedah yang mungkin boleh dilakukan ialah kaedah kitar semula sisa botol plastik dengan memprosesnya untuk dijadikn bahan mentah atau digunakan sebagai komposit di dalam polimer plastik. Walaubagaimanapun, botol plastik kitar semula jarang digunakan kerana sifat makanikal dan termal bahan kitar semula akan berkurang disebabkan oleh degradasi dan penguraian polimer semasa proses kitar semula. Dalam penvelidikan ini, polietilena terephthalate kitar semula (rPET) digunakan sebagai penguat di dalam matrik polietilena berketumpatan tinggi (HDPE). Tujuan penyelidikan ini ialah untuk menghasilkan komposit rPET/HDPE berkekuatan mekanikal yang dipertingkatkan, dan juga bertujuan untuk menyelidik kesan penambahan rPET dan ejen gandingan maleik anhidrida (MAPE) ke atas komposit rPET/HDPE. Kerja makmal dimulakan dengan proses menekan panas campuran rPET dengan HDPE menggunakan mesin penekan panas untuk menghasilkan komposit rPET/HDPE dengan peratus pengisian penguat rPET masing-masing sebanyak 10%, 30%, dan 50%. Sampel komposit rPET/HDPE dengan penambahan 5% dan 10% MAPE juga disediakan dalam kajian ini. Sampel komposit rPET/HDPE dibahagi dengan tiga jenis sampel utama jaitu Jenis I. Jenis II dan Jenis III, masing-masing mewakili rPET/HDPE/0% MAPE, rPET/HDPE/5% MAPE dan rPET/HDPE/10% MAPE. Tambahan kepada jenis utama di atas, kod A, B, dan C telah diberikan untuk merujuk kepada sampel yang mengandungi masing-masing sebanyak 10%, 30%, dan 50% rPET. Secara keseluruhannya, terdapat sembilan sampel komposit yang disediakan dengan label nama sebagai IA, IB, IC, IIA, IIB, IIC, IIIA, IIB, IIIC bagi setiap set. Sifat tegangan komposit rPET/HDPE diuji menggunakan mesin ujian menyeluruh (UTM). Sementara itu, kestabilan termal diuji dengan menggunakan analisis termo gravimetri (TGA). Selain itu, analisis morfologi permukaan retak tegangan dilakukan dengan menggunakan mikroskop electron imbasan (SEM), sementara itu, spektroskopi inframerah transformasi fourier (FTIR) digunakan untuk menganalisis pengaruh MAPE dalam meningkatkan ikatan antara muka komposit rPET/HDPE. Daripada hasil eksperimen, kekuatan sifat mekanikal komposit rPET/HDPE telah meningkat dengan sebanyak 156.270MPa diperolehi daripada sampel tegangan tertinggi 10%rPET/HDPE/10%MAPE (Jenis IIIA). Sementara itu, kestabilan termal bagi komposit rPET/HDPE dengan penambahan MAPE, Jenis II dan Jenis III didapati lebih rendah berbanding HDPE tulen dan komposit Jenis I. Ini mungkin disebabkan oleh rantaian yang terputus dalam polimer yang disebabkan oleh interaksi antara kumpulan anhidrida MAPE dan kumpulan hidroksil (OH) rPET. Secara keseluruhannya, daripada vang dijalankan. sifat-sifat makanikal komposit rPET/HDPE telah analisis menunjukkan peningkatan dengan adanya penambahan ejen gandingan MAPE tetapi pada masa yang sama telah mengurangkan kestabilan termalnya. Penemuan baru yang diperolehi daripada penyelidikan ini diharapkan dapat menggalakkan para penyelidik untuk menggunakan bahan kitar semula seperti rPET sebagai penguat di dalam bahan komposit. Komposit rPET/HDPE berpotensi untuk digunakan sebagai bahan pembungkusan yang bermanfaat terutamanya di dalam industri pembungkusan plastik.

ABSTRACT

Nowadays, the large amount of waste plastic bottles in landfills has become a major global environmental issue. This issue occur because the industry plastic production produce plastic continuously. It is well known that one of the possible methods for recycling these plastic bottles is to process them for use as raw materials or reinforced polymer plastic. However, recycled plastic bottles are rarely used because the mechanical properties of the recycled materials would decrease due to the degradation and decomposition of the polymer during recycle process which effect the mechanical and thermal properties. In this research, recycled polyethylene terephthalate (rPET) were used as a reinforcement in a high-density polyethylene (HDPE) matrix. The aim of the study is to fabricate rPET/HDPE composites with enhanced mechanical properties, and also to investigate the effect of the rPET filler loading and maleic anhydride grafted polyethylene (MAPE) coupling agent on the rPET/HDPE composite. The lab work started by hot pressing the mixture of rPET and HDPE using hot pressing machine to produce rPET/HDPE composite at different rPET filler loading of 10%, 30%, and 50%, respectively. Samples of rPET/HDPE composite with the addition of 5% and 10% of MAPE were also prepared in this study. The samples of rPET/HDPE composite were divided into three main types, namely Type I, Type II and Type III which refer to rPET/HDPE/0%MAPE, rPET/HDPE/5%MAPE and rPET/HDPE/10%MAPE. Additionally, Code A, B, and C were assigned referring to the percentage of rPET filler loading, which are 10%, 30%, and 50%, respectively. Overall, there are nine samples of composite prepared which labelled as IA, IB, IC, IIA, IIB, IIC, IIIA, IIB, IIIC in each batch. The tensile properties of the rPET/HDPE composites were tested by Universal Testing Machine. While, thermal stability were tested by using Thermo-Gravimetric Analysis (TGA). Other than that, analysis on the morphology of the tensile fractured surface was done using Scanning Electron Microscope (SEM), while Fourier Transform Infrared Spectroscopy (FTIR) was used to analyze the influence of MAPE in enhancing interfacial bonding of the rPET/HDPE composite. From the experimental result, the mechanical properties of rPET/HDPE/MAPE composite has been improved with the highest tensile strength of 156.270 MPa was observed in a specimen with 10% rPET/HDPE/10%MAPE (Type IIIA). Meanwhile, the thermal stability of the rPET/HDPE composites with the addition of MAPE, Type II and Type III composites were decreased if compared to pure HDPE and Type I composite. This might be due to the broken chains in the polymers that resulted from the interactions between the anhydride groups of the maleated coupling agent and the hydroxyl groups (-OH) of the rPET. Overall, from the analysis, it was demonstrated that the mechanical properties of the rPET/HDPE composite were improved with the addition of the MAPE coupling agent but at the same time reduced its thermal stability. From this research, new information obtained can encourage other researchers to possibly used recycled material such as rPET as a reinforcement in the composite materials. The rPET/HDPE composite could be useful as packaging materials in plastic packaging industry.

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LIST OF SYMBOLS

Т	Temperature
Tm	Malting temperature
Tg	Glass transition
Te	Crystallization temperature
To	Onset temperature
Ts	Start Temperature
Те	End temperature
ΔH	Enthalpy Change
К	Calorimetric constant
А	Area
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DTG	Derivative Thermo-Gravimetric		
DSC	Differential Scanning Calorimetry		
FTIR	Fourier Transform Infrared		
LDPE	Low density Polyethylene		
MAPE	Polyethylene-graft-maleic anhydride		
PE	Polyethylene		
PP	Polypropylene		
PS	Polystyrene		
PVC	Polyvinyl chloride		
SEM	Scanning Electron Microscope		
TGA	Thermo-Gravimetric Analysis		

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Polyethylene terephthalate (PET) are mainly used in the production of beverage bottles. PET is one of the famous thermoplastic and has number one symbol as its recycling. Plastic bottle (PET) can be recycling because it is can be melted, molded and extruded to form any shape for new products. Most of the plastic bottles are nonbiodegradable and some of them may take hundreds of years to decompose, thus it is considered as a material pollution and affects the environment. To overcome this problem, two common solutions come to mind; firstly, to reuse the disposed materials for some suitable application, and secondly to recycle it to achieve new materials that can be applied in another industry (J. C. Chen et al., 2011).

The recycling PET have several challenge and difficulty due to mechanical properties of the recycled materials would decrease due to the degradation and decomposition of the polymer during recycled process. However, this problem have been discovered by few of study reported recycled PET problems can be control by combine with other polymer or by introduce to additive of coupling agent. Potential of this solution for recycled PET mixed polymer may improve their properties in mechanical, thermal and also interfacial adhesion. Generally, the recycled PET (rPET) can produced more products and are widely used in different applications such as in building materials, films and reinforcement.

In this study, a (HDPE) composites reinforced with different percentages of (rPET) were prepared by hot pressing. The thermal stability and mechanical properties of the rPET/HDPE composites with different percentages of rPET and with the addition of coupling agent Polyethylene-graft-maleic anhydride (MAPE) of 5% and 10% were investigated. A thermal analysis was used to characterize the thermal stability of the

RPET/HDPE composites by Thermo-Gravimetric Analysis (TGA) while a tensile test was used to describe their mechanical properties.

1.2 Problem Statement

Due to environmental concerns, plastic wastes have high price of petroleum and environmental concerns (Salleh et al., 2013). PET is one of the major types of plastic waste with their annual usage rates continuing to increase, especially in the plastic bottle industries (R. S. Chen, Ab Ghani et al., 2015). One possible solution for this plastic bottle waste is recycling because it is known that, rPETs can be melted, molded and extruded to form any shape for new products. However, recycled plastic bottles are rarely used because the mechanical properties of the recycled materials would decrease due to the degradation and decomposition of the polymer (Grigore, 2017). Moreover, rPETs have other limitations such as, difficulty of the process ability, and decreased mechanical properties and molecular weight. However, this problem might be solved by mixing rPET with others polymers as reported by Karsli, Yesil, and Aytac, (2013). Another concern reported by Imamura et al., (2014), the degradation in polymer during recycled can be control by introducing additives or coupling agent. The literatures also reported, the usage of coupling agent as third polymer component for compatibilized PET improved the mechanical properties, thermal stability, and interfacial adhesion of the polymer (Imamura et al., 2014).

Previous studies of PET/HDPE mainly focused on improving compatibility between PET and HDPE since they are basically incompatible. Some studies also focused on combining HDPE with rPET to improve its stiffness. HDPE/PET composites exhibit intermediate properties of its two plastic components which are stiffer than HDPE and less brittle than PET alone (R. S. Chen et al., 2014 and McKeen, 2016). However, there are very few studies being done on polymer composites based on recycled polymers as a reinforcement or filler, especially rPET. Reported by R. S. Chen, et al., (2015) and Jarukumjorn et al., (2007) found that the tensile properties for recycled HDPE (rHDPE) and rPET which was made by melt-mixing in a twin-screw extruder was higher than rHDPE or rPET alone. The thermal and mechanical properties of recycled PET as a filler or reinforced in polymer composite still not widely explored especially with hot pressing method, there are not much input on the properties. Thus, study on thermal and tensile properties of this polymer composite especially to identify the effective new plastic composite using recycled PET as filler in HDPE is necessary.

1.3 Research Objective

The research aim is directed towards understanding the effect of rPET on thermal stability and mechanical properties of the rPET/HDPE composites prepared using hot pressing. The measurable objectives of the work are as follows:

- To fabricate difference content various percentage of rPET and MAPE of rPET/HDPE composites.
- 2. To characterize the samples produce of rPET/HDPE composite by mechanical properties and thermal stability.

1.4 Scope of Project

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The scope of this project is to fabricate rPET/HDPE composite with different percentages of rPET and with the addition of the MAPE coupling agent. There are three different percentages (10%, 30%, and 50%) of rPET used to prepare the rPET/HDPE composites. In other sample preparations with the same rPET percent loading, the MAPE coupling agent was introduced into the rPET/HDPE composites at two different percentages (5% and 10%). Then, each samples of rPET/HDPE were characterized their mechanical properties and thermal stability. Tensile test were done to examine the mechanical properties of each type of composite and then the TGA were used to analyse thermal stability of each rPET/HDPE samples. The tensile test and thermal stability result of each composite samples were tabulated. To support the result presented, SEM and FTIR test were done.

1.5 Thesis outline

The thesis layout begins with introduction of research background of study, problem statement and objective of this study in Chapter 1. A review from literature presents in Chapter 2, which are highlight topic about Polyethylene, Polyethylene terephthalate (PET), and polymer composite related with their mechanical properties and thermal stability using Thermo-gravimetric analysis (TGA) from previous studies. This chapter also including review topic about the additional of coupling agent in composite. Other than that, the bonding between matrix and filler of polymer composite using scanning electron microscope (SEM) and Fourier Transform Infrared (FTIR) also review in this chapter. In Chapter 3, the explanation about methods and procedures of rPET/HDPE composite preparation and characterization or testing. All the result from the mechanical and thermal testing are presented and discussed in Chapter 4. Lastly the conclusion of the research objective and also some recommendation for future works are describe in Chapter 5.

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CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter presents a review of previous studies and recent literature that are significant and related to polymer composites, coupling agent in composites and characterization of composites. Several studies as well as experimental works around the topic of polymer composites related to HDPE and rPET are reviewed. The present study highlights topics related to thermal stability and mechanical properties of the polymer composites. At the end of the chapter, the physical chemical explanations related to polymer composites using SEM and FTIR are also included. It is expected that the line and direction of the present research can be generated from relevant information from this literature review.

