

**DEVELOPMENT OF BIOCHAR FILLED HIGH DENSITY
POLYETHYLENE COMPOSITE**

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**A project report submitted in partial fulfilment of the
requirements for the award of Bachelor of Engineering
(Hons.) Petrochemical Engineering**

**Faculty of Engineering and Green Technology
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April 2016

DECLARATION

I hereby declare that this project report is based on my original work except for citations and quotations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

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ABSTRACT

Insufficient recycling and recovering of most diversely used high density polyethylene (HDPE) has drastically increased the amount of plastics waste. Besides, the growth in oil palm industry has led to a sharp increase in the amount of waste from palm oil mill effluent (POME), which leads to much environmental pollution. New inventions in utilization of waste materials as an alternative for reservation of non-renewable resources have been of prime aim. Thus, in this research work, the characteristics and potential of Biochar (BC) derived from oil palm sludge as filler in high density polyethylene was studied. BC filled high density polyethylene (HDPE/BC) composites were prepared through melt mixing using a Brabender internal mixer. Small size, individual and loose aggregate structure, high porosity and compatibility of BC in HDPE attribute to the improved processability, tensile strength, tensile modulus, toluene resistance and thermal stability of HDPE/BC composite in comparison to neat HDPE. However, elongations at break and water resistance of HDPE/BC composite were reduced when BC loading increased. It was studied that the optimum BC loading in HDPE/BC composite is 2.5 wt% as it showed the highest tensile strength, improved modulus strength, thermal stability, toluene resistance and comparable processability although deterioration occurred in water resistance and elongations at break.

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LIST OF SYMBOLS / ABBREVIATIONS

ΔH_m	melting heat (J/g)
ΔH_{100}	melting heat for 100% crystalline poly(ethylene), 293 J/g
BC	biochar
BOD	biochemical oxygen demand
CaCO ₃	calcium carbonate
COD	chemical oxygen demand
DSC	Differential Scanning Calorimetry
FTIR	Fourier Transform Infrared Spectroscopy
HDPE	high density poly(ethylene)
LDPE	low density poly(ethylene)
M_i	initial mass of sample prior to water immersion
M_s	final mass of sample after absorbing water
NIR	Near Infrared Radiation
PA	poly(amide)
PE	poly(ethylene)
PET	poly(ethylene terephthalate)
POME	palm oil mill effluent
PP	poly(propylene)
PS	poly(styrene)
PSA	Particle Size Analysis
PVC	poly(vinyl chloride)
SEM	Scanning Electron Microscopy
SiO ₂	silicon dioxide
TGA	Thermogravimetric Analysis
W_p	weight fraction of polymer in sample
wt%	weight percent
X_c^m	degree of crystallinity

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CHAPTER 1

INTRODUCTION

1.1 Overview

Biochar (BC) is the ancient secret discovered by Amazonian back in the 16th centuries. The black and fertile soil (terra preta) at Amazon Basin had received the attention of scientist to discover the great usage of terra preta in soils amendment. The earth's dark black colouring of terra preta contains the most important ingredient, which is charcoal, to fertilize soil and double the harvest as compared to normal chemical fertilizer (Wayne, 2012). BC can be produced by charring of agricultural waste through pyrolysis or thermochemical conversion in oxygen limited environment (Biochar-international.org, 2015). Besides improving soils' quality, BC also acts as a significant role in the global carbon cycle by which carbon content in BC resists degradation in soil for thousands of years and reduces the emissions of methane gas and nitrous oxide to the environment (Biochar.org, 2006).

“Go Green”, the mostly promoted slogan nowadays around the world. In order to accomplish the “Go Green” target by fully utilizing waste, investigation on the potential development of BC filled in various applications has been carried out. For instance, the potential of BC papers consist of BC and paper pulp blending has been investigated in Rochester, New York (Draper, 2014). According to Chemical Industry News, the global polymer demand especially on thermoplastic such as high density polyethylene (HDPE), low density polyethylene (LDPE), polyvinyl chloride (PVC) and polystyrene (PS) are in drastically increasing trend. Global demand for plastic has led to pollution problems such as emission of toxic intermediate to

surrounding when plastic is being disposed or decomposed inappropriately (Pollution Issues, 2015). Besides the challenges in recovering and recycling of plastics, incineration and biodegradation of plastics are the alternative routes to reduce plastic wastes which is also expensive and hazardous (Eze et al., 2013). Due to high recycled plastic contamination risks through polymer recycling, reinforce polymer with organic fillers such as natural fibre is able to improve the biodegradability of polymer which causes it to be more environmentally friendly and having low processing cost (Liu et al., 2009).

By far, few researches have been done on the utilization of BC as filler in manufacturing polymer composites. For example, BC was used as filler in polymer such as wood polymer composites i.e, epoxy/BC composites (Ahmetli et al., 2013). Researches have been carried out in order to manufacture a more sustainable, resilient and financially viable bio-based polymer other than just being used as soil enhancer (Das et al., 2015). The integration of BC as filler into the polymer is a powerful method to mitigate climate change as it is not only substituted the use of fossil fuels but also sequestered carbon as carbon sink and led to negative emission of carbon (Biochar.org, 2006). However, the drawbacks of using bio-filler based polymer are the poor strength and stiffness possesses by organic filled polymer composites as compared to inorganic filled polymer composites (Das et al., 2015). Thus, mechanical properties of organic filler filled polymer composites can be improved by adjusting the filler contents and reducing the filler particle size (Nwanonenyi et al., 2013) as well as with the addition of additives to enhance the performance of polymer (Industry Liaison Office, 2015).

Malaysia is a tropical country with high temperatures and humidity throughout the year that eases the cultivation of tropical oil palm tree in Malaysia. The fruit of oil palm tree can be derived into edible vegetable oil with high saturated fats (Wwf.org.au, 2016). Besides, oil palm has the highest oil yielding and required less plantation land as compared to the other types of crops derived vegetable oil such as soybean, rapeseed and sunflower which can be verified in Table 1.1 (Sumathi et al., 2008). Therefore, when the demand of oils and fats increased, Malaysia has become one of the largest vegetable oil contributors in the world. As illustrated in Figure 1.1, the production of palm oil in Malaysia for the past 50 years

showed rapid increasing pace from year to year. In year 2000, the oil palm production was 12,000 million tons, whereas in year 2010, the oil palm production already shot to 18,000 million tons. As of year 2015, the production of palm oil has already reached 20,000 million tons. Therefore, the sharp growth of palm oil industry in Malaysia has led the oil palm plantation to boast significantly in the recent year.

According to Malaysian Palm Oil Board, the plantation area of palm oil has increased nearly to 5.0 million hectares in year 2011. As shown in Figure 1.2, the planted area of palm oil has increased in a rapid pace, from 0.5 million hectares in year 1975 to 4.7 million hectares in year 2010. It was forecasted that the demand of palm oil will continuously increase in years to come as if the demand of world total oils and fats increased (Sumathi et al., 2008). However, large of amount palm oil mill effluent (POME) is generated during the production of crude palm oil. POME contains high organic carbon content by possessing high value of biochemical oxygen demand (BOD), which makes it commonly to be converted and used as a fertilizer (Sumathi et al., 2008). Besides, due to the carbon rich features of POME, it was being converted into BC through thermal decomposition at 400 °C and used as a potential filler to accommodate HDPE to form HDPE/BC composites in this research.

Table 1.1: Oil Production Analysis of Different Oil Crops (Sumathi et al., 2008)

Oil crop	Production (million tons)	% total production	Average oil yield (tons/ha/year)	Total area (million ha)	% Area
Oil palm	36.90	35.90	3.74	9.86	4.50
Soybean	35.19	34.24	0.38	92.63	42.27
Rapeseed	18.34	17.84	0.67	27.29	12.45
Sunflower	11.09	10.79	0.48	22.95	10.47

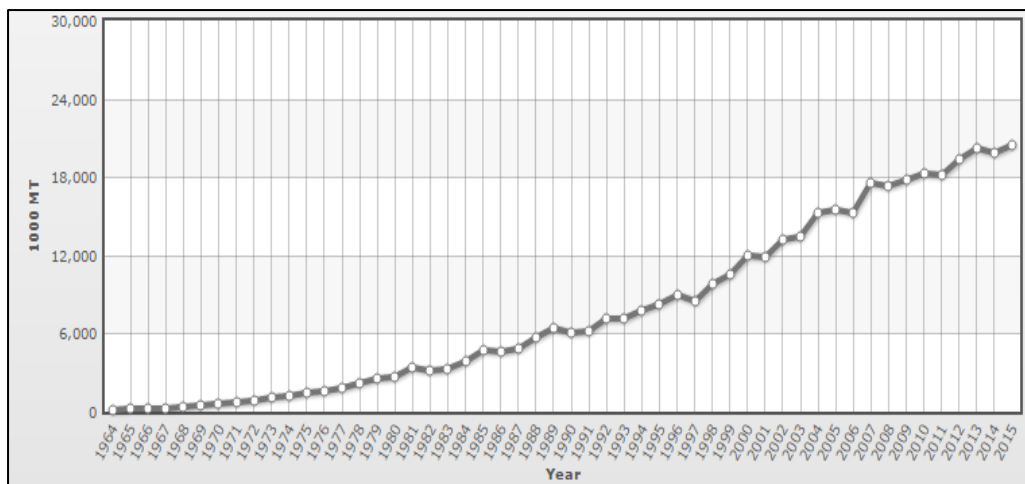


Figure 1.1: Malaysia Palm Oil Production by Year (Indexmundi, 2016)

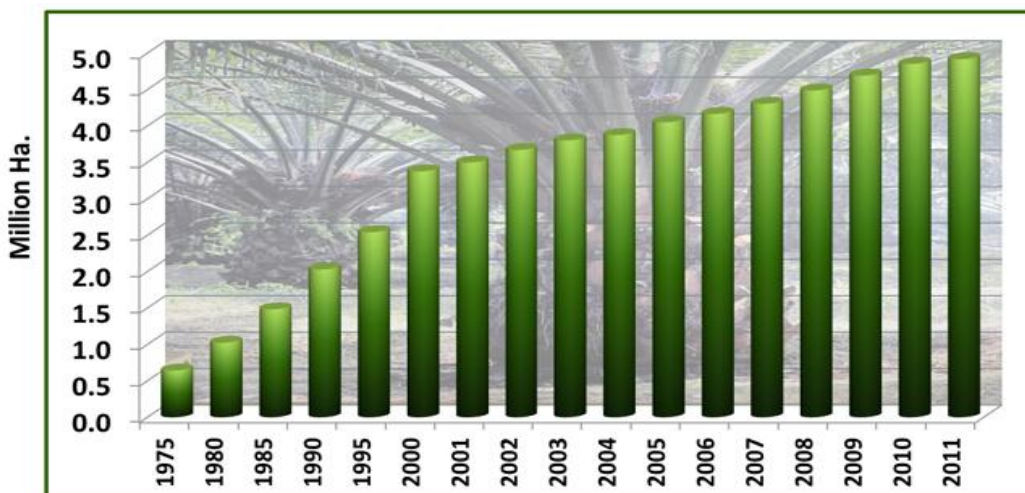


Figure 1.2: Planted Area of Palm Oil in Malaysia (Palmoilworld, 2016)

In this research, BC derived from palm oil mill effluent (POME) was used as potential filler in HDPE to form HDPE/BC composites. POME was first undergoing pyrolysis in a carbonization unit at 400 °C for 117 min of holding time and mixed with HDPE resins to produce HDPE/BC composites. In addition, HDPE and BC were mixed and blended at different BC loading: unfilled HDPE, HDPE/1.0 BC, HDPE/2.5 BC, HDPE/5.0 BC and HDPE/10 BC. Furthermore, a series of characterizations such as particle size analysis (PSA), fourier transform infrared

spectroscopy (FTIR), thermogravimetric analysis (TGA), scanning electron microscopy (SEM) were conducted on BC produced, whereas FTIR, density test, differential scanning calorimetry (DSC), SEM, water uptake and toluene swelling test, tensile test and TGA were conducted on HDPE/BC composites produced. The main purposes for this research are to study the potential of BC as filler in HDPE polymer and the effect of BC loading on the properties of HDPE/BC composites. Besides, addition of BC was expected to improve the thermal stability, toluene swelling resistance, tensile strength and tensile modulus of material of HDPE/BC composite.

1.2 Problem Statements

1.2.1 Environmental Problems Caused by POME

Oil palm plantation area in Malaysia has grown in rapid pace from about 3.38 million hectares in the year of 2000 and is forecasted to increase to 5.10 million hectares by the year 2020 (Jalani et al., 2002). Palm oil mill effluent (POME), which is resulted from the waste of palm oil mill industry, is normally discharged into nearby rivers or land after oil palm fruit processing. Consequently, the discharged of huge amount of POME has resulted pollution problems and brought significant impact to the environment due to its high chemical oxygen demand (COD) as well as high concentration of biochemical oxygen demand (BOD) (David et al., 2014).

As the awareness of environmental issues caused by POME increased, the involvement on managing POME has been changed from disposal of POME to full utilization and gain of beneficial from POME and its by-product. Therefore, recovering of palm oil sludge, the suspended or dissolved solids in POME, is one of the utilization methods to turn POME into valuable bio-resources (Madaki and Seng, 2013). Palm oil sludge can be converted into useful material such as biochar, through pyrolysis technique (Thangalazhy et al., 2015).

1.2.2 Insufficient Recovering and Recycling of Plastics

Gourmelon (2015) reported that the global plastic consumption is continually raised while plastic recycling lags. The insufficient recovering and recycling of plastics caused most of the plastic wastes ended up being landfilled and the original resources of plastics are wasted (Punčochář et al., 2012). To overcome the non-biodegradable problem for most of the conventionally used thermoplastics such as polyethylene (PE), polypropylene (PP) and polyvinyl chloride (PVC), manufacturing of polymers that can biodegrade such as bio-plastics has been developed (Tokiwa et al., 2009).

Environmental issues such as emission of greenhouse gases arise which resulted from the increasing plastic consumption can be conquered with the addition of BC as filler in polymer to produce bio-plastics (Das et al., 2015). Utilization of organic wastes derived BC in polymers helps to prevent environmental catastrophe as BC is able to sequester carbon back to its original plant source (Biochar-international.org, 2015). Besides making green environment, BC is also able to optimize the usage of organic wastes at minimum cost due to the abundance of biomass waste in oil palm plantation (Kong et al., 2014). This makes BC as an accessible feedstock in comparison with nearly depleted fossil fuels to produce polymer composites that can biodegrade. Lastly, BC filled polymer is a promising solution to the plastic disposal issues as it alters the biodegradability of polymers (Tokiwa et al., 2009) and can be disposed into landfilling without potentially endangering the ecosystem.

1.2.3 High Cost and Incompatibility of Commercial Fillers in Polymers

Carbon black, silica, calcium carbonate and various clay minerals such as talc, kaolin and china clay are used extensively in polymers (Dyson, 1990). However, there are few limitations that caused these commercial fillers to be incompatible to be used in polymers.

- i) Silica and clay are one of the commonly used filler in polymers. However, due to its hydrophilic properties, it is incompatible in hydrophobic polymer such as thermoplastic olefins as it will result in low mechanical properties. Therefore, coupling agents, compatibilizers and chemical surface treatment are needed to improve silica and clay filled polymers and undesirably increases the processing cost (Mittal, 2011).
- ii) Even though carbon black is able to enhance the mechanical properties of polymers, however, it is costly and expensive as it is sourced from petroleum feedstock. Besides, carbon black is naturally dark in colour, as a consequence, the product made up from carbon black polymers cannot be tailored or changed colour (Katz and Milewski, 1987).
- iii) Calcium carbonate is one of the popular non-reinforcing fillers used in polymers. However, calcium carbon increases the modulus but reduces the properties due to its large particle size which will cause agglomeration problems during moulding (Meyer, 1987).