2.2 Polymer

Polymers are used to replace traditional materials such as wood, glass, and metals because its properties can be modified to achieve the designer's needs and also because it can be processed for produce a variety of products (Mamoor et al., 2013). There are two major classifications of polymers, which are thermoplastics and thermosets.

Thermoplastics soften when heated and harden when cooled, and these processes are totally reversible and may be repeated process undergo reheating, melt again, and change shape. This allows for additional processing of the same material, even after being prepared as a solid. Thermoplastic can be processes by extrusion, thermoforming, and injection moulding. Some examples of thermoplastic are polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC) and polyethylene terephthalate(PET) (Strong,2008).

Thermoplastics are versatile materials that can be used for anything start from plastic carrier bag to high stress bearing and also mechanical parts. This because, thermoplastic have high-strength, flexibility and resistant to shrinkage. Moreover, thermoplastic are recyclable and reusable by the application of heat and/or pressure (Ibeh, 2011).

On the other hand, thermosets are permanently hard during their formation and do not soften upon heating. Generally, thermosets are harder and stronger than thermoplastics and have better dimension stability. Thermosets generally yield higher chemical and heat resistance, as well as a stronger structure that does not deform easily. Examples of thermosets are rubber, epoxies, phenolic and some polyester resins.

2.2.1 Polyethylene

Polyethylene (PE) is the most common type of polymer used. It is used in a wide range of applications such packaging (plastic bag, plastic film) and containers including bottles. PEs have the simplest basic molecular structure compared to other polymers (a repetition of CH₂ units), as shown in Figure 2.1.

 $CH_2 - CH_2 + n$

Figure 2.1 Chemical structure of polyethylene Source: Ronca (2016)

The advantages of PE are that its low cost, excellent electrical insulation, very good chemical resistance, rigidity, and toughness (Ronca, 2017). PE also has a high ductility and impact strength while also having low friction (Kaseem et al., 2015).

There are two types of PE which are, high density polyethylene (HDPE) and low density polyethylene (LDPE). HDPEs are harder, stronger than LDPE and also less elastic than LDPEs. LDPEs are normally used in applications such as plastic grocery bags, lining of the milk carton, and also plastic inside cereal boxes. The LDPE melting point is normally in the range between 105°C to 115°C. HDPEs have excellent mechanical properties, ozone resistance, chemical resistance and good electrical properties (Rajak Hamim et al., 2016). The melting point of HDPE is typically in the range of 120°C to 180°C. HDPEs are commonly used in the production of piping, packaging, children toys and milk or detergent bottles.

2.2.2 Poly (Ethylene Terephthalate) (PET)

Polyethylene terephthalate (PET) is a polymer that is formed from the combination of two monomers called modified ethylene glycol and purified terephthalic acid. Figure 2.2 shown typical chemical structure of PET.

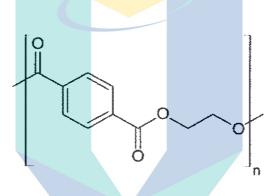


Figure 2.2 Chemical structure of PET Source: Geyer et al. (2016)

PET are known as thermoplastic polymers, it has a slow rate of crystallization but a high melting point and good ability for melting process, making its final morphology easier to control. PETs have been widely used in the manufacturing of fibres, bottles, films and other engineering plastic parts (Hegde et al., 2013;Haji et al., 2012 and Kusuktham, 2012). PETs have good mechanical and chemical properties in comparison to fibres and fabrics, with special quantities such as light weight, flexibility, easy disposability, recyclability and resistance to shrinkage. Other than that, PETs haves an excellent tensile and impact strength, chemical resistances, process ability, colour ability and reasonable thermal stability.

In recent year, PET is widely used for making soft drink bottles. The increasing production of plastic bottles has caused the plastic bottle waste to increase progressively every year with a large amount ending up at landfills. Furthermore, most of the plastic bottles are not biodegradable, and some of them may take hundreds of year to decompose.

One possible solution for this plastic bottle waste is recycling because it is known that, rPETs can be melted, molded and extruded to form any shape for new products. There are a number of uses that have been found for rPET applications such as in fabric automotive parts, fibre fills, industrial strappings, sheets, films and new containers (Oromiehie and Mamizadeh, 2004). The reason is mainly attributed to its transparency, thermal stability, chemical resistance, and excellent barrier properties of PET. On the other hand, a cap of the bottles is made from polyethylene (PE) or polypropylene (PP) due to the flexibility and formability while a label produces from polystyrene (PS) film. In recycling process, it is important to remove the PP or PE caps and PS labels from waste PET bottles in order to get the high purity of recycled-PET (RPET) flake materials.

PETs generally show a loss of mechanical, thermal and rheological properties after recycling (Badia, Strömberg et al., 2012). Despite that, recycle PET have potential as polymer composite as reported by Mohammad and Arsad, (2013).

2.3 Polymer composite

A composite is combination of more than one material, either a polymer or nonpolymeric component. Composites generally consist of two phases, the matrix phase and the reinforcement phase. The matrix phase is the internal structure of a composite, for example metals, ceramics, or polymers. Meanwhile, the reinforcement phase is the connected material to the matrix phase. Fibres that are commonly used for reinforcement are carbon fibres, glass fibres, cellulose fibres (paper fibre, straw, wood) and also high strength polymers (Mohajerani et al., 2019). Composites from polymer materials are commonly used because of their properties such as high strength and stiffness, low density, good surface hardness, improved fatigue life and corrosion resistance.

2.3.1 rPET in composite

Studies on the use of rPETs in composite materials have increased in the past few years. In an early research, the properties of a polymer concrete made from rPET mixed with gravel and concrete was investigated by Rebeiz (1995). This would allow energy savings and reduce the cost of polymer concrete products. In a previous study, it was observed that rPETs used as filler for a natural rubber compound increased the tensile modulus and temperature for thermal degradation (Nabil, Ismail, and Azura, 2011)

In another study, polypropylene reinforced with rPET fibre was found to offer a better option for recycling because of the improved properties (Zhu, et al., 2015). Besides that, rPETs were also used as a matrix with fibre glass resulting in a composite with a very high tensile strength and fracture toughness (Ronkay and Czigány, 2006).

Generally, the properties of recycled plastic tend to slightly degrade compared to pure materials, which also affect its mechanical properties. In order to have good mechanical properties, combinations of rPET with other thermoplastics as polymer composites have been studied with several polymer materials such as polyethylene, polypropylene, and polystyrene (Thodsaratpreeyakul et al., 2018). In a previous study, Fraïsse et al., (2005) reported that the rPET waste experienced polymer backbone degradation and lost their properties. However, rPET with the addition of polycarbonate (PC) has better properties than pure PET and can limit the degradation consequences of rPET. The rPET was mixed with PC with three difference percentages of rPET/PC which are, 80/20, 70/30 and 50/50 wt. %. The preparation of this composite was done using a twin screw extruder.

In another study, polypropylene (PP) was also one of the materials used to reinforce rPETs (Santos et al., 2003 and Zhu, et al., 2015).PP is a type of thermoplastics that is widely used. Other than that, rPET was used a filler in HDPE through crystallization and grinding (Demir and Tinçer, 2001). There was a weak interaction between the filler PET with the HDPE that caused weak mechanical properties. However, some further studies introduced a coupling agent to effectively improve the

interaction between polymer and filler which automatically improved the mechanical properties.

2.3.2 HDPE in composite

May previous studies on plastic composites used HDPE as a matrix such as in nanostructure polymer composites (NPC), plastic wood composites (WPC), natural composites, clay composites, carbon nanotubes, and composites with others polymers.

Composites made with polyethylene and natural fibres or filler have obtained good results in many studies (Marcovich et al., 2003 and Lei et al., 2007). There are many studies on mechanical properties, dimensional stability, interfacial bonding, and also durability of filler in polyethylene (Adhikary, Pang, and Staiger, 2008). Some studies found that adding natural fibres into HDPE plastic increased the tensile strength. Unfortunately, the composite polymer and natural fibre have some disadvantages such as incompatibility between fibre and polymer matrices (Mohammed, et al., 2015) and limited manufacturing technology (Ouarhim et al., 2018), Other limitations of this include the dispersion of the fibre into the matrix and the poor resistances to moisture and the tendency to form aggregates during processing that reduced the usefulness of natural fibre as reinforcement in polymers (Pracella et al., 2010). This incompatibility may causes low thermal and mechanical properties (Pracella et al., 2006 and Rizal et al., 2018).

Some studies have been published on polymer clay composites based on a single polymer matrix. Polyethylene (PE) has also been use as a matrix in polymer clay. For example, by David et al., (2011) PE were used with polybutylene terephthalate and clay. The disadvantage of these clay polymers is that they have poor miscibility with polymers which results in difficulty in exfoliating clay layers into a polymer matrix. A previous study have shown that the rHDPE/rPET decreased mechanical properties when the clay was incorporated, and have bad dispersion of clay within the polymer matrix and also bad compatibility (R. S. Chen et al., 2015).

2.3.3 Coupling agent in composite

Coupling agents are a very important element in high performance polymer composites. There are several coupling agents being used in previous research to improve the properties of the composites, such as ethylene–glycidyl methacrylate copolymers (E-GMA), maleic anhydride grafted styrene–ethylene–butylenes–styrene (SBS-gMA), ethylene–acrylic acid copolymers (EAA), maleic anhydride grafted polyethylene (MAPE), butyl acrylate and maleic anhydride (E-BA-MA). Among these coupling agents, the most efficient coupling agent that improved the properties of polymer composite, especially when HDPE was used as a matrix is polyethylene grafted with the MAPE coupling agent (Dencheva et al., 2008 and Liu et al., 2014).

Work research by Rajak Hamim et al., (2016) about recycled high density polyethylene (RHDPE)/ethylene vinyl acetate (EVA) with different compositions and coupling agent were prepared by using melt blending technique. The coupling agent of RHDPE/EVA were enhanced by the addition of polyethylene-grafted-maleic anhydride (PE-g-MAH) or (MAPE) as coupling agent. The results also revealed that there was good compatibility between RHDPE/EVA with addition of PE-g-MAH lead to improvement in tensile properties, swelling behaviour and display better interfacial adhesion due to good dispersion and interaction between RHDPE and EVA phase compared to RHDPE/EVA without the presence of coupling agent. Figure 2.3 present the improvement of interfacial adhesion as PE-g-MAH was added due to reaction of carbonyl group in PE-g-MAH to ester group of EVA, which would form covalent bonds, enhanced the improvement and efficiency of stress transfer from RHDPE to EVA matrix. This reaction was similar to the study research by Shabbir et al., (2013) which agreed that with accumulation of coupling agent will helped to increase the tensile strength.

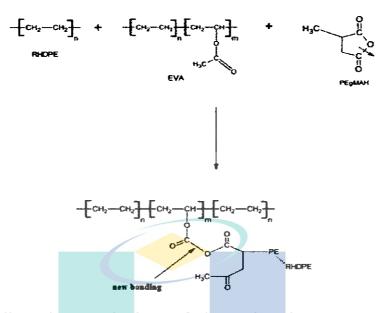


Figure 2.3 Illustration mechanism of interaction between PE-g-MAH and RHDPE/EVA

Source: Rajak Hamim et al. (2016)

Another study (Ouarhim et al., 2018) used three different percentages of MAPE which are 5%, 10% and 15%. The study found that polyethylene composites modified with added MAPE increased the overall crystallinity when compared to unmodified polyethylene. other than that, reported by Imamura et al., (2014) in the literatures, the usage of coupling agent as third polymer component for compatibilized PET improved the mechanical properties, thermal stability, and toughness of the polymer.

In another work (Minkova, Yordanov, and Filippi, 2002), the interfacial tensions of PE/PA6 with and without coupling agent were measured. As a result, the PE/PA6 with the addition of a coupling agent reduced the interfacial tension significantly. The presence of coupling agents in the composite made with fibre and HDPE showed greater stabilities than the individual components (Mohanty, Verma, and Nayak, 2006). Rodrigues (2010) has investigated that the addition of a coupling agent into PA6/PE which significantly decreased the PE domains and improved impact strength and the adhesion between PA6 and the PE phase. There are several studies on the use of coupling agents in HDPE/PET composites. In Jarukumjorn and Chareunkvun (2007), MAPE or (PE-g-MA) coupling agents were added to a R-HDPE/R-PET blend and prepared using a twin extruder. The study found that the mechanical properties of the RHDPE/RPET improved with an increase in MAPE content. Moreover, the increasing addition of MAPE to the RHDPE/RPET also improved the composite's morphology by decreasing the dispersion phase size. This was explained due to the interaction between the matrix and dispersed phase of maleic anhydride (MA) functional group of MAPE.

2.4 Mechanical testing of composites

There are several factors that can influence the mechanical properties of composites such as the shape of the composite, orientation of the reinforced fibre and also the interfacial adhesion between the fibre and the matrix (Tezara et al., 2016).

2.4.1 Tensile test

The tensile test is the common mechanical testing used in polymer studies. The ASTM D638 is one of the standardized tests available to evaluate the stress-strain behaviour of polymeric materials. Figure 2.4 show the optimal stress strain curve in tensile test. The ASTM D638 also uses one rate of deformation per material to measure the modulus, with brittle materials having a slow speed is while ductile material shaving a fast speed (ASTM D638, 2015). Tensile elongation and tensile modulus measurement are the most widely specified properties of plastic materials. Tensile test uses a measurement instrument that is able to stretch stand force materials and then pull it apart to identify what extant the material stretches before breaking.

HDPE is one of the thermoplastics that has excellent mechanical properties (Y. Chen et al., 2014). As reported by Hamid et al., (2013) and Adhikary et al., (2008), the tensile strength of HDPE values are in the range of 23.00 to 29.5 MPa. Table 2.1 shows the range of mechanical properties of HDPE.

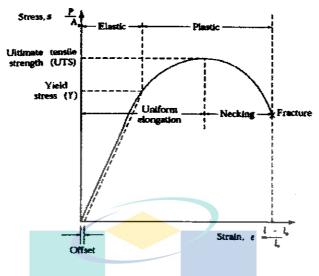


Figure 2.4 Optimal stress strain curve Source:Kalpakjian, Schmid, and Sekar, (2014)

Table 2.1The med	nanical prop	erties of HDPE
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	Value	Unit
Tensile strength	20-32	MPa
Young's modulus	600-1400	MPa
Elongation	180-1000	%
Fatigue	18-20	MPa

-

Source: Siti Amni (2013)

Many studies used HDPE as the matrix in polymer composites. In a previous study by Supri and Lim (2009), the addition of filler in the matrix HDPE made it become more rigid. At the high strain rate, the polymer chain was restricted due to the insufficient time for reorientation, thus increasing the rigidity and also accumulation of the intermolecular force that gives strengthening to the polymer. In another study, pure polypropylene (PP) with 20%, 30%, and 50% pure HDPE were combined and prepared by twin screw extruder and injection moulding machine, and the mechanical properties were examined. A tensile strength test was conducted using a universal testing machine (UTM 3382, Instron, UK) following the ASTM D638 standard at a cross head speed of 50mm/min. The results in Figure 2.5 showed a higher value (\approx 35MPa) of tensile

strength from PP, while the tensile strength of the HDPE matrix value was reported at \approx 22MPa. The tensile strength of the composite was increased by 29% for HDPE50-PP50 and a maximum value among the polymer composite. The tensile strength was improved with the reinforcement of PP to HDPE due to the dispersion of PP in HDPE (Sutar et al., 2018).

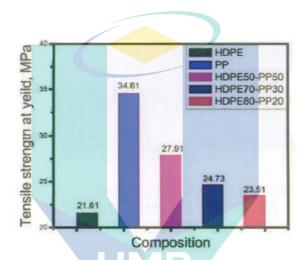


Figure 2.5 Tensile strength of polymer composite Source: Sutar et al. (2018)

The HDPE matrix was also used with wood fibre. A previous research investigated the effect of different compositions of high-density polyethylene (HDPE)wood fibre (WF) composite on its tensile properties. Six different compositions of HDPE-WF composites (100% HDPE + 0% WF, 90% HDPE + 10% WF, 80% HDPE + 20% WF, 70% HDPE + 30% WF, 60% HDPE + 40% WF, and 50% HDPE + 50% WF) were fabricated by using a hot-press machine. The tensile properties of HDPE-WF composite are investigated with following ASTM D638-98 with a crosshead speed of 5 mm/min. The tensile properties of HDPE-WF composite show the highest tensile properties at 100% HDPE+0% WF whiles the tensile properties results are decreased as the composition of HDPE is decreased from 90% to 50%. This is due to the weak bonding of the HDPE-WF composite, the presence of voids, and the fibres pull-out as shown in Figure 2.6 when the percentage of HDPE decreases and proves that the composition of the HDPE-WF composite can affect the decrease in tensile strength (Gulitah and Liew, 2019).

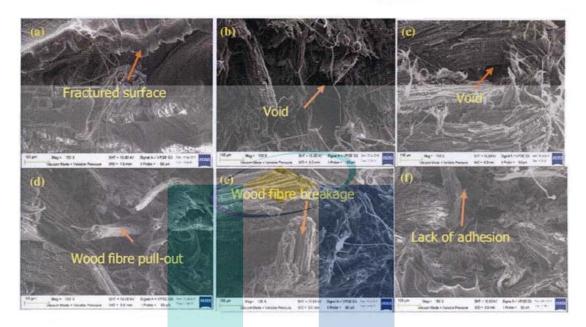


Figure 2.6 SEM micrograph from tensile fracture of HDPE-WF (a) HDPE-WF (100:0), (b) HDPE-WF (90:10), (c) HDPE-WF (80:20), (d) HDPE-WF (70:30), (e) HDPE-WF (60:40), (f) HDPE-WF (50:50)

Source: Gulitah and Liew (2019)

The maximum tensile strength value of PET as listed in the material data book (Department CUE, 2003) is in between 48.3 and 72.4MPa. a study by Cinelli et al., (2016) reported a PET strength of 150 MPa. Studies on composites using rPET have been done with several polymers such as using polyimide by Ding et al, (2012). There are still only a few studies on HDPE composites containing rPET. A previous study by R. S. Chen, et al., 2014a and Ávila, 2001), on the mechanical properties of a rPET/HDPE composite used rPET as a matrix and was prepared by extrusion. The Young's modulus of their rPET/HDPE for the 80/20 composition is 1.46 MPa which is an increase in stiffness compared to pure HDPE due to the large amount of rPET. Another research investigated the incorporation of PET in polymers such as PP, showing an increase in tensile properties and improved matrix-fibre interface adhesion that indicated better mechanical properties (Lopez-Manchado and Arroyo, 2001). Some researchers have tried to improve the mechanical properties of the recycled materials by introducing additives or coupling agents. In a study by Imamura et al., (2014) the

addition of additives in recycled materials can improved their mechanical properties. (Lei et al., 2009) reported that a recycled HDPE/PET in situ micro-fibrillar composite with a composition of 75/25 wt/wt through extrusion and stretching exhibited increased elongation at break from 7% to 60% when 5% of ethylene-glycidyl methacrylate (E-GMA) was introduced. Another study was done on the mechanical properties of PP/rPET composites with different percentages of rPET and compatibilizer of maleic anhydride grafted polypropylene (PP-g-MA). The percentage of PP/rPET composites used in the study was 5%, 10%, and 18% which were then added with 4% PP-g-MA. The tensile test was carried out by using a Universal Testing Machine-Instron 2267 with a crosshead speed of 5 mm/min. The tensile strength of PP/rPET composites with 5%rPET obtained 30.59 MPa and increased to 31.32 MPa as the percentage of rPET increased to 10%. When the percentage of rPET was up to 18%, the tensile strength of PP/rPET composites was decreased to 28.80 MPa. The increase of rPET in PP/rPET composites led to a decrease of tensile strength but the compatibilizer still increased the tensile strength of PP/rPET composites if compared to the tensile strength of pure polypropylene (28.71 MPa) (Nonato and Bonse, 2016). There were some researchers who studied the mechanical properties of rPET/ABS composites with the addition of kenaf fibre with four different weight percentages of 0%, 5%, 10%, and 15%. The tensile test was carried out by using a Universal Testing Machine (Instron 5567) with a high crosshead speed of 50 mm/min. The tensile strength of rPET/ABS/kenaf fibre composite was reported in Figure 2.7. The tensile strength of rPET/ABS/kenaf fibre composite showed a decrease in strength at 10 wt% and 15 wt% as compared to rPET/ABS/kenaf fibre composite with 0 wt% and 5 wt%. Moreover, the tensile modulus of rPET/ABS/kenaf fibre composite obtained an optimum modulus of 17.42 GPa at 5 wt% compared to 0 wt% kenaf fibre with 3.10 GPa. The tensile modulus of rPET/ABS/kenaf fibre composite was decreased at 10 wt% and 1 5wt% kenaf fibre because of more kenaf fibre contents in rPET/ABS/kenaf fibre composite led to the decreasing of their mechanical properties. This degradation phenomenon also occurs during the elongation at break of the rPET/ABS/kenaf fibre composite as the increase in the content of kenaf fibres inhibits the movement of molecules in the composite (Mohammad and Arsad, 2013).

In another study, rPET/HDPE composites with different compositions (5, 19, 15, and 40%) of rPET into HDPE were prepared by melt mixing then hot pressing at 200°C in between steel plate compression-molds. The tensile test was conducted by an Instron tensile testing machine on a standard cut dumbbell shape specimen with 2 mm thickness and a gauge length of 3.5 cm, at 50 mm/min rate. The result showed that the addition of PET improved the tensile strength and elastic modulus while reducing the ultimate elongation. However, the rPET/HDPE composite with 40% rPET composition has low tensile strength due to the weak adhesion between the two polymers (Demir and Tinçer, 2001).

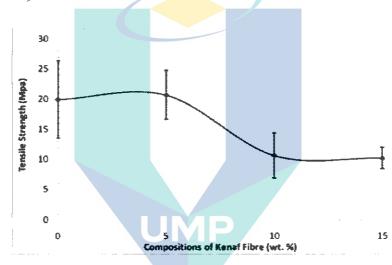


Figure 2.7 Tensile strength of rPET/ABS/kenaf fiber composite Source: Mohammad and Arsad (2013)

Thermal analysis

2.5

Thermal analysis technique is widely used to determine the thermal stability and characteristics of the polymers. The differential scanning calorimetry (DSC) and thermo-gravimetric analysis (TGA) technique are commonly used to study the thermal behaviour.

2.5.1 Differential Scanning Calorimetry (DSC)

DSC is a thermo-analytical technique in which the difference in the amount of heat required to increase the temperature of a sample and the reference area is measured as a function on temperature. DSC is usually used to study the properties of polymers upon a heating range at a specific rate. Normally, the temperature increases linearly as a function of time. This technique was developed by E.S Watson and M.J O'Neil in 1960 and introduced commercially in 1993 by Perkin Elmer at Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy. The DSC function is to determine the thermal transition of polymers in a range of temperatures between 180°C until 600°C (Mishra, 2007).

The basic principle of this technique is that when the sample undergoes a physical transformation such as phase transition, more or less heat will be needed to flow to it and the reference to maintain both at the same temperature. The flow of more or less heat to the sample depends on whether the process is exothermic or endothermic. In the endothermic process, the phase transition from solid to liquid absorbs of energy, while the exothermic process is a transition which releases energy.

Sample or reference materials are heated and cooled in DSC in a defined manner. DSC is used to study the melting of crystallization polymer or the glass transition (At, 2006). DSC can be used to measure a number of characteristic parameters of a sample. This technique can also be used to observe fusion and crystallization events as glass transition temperatures, T_g . This method can also be used for the determination of oxidative stability and glass transition temperature, T_g . A glass transition may occur as an amorphous solid is increased and is characterized by a decrease in viscosity. When the temperature increases, an amorphous material will become less viscous. This is known as the crystallization temperature, T_c because at this point, the molecules will have enough freedom of motion to spontaneously arrange themselves into a crystalline form. For crystalline polymer such as PE and PP (T_g) is

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not relevant (Mohammadzadeh, 2009).

2.5.1.1 DSC curve

Normally the DSC experiment involves a heating or cooling curve. This curve is used to calculate the enthalpies of transition. The integrating peak corresponds to give the transition. The Figure 2.8 shows a schematics DSC curve demonstrating the appearance of Different Transition. The enthalpy of transition can be shown using the following equation:

$$\Delta H=KA$$
 2.1

The ΔH is the enthalpy of transition. K is the calorimetric constant, and A is the area under the curve. The calorimetric constant may be different form instrument to instrument, but can also be determined by analysing a well characterized sample with known enthalpies of transition (Mishra, 2007).

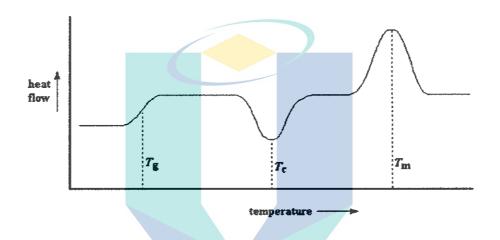
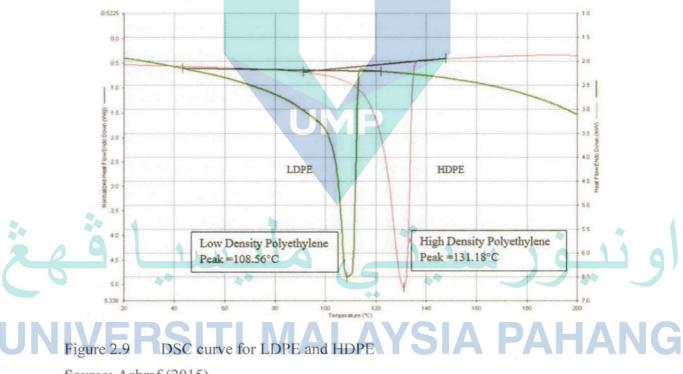


Figure 2.8 A schematic DSC curve demostrating the appearance of different transition Source: Mishra (2007).