Thus, solutions are found to replace the commercial fillers with alternative fillers from natural resources which are abundant, low in cost, easily processed, environmentally friendly and can substitute commercial fillers without reducing or deteriorating the properties of polymer (Vroman and Tighzert, 2009). In this research, BC was used as filler to prepare HDPE/BC composites. BC used is derived from palm oil sludge which is abundantly available in all palm oil mill, simple processing and low in cost as it is processing from waste. Besides, BC is potentially to improve the mechanical and thermal properties due to high porosity BC particles. Furthermore, high carbon content of BC also able to act as similar to carbon black, whereas smaller particle size of BC particles compared to other types of filler material may also potentially increase properties significantly with very low loading, which can help in colour tailoring of the final product.

1.3 Project Objectives

The ultimate goal of this project is to produce, characterize and study the potential of BC as filler in HDPE polymer. The other objectives on this study are:

1. To produce biochar through carbonization process of palm oil mill effluent (POME).
2. To characterize the physiochemical properties of biochar.
3. To prepare biochar filled HDPE composites and study the effect of biochar loading on the processing and properties of HDPE/BC composite.

CHAPTER 2

LITERATURE REVIEW

2.1 Plastic Recycling

Plastics are synthetic or semi-synthetic materials manufactured from long-chain polymers, which are derived from oil and natural gas. Plastic production on 1950 was 1.7 million tons; it is increased averagely at a rate of 8.7 percent per year until the production of plastic reaches 300 million tons of years 2012 (Plastics Europe, 2013), which can be seen in Figure 2.1. China is the largest plastic production country with 24 % by weight of plastic has been solely produced; other countries in Asia has 40 % plastic by weight of world production of plastic; whereas Europe and North America have 20 % weight of world plastic production (Velis, 2014).

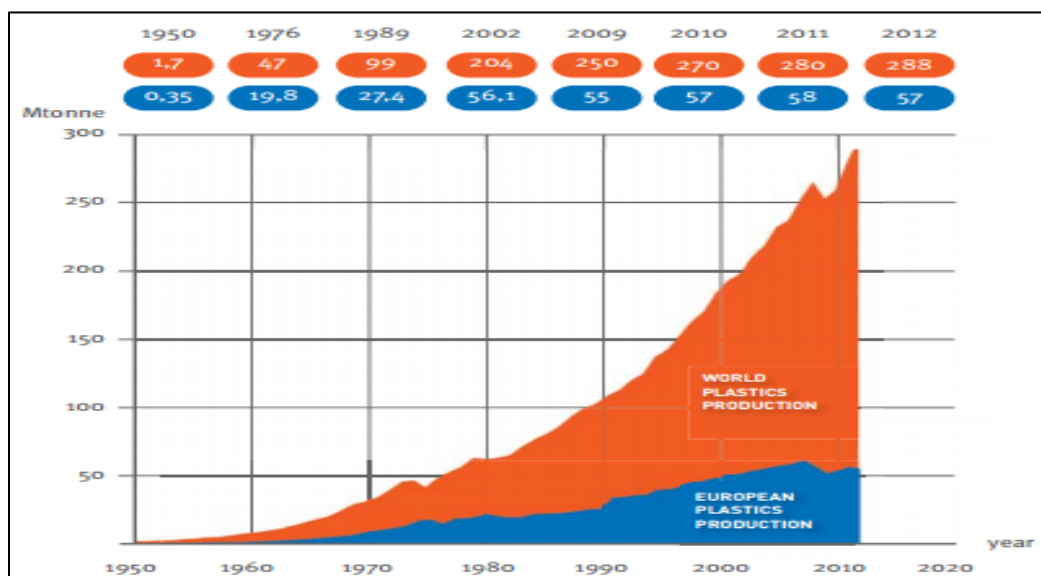


Figure 2.1: World Plastic Production (Plastics Europe, 2013)

As illustrated in Figure 2.2, there are approximately about 40 % of plastics are being used in short-lifespan applications which is also known as the single-use disposal plastic such as food packaging and films in agricultural. On the other hand, around 20 - 25 % of plastics are used for long-term infrastructures such as cable insulation, piping system and structural materials, whereas the remainder plastics are used for durable plastic applications due to its intermediate lifespan such as electronic goods, vehicles and furniture (Hopewell et al., 2009).

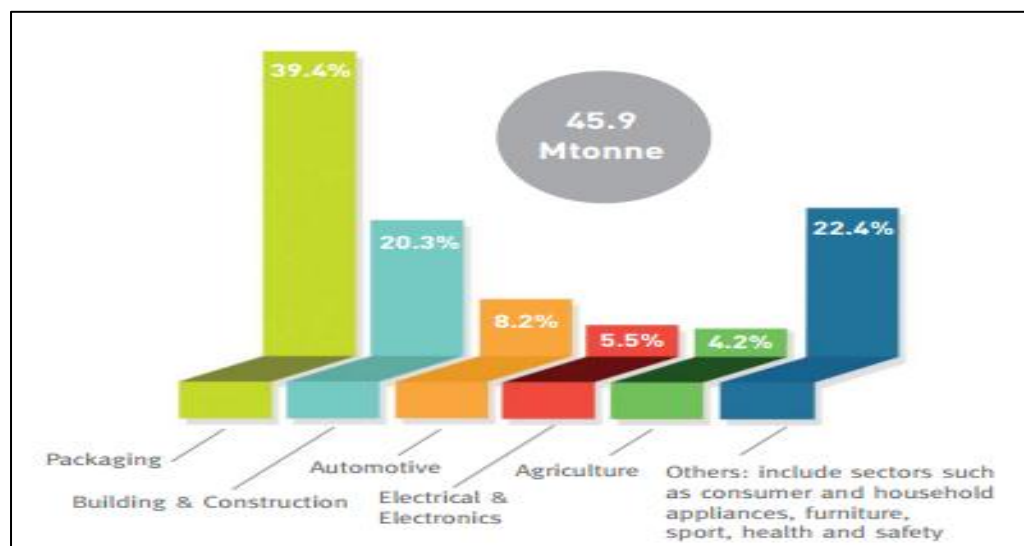


Figure 2.2: Consumption of Plastic by Segment (Plastics Europe, 2013)

The large quantities of plastic consumption bring significant impacts to the environment as the recovery and recycling of plastics remain insufficient and inefficient because of the disposal by landfilling of the most plastic materials (Gourmelon, 2015). In consequence, more lands are wasted for landfill and plastic's valuable resources are gone into vain as well. Therefore, recycling of plastic would be very important not only because it reduces the problem of plastic incineration and landfilling but also converts the waste plastics into useful products as well as to minimize the waste (Ecologycenter.org, 2015).

2.2 High Density Polyethylene (HDPE)

2.2.1 HDPE Structure

Polyethylene, the popular thermoplastic produced from polymerization of ethylene monomers, is commonly used in producing consumer products. High density polyethylene (HDPE), is also known as linear polyethylene, it has a linear polymer structure which is produced from ethylene monomers through Ziegler-Natta catalytic reaction. Furthermore, the joining of carbon and hydrogen atoms is linear in HDPE structures which result in high molecular weight thermoplastic materials. In addition, HDPE is a long chain ethylene polymer lined up regularly to form semi-crystalline structure with low degree of branching (Bbc.co.uk, 2014). Degree of branching determines the crystalline proportions in HDPE structure, which may affect the density and strength of HDPE (Lester, 2015). The low degree of branching causes the HDPE polymer chains to be packed closely and tightly, resulting in a high density polymer with high crystalline structure which also gives high strength and moderate stiffness to the thermoplastic (Encyclopedia Britannica, 2015).

Figure 2.3 illustrates the difference between the chemical structure of HDPE and LDPE. As illustrated in Figure 2.3, LDPE is a long polyethylene chain with a high degree of branching, whereas HDPE has a low degree of branching. Therefore, the intermolecular forces between HDPE molecules are stronger as compared to LDPE. Thus, HDPE possesses better mechanical and higher tensile strength as compared to LDPE (Plasticmoulding.ca, 2015).

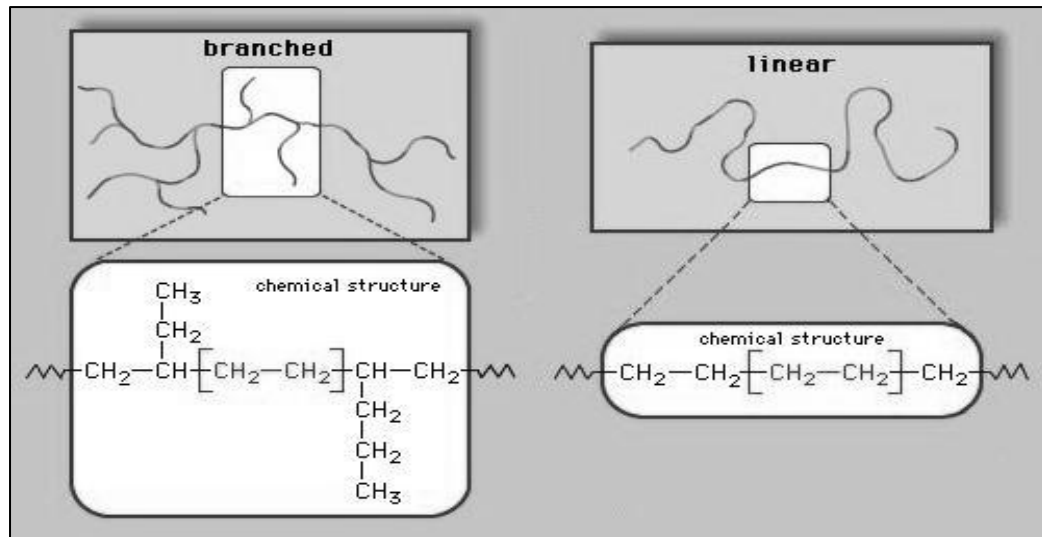


Figure 2.3: Chemical Structure of LDPE and HDPE (Encyclopedia Britannica, 2015)

2.2.2 Properties and Applications of HDPE

HDPE is comparatively denser than other derivatives of polyethylene with a specific gravity of 0.95. Furthermore, HDPE has good mechanical strength with relatively hard and high impact properties. Besides, HDPE are chemically inert and has a very high resistance to chemicals and corrosion. In addition, HDPE is able to withstand high temperature up to 120 °C without properties being affected (Thomas, 2013). The melting point of HDPE is defined when the crystalline structure completely transformed into amorphous state. When HDPE is being stretched, the internal arrangement structure of HDPE will elongate and the molecular chains will start to slip over one another. In consequences, deformation in structure may result on fracture and the stiffness of HDPE will be reduced when ultimate tensile strength of HDPE is reached (Lester, 2015).

The inherent properties of HDPE raised the market demand and consumption as compared to other polyethylene derived thermoplastics. The durability of HDPE contributes to its widely use in blow and injection moulding applications in polymer industry (Icis, 2010). In blow moulding application, HDPE resins are being melted

and emerged to the mould as hollow under high pressure to manufacture plastic films, bottles, containers, automotive fuel tanks and watering cans (British Plastics Federation, 2015). Apart from that, injection moulding process of HDPE is able to manufacture various types of plastic applications such as bottle caps, toys, packaging containers and household goods. On the other hand, extrusion process of HDPE are used to produce products such as insulator and long profile HDPE pipes, which is commonly applicant for water, natural gas and drainage system in the world (Icis, 2010).

2.2.3 Recycling of HDPE

As the demand of plastics increase globally, the plastics manufacturing rate is up to 100 million tons annually. However, due to most of the ubiquitous and versatile plastics are non-biodegradable, therefore, recycling of plastics is introduced globally to reduce the waste and plastic resources. Plastics have become one of the toughest to collect and recycle materials in the world, where polyethylene terephthalate (PET) and HDPE are the most dominant recyclable plastic in the market. Yet, there is only 31 % of PET and 28 % of HDPE being recycled in the past few years (Szaky, 2015). Thus, it is important to make plastics to be economically and environmentally sustainable to conserve the resources and reduce the plastics waste by recycling and recovering the waste to other useful products (American Chemistry Council, 2015).

Recycled HDPE is firstly to be sorted according to their densities and cleaned to remove dirt and ducts on unwanted plastics. Near Infrared Radiation (NIR), is one of the popular technologies to sort out HDPE from other types of plastic by irradiating infrared radiation to the rigid plastic, the detector will base on the electromagnetic energy passes through it to determine the spectrum of plastic to achieve sorting purposes. However, NIR sorting technique is not applicable in dark colour because dark coloured product plastic is unable to absorb the infrared waves irradiated by the camera (Maris et al., 2012). After sorting, recycled HDPE will be shredded into small pieces and further reprocessed into pellets after melting of shredded pieces (Thomas, 2013).

Commonly, recycled HDPE is used in manufacturing of non-food application bottles, plastic piping, flower cans and trash cans (Heathland, 2009). Due to the nature attributes of HDPE, recycled HDPE materials have wide range of applications in industry. The strong wear resistance and ability to withstand moisture attack properties of HDPE allow it to be used in marine manufacture such as boat seating, decking and hull construction. In addition, recycled HDPE can also be used as partition for bathroom, signage and recreation construction such as playhouse structures (Metemplastics, 2015).

Apart from being recycled, HDPE waste is being converted into useful energy resources through recovering the potential energy generated from waste incineration process and landfilling. The released landfill gas contributes to around 2 % of greenhouse gas emissions annually in the global. The major emitted landfill gas from landfilling is methane gas, which is the second most prevalent greenhouse gas. The energy recovery process is completed by using sophisticated system in landfilling sites to collect the released methane gases. The collected methane gas is later being treated and used as fuel sources or converted into carbon dioxide gas, which is released to the atmosphere (Klinghoffer and Castaldi, 2013). Recovering energy from waste HDPE is not only able to conserve the resource, it also protect human health by reducing the emission of greenhouse gases to the environment.

2.3 Biochar

2.3.1 Biochar Production Methods

Biochar (BC), a carbon enriched charcoal which produced from thermochemical decomposition of biomass (Biochar-international.org, 2013). Woodchips, animal manure and crop residues are the examples of biomass which can be convert into BC (Tang et al., 2013). BC is normally being produced through thermochemical conversion of biomass, the most popular and convenient method to convert biomass as a potential renewable energy source (Thangalazhy et al., 2015). Thermochemical conversion of biomass includes the process of combustion, gasification, liquefaction

and carbonization of biomass to decompose it into three different solid, liquid and gaseous fractions product (Özçimen and Karaosmanoğlu, 2004).

Pyrolysis is the most common thermal conversion process to produce BC from biomass. It involves heating of biomass under oxygen-limiting conditions to produce bio-oil, char and non-condensable gases (Ronsse, 2013). Thermal decomposition of the polymeric constituents in biomass starts when the combustion temperature reaches around 350 - 550 °C. The rate of decomposition of biomass for the distributions and yield of BC is depending on the process parameters: heating rate, heating temperature, pressure and types of feedstock (Jahirul et al., 2012). For instance, fast pyrolysis with high heating rates will maximize the production of liquid bio-oil due to the low vapour residence time during combustion of biomass (Ronsse, 2013). On the other hand, in slow pyrolysis, vapours have higher residence time to react with the solid phase and produce more BC compared to fast pyrolysis. To summarize, the content of carbon percentage in BC is increased with the temperature and heating rate of pyrolysis (Mohan et al., 2014). The parameters used in this research was modified from the research of Sukiran (2011), where POME was pyrolysis at 400 °C with 27 °C/min heating rate and 117 min retention time without the presence of oxygen in order to maximize the carbon content of BC produced.