Referring to the Figure 2.8, the T_g is known as the glass transition temperature which is shown by the overlapping endothermic peak. This T_g is also a reversible transition that occurs when an amorphous material is heated or cooled in a particular temperature range. The T_g is exhibited by semi crystalline or completely amorphous solids and can be reshaped or moulded without braking. During the increasing temperature, an amorphous solid will become less viscous, then the molecule will have enough freedom of motion to impulsively arrange themselves into a crystalline form and that called the crystallization temperature, T_c . Usually, the T_c is observed in the DSC as an exothermic peak in the heat capacity (Baird and Taylor, 2012). When the temperature increases the sample eventually reaches its melting temperature, T_m . The melting process result in an endothermic peak in the DSC curve as shown in Figure 2.8. Meanwhile, not everything shown in the DSC curve (Figure 2.8) will be plotted on every graph of other samples. For example, for the polymers that can form crystals, only the crystallization and the melting peak will appear. Meanwhile, completely amorphous polymers will show any crystallization and melting. However, polymers with both crystalline and amorphous domains will have all the features shown in Figure 2.8.

2.5.1.2 DSC of Polyethylene

The DSC curve for the polyethylene showed that for HDPE, the melting point, $T_m \approx 131^{\circ}$ C by Manivannan and Seehra (1997) and T_m in range 114°C -135°C discussed by Ashraf (2015). Figure 2.9 show an example presenting a single, sharp thermal transition due to melting point of LDPE and HDEP samples.



Source: Ashraf (2015)

Many studies on polymer composites used the DSC technique to identify their melting temperature and glass transition change. Most of the composites with HDPE as a matrix resulted in a reduced temperature change. For example in a study by Banat and Fares (2015), the DSC result showed that the addition of a natural fibre (olive shell

flour) in a HDPE polymer matrix reduced the melting temperature of the HDPE composite. This is because of the fibre interaction with the polymer matrix (Waldman, Paoli, and Arau, 2008).

2.5.1.3 DSC of Polyethylene terephthalate

Polyethylene terephthalate (PET) can be either amorphous or semi crystalline depending on the processing. Typically, glass transition T_g for PET is between 70°C to 80°C, and the melting transition range is between 250°C to 260°C. The pure PET exhibits two melting peaks because of the reorganization of the crystal during the heating time on DSC (Elamri et al., 2015). The DSC test is also used to determine the melting point between pure PET and rPET. The melting point of pure PET shows a higher result than the recycled PET, because of the limitation of impurities in rPET flakes (He, Wei, at al., 2014). A typical semi crystalline PET pellet is expected have 80 °C of glass transition temperature, around 160°C of crystallization temperature and around 250°C of melting temperature (Giles, 2003).

2.5.2 Thermo-gravimetric analysis TGA

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Thermo-gravimetric analysis (TGA) is used to find the change in weight related to changes in temperature which is also known as thermal stability. TGA is a thermal analysis technique that measures the weight change of a sample under a certain temperature time, working on the principle of a beam balance (Naranjo et al, 2008). The TGA analysis is able to evaluate weight changes caused by the following thermal events such as vitalization of moisture, decomposition of polymers and additives and decomposition of some mineral fillers.

2.5.2.1 TGA of polyethylene ALAYSIA PAHANG

TGA is commonly used in studies on the thermal stability of plastic composites. The thermal stability may be related to their potential used as a composite, where low thermal stability of fibres could be a limitation to their composites (Mengeloglu and Karakus, 2008), (Monteiro et al.,2012). The thermal properties of natural fibres in a HDPE matrix showed that the composite is more stable (Waldman et al., 2008), (Ren et

al., 2014). Other than that, a previous study used polyamide 6 (PA6) in a HDPE matrix with and without the addition of coupling agent. The thermal stability was compared and the result showed that the TGA of the PA6/HDPE composite was improved after the addition of a coupling agent (Hamid et al., 2013). In comparison, (Banat and Fares, 2015) found that the addition of the natural fibre olive shell flour (OSF) into the HDPE matrix reduced the melting temperature, melting enthalpy and crystallinity of the HDPE composite, but the addition of a coupling agent did not significantly affect the melting temperature and only slightly (10%) decreased the melting enthalpy of the polymer composite. Figure 2.10 shows that the HDPE was thermally stable up to a temperature of 400°C, then it start to degrade dramatically followed by one step maximum weight lost rate at 478°C at the DTG curve as shown in Figure 2.10.

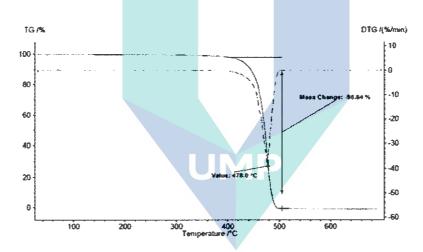
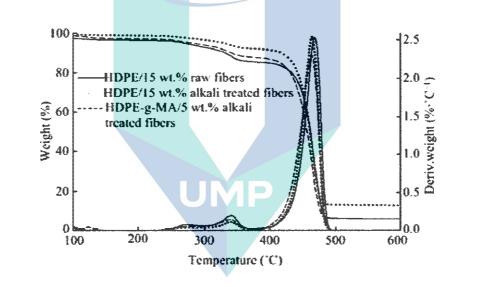


Figure 2.10 TG and DTG thermograph of pure HDPE Source: Banat and Fares (2015)

Figure 2.11 shows the TGA curve of a HDPE reinforced with natural fibre (Ouarhim et al., 2018). As shown in Figure 2.8, the degradation temperature shifted from 455°C to 467°C after the addition of the maximum (15 wt.%) of raw fibres and continued to decrease around 464°C after addition of the coupling agent. The composite with added coupling agent showed less stability than the composite without the coupling agent. This happened due to the interaction between the coupling agent group on the fibre surface (Essabir et al., 2016) and (Essabir, Boujmal, et al., 2016).

Another study by Yong Lei et al., (2009), on recycled HDPE (rHDPE) and rPET blends through reactive extrusion also used TGA at 10°C /min in nitrogen gas to determine the thermal stability of the rHDPE/rPET. The result showed that the TGA of pure rHDPE at the onset of decomposition temperature was about 442°C, and degradation temperature was about 470°C. For the rPET, the onset temperature was at 387°C and degradation temperature at 425°C as shown in Figure 2.12. However, the thermal stability of this composite improved with the addition of methylenedi (phenyl isocyanate) (MDI) for rHDPE/ rPET (50/50) while no obvious improvement was seen for the sample with added styrene and ethylene/butylene (SEBS), and maleated polyethylene (PE-g-MA).



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Figure 2.11 TGA curve of HDPE composite Source:Ouarhim et al. (2018)

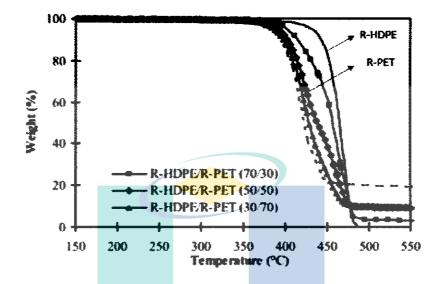


Figure 2.12 TGA curve of pure R-HDPE and R-PET Source: Yong Lei et al. (2009)

2.6 Microstructure

The scanning electron microscope (SEM) is type of electron microscope that can produce images of samples by scanning on the surface with a beam of focussed electrons. The electrons and atoms interact in the sample, which then produced signals that contain information about the samples composition and surface of the shapes and features.

The SEM of the fractured surface of composites that used HDPE as a matrix showed a large number of gaps between the fibres and the matrix. This is because of the poor interfacial adhesion with the HDPE matrix as mentioned in (Mohanty et al., 2006). Another study found that a HDPE composite with added MAPE also showed the layers of matrix material were pulled out together with the fibre during the tensile fracture, which proved that the MAPE caused cohesive coupling between the fibre and the HDPE matrix (John et al., 2003).

A (Dimitrova et al., 2000) stated that a morphological study of PET/PE was needed, as they knew these two components showed incompatibility. The SEM micrograph in a paper by Navarro et al. (2008) showed that the fracture surface had two different phases, with the PE located on the outside of the section and the PET remaining in the centre area. In another work by W. G. Yong Lei, Qinglin Wu, et al. (2009), the morphology of the fracture surface of a rHDPE/rPET blend at different compositions was discussed. Figure 2.13 shows that the rHDPE/rPET (70/30) had a typical morphology that suggests an incompatible system with poor distribution and no adhesion between the rHDPE and rPET. The increase in rPET content up to 50% in Figure 2.14 showed a coarse co-continuous morphology form and when the rPET was added up to 70% as shown in Figure 2.15, the HDPE phase became the dispersed phase with a wide diameter distribution.

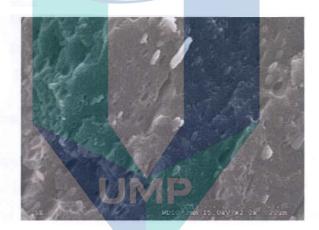


Figure 2.13 Morphology of the fracture surfaces of the R-PET/R-HDPE (30/70 w/w) Source: W. G. Yong Lei et al. (2009)



Figure 2.14 Morphology of the fracture surfaces of the RPET/R-HDPE (50/50 w/w) Source: W. G. Yong Lei et al. (2009)

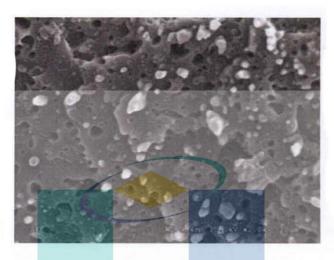


Figure 2.15 Morphology of the fracture surfaces of the RPET/R-HDPE (70/30 w/w) Source: W. G. Yong Lei et al. (2009)

2.7 Fourier Transform Infrared (FTIR)

The FTIR spectra are used to imply interfacial bonds between filler and matrix in a composite. Much research have been done on the characterization of the hydrogen bonds in reinforcing materials using FTIR and most of it have proved its usefulness (Hinterstoisser and Salmén, 2000). Furthermore, the FTIR is also used to determine the chemical composition of modified fibres. FTIR can also be used to effectively identify changes in chemical composition, interface and properties of fibres and composites.

The FTIR scans from 400 cm⁻¹ to 4000 cm⁻¹ depending on the differences of the observed peak. The typical wavelength of polyethylene analysis is in the region of 3000-2800 cm⁻¹,1550-1400 cm⁻¹, and 750-650 cm⁻¹ (Gulmine et al., 2002). These wavelengths for polyethylene are related to the C-H bonds for each peak.

In a study by Chaiwutthinan et.al (2018), samples containing rPET were analysed using FTIR and showed the characteristic peaks of the carbonyl group (C=O) at 1714 cm⁻¹, asymmetric C-C-O stretching at peak 1240 cm⁻¹, asymmetric O-C-C stretching at 1092 cm⁻¹, C-H wagging at 722 cm⁻¹, C-H stretching at2950 cm⁻¹, 2918

and 2836 cm⁻¹, at peak 1450 cm⁻¹ CH₂ was formed, and symmetric of CH₃ deformation at 1375 cm⁻¹. In Figure 2.16, the first line, (a), shows the FTIR spectra of rPET.

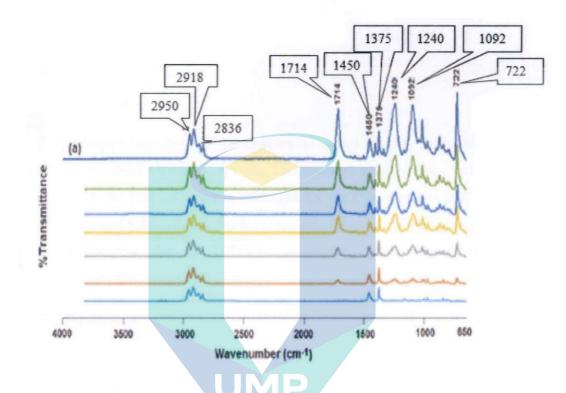


Figure 2.16 FTIR spectra of (a) rPET Source: Chaiwutthinan et.al, (2018)

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CHAPTER 3

METHODOLOGY

3.1 Introduction

This chapter explains the procedures in detail for the understanding of the fabrication of the rPET/HDPE composite. The research methodology will describe the raw materials in the first sub section, followed by the DSC thermal transition analysis of raw materials and fabrication procedures including parameter temperature setting and methods to examine the rPET/HDPE composite. Figure 3.1 summarizes the methodology in an illustrated flowchart.

3.2 Raw materials

Raw materials is the important things in the process fabrication of composite .The raw materials used in this study are rPET flakes as a filler, HDPE matrix and MAPE coupling agent. With regards to these materials, the following subsections provide their properties and justification.

3.2.1 Polyethylene (HDPE) matrix

As for the matrix, HDPE was selected due to its being widely used as a matrix and ease in processing. The HDPE was purchased from Lotte Chemicals Titan (M) Sdn. Bhd. Table 3.1 shows the specification of the raw HDPE, while Figure 3.2 shows the image of pure materials, indicated as types of pellets.

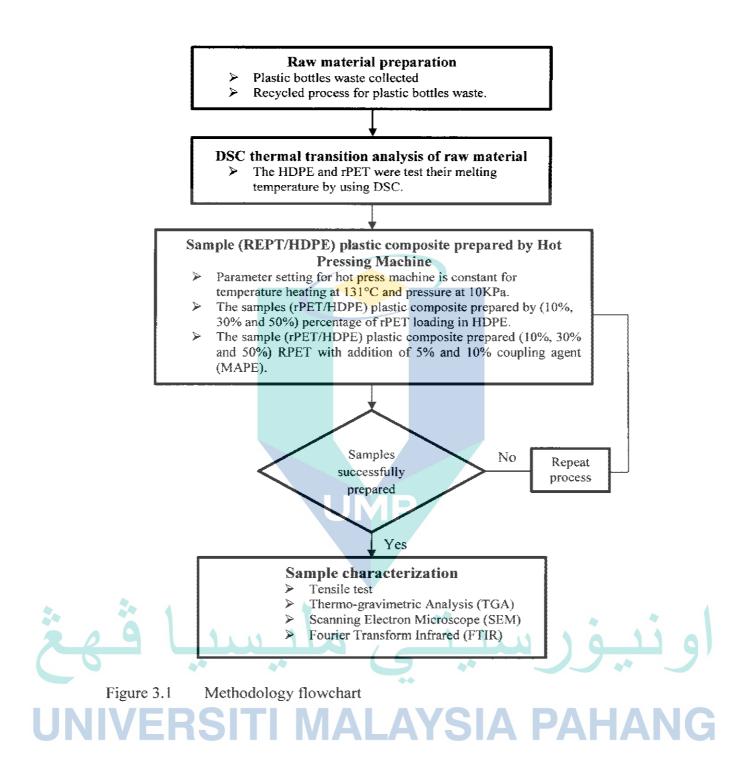




Figure 3.2 The pure HDPE

3.2.2 Preparation of recycled PET

In this study, the recycling process started by collecting the waste polyethylene terephthalate (PET) plastic bottles around UMP, for about three months. After that, the plastic bottles were sorted from their caps and labels, and only the plastic bottles itself was used as shown in Figure 3.3.



Then, the plastic bottles were crushed into flakes using a crusher machine as shown in Figure 3.4. Next, the plastic flakes were washed to remove any dirt using water. Finally, the plastic flakes were dried using normal environment which is dry air for at least two days. The appearance of the plastic flakes after the washing and drying process is shown in Figure 3.5. The sizes of the flakes were measured was to be in a range of 3 mm to 9 mm.





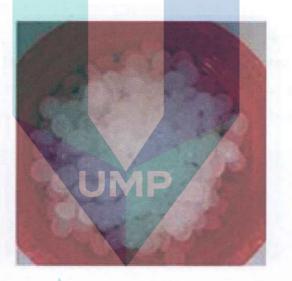


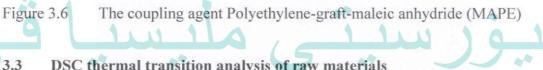
Figure 3.5 Recycled plastic bottled PET flakes after wash and dry process

UN 3.2.3 MAPE coupling agent ALAYSIA PAHANG

The polyethylene-graft-maleic anhydride (MAPE) coupling agent was purchased from Sigma-Aldrich. The specifications of MAPE that was purchased are shown in Table 3.2 and Figure 3.6 shows the image of MAPE pellets. The addition of this coupling agent is to improve the compatibility and mechanical strength of the interface region between the rPET and the HDPE matrix.

MAP	Έ
Appearance (Form)	Beads or Pellets
Appearance (Colour)	White to Off-White
Chemical formula	$C_{20}H_{30}N_8O_9$
Density	0.92g/mL at 25°C
Viscosity	140°C
Melting point	80°C
Melting temperature (DSC)	107°C
Solubility in water	Insoluble





DSC thermal transition analysis of raw materials

The test method for the raw materials used is the Differential Scanning Calorimetry (DSC) test. The DSC thermal test is to identify the melting temperature for the rPET flakes and HDPE pellets before the start of the hot press process. This melting temperature is important in order to set the temperature parameters during the hot press process.

3.3.1 Differential Scanning Calorimetry (DSC)

The differential scanning calorimetry (DSC) (TA instrument DSC model Q100) was used to study the melting temperature (Tm) of the rPET and HDPE in a nitrogen atmosphere. This test followed the ASTM 3418 standard. Figure 3.7 shows the DSC instrument used in this study.

For the DSC analysis, the plastic samples weighing less than 3 mg were put into typical aluminium pans and then sealed. As a reference, an empty sealed aluminium pan was analysed together with the samples in the DSC. The samples were put through a heating program at a constant rate of 10° C/min and heated from room temperature to 300°C, and then held for about 5 minutes at this temperature to erase the thermal history during the processing. This step is also known as 1st heating scan. Afterwards, the samples were heated for second time (2nd heating scan) at the same rate of 10°C /min up to 300°C to find the melting temperature of the samples. The typical DSC of pure HDPE and rPET values of the melting temperature (Tm) were obtained.



3.4 RPET/HDPE composite preparation

The sample preparation included two main processes which were mixing of raw material, and pressing the sample using a hot press machine. Manual mixing method was used to mix the rPET and HDPE. Table 3.3 specifies the different rPET loadings in

the HDPE matrix. There were three types of rPET/HDPE composites which were: Type I, Type II and Type III.

The rPET/HDPE composite samples were thermoformed by a hot pressing machine model LS22025 as shown in Figure 3.8 with a thickness of 1 mm. The operation temperature was 135°C with constant pressure 10kPa for 10 minutes of pre heating, 15 minutes of compression and cooling until the temperature was reduced to room temperature for approximately 20 minutes.

The moulds used in the preparation were made from the aluminium plate hot press machine as shown in Figure 3.9. The dimensions of one aluminium frame are 140 mm x 140 mm x 1 mm and two aluminium plates were used, one on the top and one on the bottom.



Type of	Code		
rPET/HDPE	of	Composition (%)	Weight(g)
composite	samples		
HDPE		100 % HDPE	50
rPET		100 % rPET	50
Type I	IA	90%HDPE + 10%rPET	(0.9 x 50) + (0.1 x 50)
	IB	70% HDPE+ 30%rPET	(0.7 x 50) + (0.3 x 50)
	IC	50% HDPE+50%rPET	(0.5 x 50) + (0.5 x 50)
Type II	IIA	90% HDPE+ 10%rPET + 5%MAPE	(0.9 x 50) + (0.1 x 50)
			+(0.2 x 5)
	IIB	70% HDPE+ 30%rPET +5%MAPE	(0.7 x 50) + (0.3 x 50)
			+ (0.2 x 5)
	IIC	50% HDPE+ 50%rPET +5%MAPE	(0.5 x 50) + (0.5 x 50)
			+(0.2 x 5)
Type III	IIIA	90% HDPE+ 10%rPET +10%MAPE	(0.9 x 50) + (0.1 x 50)
			+ (0.2 x 10)
	IIIB	70% HDPE+ 30%rPET +10%MAPE	(0.7 x 50) + (0.3 x 50)
			$+(0.2 \times 10)$
	IIIC	50% HDPE+ 50%rPET +10%MAPE	$(0.5 \times 50) + (0.5 \times 50)$
	1.0	110, 11	+ (0.2 x 10)
	•	* 5 *	- J

Table 3.2 rPET reinforced HDPE composite composition

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Figure 3.9 Aluminium mould and plate (140mm x 140mm x 1 mm)

3.5 Sample characterization

The rPET/HDPE composites were characterized for their mechanical, morphology, thermal and structure properties. The characterization tools used in this study are listed below:

- i. Mechanical study: Tensile test
- ii. _ Thermal study: TGA

Morphological and structure characterization study: SEM, FTIR

3.5.2 Tensile testing

iii.

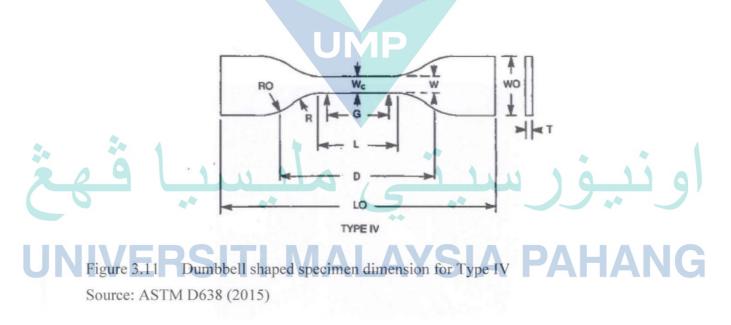
The properties such as tensile strength, elongation at break and modulus were determined using a Shimadzu Universal Testing Machine (Model: Autograph AG-X) as shown in Figure 3.10. The maximum setting of force for the machine was 5000 N.

The tests were conducted with a crosshead speed of 2 mm/min. The specimens were placed vertically in the grips of the testing machine. The precise five results were chosen for each loading of plastic rPET/HDPE matrix for each percentage. According

to ASTM (D638), a dumbbell shape (type IV) specimen was needed for the reinforced composite testing. Details of the dimensions are shown in Figure 3.11 and Table 3.5.



Figure 3.10 Shimadzu Universal Testing Machine (Model: Autograph AG-X)



Dimension	Value, mm (in)
Thickness ,<4mm (0.16in),T	$1.00 \pm 0.4 \ (0.13 \pm 0.02)$
Width of narrow selection, W	6 (0.25)
Length of narrow selection, L	33 (1.30)
With overall, WO	19 (0.75)
Length overall, LO	115 (4.5)
Gauge length, G	25 (1.00)
Distances between grips, D	65 (2.5)
Radius of fillet, R	14 (0.56)
Outer radius (Type IV),RO	25 (1.00)

Table 3.3 Dumbbell shaped speciment dimension for Type IV

Source: ASTM D638 (2015)

3.5.3 Scanning Electron Microscope (SEM)

The morphology of the fractured specimens of the rPET/HDPE composites were studied by using a SEM (FEI Quanta 450) as shown in Figure 3.12. The procedure for this SEM included coating the sample surface with a thin layer of titanium before examination to avoid electrostatic charge.



Figure 3.12 FEI Quanta 450 Scanning Electron Microscope (SEM)

3.5.4 Thermo-Gravimetric Analysis (TGA)

The thermal stabilities of the samples were characterized by using a Thermogravimetric analysis (TGA) (Hitachi STA7200) as shown in Figure 3.13. The samples were weighed to approximately 4-6 mg and put in a typical aluminium pan, and then sealed. The sample were heated in the TGA chamber from room temperature to 600^oC under nitrogen atmosphere and at 10^oC/min heating rate and 50 ml/min flow rate for each sample. The values for the onset degradation temperature, start degradation temperature and end degradation temperature were determined from the TGA curve.



Figure 3.13 Thermo-Gravimetric Analysis (TGA) model Hitachi STA7200

3.5.5 Fourier Transform Infrared (FTIR)

The FTIR spectroscopy technique was used to characterize the bonding interactions among the polymer. The FTIR machine (Thermo scientific Nicolet iS50) is shown in Figure 3.14.

Figure 3.14 FTIR Thermo scientific Nicolet iS50

The FTIR analysis technique was used to identify polymeric materials. The sample was scanned from 400 cm⁻¹ to 4000 cm⁻¹ for 2 to 4 times depending on the observed peaks for each sample. The method used was infrared light to scan test samples and observe the chemical properties. The FTIR spectra with transmittance (%T) versus wavelength (cm⁻¹) were gained from the scanning process.

There were four types of samples that were observed in this analysis technique which were high density polyethylene (HDPE), high density polyethylene (HDPE) and recycled polyethylene terephthalate (rPET) plastic composite, rPET/HDPE plastic composite with the addition of 5% coupling agent (MAPE), and rPET/HDPE plastic composite with the addition of 10% coupling agent (MAPE).

3.6 Summary

The explanation and details of the procedures, samples fabrication, tools used and characterization analysis on rPET/HDPE composite samples were presented in this chapter. All of the rPET/HDPE samples were examined for mechanical properties and thermal stability. Then, the bonding between the matrix and filler was characterized via microstructure. All of the results are analysed and discussed in the following Chapter 4.



CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

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This chapter starts with the results of raw materials test used DSC analysis. Then, the tensile test results for three different types of rPET/HDPE composite which are, Type I (rPET/HDPE/0%MAPE), Type II (rPET/HDPE/5%MAPE) and Type III (rPET/HDPE/10% MAPE) were compared and discussed. After that, the SEM micrographs of fracture specimens from the tensile test were observed and discussed. In the next subsection, the thermal stability results from TGA test for each types of rPET/HDPE composites were analysed. Lastly, the FTIR analyse are included to see the interfacial interactions that affect the tensile properties between the rPET and HDPE and after MAPE was added to the composite.

4.2 DSC thermal transition analysis of raw materials

The DSC thermal test was performed to identify the melting temperature (T_m) of rPET and polyethylene (HDPE). Recycled PET flakes and HDPE pallets were tested using this DSC analysis before the hot press process were done.

The results of the DSC characterization test on pure HDPE and rPET flakes before the start of the hot pressing process are shown in Figure 4.1 and Figure 4.2. Figure 4.1 shows the melting peak (T_m) of rPET is at 250.11°C. rPET is a semi crystalline structure with a melting temperature and glass transition temperature (T_g) of 82.25°C. In Figure 4.2, the HDPE pellet sample showed a melting peak at 131.08°C with the heat of melting of 21.63 J/g. Based on the DSC result, the suitable temperature for hot press can be set to start at 131°C until 135°C.