Liquefaction is another method of producing BC from biomass. Thermochemical liquefaction is a low temperature and high pressure process to produce BC and bio-oil from biomass with solvent such as methanol and ethanol participation. Temperature uses in liquefaction is ranging from 260 - 350 °C with pressure of 5 - 20 MPa. BC acts as a by-product in biomass liquefaction process, whereas bio-oil is the main products from the yield. However, BC produced from liquefaction process contains high contents of oxygen functional groups in its constituents. Therefore, in comparatively, pyrolysis gives higher BC yield than liquefaction process, but liquefaction BC has better performance than pyrolysis process due to the high content of oxygen-containing functional groups in BC constituents (Leng et al., 2015).

2.3.2 Properties and Applications of Biochar

Biochar is a char particles enriched with carbon and has high porosity with large specific internal surface area in its structure. The large internal surface area allows BC to have better retention power in storing water and nutrients (Tang et al., 2013). Besides, the physical properties of BC are depending on the original biomass used and also the BC conversion process through carbonization or pyrolysis system (Lehmann and Joseph, 2009).

BC is categorized into three categories based on the carbon content in it: Class 1 BC, more than 60 % of carbon content; Class 2 BC, carbon content ranges from 30 - 60 %; Class 3 BC, carbon content ranges from 10 - 30 %. Carbon content in BC may vary depends on the process conditions of residence time and pyrolysis heating rate (Mohan et al., 2014). According to Sukiran (2011), BC produced from empty fruit bunches at 400 °C with 30 min/°C heating is belong to class 1 BC as the content of carbon was 65 %. Thus, it is envisaged that BC produced in this research is belong to class 1 BC. In addition, process conditions also alter the structural arrangement of BC produced. This includes the pre- and post-handling of BC, temperature, material used and heating rate during the conversion process. For instance, BC produced from high pyrolysis temperature has larger surface area and provides better adsorption ability than those produced from low pyrolysis temperature (Tang et al., 2013). Furthermore, the mechanical strength possessed by BC is determined through its density, whereas the density of BC is determined by its degree of porosity. As illustrated in Figure 2.4, BC has highly porous structure with large internal surface area within it.

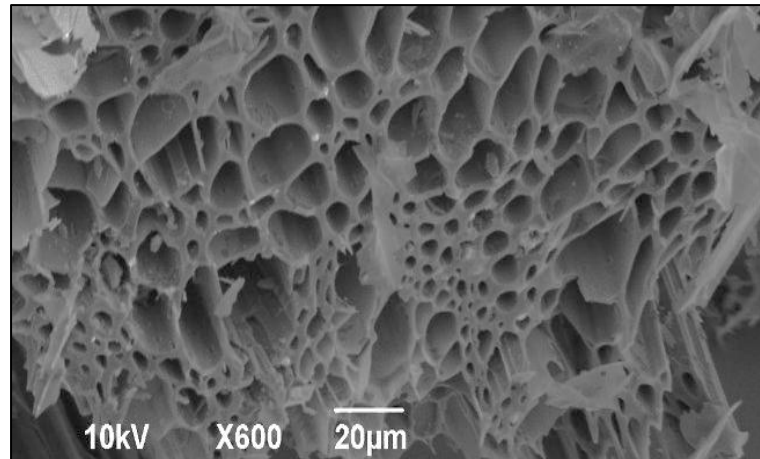


Figure 2.4: Internal Surface and Porosity of BC (Australian Sustainable Business - The Switch Report, 2015)

The advantageous properties of BC make it popular to be used in soil amendment applications as the high specific surface area of BC improves its moisture and nitrogen retention in soil (Tang et al., 2013). Due to its adsorption and retention capability, BC is widely used in agriculture as soil amendment for nutrient supplements or fertilizers. It is reported that the yield has significantly increased with the application of BC as soil amendment in agriculture due to the capability of BC in improving nutrient uptake of plants with its large internal surface area (Schmidt et al., 2014).

Apart from that, BC is also widely used as an adsorbent in water remediation. The sorption capacities of BC make it useful in removing organic and inorganic contaminants from water by using biological methods. Chemical precipitation, the most commonly used method to remove contaminants from water, uses hydroxide, sulphides, carbonate, and phosphate in the water treatment process. However, the drawback of chemical precipitation is the disposal problems of sludge produced from the precipitation. Therefore, removing contaminants in water with biological methods has been introduced by using selective adsorption with biological materials such as mineral oxides and activated carbon for water treatment (Schmidt, 2012).

Activated carbon is expensive due to its high processing cost, which have raised the market attention and demand of BC in water remediation. BC is a more sustainable and low cost derivatives of carbon possessing high adsorption towards hydrocarbons, organic and inorganic ions. BC can be easily produced through carbonization process by using agricultural waste materials, fibers from plants and also waste from oil palm processing. The large internal surface area and capacity to exchange cation makes BC adsorb and bind effectively with inorganics components and ammonium (Schmidt, 2012). The use of BC as adsorbent is not only for removing contaminants from water; it also adsorbs nutrients within it and can be subsequently used as soil amendment in agriculture to fertilize plants (Mohan et al., 2014).

2.3.3 Applications of Biochar in Polymer

Apart from being soil amendment and adsorbent, BC also acts as potential filler in polymer composite preparation which capable of enhancing the physical and mechanical properties of BC filled polymer composites (Biocharnow.com, 2015). Demand of fossil fuels increases with the growth of population, and causes the depletion of the non-renewable resources in the world. Thereby, the aid of BC as filler in polymer is not only able to improve composites' performance in sustainable way; but also reduces the dependence on using oil-based consumption in making polymer to conserve the environment (Biocharnow.com, 2015). Polymer has either crystalline or amorphous or semi-crystalline structure, which causes the mechanical strength of polymers to be varied from each other. Therefore, the introduction of fillers into polymer as reinforcing agent may imparts many benefits through improving both mechanical and chemical strength and also dimensional stability of the neat polymer (Shenoy, 1999). While optimizing the function of polymer, the aids of fillers in polymer also help to minimize the cost of the product and to improve the processability of the composite material.

Wood polymer biochar composites, is an example of BC filled polymer composite development in recent year. Wood polymer biochar composites are widely used in manufacturing furniture or act as construction material for building

and automotive mobile (Ashori, 2008). The high internal surface area, high carbon content and hydrophobic properties of plant/woody biomass converted BC makes it potential filler in wood and polymer composites, by lowering the moisture absorption of wood polymer biochar composites. Furthermore, BC is co-injected into wood and polymer composites due to the high thermal degradation temperature of more than 200 °C which makes it more thermally stable than commercially used wood (Das et al., 2015).

The processing of wood polymer composites with BC filler involve the compounding process at slightly higher melting temperature of polymer and moulding the mixture under high pressure and temperature into desire products. Composite wood solely into polymer gives high impartment force for the product while it only requires low cost of production. The tendency of wood to attract water is the largest drawback because it causes swelling in the thickness and dimensional stability of wood polymer composite decreases due to the poor wood fiber dispersion in the matrix (Ashori, 2008). This diminished the outdoor usage of wood polymer composite. Therefore, coupling agent is introducing to bind the wood fiber in the polymer for the mechanical strength enhancement purposes. However, this increase the production cost of wood polymer composite which is undesirable (Das et al., 2015).

Biochar are desired more as filler material in producing polymer composite due to its advantageous properties: low in cost, easy to obtain and able to reduce the dependence on using fossil fuels as resources (Biocharnow.com, 2015). Ahmetli et al. (2013) has reported that the char particles derived from plastic waste, wood shavings and pine cone connected well in the matrix of epoxy/char composites. According to Ahmetli et al. (2013), the epoxy/char composites displayed uniform BC distribution on the fracture surface under scanning electron microscopy (SEM); however, the high brittleness of BC reduce the percentage elongation and increase the surface coarseness of composites. The image of fracture surface of plastic waste derived char filled epoxy composite is shown in Figure 2.5. Besides, the epoxy composites filled with char filler derived from different sources (plastic waste, wood shavings and pine cone) was not only led to the improvement in mechanical and thermal

properties, but also decreased the moisture diffusivity of epoxy/char composites (Ahmetli et al., 2013).

In addition, the organized distribution of BC aligned well to each other and also with the epoxy matrix in the epoxy/char composites in the research conducted by Ahmetli et al. (2013). With the good reinforcing force due to good alignment between char filler and epoxy matrix, the composite formed has high impact strength and resilient force. It was studied that the tensile strength, Young's modulus and thermal properties improves with the increasing percentage of BC up to 15 wt% used as filler in composite. However, the elongation percentage and tensile strength of composite reduces when the filler reached the optimum and critical filler level in compounding process (Ahmetli et al., 2013).

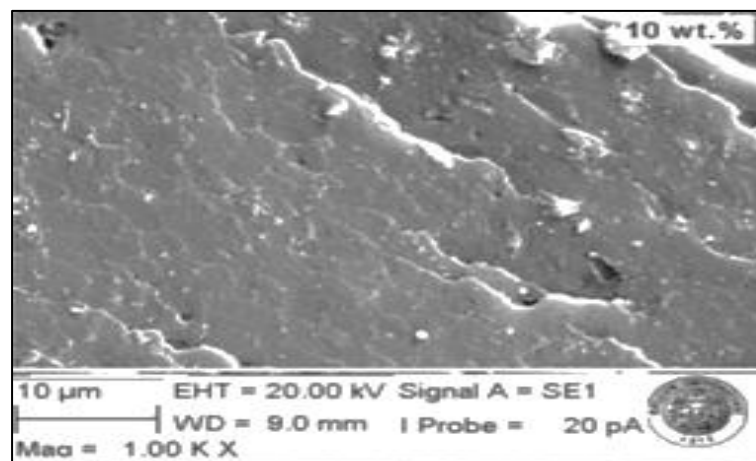


Figure 2.5: SEM Image of Fracture Surface of Epoxy Resins/ Plastic Waste Char Composite (Ahmetli et al., 2013)

Apart from that, Ho et al. (2015) has reported that the mechanical properties of polylactic acid reinforced with bamboo charcoal derived from bamboo plants increased with the content of bamboo charcoal up to 7.5 wt%. Besides, it was found that the polylactic acid/bamboo char composites possessed low decomposition rate and excellent absorption capacity compared to pure polylactic acid, which made the composite suitable to be used in food storage applications (Ho et al., 2015). In addition, it was also reported that the bamboo char filler has neat and good

dispersion in polylactic acid matrix, which is similar to Ahmetli et al. (2013)'s finding, where the char derived from plastic waste, wood shavings and pine cone distributed uniformly in the epoxy's matrix. Thus, the addition of bamboo charcoal in polylactic acid were found to improve the mechanical, thermal and optical properties of polylactic acid/bamboo char composite as the tensile strength, flexural and ductility increased when the bamboo char loading was increased to 7.5 wt% (Ho et al., 2015).

Furthermore, the development of polyvinyl alcohol/BC composite was conducted by Nan et al. (2015) with the mixed hardwood derived BC. It was reported that the addition of hardwood char into polyvinyl alcohol showed similar electrical conductivity with carbon nanotubes and graphene filled polyvinyl alcohol composites. Besides, it was also reported that the polyvinyl alcohol/BC composites possessed high thermal stability as the decomposition and degradation temperature of polyvinyl alcohol/BC composites were relatively high but the mechanical strength of composite were reduced. In addition, polyvinyl alcohol/BC composite has higher electrical conductivity than carbon nanotubes and graphene filled polyvinyl alcohol composites. Apart from that, Nan et al. (2015) also reported that BC was distributed homogenously throughout the polyvinyl alcohol matrix at 2 wt% and 6 wt% BC loading. Thus, the author has concluded that BC can be alternative filler that used to replace high cost carbon nanotubes and limited performance graphene filler in manufacturing electrical utilization such as electrical type sensors.

2.4 Thermoplastic

2.4.1 Introduction to Thermoplastic

Thermoplastic is made up from intermolecular linked polymers with Van der Waals forces above transition temperature to form polymer with linear or branching structure on its backbone. The properties of thermoplastic are depending on the molecular arrangements and the degree of interaction between molecules in the polymer chains. Therefore, thermoplastic is classified into two categories based on

the crystallinity concentration is its structure, which can be divided into amorphous and crystalline structure (Adhesiveandglue.com, 2015). In addition, thermoplastic is able to be melted and reformed into various shape upon cooling from the viscous phase; unlike thermoset, which is which is hard and irreversibly heating polymer (OpenLearn, 2011). As illustrated in Figure 2.6, molecules linked to one another to form long polymer chain without cross-linkage in between.



Figure 2.6: Linkage of Polymer in Thermoplastic (Adhesiveandglue.com, 2015)

Generally, polymers dominant with amorphous in structure are hard, brittle and stiff at high temperature. The random arrangement of polymer chains can indirectly affects the elasticity of thermoplastic materials (Adhesiveandglue.com, 2015). Besides, amorphous polymer is also termed as ‘glassy’ when it is below the glass transition temperature with disordered polymer chains arrangement. On the other hand, when amorphous polymers are above the glass-transition temperature but below the melting temperature, it becomes rubbery and possesses good elongation properties with low loading. This causes most of the amorphous polymers are used below the transition temperature.

When amorphous polymers are heated above the melting temperature, it becomes viscous in behaviour; however, the viscosity decreases with the increasing temperature and rate of strain and gives visco-elastic behaviour (Furness, 2014). Due to the random polymer chains arrangement, amorphous thermoplastics exhibit poor fatigue and wear resistance. Besides, the random polymer chain structure causes chemicals to penetrate in the structure, thereby; it has poor chemical resistance

properties. Polyvinyl chloride, polystyrene and polycarbonate are the examples of amorphous thermoplastics (Psgtech.edu, 2015).

Apart from that, thermoplastic materials with high crystallinity ranging from 20 - 90% are known as semi-crystalline polymers (Xanthos, 2010). Unlike amorphous structure, semi-crystalline is compact and has better polymer chain alignment in its structure and it is normally processed above the melting temperature. The well aligned polymer chains in the crystalline region help in improving the strength of thermoplastic, enable it to withstand high mechanical loading (Furness, 2014). Semi-crystalline thermoplastic is opaque with good fatigue toughness and wear resistance. However, semi-crystalline polymer has low elasticity compared to amorphous polymer due to the crystalline region in its structure. Examples of semi-crystalline thermoplastics are PE, PP and polyamide (PA) (Psgtech.edu, 2015).

Figure 2.7 illustrates the amorphous and semi-crystalline structure of thermoplastic. As illustrated in figure, amorphous thermoplastic has random polymer chains arrangement which provides loosen polymer structure whereas semi-crystalline structure has well-aligned polymer chains which is compact and tightly packed structure compared to amorphous thermoplastics.

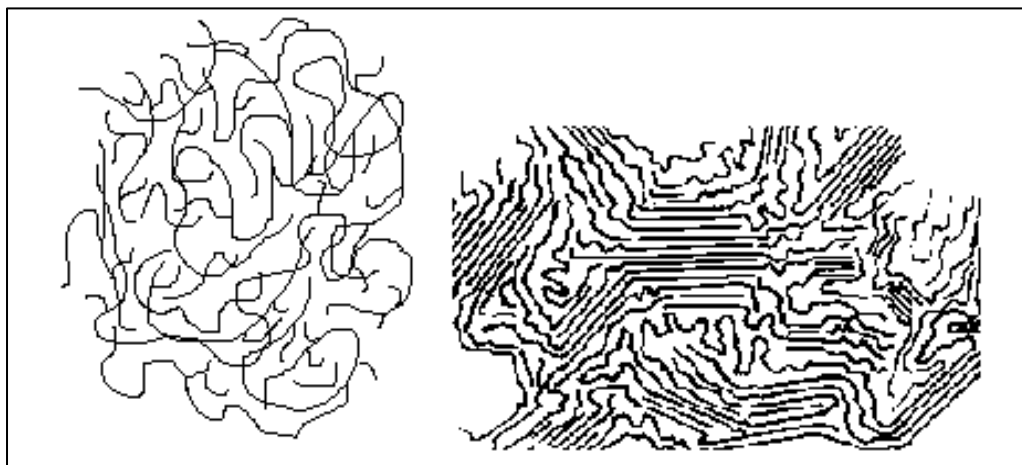


Figure 2.7: The Amorphous and Semi-Crystalline Structure in Thermoplastic (Polymerexpert.biz, 2015)

Extrusion and injection moulding are the most widely used method for processing thermoplastic into useful applications. In extrusion process, the thermoplastic resins are being melted and extruded in a barrel with uniform cross-sectional area through a die to form a long profile thermoplastic product. Whereas in injection moulding, thermoplastics resins are firstly to be melted and flow under pressure to fill in the mould through die to form desired shape at the end of the chamber. When the mould filled with hot melted thermoplastic is hydraulically cooled, the thermoplastics product will be ejected from the mould and further process to the final product (Vichem, 2015).