The comparison value of melting temperature, T_m in some literature that value melting temperature of HDPE are around 114°C -135°C and for PET around 250°C -

255°C. Based on this result it can be conclude that the result show in approximately value almost the same with the literature values by Ashraf, (2015) and Elamri et al., (2015)

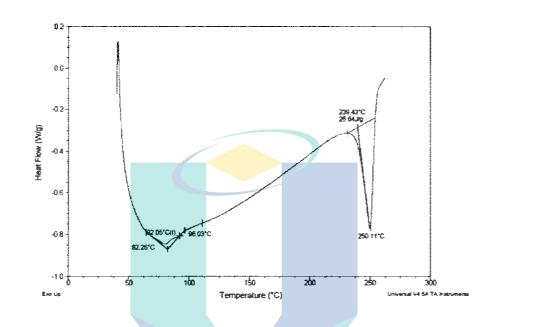


Figure 4.1 DSC curve for recycled PET flake

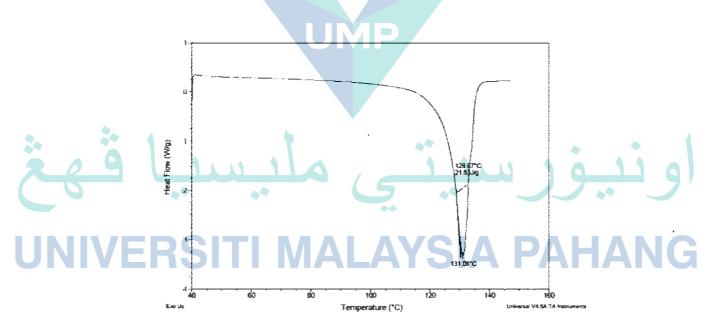


Figure 4.2 DSC curve for high density polyethylene (HDPE) pellets

4.3 Tensile properties

The tensile test were carried out on three types of sample which were, Type I (rPET/HDPE/0% MAPE), Type II (rPET/HDPE/5% MAPE) and Type III (rPET/HDPE/10% MAPE) and each type have difference percentages of rPET (10% 30% and 50%) in HDPE. All Table 4.1 and Figure 4.3 show the average result of tensile strengths for all samples.

Туре	Code of samples	MAPE (%)	rPET (%)	Tensile Strength (MPa)
HDPE			-	24.256
	IA		10	7.412
·T I	IB	0	30	7.356
Type I	IC	0	50	4.449
	IIA		10	116.937
Tumo II	IIB	5	30	102.502
Type II	IIC	3	50	75.717
	IIIA		10	156.271
Type III	IIIB	10	30	122.370
- 1	IIIC	UMP	50	86.823

Table 4.1	Average of tensile strength

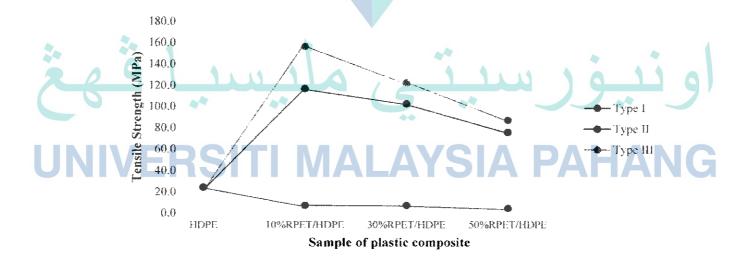


Figure 4.3 The average tensile strength graph of rPET/HDPE composite

It was observed that the mechanical properties of rPET/HDPE (Type I) composite decreased linearly with the increasing filler (rPET) loading of 10%, 30% and 50%. This decrease in the mechanical properties at high filler (rPET) loading was due to the poor filler-matrix adhesion which promoted weak spots at the interface as well as ununiformed stress transfer due to filler (rPET) loading within the matrix (Thwe and Liao, 2003). Figure 4.3 shows that the Type I (rPET/HDPE/0% MAPE) composite had a lower tensile strength compared to pure HDPE (24.256 MPa). The lowest tensile strength for the TypeI sample is the plastic with 50% rPET (IC), the value for this sample is about 4.4 MPa, while for the 10% rPET (IA) and 30% (IB) they are about 7.4 MPa.

A similar pattern seen by Kusuktham and Teeranachaideekul (2014) which suggested that the decreasing pattern is due to the high filler content. High filler to matrix content affects the strength due to interactions between the filler and the matrix. As the percentage of filler content increased, the interaction between the filler increased and results in agglomeration of the filler. Agglomeration of the filler leads to stress concentration points within the composite and can cause weak composites (Han-Xiong Huang, 2009).

The result for Type II composites with (5% MAPE) showed that the highest tensile strength was from the sample IIA (10% rPET/HDPE) is 116.937 MPa, which increase of about 92.7 MPa from pure HDPE. Meanwhile, for the sample IIB (30% rPET/HDPE), the tensile value slightly decreased about 14 MPa compared to the IA sample. The tensile strength of IIC (50% rPET/HDPE) sample is 75.72MPa which is the lowest tensile strength among Type II composites but still higher than pure HDPE and Type I composites. However, the Type III composites with 10%rPET loading in HDPE (IIIA) have the highest tensile strength compared to other samples. The samples IIIA has a tensile strength value of 156.27 MPa which is an increase of about 132 MPa higher than pure HDPE.

Overall, the tensile strength increased drastically after the addition of the coupling agent (MAPE) for Type II and Type III composites. This is because the coupling agent gives stronger bonding due to the sufficient maleic anhydride groups

present in the coupling agent having better interaction with the –OH group present on the fibre surface and have a sufficient tail length for better mix-up with the matrix (Mohanty et al., 2006). Other reason is the composite of rPET/HDPE increased with the addition of coupling agent (MAPE) due to the strong interaction developed between the polymer interphase (Mir et al, 2011).

Figure 4.4 shows the average tensile modulus of all types of samples and are summarize in Table 4.2. Figure 4.4 show that the average tensile modulus of this composite exhibit same behaviour with the tensile strength. The value of tensile modulus for pure HDPE measured in this experiment was 4.44GPa.

	Table 4.2	Average of	tensile mo	dulus			
•	Туре	Code of	MAPE	(%)	rPET (%)	Tensile Modulus	
		sample					
-	HDPE		-		-	4.437	
	Type I	IA	0		10	1.444	
		IB			30	1.211	
		IC			50	0.933	
	Type II	IIA	5		10	12.074	
	-	IIB			30	10.000	
2	09	IIC		3	50	7.8333	
	5	**	**		5 *		7
	Type III	IIIA	10		•• 10	14.111	
IN	IIVE	B	і пл	ΔΙ	30	A D ^{12.833}	G
		HIC			50	9.250	

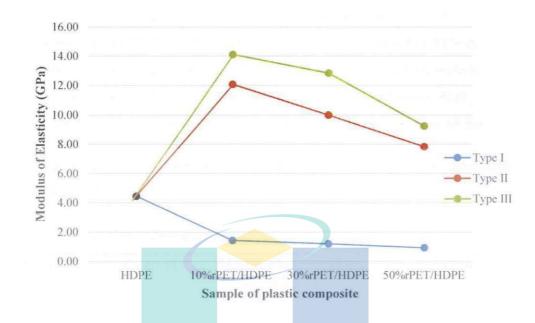


Figure 4.4 The average modulus of elasticity of rPET/HDPE composite

From the results obtained in Figure 4.4, the Type I composite showed the lowest value of tensile modulus for each type of sample. In the Type I composites, the value of tensile modulus continuously dropped as the percentages of rPET increased up to 30% and 50%. The lower tensile modulus seen at this point is most probably due to the high percentage of rPET in HDPE causing agglomeration and thus serving as weak spots in the composite. This observation is in agreement with (Albano et al., 2009).

Meanwhile, the tensile modulus increased drastically when the coupling agent MAPE was added into the rPET/HDPE composite, as shown for Type II and Type III in Figure 4.4. The tensile modulus value for rPET/HDPE with 5%MAPE (Type II) are, 12.074GPa for samples IIA (10%rPET/HDPE), 10.000GPa for IIB (30%rPET/HDPE), and 7.8333GPa for IIC (50%rPET/HDPE). In Type III, the tensile modulus showed the value of 14.111GPa for the IIIA sample, while for the IIIB, it decreased by about 1.28GPa from the IIIA sample. The IIIC showed a 9.250GPa of tensile modulus. In terms of rPET percentage, the highest value average of tensile modulus was seen in the Type III (rPET/HDPE/10% MAPE). Meanwhile, as seen in the rPET/HDPE composite Type I, the value of tensile modulus dropped with the increasing of rPET percentage. A significant increase in tensile modulus of Type II and Type III composite was due to the addition of MAPE which enhanced the interfacial bonding between rPET and HDPE matrix by coupling the rPET and HDPE. Similar observations were also found in (Rajak Hamim et al., 2016),(R. S. Chen et al, 2014) and (Adhikary et al., 2008). The details of the rPET/HDPE bonding analysis using FTIR were discussed in Section 4.6.

The average of tensile elongation result show in Figure 4.5 and the details value were summarize in Table 4.3.

	rage of tensile			
Туре	Code of	MAPE (%)	rPET (%)	Elongation At
	sample			Break (%)
HDPE		-	-	1.577
Type I	IA	0	10	1.822
	IB		30	2.007
	IC		50	3.243
		UMP		
Type II	IIA	5	10	1.284
	IIB		30	1.430
	IIC		50	1.811
20 1			-4	
Type III	IIIA	10	10	1.105
6	IIIB	- (5	30	2.007
-	IIIC	**	50	3.243
		ΛΙΛ		

 Table 4.3
 Average of tensile elongation

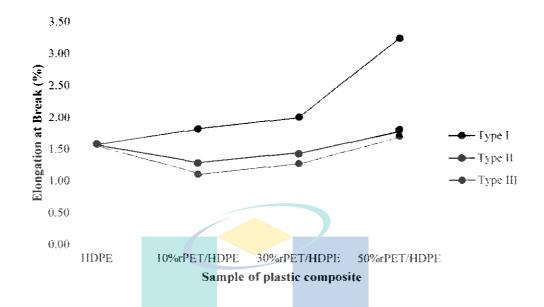


Figure 4.5 The average of elongation at break of rPET/HDPE composite

Otherwise, the elongation at break in Figure 4.5 was observed decrease when the coupling agent (MAPE) was added in rPET/HDPE composites. The results for the compositions with coupling agent (MAPE) showed a continuous decrease as the coupling agent increased to 10% in the Type III composites. A major decrease of 1.10%, was shown for the composite with 10% MAPE added into sample IIIA. These results suggest that the incorporation of MAPE with rPET in HDPE dramatically decreases the values as also observed by Santos and Pezzin (2003), for all compositions with rPET in relation to pure HDPE. This observation is normal for fibre reinforced composites as discussed by Laura et al. (2002). The high value of elongation shows higher ductility of the composite rPET/HDPE materials .This shows that the recycled PET filler in HDPE has influenced the ductility of the composite materials at sample IC (50%rPET/HDPE). Meanwhile, the composite rPET/HDPE Type II and Type III with the added coupling agent (MAPE) showed less ductility.

This result proved that this rPET/HDPE composite can be an efficient way to recycle PET because the mechanical properties of HDPE were increased. The best sample of the tensile test in this study is Type IIIA, with high value of tensile strength and Young elongation show it has good mechanical properties.

4.4 Morphology Analysis

Figure 4.6 shows the chemical elements of rPET and HDPE in the rPET/HDPE composite as screened using Energy-Dispersive X-ray (EDX), demonstrated by EDX peaks and different morphologies of the rPET and HDPE. This EDX image used as reference image to show rPET and HDPE element or surface look like for fracture surface of each Types of rPET/HDPE composite in SEM result.

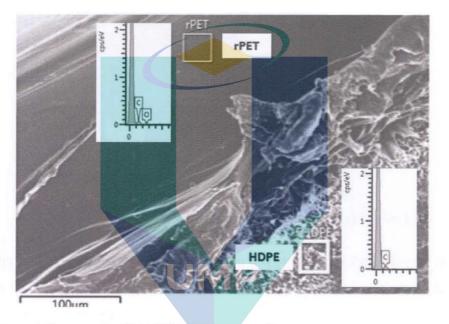


Figure 4.6 Micrograph of rPET/HDPE composite

The SEM morphology analysis of the tensile fracture surface of the rPET/HDPE composite shown in Figure 4.7. Figure 4.7 (a), (b), and (c) represent IA (10% rPET/HDPE), IB (30% rPET/HDPE), and IC (50% rPET/HDPE) composite, this samples were prepared without added any coupling agent (Type I).

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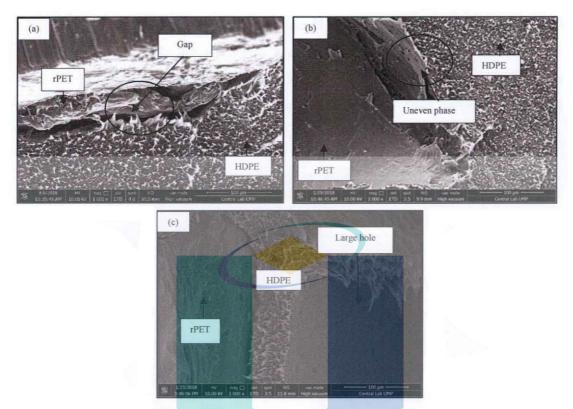


Figure 4.7 Micrograph of rPET/HDPE composite Type I (a) IA (b) IB (c) IC

Figure 4.7(a) shows that the IA sample has poor interfacial adhesion with clear gaps seen in between the rPET and HDPE phases. The poor interfacial adhesion has caused the tensile strength to be lower than the pure HDPE. The weak filler-matrix interface between rPET and HDPE also eased the pull out of rPET when stress was applied during the tensile test. Figure 4.7(b) shows that the samples IB composite has uneven phases and unstable structure due to uniformly dispersed of recycled PET in HDPE, may be caused too much composition of rPET in HDPE that made it difficult to bond. Meanwhile, Figure 4.7 (c) shows that the sample IC composite has a large hole created after the rPET pull out, meaning the sample has a low tensile strength because of the weak bonding between the rPET and HDPE. This happened because of the large difference in bonding of the rPET surface to the HDPE matrix (Mohanty et al., 2006). This is also due to the properties of rPET degrading after the recycling process as mentioned in (Khoramnejadian, 2011). Thus it can be concluded that with more percentage of rPET added, the bonding between HDPE and rPET becomes weaker.