2.4.2 Filler in Thermoplastic

Filler is the inorganic or organic materials that are added into polymer not only to strengthen the composite, but also to reduce the product cost. Non-reinforcing filler acts as extenders that improve the viscoelasticity of composite but does not exhibit reinforcing effect on the composite. Calcium carbonate and clay are the examples of non-reinforcing fillers which help to impart composite's colour as well as to increase the viscosity of composite. On the other hand, reinforcing filler improves the performance of composites by increasing the fracture resistance and stiffness of composite. The most commonly used reinforcing fillers are carbon black and silica, which enhances the mechanical properties of composites by improving the matrix of polymer composites (Visakh et al., 2013).

In addition, organic filler are materials that contain cellulose, lignins, proteins and synthetics; whereas inorganic fillers are materials that contain carbonates, oxides, silicates, sulphates and carbon (Shenoy, 1999). Calcium carbonate and aluminium trihydrate are the examples of inorganic fillers which are commonly used in industry due to their ability in enhancing composites' strength, abundant and cheap properties. On the other hand, the low specific gravity and with lignins and cellulose shell flour, wood flour and char are the examples of organic fillers used in polymer (Carragher and Sperling, 1983).

Generally, fillers are acted as additives to moderately increase the polymer modulus and improve mechanical properties of polymer. Besides, filler is an inert material that dispersed physically in the polymer matrix without affecting the molecular structure of composites. The major advantageous of filler is it lowers the cost of materials required by reducing the usage of polymer while giving better polymer modulus. In addition, the properties of polymer can be altered by the types of filler used (Xanthos, 2010).

Apart from lowering the cost, fillers also reduce strain and increase stiffness of composites when it pinches to the polymer matrix. The effectiveness of filler in reinforcing polymer is characterized by the aspect ratio of fillers. High surface area ratio of filler to its volume will enhance the reinforcement effectiveness of fillers in composite. Moreover, the interfacial bond between fillers and polymer in the interfacial region is the key of improving mechanical strength in the composites. The strong adhesion by Van der Waals force between fillers and polymer causes the formation of strong chemical bond within the composite. Consequently, it reinforces the interaction forces between polymer and filler, thus, improves the reinforcing effects (Xanthos, 2010).

2.4.3 Common Fillers in Thermoplastic

Carbon black, silica, calcium carbonate (CaCO_3) and mineral clays such as china clay, talc and kaolin are among the common used fillers in polymer. The dark coloured filler, carbon black is commonly being compounded as reinforcing, colouring and opacifying agent in thermoplastics. The planal hexagonal nets of carbon atoms in carbon black makes it crystalline in nature and gives it chemically and physically strong properties which is suitable to be used as reinforcing agents in thermoplastics. Besides reinforce the mechanical properties of thermoplastic end products, carbon black is able to increase the thermal conductivity and stabilize against ultraviolet light or ultraviolet protection. However, the drawbacks of using carbon black fillers are unable to change the end product's colour and it is expensive in cost (Katz and Milewski, 1987).

The synthetic silica is one of the common used filler in thermoplastic. The amorphous silicon dioxide structure of SiO_2 causes it to be wide range of diameter particle sizes (Drobny, 2007). Due to large particles in size and may form aggregated structure between hydrogen bond and silanol groups surface, therefore, it is a well-known non-reinforcing filler and good coupling agent in thermoplastics (Thomas, 2012). The main function of SiO_2 filler in thermoplastics are to reduce the shrinkage and cracking in thermoplastic product, improve the dimensional stability of thermoplastic under heat and prevent film blocking in the thermoplastic matrix (Drobny, 2007). The applications of SiO_2 filled thermoplastics are to be used as thickening in paints and coatings, and also anti-block agent in packaging films (Thomas, 2012).

CaCO_3 is simple to reduce into a specific particle size to compatible with the polymer resins in compounding (Ktron, 2014). CaCO_3 is widely used as filler in the applications of PVC, PP and PE. The reasons for it to be popular among other fillers are mainly due to its abundant and low cost properties. Besides giving economy, CaCO_3 also exhibits mechanical modification properties in polymer (Xanthos, 2010). Furthermore, CaCO_3 has relatively high refractive index which provides good optical properties compared to other filler and this makes it suitable to be an opacifying pigments in polymer. In addition, CaCO_3 filler also helps in improving both impact strength and stiffness of polymer when the filler size is compatible to the resins in compounding (Ktron, 2014). However, CaCO_3 is soft with poor abrasion resistance and poor stability in acidic conditions due to its alkalinity (Ciullo, 1996).

Generally, the fine granulometry of fillers enables it to be well distributed in polymer matrix when it is introducing into polymeric material. As illustrated in Figure 2.8, CaCO_3 is presented in irregular shape with coarse granulometry. Therefore, this causes agglomeration of CaCO_3 particles in polymer matrix during compounding which can be seen in Figure 2.9. Moreover, Figure 2.10 illustrates the poor interaction of CaCO_3 fillers in polymeric matrix. The agglomeration of fillers in polymer matrix lead to poor interaction of filler with the polymer will reduce the strength and cause early deformation of polymeric products (Sant'Anna et al., 2008). As the CaCO_3 filler has low interaction and poor mechanical adhesion to the

polymer matrix, therefore, it needs to be sieved into defined particles size before using as fillers in polymer.

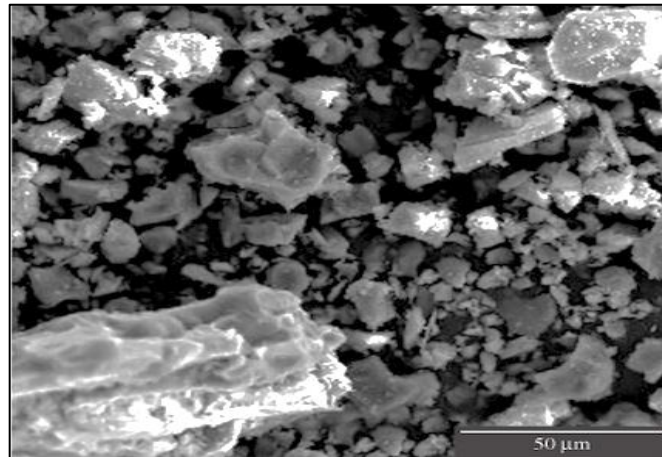


Figure 2.8: Structure of Commercial Calcium Carbonate under Microscopy
(Sant'Anna et al., 2008)

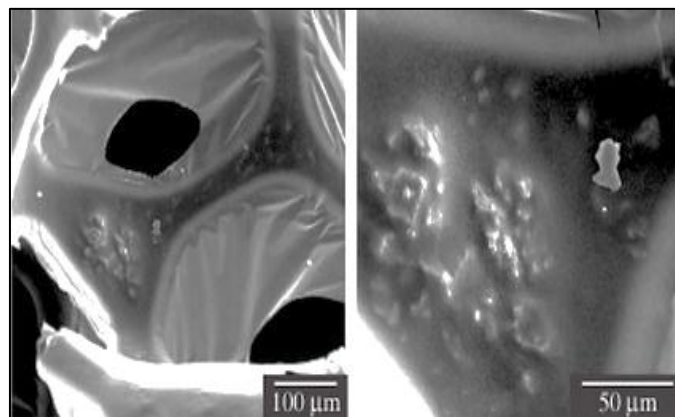


Figure 2.9: Polyurethane Foam Filled with Calcium Carbonate Filler
(Sant'Anna et al., 2008)

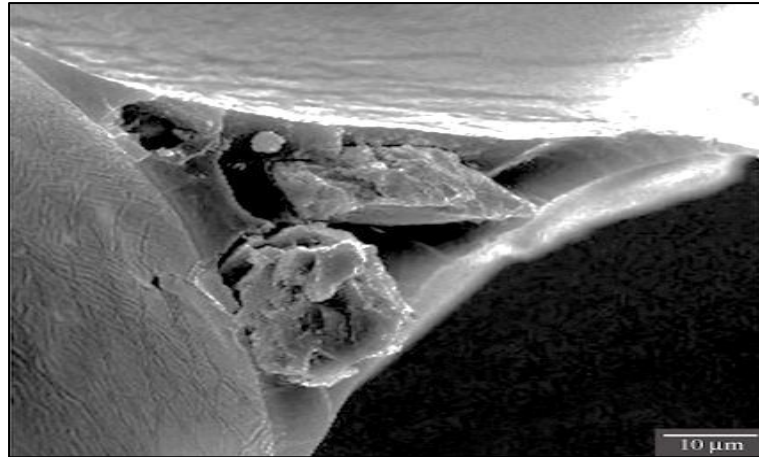


Figure 2.10: Interaction of Calcium Carbonate Filler in Polyurethane Foam Matrix (Sant'Anna et al., 2008)

2.4.4 Current Development of Thermoplastic

Thermoplastic starch has currently been developed due to its biodegradability. Starch is a low cost material produced from maize, wheat, rice and potato (Xie et al., 2014). Large scale of starch is transformed into polymeric state with entangled polysaccharide chains of amylose and amylopectin through structural degradation of starch at low temperature with sufficient quantity of plasticizer such as glycerol and water (Saiah et al., 2012).

Starch is made up from spherical or oval granules in different sizes with smooth surface, low volume of porosity and free from crack properties. The hydrogen bonding between starch molecules destruct during plasticization, while new hydrogen bonds between plasticizer and starch molecules are formed simultaneously (Saiah et al., 2012). Thereby, thermoplastic starch is produced as film through extrusion process. The semi-crystalline structure of extruded thermoplastic starch under microscopy is illustrated in Figure 2.11.

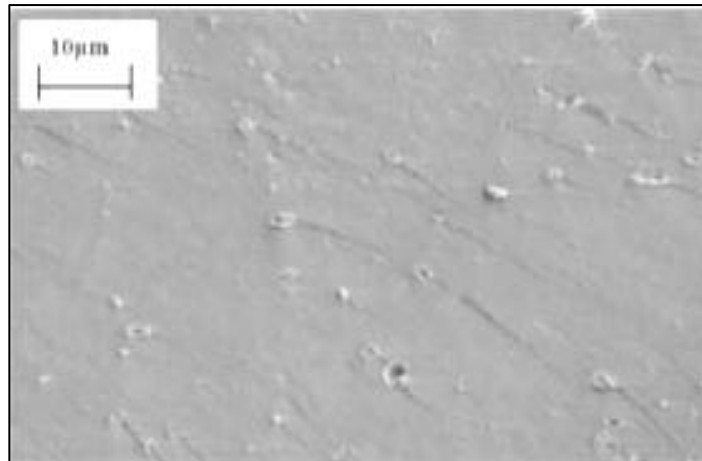


Figure 2.11: Scanning Electron Microscopy of Extruded Polyethylene Starch Film (Saiah, Gattin and Sreekumar, 2012)

The relatively good enhancement properties such as good barrier and thermal properties of having starch in thermoplastic has widen its application in market such as bags, flower arrangement accessories, packaging film, planting pots and tapes (Smith, 2005). Apart from biodegradable and low costing required characteristics, the reasons for starch to be used in thermoplastics are also due to its abundance and easily available properties. However, there are few limitations of thermoplastic starch: water soluble, poor resistance and mechanical strength compared to other thermoplastic (Cyras et al., 2008). The poor water resistance properties of thermoplastic starch are due to the hydroxyl groups in the structure causes swelling of starch when it is exposed to water (Mohammadi Nafchi et al., 2013).

Even though thermoplastic starch can be widely used in various products, however, the improvement on water resistance and mechanical properties still need to be explored and researched. One of the ways to overcome the weakness of thermoplastic starch are by modifying and blending the starch with other thermoplastic polymers to provide superior mechanical properties to it (Saiah et al., 2012). As thermoplastic starch is a type of bio-plastic, which is biodegradable plastic, hence, more studies on the thermoplastic starch are currently being carried out in order to widen its application to niche market and maintain a green environment (Xie et al., 2014).

Apart from that, HDPE composites reinforced with hybrid inorganic fillers is one of the current thermoplastic developments that use the combination of talc and glass fiber. Besides, the main objectives of using the combined talc and glass fiber in HDPE are to make low cost composite with the aids of talc and mechanical properties enhancement on HDPE with the reinforcement of glass fibers. The combined talc and glass fiber and blended with HDPE to form HDPE composites. In HDPE composites, glass fibers are bounded nicely and arranged perpendicularly to the HDPE matrix whereas talc is bounded in parallel and perpendicularly to the HDPE composites and form little bonding within the fracture surface which is illustrated in Figure 2.12. Hence, HDPE composites reinforced with combined talc and glass fibers improves the mechanical properties and modulus of HDPE composites due to less available void in HDPE matrix. Furthermore, it also performs good thermal expansion by reducing the deformation or dimension changing of composites when exposed to heat (Huang et al., 2013).

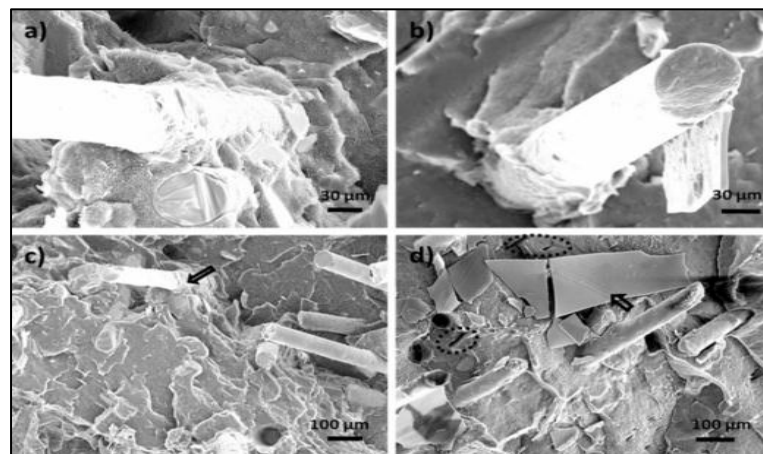


Figure 2.12: Morphology of Fracture Surface HDPE Composites Reinforced with Combined Talc and Glass Fibers Filler (Huang et al., 2013)

However, the mechanical properties of combined talc and glass fibers reinforced HDPE composites are varied with the proportions of talc and glass fibers in filler mixture. Large portion of glass fibers in mixture will lead to better mechanical performance in composites whereas increase in talc proportion will reduce the performance of composites but increase the recyclability and reduce cost of composites (Huang et al., 2013).

CHAPTER 3

MATERIALS AND METHODOLOGY

3.1 Introduction

This chapter includes the details of raw materials being used for the preparation of HDPE/BC composite, source of materials and composite preparation method specified with the parameters. Besides, this chapter also includes the preparation of BC, HDPE/BC composite, characterization of BC and characterization and testing of HDPE/BC composites.