At the same composition, the Type II composites with added 5% MAPE in rPET/HDPE composite are shown in Figure 4.8 (a-c). Overall, the SEM images of rPET/HDPE sample with the addition of 5% MAPE shows that the interfacial adhesion between rPET and HDPE was significantly improved then samples rPET/HDPE without MAPE.

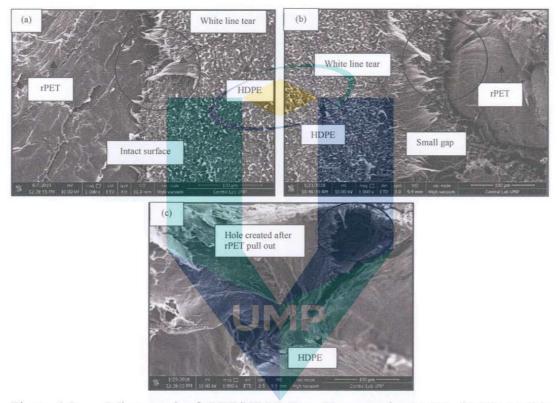
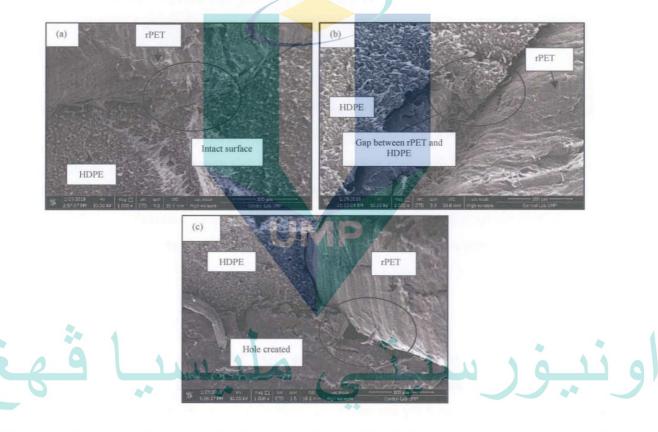


Figure 4.8 Micrograph of rPET/HDPE Type II composite (a) IIA (b) IIB (c) IIC Figure 4.8 (a) shows the sample of Type IIA was improved with the intact surface. Meanwhile, the prominent white line tear exposed the fact that HDPE was also pulled out during the tensile test, indicating a strong adhesion between the HDPE and rPET, as thus increased the strength of the rPET/HDPE composite Figure 4.8(b) and 4.8(c) show SEM micrographs of tensile fracture surfaces of rPET/HDPE with added 5% MAPE at different percentages of rPET. These figures show there are also interface sites with small gaps between the rPET and HDPE in Type II composite especially in sample with 30% and 50% rPET content. This may be caused by the too high composition of rPET in HDPE interfering with the bonding with the coupling agent. However, the SEM images of the rPET/HDPE samples with the added 5% MAPE showed that the interfacial adhesion between rPET and HDPE was significantly better than samples of rPET/HDPE without MAPE. Thus, the addition MAPE improved the interfacing between the two phases of the polymer (Rajak Hamim et al., 2016).

The Type III composites with added 10% MAPE at the same composition are shown in Figure 4.9. The highest tensile strength of the composites in this study was from the HDPE/10% rPET with added 10% MAPE coupling agent. The SEM proved this as shown in Figure 4.9(a) where the interfacial bonding between HDPE and rPET become stronger with the addition of 10% MAPE.



. V E Micrograph of rPET/HDPE composite Type III (a) IIIA (b) IIIB (c) IIIC

Figure 4.9(a) shows the micrograph of the fracture surface of IIIA. An intact surface between the HDPE and rPET phase was observed, indicating a good interfacial bonding. This is because the coupling agent (MAPE) gave stronger bonding due to the sufficient maleic anhydride groups present in the coupling agent for better interaction with the functional group to be coupled and bonded with HDPE. As shown in Figure 4.9(b) and Figure 4.9(c), there are small holes and gaps in composite samples with more

than 10% of rPET. Similar observations were seen in the sample IIB and IIC as shown in Figure 4.8(b) and Figure 4.8(c). This also can be explained by the rPET being weakly bonded to the HDPE matrix and thus pulled out from the matrix during the fracture. Furthermore, when the percentage of rPET increased, the HDPE matrix is no longer continuously distributed and many of the rPET filler are in direct contact with one another, resulting in poor bonding at adhesion at the interface (Adhikary et al., 2008). Particularly, the higher percentage of MAPE up to 10% in rPET/HDPE composite resulted in higher tensile strength as observed in the tensile test. Thus, the micrographs showed that the recycled PET can improve the mechanical properties of HDPE but with the addition of additives or coupling agents.

4.5 Thermal stability (TGA) of the rPET/HDPE

In this section, the thermal stabilities of the rPET/HDPE composites without coupling agent and rPET/HDPE with coupling agent (MAPE) were determined by analysing the weight change that occurred as the samples were heated in nitrogen with a heating rate 10°C/min. The thermo-gravimetric weight loss curve TG (%) were recorded as a function of temperature. The thermal decomposition of the HDPE sample occurred in a one stage pattern, with a maximum decomposition rate occurring between 300°C to 500°C.

4.5.1 Type I, (rPET/HDPE/0%MAPE) composite

Figure 4.10 shows the TGA curve of pure HDPE and Type I rPET/HDPE/ 0%MAPE composites. The shapes of the TGA curves observed in Figure 4.10 for HDPE and rPET/HDPE are almost the same. From the TGA curve, it was observed that raw HDPE undergoes thermal degradation beginning at 350°C. From this temperature, the HDPE process of thermal decomposition occurred at one stage until 500°C. The onset temperature T_0 of the rPET/HDPE/0% MAPE composite (Type I) are also observed to start at the same temperature as pure HDPE (350°C). Figure 4.10 shows the starting temperature of degradation decreased at high percentages of rPET. As observed in the result, the start temperature of degradation for IB (30% rPET/HDPE) and IC (50% rPET/HDPE) is 390°C, while for the IA (10% rPET/HDPE), the temperature is the same as for the HDPE which is at 400°C. There have possibility the addition of rPET flakes can hold accumulation heat that used as a heat source to accelerate the degradation process, as thus reduced the thermal stability as seen in Type I composite (Beyler and Hirschler, 2002).

The percentage of weight loss increased as the temperature increased, and completely decompose at 490°C, as indicated in Figure 4.10. The details in variation of decomposition temperatures for all samples at 50% weight loss are summarized in Table 4.4. However, the temperature of the rPET/HDPE composite at 50% weight loss, T (0.5) shifted to lower temperatures by an average of 17°C. Figure 4.10 and Table 4.4 show the temperatures for the start of degradation decreased when the percentage of rPET increased up to 30% and 50%. At temperature 200°C, all of the rPET/HDPE samples and HDPE samples were observed to experience a typical \approx 2-3% of weight loss, which can be attributed to components such as impurities and moisture i.e. oxygen start to evaporate at such low temperatures (Mohanty et al., 2006). The sample degradation can be explained by the fact that the residual water moisture started to evaporate at such low temperatures (Dimitrov et al, 2013).

Another important information that can be extracted from the analysis in Figure 4.10 and Table 4.4 is the residue weight percentage which was lower as compared to the actual weight added during process. This is possibly due to the decomposition of rPET that were compacted with the HDPE matrix that resulted from the hot compression moulding or this might be due to the non-uniform filler distribution in the test sample. Meanwhile, the remaining residue may be attributed to the high thermal

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stability.

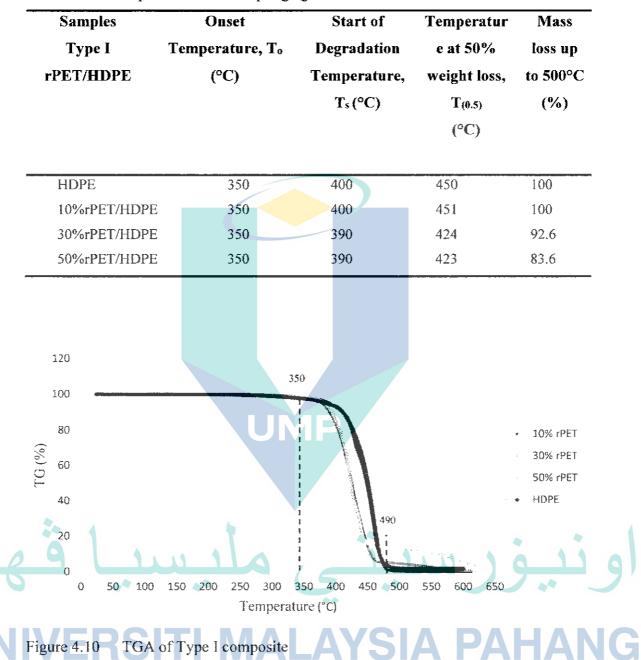


Table 4.4Onse temperature, To and 50% weight loss and residue mass for Type I,rPET/HDPE composite without coupling agent at various filler content.

4.5.2 Type II, (rPET/HDPE/5%MAPE) composite

Figure 4.11 shows the TGA curve of the HDPE and Type II, rPET/HDPE composite with added 5% MAPE coupling agent, (rPET/HDPE/5%MAPE). The result showed that the onset temperature of these Type II composite samples decreased at 340° C. The onset temperature, T₀ shifted to a lower temperature by 10° C lower than

HDPE and rPET/HDPE/0%MAPE, (Type I) composite. The TGA curve showed that the starting degradation temperature was faster than the HDPE for 10% 30% and 50% rPET, which was at 380°C.

Table 4.5 summarized the decomposition temperatures for the HDPE and rPET/HDPE composites at 50% weight loss, T (0.5). In Figure 4.11, the Type II composite were seen to have lesser changes in temperature compared to the TGA curve for the Type I (rPET/HDPE/0% MAPE) composite. Table 4.5 and Figure 4.11 showed that the temperature of degradation at 50% weight loss, T (0.5) decreased when the rPET percentage increased, this happened due to the low interaction between rPET and HDPE (Saeed, Eltahir et al., 2018).

Table 4.5Temperature at 10% weight loss, 50% weight loss and residue mass forTypeII, rPET/HDP/5%MAPE at various filler content.

Samples Type II rPET/HDPE/5%	Onset Temperature,	Start degradation	Temperatur e at 50%	Mass Joss up
MAPE	T. (°C)	Temperature, Ts (°C)	weight loss, T(0.5) (°C)	to 500°C (%)
HDPE	350	400	450	100
10%rPET/HDPE	340	380	447	100
30%rPET/HDPE	340	380	421 💊	88.0
50%rPET/HDPE	340	380	421	87.6

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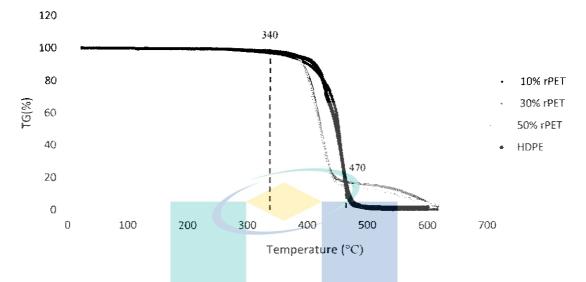


Figure 4.11 TGA of Type II composite

4.5.3 Type III, (rPET/HDPE/10%MAPE) composite

From the analysis in Figure 4.12, it was found that with the addition of coupling agent (MAPE) into the rPET/HDPE composite, the onset temperature, T_0 shifted to a lower temperature by 10°C which is the same temperature as Type II (rPET/HDPE/5%MAPE), compared to Type I composite and pure HDPE. The starting degradation temperatures of the rPET/HDPE/10%MAPE composite (Type III) are also observed to have the same temperature as Type II at 380°C. Figure 4.12 displays the TGA curve of the HDPE and Type III rPET/HDPE composite, while Table 4.6 summarizes the decomposition temperature for the HDPE and rPET/HDPE Type III, (rPET/HDPE/10%MAPE) composites at 50% weight loss, T (0.5). The temperature of the rPET/HDPE composite at 50% weight loss, T (0.5) decreased when the rPET percentage increased by an average of 11°C.