3.2 Raw Materials

3.2.1 High Density Polyethylene (HDPE)

The HDPE resins used were supplied by Lotte Chemical Titan (M) Sdn. Bhd.

3.2.2 Palm Oil Sludge (Precursor of Biochar)

The palm oil sludge used to convert biomass was obtained from Tian Shiang Oil Mill (Air Kuning) Sdn. Bhd., which is located in Air Kuning, Perak, Malaysia.

3.3 Biochar Preparation

Firstly, the fresh palm oil sludge obtained was dried in oven at 110 °C for 24 hours to remove moisture. Then, the dried sludge was undergoing pyrolysis at 400 °C for 117 min with 27 °C/min heating rate in a carbonization unit. BC was then being crushed and grinded into less than 45 µm particle size. The preparation of BC is showed as in Figure 3.1.

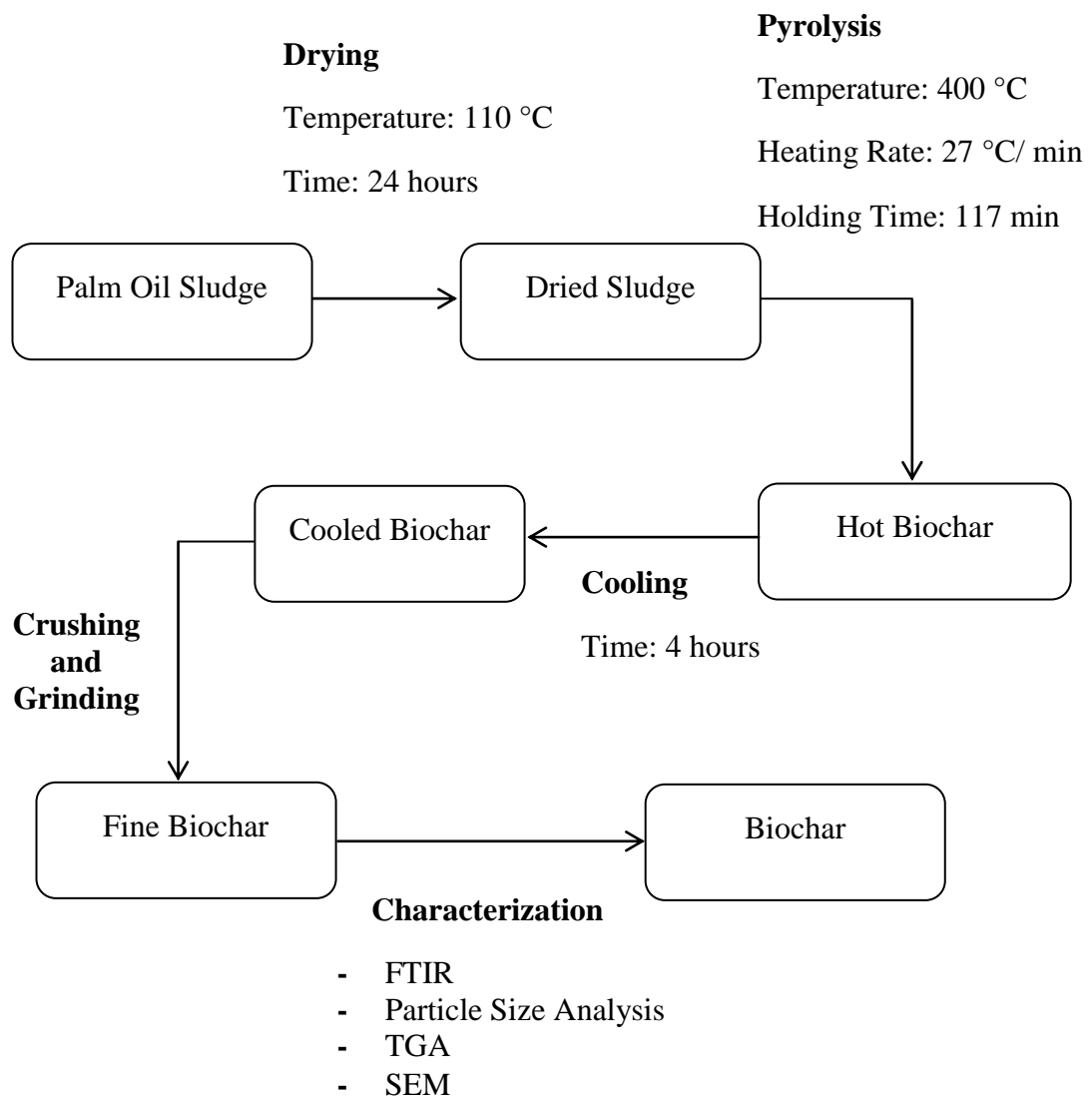


Figure 3.1: Flowchart of Biochar Preparation

3.4 HDPE/Biochar Composite Preparation

HDPE resins and BC were pre-dried in vacuum oven for 24 hours at 80 °C. HDPE/BC composites were produced by melt mixing method using rheometer Brabender® Plastograph® EC 815652. The composite mixing was carried out based on the compounding formulation as in Table 3.1 at melting temperature of HDPE, 160 °C for 8 min at 60 rpm rotation.

Table 3.1: Compounding Formulation of HDPE/BC Composites

Compound	HDPE (wt%)	Biochar (wt%)
1	100.0	0
2	99.0	1.0
3	97.5	2.5
4	95.0	5.0
5	90.0	10.0

The graph of processing torque of the composites was obtained from the Brabender internal mixer. The HDPE/BC composites were pressed into sheets using hydraulic hot and cold press machine GT-7014-A30C at 170 °C. The lumps of composites were preheated for 5 min and pressed for 3 min, followed by 2 min of cooling. The preparation of HDPE/BC composites is illustrated as in Figure 3.2.

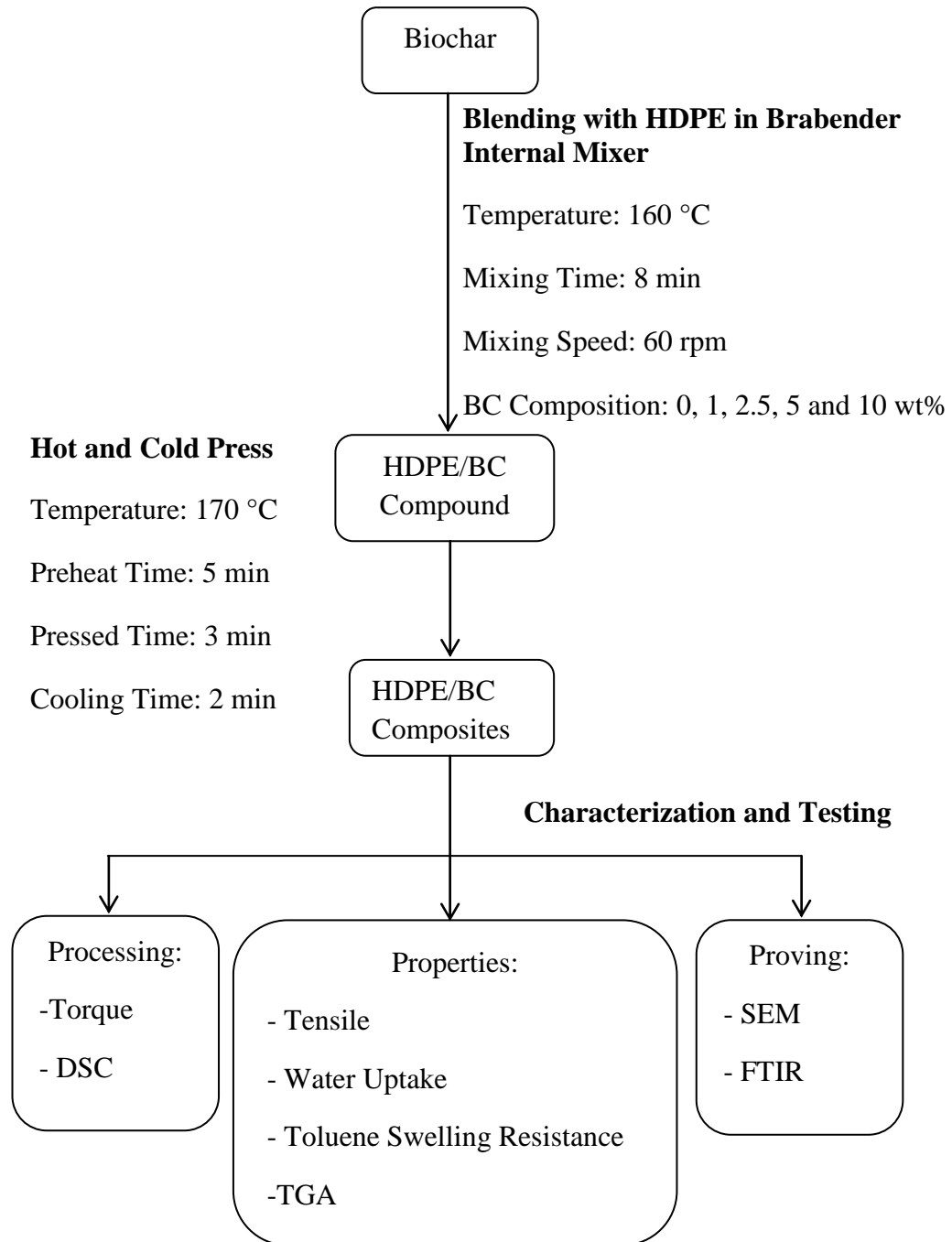


Figure 3.2: Flowchart of HDPE/BC Composite Preparation

3.5 Characterization of Biochar

3.5.1 Particle Size Analysis (PSA)

Particle size analysis (PSA) was a size indication of a particles presented in proportions from the total amount of 100 % in the particle sample group. In PSA test, volume, area length and amount were used as the standard dimension to determine particle amount (Shimadzu Corporation, 2015). The cumulative distribution of particles passing the sieve expresses the percentage of the particles amount from specific particles sizes or below. Mastersizer 2000, Hydro 2000 MU (A) was used to analyse the particle size distribution of BC in this research.

3.5.2 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR was carried out by using Perkin Elmer Spectrum ex1 to identify the types of chemical bonds and functional groups in BC. BC was mixed homogeneously with KBr and pressed into pellet form for FTIR test. The analysis was carried out to determine the absorption band with a wavelength from 4000 - 400 cm^{-1} with 4 scans at a resolution of 4 cm^{-1} .

3.5.3 Thermogravimetric Analysis (TGA)

TGA was performed to determine the decomposition temperature and thus, the thermal stability BC. Measurements were carried out under a nitrogen atmosphere using a heating rate of 20°C/min from 30 - 600 °C using Mettler Toledo TGA SDTA851 E.

3.5.4 Scanning Electron Microscopy (SEM)

The morphology of BC was characterized by using SEM at accelerating of 2 kV voltage. Prior to scanning, BC was placed on a disc and held in place using a double-sided carbon tape then coated with platinum particles to avoid sample charging. The model of equipment used was JOEL JSM 6701F.

3.6 Characterization and Testing of HDPE/Biochar Composite

3.6.1 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR was carried out by using Perkin Elmer Spectrum ex1 to identify the types of chemical bonds and functional groups in HDPE/BC composite. The analysis was carried out to determine the absorption band with a wavelength from 4000 - 400 cm^{-1} with 4 scans at a resolution of 4 cm^{-1} .

3.6.2 Differential Scanning Calorimetry (DSC)

Mettler Toledo TOPEM was used to determine the melting points, crystallinity and crystallizing temperatures of HDPE and HDPE/BC composites. The samples were heated from 25 - 300 $^{\circ}\text{C}$ at a rate of 10 $^{\circ}\text{C}/\text{min}$ under nitrogen flow of 10 ml/min and immediately cooled back to 25 $^{\circ}\text{C}$.

Crystallinity was calculated by using equation 3.1.

$$X_c^m = \frac{\Delta H_m}{W_p \times \Delta H_{100}} \times 100 \% \quad (\text{eq. 3.1})$$

Where,

X_c^m = Crystallinity (%)

ΔH_m = Melting heat (J/g)

ΔH_{100} = Melting heat for 100 % crystalline polyethylene, 293 J/g (Ibeh, 2011)

W_p = Weight fraction of polymer in sample

3.6.3 Scanning Electron Microscopy (SEM)

The morphology of HDPE/BC composites was characterized by using SEM at accelerating voltage of 2kV. The model of equipment used was S-3400N. Prior to scanning, HDPE/BC composites were placed on a disc and held in place using a double-sided carbon tape then coated with platinum particles to avoid sample charging.

3.6.4 Water Uptake and Toluene Swelling Resistance

HDPE/BC composites specimens with the dimensions of 30 x 5 x 2 mm were cut from the compression moulded sheet and the swelling test was carried out using distilled water and toluene as a solvent in accordance with ASTM D471-79. The test pieces were weighed using an electronic balance and initial mass (M_i) of the specimens in gram were recorded. The test pieces were then immersed in toluene for 72 hours and conditioned at 25 °C, in dark place. After 72 hours, the test pieces were weighed again and the mass of the specimens after immersion (M_s) in distilled water and toluene were recorded. Water and solvent resistance of HDPE/BC composite was evaluated from the swelling percentage of composite in distilled water and toluene. The lower swelling percentage indicates the higher water and solvent resistance of HDPE/BC composite. Swelling percentage was calculated based on equation 3.2.

$$\text{Swelling Percentage} = [(M_s - M_i) / M_i] \times 100 \% \quad (\text{eq. 3.2})$$

3.6.5 Tensile Test

Tensile test was carried out according to ASTM D638 under ambient condition to measure the elastic modulus, ultimate tensile strength and elongation at break of HDPE/BC composites. The test was conducted by using Tinius Olsen H10KS-0748 with a load cell of 450 N, at a crosshead speed of 50 mm/min.

3.6.6 Thermogravimetric Analysis (TGA)

TGA was performed to determine the decomposition temperature and thus, the thermal stability HDPE/BC composites. Measurements were carried out under a nitrogen atmosphere using a heating rate of 20 °C/min from 30 - 600 °C using Mettler Toledo TGA SDTA851 E.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

This chapter includes the results and discussion on the characterization and evaluation on HDPE/BC composite as compared to BC and unfilled HDPE. In addition, results for characterization and testing such as particle size analysis, processing torque, differential scanning calorimetry (DSC), fourier transform infrared (FTIR), water uptake and toluene swelling test, thermo gravimetric analysis (TGA), tensile test and scanning electron microscopy (SEM) were interpreted with respect to the past research works done. Furthermore, all characterization and testing were conducted based on the ASTM standards to ensure the controlled testing condition. Results and data obtained from testing were tabulated and summarized in this chapter as the support for the explanation and discussion on the tests performed.

4.2 Characterization of Biochar

4.2.1 Particle Size Analysis (PSA)

Particle size analysis was performed on BC particles to determine the mean particle diameter, specific surface area and the particle size distribution which is crucial in studying the effect of BC as potential filler in HDPE. Figure 4.1 illustrates the particle size distribution of BC. Based on the data obtained from particle size analysis, the particle size of BC ranges from 0.2245 - 148.2635 μm . However,

the BC particle used in composite preparation was limited between 0.2245 - 45 μm by sieving. This is to ease and control the processing of HDPE/BC composites and to reduce the tendency of agglomeration of larger BC particles at higher BC loading.

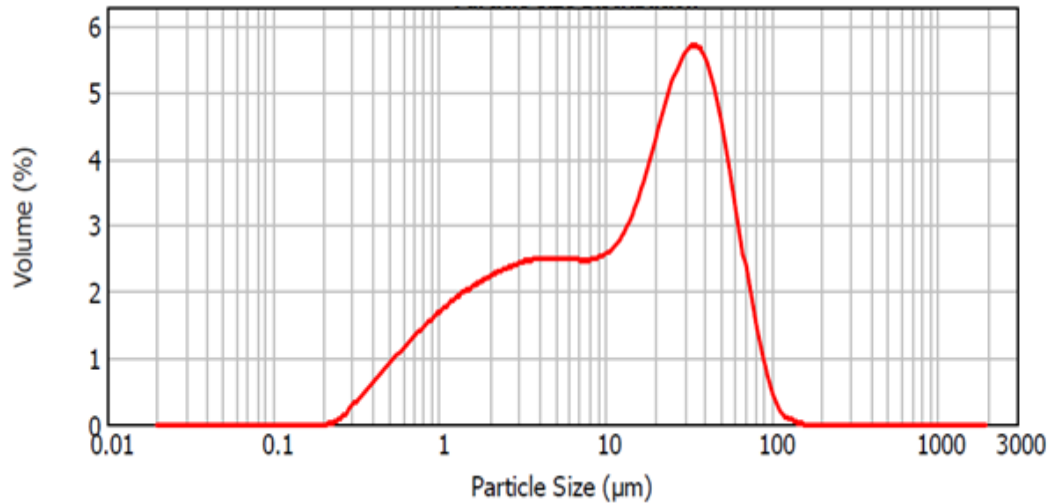


Figure 4.1: Particle Size Distribution of BC

Table 4.1 tabulates the comparisons between the physical characteristics of BC as compared with carbon black, silica and CaCO_3 through particle size analysis. BC has broad particle size distribution as compared to commercial fillers carbon black, silica and CaCO_3 . Broad particle size distribution may contribute to more diversity in application of BC which requires different particle size range. Furthermore, across the broad particle size distribution, the mean diameter of BC is 14.73 μm , whereas the mean diameter of carbon black, silica and CaCO_3 are 4.60 μm , 20.02 μm and 8.54 μm respectively.

Comparatively, BC has the largest specific surface area of 1.740 m^2/g , whereas carbon black, silica and CaCO_3 having specific surface area of 1.340 m^2/g , 1.138 m^2/g and 0.896 m^2/g . Specific surface area represents the surface area of filler exposed in the unit weight of the filler which is responsible for any sort of interaction with polymer matrix. According to Rothon (2002), the specific surface area of filler is closely related to the density, shape and particle size distribution of fillers. Thus, high specific surface area indicates high porosity of BC and leads to

small BC particle size as compared to carbon black, silica and CaCO₃, which reveals the potential of BC as reinforcing filler in polymeric composites.

Table 4.1: Physical Characteristics of BC, Carbon Black, Silica and Calcium Carbonate

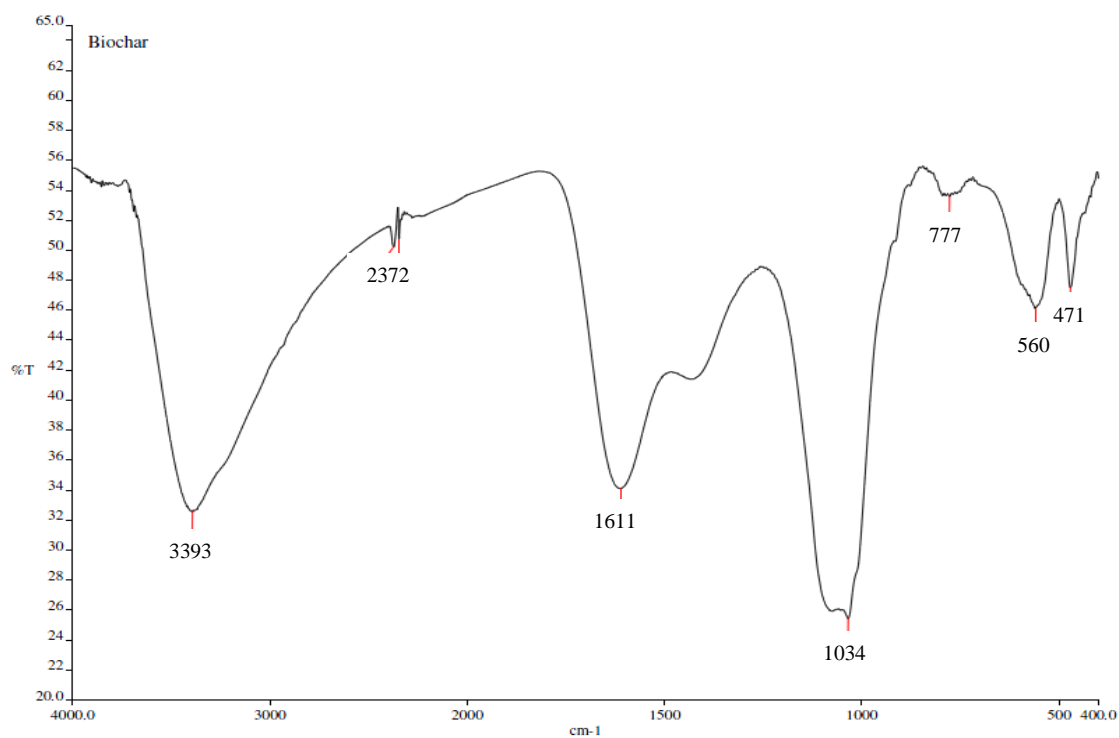
Properties	Filler			
	Biochar	Carbon Black	Silica	Calcium Carbonate
Particle Size Distribution (µm)	0.22 - 148.26	0.24 - 58.66	7.96 - 63.94	1.22 - 37.84
Mean Diameter (µm)	14.73	4.60	20.02	8.54
Specific Surface Area (m²/g)	1.740	1.340	1.138	0.896

4.2.2 Fourier Transform Infrared Spectroscopy (FTIR)

The functional groups of BC was analysed by FTIR. Table 4.2 tabulates the information of chemical structures on BC based on Lambert (1987) whereas Figure 4.2 illustrates the peaks of BC shown in FTIR. Amides group was appeared in BC as medium peaks at frequency 3393 cm⁻¹ and 1611 cm⁻¹ were clearly observed in the figure. Besides, silicon compounds were detected in BC due to the presence of Si-H stretching at 2372 cm⁻¹ and 2345 cm⁻¹, and Si-O-C stretching at 1034 cm⁻¹. Furthermore, the S-S stretching at 560 cm⁻¹ and 410 cm⁻¹ indicates the presence of disulphides in BC. Apart from that, the absorption band identified at 1611 cm⁻¹ and 1034 cm⁻¹ indicated the presence of aromatic compounds in BC, which corroborated with the findings conducted by Ahmetli et al. (2013), where aromatic compounds are found in chars derived from different materials.

Table 4.2: FTIR Analysis of BC (Stuart, 2004)

Frequency (cm^{-1})	Peak Assignments
3400 - 3380	Primary amides group with N-H stretching
2400 - 2000	Silicon compounds with Si-H stretching
1650 - 1610	Primary amides group with N-H deformation
1620 - 1580	Aromatic compounds with C=C stretching
1100 - 1030	Silicon compounds with Si-O-C stretching
1045 - 1015	Aromatic compounds with CH in-plane bending
550 - 430	Disulphides group with S-S stretch

**Figure 4.2: FTIR Spectra of BC**

4.2.3 Thermogravimetric Analysis (TGA)

The thermal degradability of BC was identified by using TGA. From the data obtained, BC possessed high thermal stability as it did not fully decompose upon heating up from 30 - 600 °C. Hence, BC exhibited high thermal degradation temperature or high thermal stabilizing effect. In addition, the thermal degradation of BC happened only in one stage. As tabulated in Table 4.3, the remaining solid residue of BC after heating to 600 °C was 84.23 %, which indicated only 15.77 % of BC was burnt off from the heating. Thus, the high thermal stabilizing effect of BC has the tendency to increase the thermal stability of composite (Das et al., 2016), whereas in this research, BC is able to increase the thermal stability of HDPE/BC composite.

Table 4.3: Thermogravimetric analysis of BC

BC loading (wt%)	Maximum weight loss (%)	Residue (%)	Stabilization (%)
Raw BC	15.77	84.23	115.86

4.2.4 Scanning Electron Microscopy (SEM)

The morphology of BC was analysed with SEM. As illustrated in Figure 4.3, BC exhibit less interaction between the particles and tends to appear as an individual particles with broad particle size distribution. The individual and broad particle size distribution of BC provides good dispersion in HDPE matrix. As reported by Ahmetli et al. (2013), char particles distribute well in the matrix and provide good interaction between char and the polymer matrix. Besides, cracks also can be observed clearly on the surface of BC particles under SEM. Crack on the BC surface is not only allowed more penetration of HDPE to BC particles, but also enhanced interlocking between HDPE and BC particles. In addition, the porous structure of BC also has been analysed and shown in Figure 4.3. The highly porous structure of

BC provides good interlocking between HDPE and BC, thus, has tendency to improve tensile strength of HDPE/BC composite.

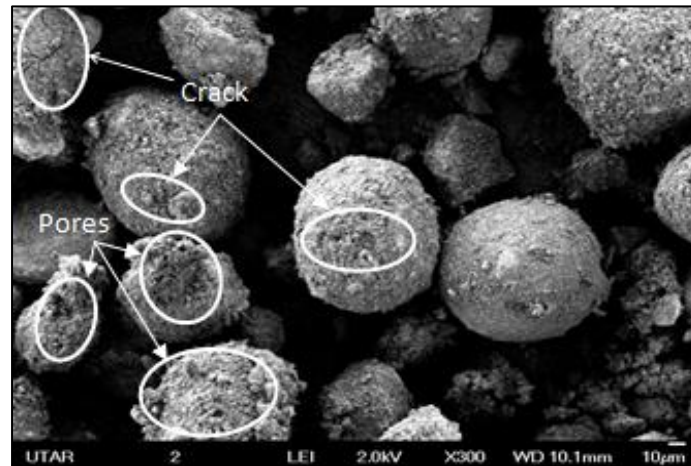


Figure 4.3: SEM Micrograph of BC at 300x Magnification

4.3 Characterization and Properties of HDPE/BC Composite

4.3.1 Processing Properties

The melt processing characteristic of HDPE/BC composites were studied through the melt mixing of HDPE pellets and BC powder in a Brabender Internal Mixer. Torque is not only indicates the viscosity of composites, but also shows the rheological behavior such as stiffness and processability of the composites formed (Demir et al., 2006). However, the torque rheometry obtained is highly depends on the operating conditions which is the temperature, pressure and rotor speed, and the structural of materials such as molecular weight and particle size (Silva et al., 2014).

In the mixing chamber, HDPE absorbs heat supplied and melts before being mixed with BC particles. Therefore, the loading peak of torque is mainly depends on the feeding amount of HDPE as the shearing action between HDPE pellets will create high frictional force, which causes the shear stress to increase and eventually results in high processing torque value. As illustrated in Figure 4.4, the loading torque values reduces from 0 - 1 wt% BC loading, which levels up and increases from 2.5 - 10 wt% BC loading. In comparison, it was observed that the HDPE/BC

composites have lower torque value compared to unfilled HDPE; however, the torque value of 10 wt% BC is the highest loading torque among all BC loading as well as unfilled HDPE.

Reducing in the feed amount of HDPE pellets signifies the reduction in HDPE charged weight and also the melt viscosity within the mixing chamber. Therefore, less frictional forces and shearing action between the molten HDPE and BC powder has yielded low loading torque in the mixer from 0 - 1 wt% BC loading in this case. Furthermore, particle size of BC is one of the factors that also influenced the torque value of composites. When the BC loading is not significant, the BC with small particle size will create insignificant frictional forces and yield low processing torque value. However, when BC loading is increased, the frictional forces due to the shearing action between HDPE/BC composites increased. As a consequence, torque increased with the amount of BC, from 1 - 5 wt%. Apart from that, 10 wt% BC loading has the highest torque as the BC added absorbed the heat required to prior melt the HDPE pellets. Thus, more energy is needed to melt and blend HDPE containing 10 wt% BC, eventually resulted in 10 wt% BC loading has the highest processing torque.

Apart from that, the stabilization torque is the stable torque value which indicates the homogeneous dispersion of filler in HDPE. The increment in stabilization torque indicates the enhancement of interaction between BC and HDPE matrix (Demir et al., 2006). Small size of BC manages to trickle in between the HDPE matrix upon the mixing, melting and blending in the chamber. It was observed that the stabilization torque of HDPE/BC composites gradually decreased with the increased of BC loading, however, the stabilization torque for 1 - 10 wt% did not exceed the unfilled HDPE. Thus, it can be postulated that the BC did not stiffen the matrix formed, while more shears were used to disperse the small size BC particles within the HDPE matrix and eventually yielding high stabilization torque with the increasing BC loading.

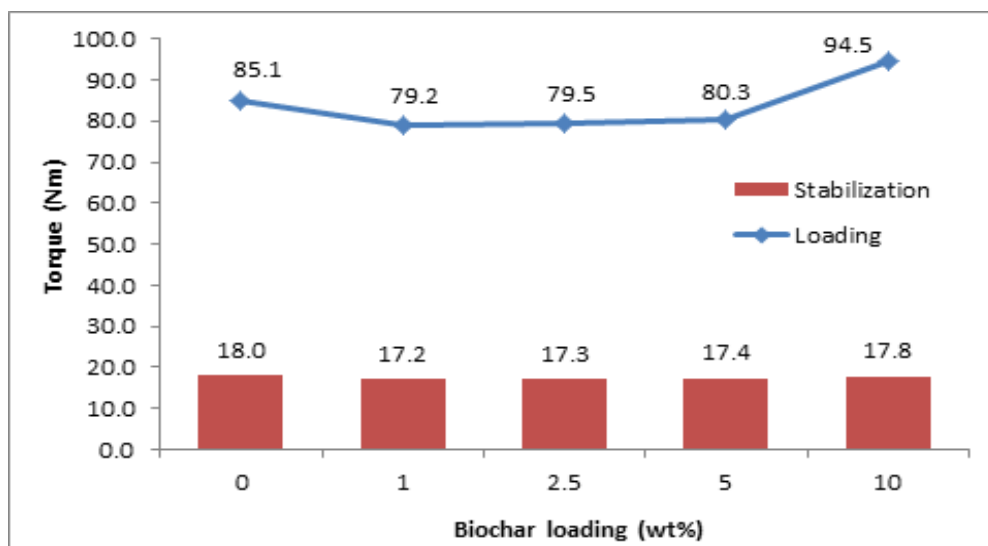


Figure 4.4: Processing Torque of HDPE/BC Composites at Different BC Loading

4.3.2 Differential Scanning Calorimetry (DSC)

Table 4.4 illustrates the DSC results obtained for HDPE and HDPE/BC composite with increasing BC loading. The effect of BC loading on the melting temperature (T_m), crystallizing temperature (T_c) and degree of crystallinity (X_c^m) was measured. In comparison, the melting temperature has reduced 2 °C when the BC loading increased from 0 - 10 wt%. However, from Table 4.4, it can be observed that there is no significant change in overall melting and crystallizing temperature of all different loading of HDPE/BC composites.

From literature, the pure HDPE has 293 J/g of enthalpy of crystallization. The nucleating effect of BC helps the crystallization to occur sooner than pure HDPE. According to Kanagaraj et al. (2008), the degree of crystallinity in composites increased when there is nucleation site available for crystallization of polymer to happen. As shown in Table 4.4, BC acts as the nucleation side for crystal to grow, thus, degree of crystallinity of HDPE/BC composites increase at low BC loading up to 2.5 wt% due to the fast growing of crystal structure on the nucleation sides of BC.