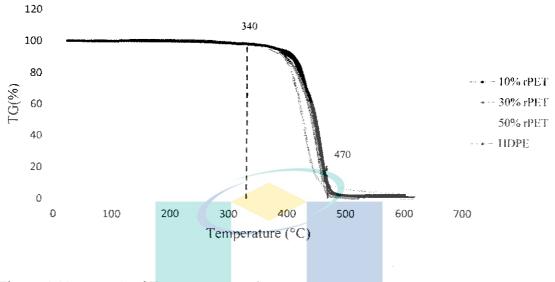


Figure 4.12 TGA of Type III composite

Table 4.6Temperature at 10% weight loss, 50% weight loss and residue mass forTypeIII, rPET/HDPE/10%MAPE at various filler content.

-	ples Type III ET/HDPE/	Onset Temperature,	Start degradation	Temperature at 50%	Mass loss
10	%MAPE	To	Temperature,	weight loss,	up to
		(°C)	Ts	T _(0.5)	500°C
			(°C)	(°C)	(%)
0		alcur	11	or un	ii.
	OPE	350	400	450	100
10	%rPET/HDPE	340	** 380	449	100
	%rPET/HDPE %rPET/HDPE	340 340		A P ⁴⁴² ₄₂₆ H	97.6 89.9

4.5.4 Summary of rPET/HDPE composite thermal stability properties.

Overall, the addition of MAPE in rPET/HDPE for Type II and Type III composites caused a shift to lower temperature of degradation. This result proved that a higher thermal stability was achieved for the composite Type I (rPET/HDPE/0%

MAPE) which are samples prepared without the coupling agent (MAPE). This is in agreement with (Mohanty et al., 2006) and (Siregar, Salit et al., 2011). With more percentage of coupling agent added in rPET/HDPE composites as shown for Type III and Type II, the onset temperature of degradation was 340°C compared to samples without MAPE which was at 350°C. The composites with 10% MAPE and 5%MAPE became less stable than the composites without MAPE because the presence of MAPE broke the perfect structure of rPET/HDPE, which consequently degraded the polymer chain and made the rPET/HDPE composites becoming less stable.

The end of degradation temperature, also known as the maximum degradation rate obtained from all of the curves was approximately at 470°C. In comparison, the maximum degradation rate of pure HDPE at nearly 100% decomposition was 500°C. This analysis suggests that the addition of rPET into the HDPE thermoplastic causes thermal degradation to occur at lower temperatures.

The MAPE coupling agent is often used in polymer composite to increase the interfacial bonding between the polymer matrix and the reinforcement fibre (Keener, Stuart, and Brown, 2004). In the present study, the MAPE was used to improve the interaction between the HDPE matrix and rPET filler. Interactions between the anhydride groups of maleated coupling agent and the hydroxyl groups (-OH) of the rPET can overcome the incompatibility problem and increase the tensile strength of rPET/HDPE composites, but at the same time decrease the thermal stability (Waldman et al., 2008). This interaction promotes more degradation sites due to the broken chain in the polymers that resulted from the coupling process. At the same time, the degradation of one component may possibly accelerate the degradation of the other

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4.6 Fourier Transform Infrared (FTIR) spectra

component as well.

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The results of the intermolecular reactions seen in FTIR also support the findings observed in the SEM scanning. For instance, Figure 4.13 shows the FTIR spectrum of pure HDPE, rPET/HDPE, and rPET/HDPE/5% MAPE and rPET/HDPE/10% MAPE.

From the Figure 4.13(a), it can be observed that the main peaks of pure HDPE arose from the vibration characteristics of the C-H ethylene group, the asymmetric and symmetric stretching at 2915 cm⁻¹ and 2847 cm⁻¹, the bending vibrations at 1471 cm⁻¹ and 1462 cm⁻¹, and rocking vibration at 716 cm⁻¹(Rajak Hamim et al., 2016). Furthermore, as can be seen in Figure 4.13(b), the addition of rPET into HDPE was confirmed with the noticeable peaks arising at 1712 cm⁻¹. The peak at 1712 cm⁻¹ is attributed to the C=O stretching of the ester group that belonged to the rPET (Merck, 2019). This 1712 cm⁻¹ peak related to the degradation of PET.

Meanwhile, Figure 4.13(c) and Figure 4.13(d) was observed that the FTIR spectra for the rPET/HDPE composite with added 5% MAPE and 10% MAPE, respectively. The intensity of C=O peak at 1712 cm⁻¹ when compared to the C-H stretching peaks at 2915 cm⁻¹ and 2847 cm⁻¹ was found to decrease with the addition of MAPE (Xinwu Xu and Ling feng Chen, 2019), suggesting the coupling reaction occurred in the rPET/HDPE composite. Notably, these changes support the stronger interfacial bonding and enhanced tensile strength seen in the rPET/HDPE/MAPE composite.

These coupling reaction between rPET and HDPE as seen in the rPET/HDPE/MAPE FTIR spectrum, support the stronger interfacial bonding as observed in the SEM analysis and enhanced tensile strength measured in the tensile test. By having good interfacial bonding between rPET and HDPE, it significantly improved the mechanical properties of the composite but at the same time reduced the thermal stability due to the perfect chain of rPET/HDPE composite were disturbed and consequently as degradation temperature decreased.

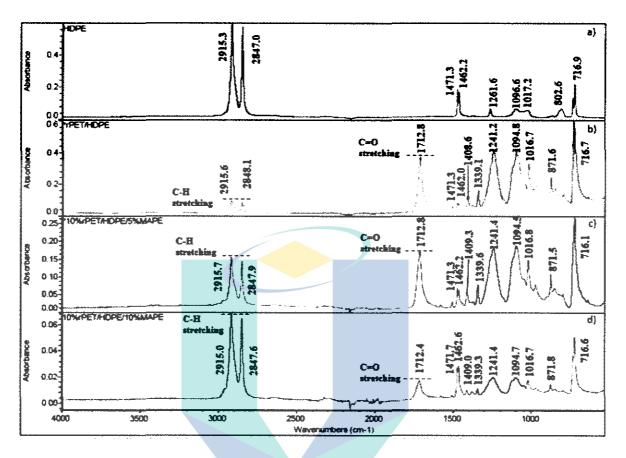


Figure 4.13 FTIR spectra of (a) HDPE, (b) rPET/HDPE, (c) HDPE/10%rPET/5%MAPE, (d) HDPE/10%rPET/10%MAPE

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CHAPTER 5

CONCLUSION

5.1 Conclusion

The results of this study shows that a useful composite with good properties could be successfully produced using recycled PET as reinforcement for the HDPE matrix. The following conclusion can be drawn based on the thermal properties and mechanical properties of the composites to the effect of recycled PET loading in HDPE polymer could be made:

- i. The rPET/HDPE plastic composite were successfully prepared by using hot pressing method with various percentage of rPET and MAPE. The addition of the MAPE coupling agent enhanced the interfacial bonding between HDPE and rPET phases, thus improving the compatibility of the rPET/HDPE composite.
- ii. The mechanical properties experiments showed that the rPET fibre improved the tensile properties of the rPET/HDPE composite for samples Type II and Type III due to the strong interaction developed between the polymer interphase. While, the thermal stability of rPET /HDPE composite Type II and Type III show less stability compare to Type I. The thermal stability of rPET/HDPE composite becomes less stable due to more interactions between MAPE and the rPET/HDPE composite and thus the perfect chain of rPET/HDPE composite were disturbed and consequently decrease the degradation temperature. Based on this, it can be concluded that rPET flakes could effectively reinforce the HDPE matrix when used in a minimal percentage and with the addition of the MAPE coupling agent.

Out of nine specimens in this study, the best specimen is Type IIIA (10% rPET/HDPE/10% MAPE) due to the enhancement of mechanical properties as proved by the test results.

5.2 **Recommendations for future studies**

Based on the experimental conclusions, several possible improvement for future studies are recommended as follows:

- i. Thermal analysis of rPET/HDPE composites could be done by using other thermal testing methods such as dynamic mechanical analysis (DMA) and thermomechanical analysis (TMA) to further understand the thermal properties of the rPET/HDPE plastic composites.
- ii. The combination of recycled PET and other types of thermoplastic matrix such as rPET/PP, rPET/PC or more than one filler/matrix could be prepared using the hot pressing method. This is to explore the possibility of the method in preparing other thermoplastic systems.

iii. Different types of coupling agents such as ethylene-glycidyl methacrylate copolymer (E-GMA) and maleic anhydride terpolymer (E-BA-MA). Could be introduced to study the effectiveness of other coupling agent in enhancing the interfacial bonding between the rPET and HDPE.

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Appendix A: The Details of Mechanical Properties

Туре	Code of samples	MAPE (%)	rPET (%)	Tensile Strength (MPa)	Standard Deviation
HDPE		-	-	24.256	0.6861
	IA		10	7.412	0.607
Type I	IB	0	30	7.356	0.800
	IC	U	50	4.449	1.180
	IIA		10	116.937	3.256
Type II	IIB	5	30	102.502	1.023
	IIC	3	50	75 .717	2.715
	IIIA		10	156.271	3.202
Type Ill	IIIB	10	30	122.370	4.762
	IIIC		50	86.823	1.695

The Average of Tensile Strength with Standard Deviation

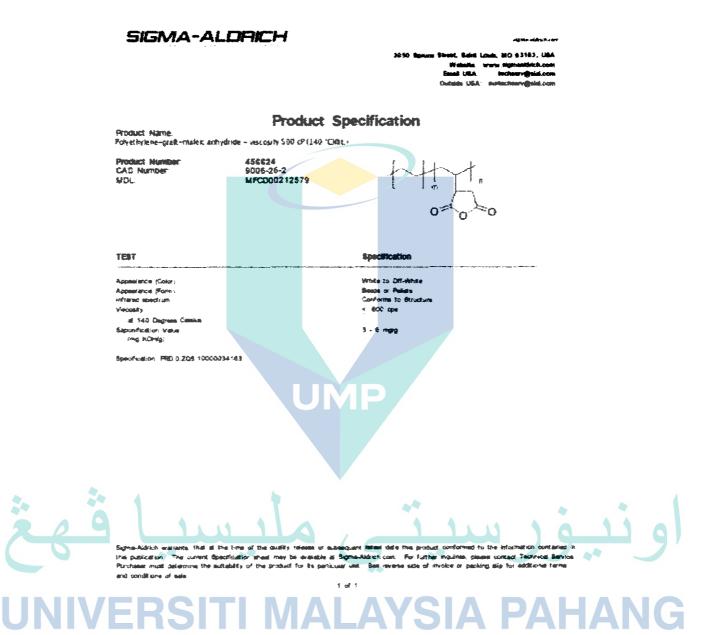


UMP

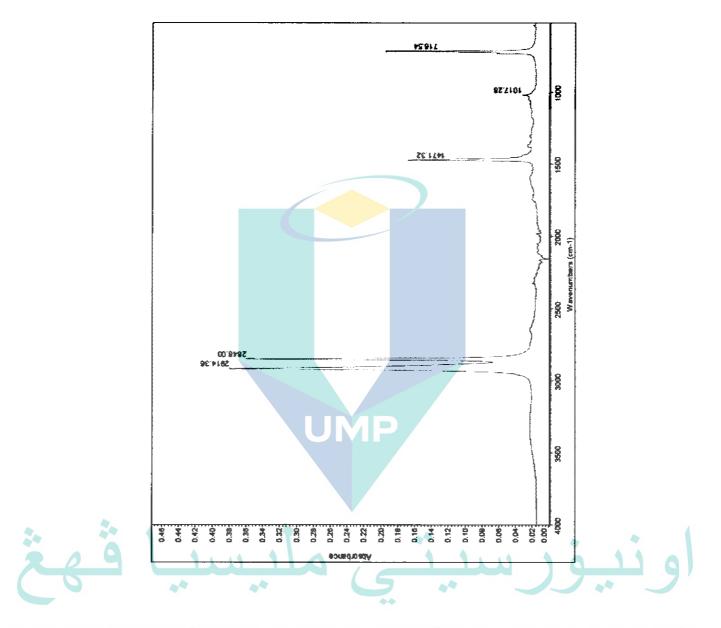
Appendix B: Data Sheet of High Density Polyethylene (HDPE) Materials

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	CEARACTER APPLICATIONS ADVANTAGES					
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Appendix C: Product Specification of Polyethylene-Graft-Maleic Anhydride



Appendix D: FTIR Curve for HDPE



Appendix E: List of Publication

- Nik Ruqiyah Nik Hassan, Noor Mazni Ismail, Suriati Ghazali, Dewan muhammad Nurzamman. 'The Effect of MAPE Compatibilizer Agent on the Tensile Strength of Recycled PET/HDPE Plastic Composite', *Materials Today:* Proceeding (In Press)(SCOPUS)
- Nik Ruqiyah Nik Hassan, Noor Mazni Ismail, Suriati Ghazali, Dewan muhammad Nurzamman. 'Thermal properties of polyethylene reinforced with recycledpoly (ethylene terephthalate) flakes', *IOP Conf. Series:* Materials Science and Engineering 342 (2018) (SCOPUS).
- 3. Nik Ruqiyah Nik Hassan, Farah Amirah Mohd Ghazali, Abdul Aziz Jaafar, Noor Mazni Ismail. 'Preparation of polypropylene thermoplastic container via thermoforming process', *IOP Conf. Series*: Materials Science and Engineering 114 (2016) (SCOPUS).
- 4. Poster presentation exhibition International Festival Innovation on Green Technology (2016)

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