However, when BC loading was increased to 5 wt% and 10 wt%, the degree of crystallinity has reduced gradually. This phenomenon may be due to the hindrance of large amount of BC particles, which retards the growth of crystalline structure within the HDPE/BC composites. The melting and crystallization of composites are mainly depending on the polymer; in this case, HDPE is the main contributor for melting and crystallization events to occur (Das et al., 2016). Therefore, when BC loading increased to 5 wt% and 10 wt%, the degree of crystallinity in HDPE/BC composites reduced.

Apart from that, the small particle size of BC has enhanced the dispersion of BC within the polymer matrix. Thus, the well dispersed of BC in HDPE/BC composites has hindered the growth of crystalline structure and caused the degree of crystallinity of HDPE/BC composites to reduce at 5 wt% and 10 wt% BC loading. The end result of DSC is in line with the finding of Das et al. (2016), where the intensity of crystallinity decreased when the amount BC loading increased. On the other hand, DSC also showed the similar trend as that of the torque. Addition of BC into HDPE results in decreased stabilization torque, comparable T_m and T_c as well as low reduction in degree of crystallinity which suggests the suitability of BC as filler in HDPE. Addition of BC does not significantly affect the processing of HDPE thus has a great potential for any HDPE applications.

Table 4.4: The Melting Temperature, Crystallizing Temperature and Crystallinity Percentage of HDPE/BC Composites at Different BC Loading

Biochar Loading (%)	W_p	T_m (°C)	T_c (°C)	X_c^m (%)
0	1.000	132.41	114.85	62.20
1.0	0.990	132.11	117.26	67.80
2.5	0.975	131.92	115.82	65.84
5.0	0.950	130.60	114.22	62.85
10.0	0.900	130.09	114.52	45.97

4.3.3 Fourier Transform Infrared Spectroscopy (FTIR)

The functional groups of HDPE/BC composites at different BC loading were analysed by FTIR. Table 4.5 tabulates the information of chemical structures on unfilled HDPE whereas Table 4.6 tabulates the chemical structures of HDPE/BC composites at different frequency based on Stuart (2004). FTIR analysis can be used to detect any changes brought in HDPE with the addition of BC, indicated by the appearance or disappearance of certain peaks of either HDPE or BC which signifies the presence of chemical interaction between HDPE and BC. On the other hand, FTIR spectra of unfilled HDPE, HDPE/1.0 BC and HDPE/2.5 BC were shown in Figure 4.5. As illustrated in Figure 4.5, peaks at all different composition of HDPE/BC composites possessed similar trend in FTIR spectra. In comparison, HDPE possess high peaks intensity from 1800 - 2500 cm^{-1} and 850 - 1200 cm^{-1} frequency compared to HDPE containing 1 wt% and 10 wt% BC loading. Furthermore, HDPE also possessed wider bands around 3000 cm^{-1} and 1460 cm^{-1} frequency than HDPE/1.0 BC and HDPE/10 BC composite. Most of the peaks shown in IR spectra of unfilled HDPE indicate the presence of C-H bending of alkane groups.

Apart from that, the peaks showed at different frequency ease the determination of functional groups in HDPE/BC composites. For instance, the absorption band at 2951 cm^{-1} was clearly detected due to the stretching of aliphatic C-H bond. With the presence of peaks at a frequency of 1462 cm^{-1} , 1369 cm^{-1} and 1305 cm^{-1} , it was identified that the alkanes group were appeared in the HDPE/BC composites. Furthermore, silicon compounds were also detected in HDPE/BC composites as Si-H stretching at 2018 cm^{-1} , 2149 cm^{-1} and 2349 cm^{-1} are presented in FTIR spectra along with the Si-O-C stretching at frequency around 1081 cm^{-1} , whereas the presence of ethers group in HDPE/BC can also be determined through the C-O-C stretching from 900 - 1300 cm^{-1} (Stuart, 2004).

According to Ahmetli et al. (2013), aromatic compounds are presented in chars derived by different materials. Likewise, as reported by Das, Sarmah and Bhattacharyya (2016), wastes such as sewage sludge and poultry litter derived BC showed aromatic mode at 1600 cm^{-1} . In similar, aromatic compounds in HDPE/BC

composites were clearly identified due to the presence of absorption band of aliphatic C-H stretching below 3000 cm^{-1} , along with the presence of overtones and combination bands from $1700 - 2000\text{ cm}^{-1}$, C=C stretching at $1430 - 1650\text{ cm}^{-1}$, the in-plane bending from $1000 - 1250\text{ cm}^{-1}$, and out-of-plane bending at $690 - 900\text{ cm}^{-1}$ in the FTIR spectra.

In comparison, bands around frequency of 2950 cm^{-1} become narrow when BC loading increased from 0 - 10 wt%, which shown in region A from Figure 4.6. Same goes to the peak around 1462 cm^{-1} , region B has become narrower when the BC loading increased. In addition, the intensity of peaks from $1800 - 2500\text{ cm}^{-1}$ decreased gradually when the levels of BC loading increased from 0 - 10 wt% as the peaks at 1896 cm^{-1} , 2018 cm^{-1} and 2345 cm^{-1} were obviously reduced. Besides, the peaks intensity at 1304 cm^{-1} and 1367 cm^{-1} also reduced when more BC was blended with HDPE resins.

On the other hand, as shown in Figure 4.6, the peaks in region C were merged and formed a broader peak, whereas peak at 721 cm^{-1} has split into two when BC loading increased from 0 - 10 wt%. However, the growth of aromatic structure in HDPE/BC composites was observed from Figure 4.5 when the levels of BC loading increased. This result is corroborated with the findings of Ahmetli et al. (2013), where composites possessed growing aromatic structure trend when chars are added. Apart from that, peak at 1590 cm^{-1} became observable when BC loading increased. The increased intensity in this peak indicates BC has induced the presence amines group with N-H bending in HDPE/BC composite.

When BC amount increased, the proportion of each HDPE blend reduced. As a consequence, the corresponding FTIR peaks have become less intensive and broaden which can be seen from Figure 4.5. Addition of BC increased the concentration of free radicals in composites (Das et al., 2016). Thus, inclusion high amount of BC steadily reduced the intensity and broaden the peaks in HDPE/BC composites. However, no new peaks have been observed in HDPE/BC composite as compared to the raw HDPE and BC, which indicated that there is no chemical reaction took place between BC and HDPE. Besides, any improvement in

mechanical properties is responsible due to any physical interaction such as interlocking of HDPE chains at BC surface cracks and porosity.

Table 4.5: FTIR Analysis of Unfilled HDPE (Stuart, 2004)

Frequency (cm ⁻¹)	Peak Assignment
2951	Alkanes with methyl symmetric C-H stretching
3000 - 2800	Aromatic compounds with aliphatic C-H stretching
3000 - 2400	Carboxyl group with O-H stretching
2000 - 1700	Aromatic compounds with overtones and combination bands
1650 - 1430	Aromatic compounds with C=C stretching
1462	Alkanes group with methylene scissoring
1369	Alkanes group with methyl symmetrical C-H bending
1305	Alkanes group with methylene wagging
1250 - 1000	Aromatic compounds with C-H in-plane bending
900 - 690	Aromatic compounds with C-H out-of-plane bending
720	Alkanes group with methylene rocking

Table 4.6: FTIR Analysis of HDPE/BC Composites at Different BC Loading (Stuart, 2004)

Frequency (cm ⁻¹)	Peak assignments
3369	Secondary amines group with N-H stretching
3000 - 2800	Aromatic compounds with aliphatic C-H stretching
3000 - 2400	Carboxyl group with O-H stretching
2951	Alkanes with methyl symmetric C-H stretching
2400 - 2000	Silicon compounds with Si-H stretching
2000 - 1700	Aromatic compounds with overtones and combination bands
1650 - 1430	Aromatic compounds with C=C stretching
1611	Secondary amines group with N-H bending
1462	Alkanes group with methylene scissoring
1369	Alkanes group with methyl symmetrical C-H bending
1305	Alkanes group with methylene wagging
1300 - 900	Ethers group with C-O-C stretching
1250 - 1000	Aromatic compounds with C-H in-plane bending
1110 - 1050	Silicon compounds with Si-O-C stretching
900 - 690	Aromatic compounds with C-H out-of-plane bending
720	Alkanes group with methylene rocking
715	Secondary amines group with NH wagging

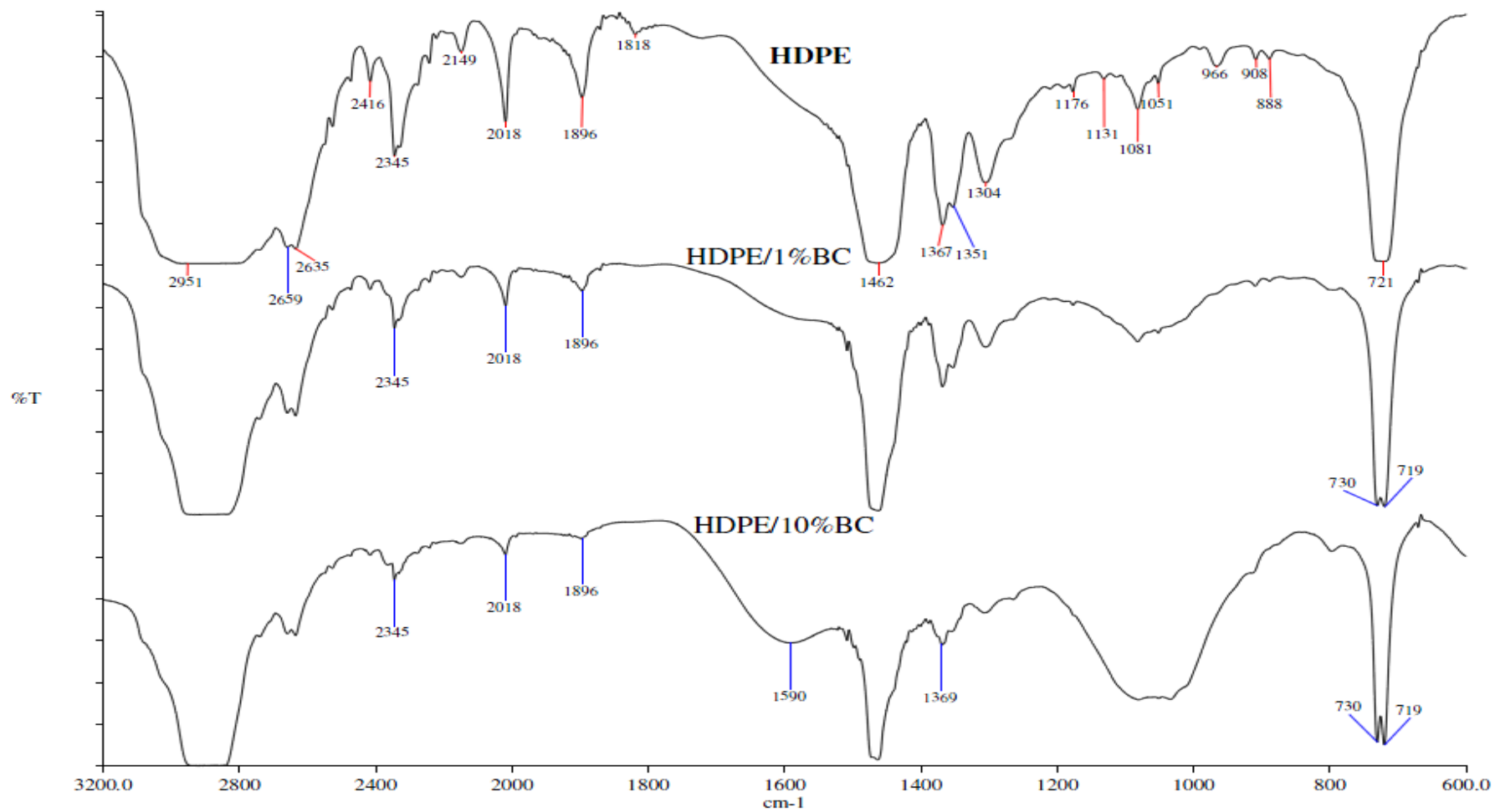


Figure 4.5: FTIR Spectra of Unfilled HDPE, HDPE/1.0 BC and HDPE/10 BC Composite

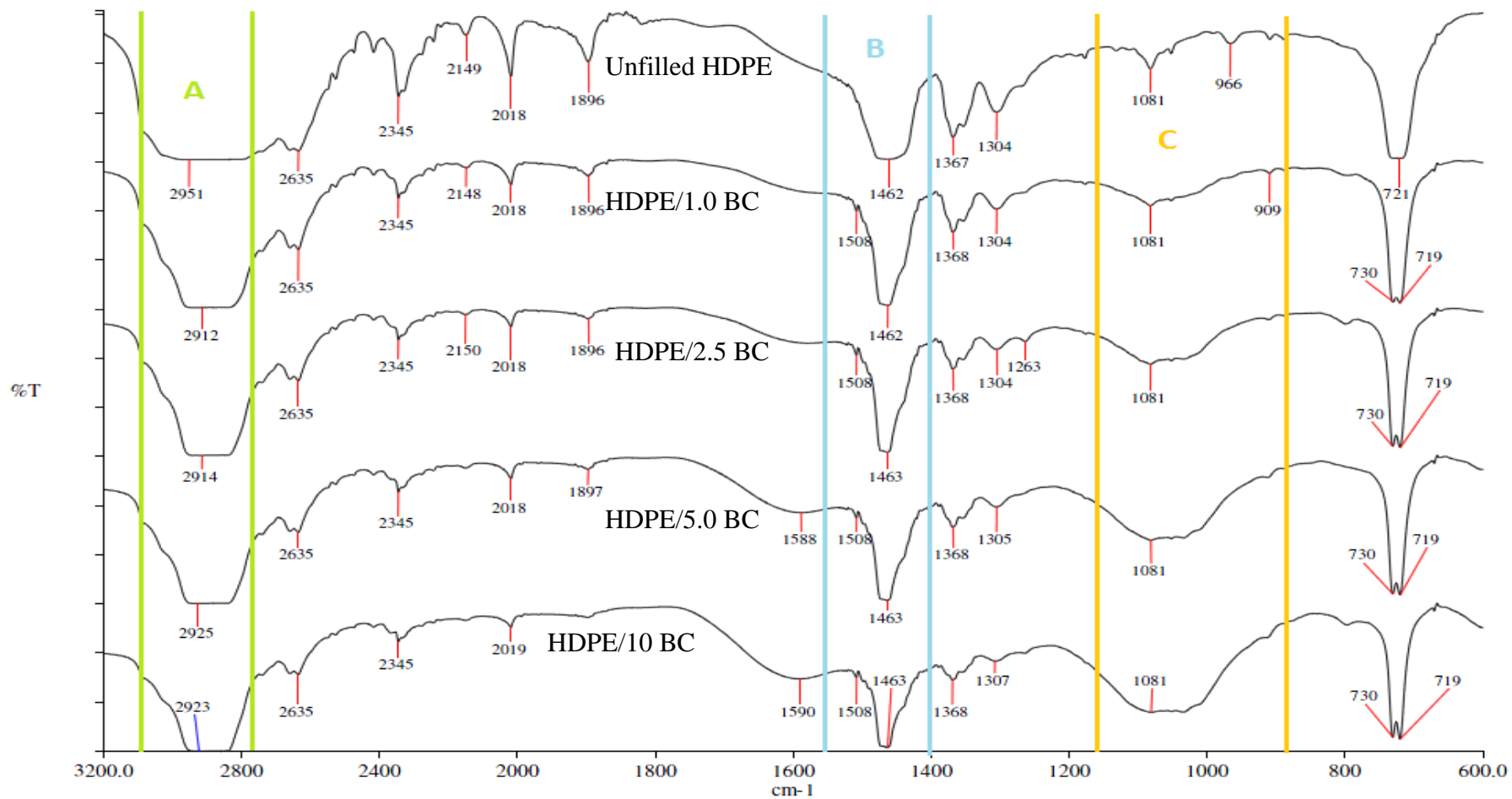


Figure 4.6: Comparison FTIR Spectra of HDPE/BC Composites at Different BC Loading

4.3.4 Swelling Test in Water and Toluene

Swelling test in water was conducted to study the water absorption capacity of HDPE/BC composite as compared to HDPE. BC is organic filler that is highly porous and capable of absorbing water. Thus, this testing is essential to determine the stability of BC in HDPE at environment that contains moisture. According to Ahmetli et al. (2013), aside leading to degeneration in mechanical and thermal properties of material, moisture diffusivity will also affect the adhesion binding on the composites. Water absorption is highly dependent on BC's surface properties such as surface area exposed, degree of porosity, oxygenated group and carbon content within BC (Behazin et al., 2015). In addition, difference in crystallinity degree of polymer, polarity of polymer, types and amount of filler used can lead to notable changes in the water sorption of composites (Ahmetli et al., 2013).

Figure 4.7 illustrates the water uptake of HDPE/BC composites at different BC loading. It can be clearly observed that the swelling path of HDPE/BC composites increased sharply at the beginning, then constant from 2.5 - 5 wt% BC loading and increased again when BC loading increased to 10 wt%. When BC is exposed to water, hydrogen bonding forms from the combination of oxygenated groups within BC and water molecules, which causes it to possess high affinity towards water molecules (Behazin et al., 2015). Thus, BC filler has acted as the penetration part for water to be absorbed into HDPE/BC composites. Comparatively, the hydrophobic and non-polar nature has caused HDPE matrix to have least affinity to water. As a consequence, HDPE/BC composites with higher BC allows more penetration parts for composites to form hydrogen bond with water compared to unfilled HDPE and HDPE/BC composites with low BC loading. In overall, the water absorption percentage of HDPE/BC composites was considered low as the highest water sorption percentage was up to around 0.2 %. Hence, it can be said that addition of BC shows negligible effect on water absorption capacity of HDPE.

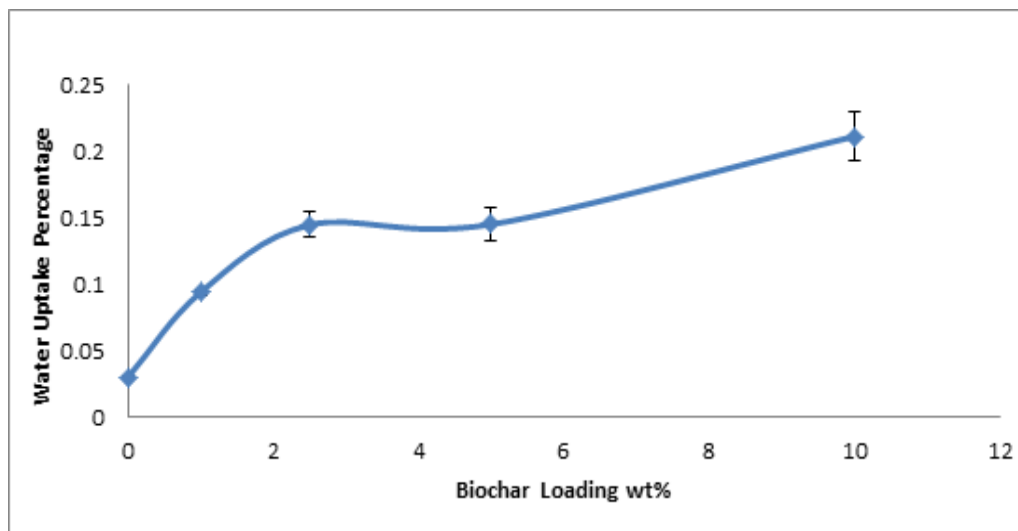


Figure 4.7: Water Uptake Percentage of HDPE/BC Composites at Different BC Loading

Apart from that, hydrophobic nature has caused HDPE to have strong affinity towards non-polar solvent such as toluene. Thus, swelling test in toluene was conducted to study the stability of HDPE/BC composite in toluene. As illustrated in Figure 4.8 the chemical swelling percentage of HDPE/BC composites was declined slowly when BC loading increased from 0 - 1 wt%. This situation happened was due to the insignificant amount BC did not affect the HDPE matrix within the HDPE/BC composites. However, when BC loading increased to 2.5 wt%, it can be observed that the toluene swelling percentage started to decline more as increase in BC amount indicates the reducing of HDPE matrix in composites. BC particles have entrapped and adsorbed on the matrix surface of HDPE during the mixing process (Gurovich et al., 2004). Thus, BC particles have reduced the mobility of matrix and blocked the HDPE matrix from absorbing the solvent and resulted in decreased toluene swelling percent. Besides, it can be observed from Figure 4.8 that 2.5 wt% of BC loading was saturated point where the toluene swelling percent started to stabilize by declining steadily. Therefore, it can be said that the toluene swelling resistance of HDPE/BC composites improved when BC loading was increased as it leads to more dispersion and interaction between BC and HDPE, and reduced the solvent penetration path into HDPE matrix.

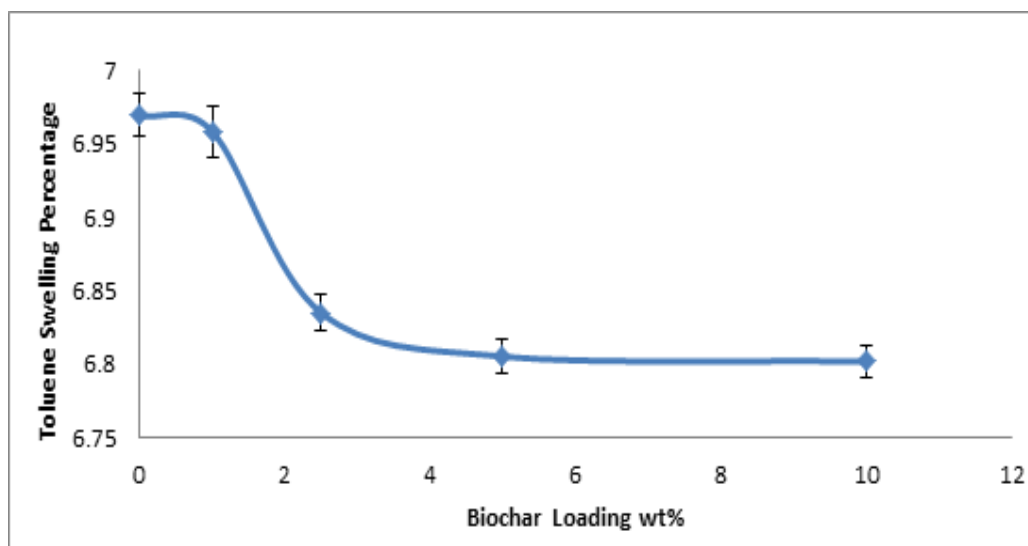


Figure 4.8: Toluene Swelling Percentage of HDPE/BC Composites at Different BC Loading

4.3.5 Thermogravimetric Analysis (TGA)

Figure 4.9 illustrates the weight loss percentage of HDPE/BC composites at different BC loadings. According to Zou et al. (2004), polymer will prior to oxidize before filler (carbon nanotube) starts to degrade in the composites, whereas in this case, HDPE will prior to oxidize before BC in HDPE/BC composites. As illustrated in Figure 4.9, it can be observed that the all HDPE/BC composites possessed multiple thermal degradation behavior, except raw BC. The initial thermal degradation happened just after 160 °C whereas second thermal degradation occurred after 400 °C. The first decomposition of HDPE/BC composites is most likely contributed by the HDPE, while the second decomposition is contributed by the degradation of BC itself.

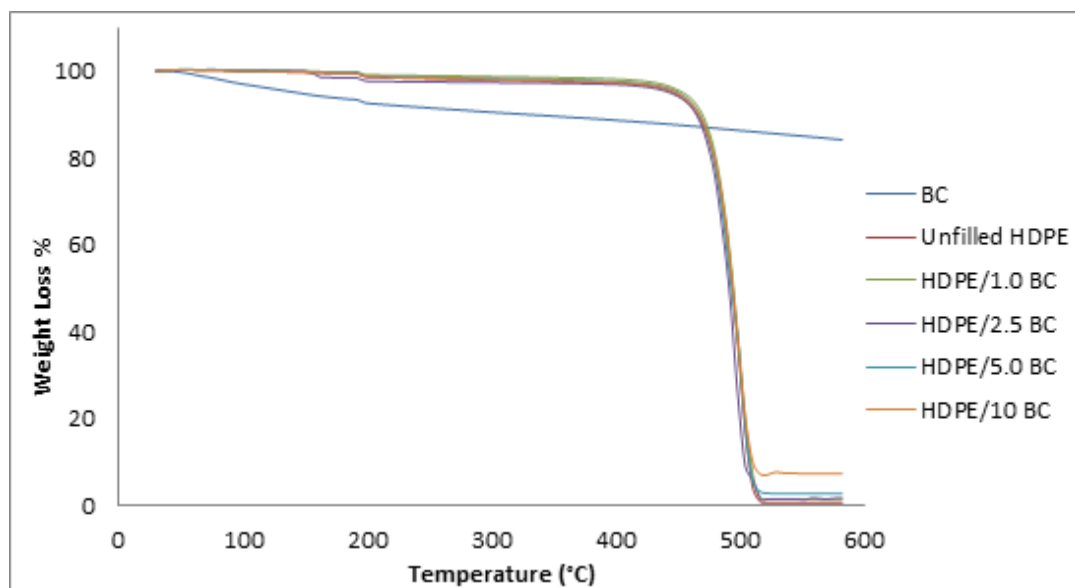


Figure 4.9: Thermo-Oxidation of HDPE/BC Composites at Different BC Loading

In general, inclusion of BC into HDPE has shifted the thermal degradation temperature of HDPE/BC composites to a higher value. As shown in Figure 4.9, it can be observed that at the highest loading of BC (10 wt%) has the highest solid remaining residue. The weight loss percentage of HDPE/BC composites at final TGA temperature increased accordingly from unfilled HDPE > HDPE/1.0 BC > HDPE/2.5 BC > HDPE/5.0 BC > HDPE/10 BC. On the other hand, the thermal stability of raw BC is high (Das et al., 2015), thus, the inclusion of BC has enhanced the overall thermal stability performance of composites (Das et al., 2016). Hence, thermal stability enhancement of HDPE by BC addition is aligned with the findings performed by Das et al. (2016).

Table 4.7 summaries the thermogravimetric analysis of HDPE/BC composites. It can be observed that the thermal stabilizing effect of HDPE/BC composites increased with the increasing BC loading. Initially, the stabilization effect of HDPE/BC composites increased gradually from 1 - 2.5 wt% BC loading; however, double increment of stabilization percentage was observed when BC loading increased to 5 wt%, whereas at 10 wt% BC loading, the stabilization percentage increased up to 9 %. Therefore, it can be said that the addition of BC in

HDPE improved the thermal stability of HDPE/BC composites, which is able to become potential area for the future research.

According to Ismail and Mathialagan (2011), high thermal stability fillers entrapped on the surface of polymer matrix will result in shifting the thermal degradation temperature of composite to a high value. Thus, the addition of high thermal stability BC into HDPE formed entrapments of BC in the interface of matrix, which hindered the diffusions of volatile by-product and shifted the thermal degradation temperature to higher value.

Besides, addition of BC into HDPE is not only increased the thermal stability due to thermally stable BC; however, when BC loading increased, the path for volatile by-product of combustion was blocked which resulted in self-extinguishing of BC and caused no further combustion on HDPE/BC composite at high temperature. Consequently, more char formation or residues at high temperature when BC loading increased in HDPE/BC composite. Besides, high BC loading containing in HDPE/BC composite may block the heat transfer and further temperature rise on the lower or below materials of BC. Thus, it reduced the tendency of the remaining solid residue from burning completely.

Table 4.7: Thermogravimetric Analysis of HDPE/BC Composites at Different BC Loading

BC loading (wt%)	Maximum weight loss (%)	Residue (%)	Stabilization (%)
0.0	99.28	0.72	-
1.0	98.52	1.48	1.06
2.5	98.23	1.77	1.46
5.0	97.25	2.75	2.82
10.0	92.67	7.33	9.18
Raw BC	15.77	84.23	115.86

4.3.6 Tensile Test

Table 4.8 summarizes the ultimate tensile strengths, tensile modulus and elongations at break of HDPE/BC composites at different BC loading. Ultimate tensile strength or tensile strength refers to the maximum stress of composite able to withstand before failure occurred when external force is exerted to pull the composite, whereas E-modulus or elastic modulus is composite's stiffness measurement or the resistance of composite to deform when stress is applied (Matinlinna, 2014). It can be observed from Figure 4.10, that the ultimate tensile strength of HDPE/BC composites increased gradually from 0 - 2.5 wt% BC loading (32.29 - 35.8 MPa), then, decreased slowly from 2.5 - 10 wt% BC loading (35.8 - 32.51 MPa).

According to Das et al. (2016), the changes in mechanical properties of composites is due to the intrinsic characteristics of BC that added into composites have resulted the interaction between composites to be varied. Thus, in this case, the addition of BC into HDPE caused HDPE/BC composites to exhibit different tensile strengths as compared to unfilled HDPE. More BC added into HDPE also indicates more carbon content in the HDPE/BC composite. The highly porous structure of BC allowed more penetration of HDPE and provided more reinforcement as interlocking between BC and HDPE increased. Hence, the tensile strength of HDPE/BC composites increased when BC loading increased from 0 - 5 wt%.

However, tensile strength of HDPE/BC composites decreased when BC loading was increased to 5 wt% and 10 wt%. This phenomenon may due to the large amount of BC particles caused agglomeration of BC happened in HDPE/BC composite. Therefore, when BC loading was too high, HDPE/BC composites were not able to withstand high stress and yielded low ultimate tensile strength. Apart from that, the addition of BC has improved the tensile modulus of HDPE/BC composites from 1235.5 MPa at 0 wt% BC loading to 1320.5 MPa at 10 wt% BC loading which can be noted in Figure 4.11. The infiltration of HDPE into BC has yielded strong mechanical interlocking in HDPE/BC composites. Thus, both strength and stiffness of HDPE/BC composites has significant increment when BC loading increased. On the other hand, as presented in Figure 4.12, the percentage elongation at break of HDPE/BC composites reduced sharply when BC loading increased.

Comparatively, unfilled has the highest elongation percentage (453.75 %) whereas the highest 10 wt% BC loading has the lowest break percentage.

It can be said that although BC has provided necessary resistance for HDPE/BC composite to overcome the deformation when stress was applied; however, the improved strength and stiffness compromised with the ductility of HDPE/BC composites. Therefore, the percentage of elongation before breaking decreased when BC loading increased in HDPE/BC composites. The results obtained from this research was similar to the past research conducted by Das et al. (2016), where the tensile strength and moduli of composites filled with organic wastes derived BC improved with increased BC loading, as well as the decrement in elongation percentage when BC loading increased.

Table 4.8: Ultimate Tensile Strengths, Tensile Modulus and Elongations at Break of HDPE/BC Composites at Different BC Loading

Parameters	BC loading				
	0	1.0	2.5	5.0	10.0
UTS (MPa)	32.29	32.86	35.80	33.33	32.51
Stdev	0.92	0.04	1.03	0.25	0.11
E-Mod (MPa)	1235.5	1256.5	1267.5	1276.5	1320.5
Stdev	41.72	53.03	37.48	4.95	4.95
Break %	453.75	231.65	145.15	80.75	21.06
Stdev	21.57	4.03	19.30	5.44	0.53

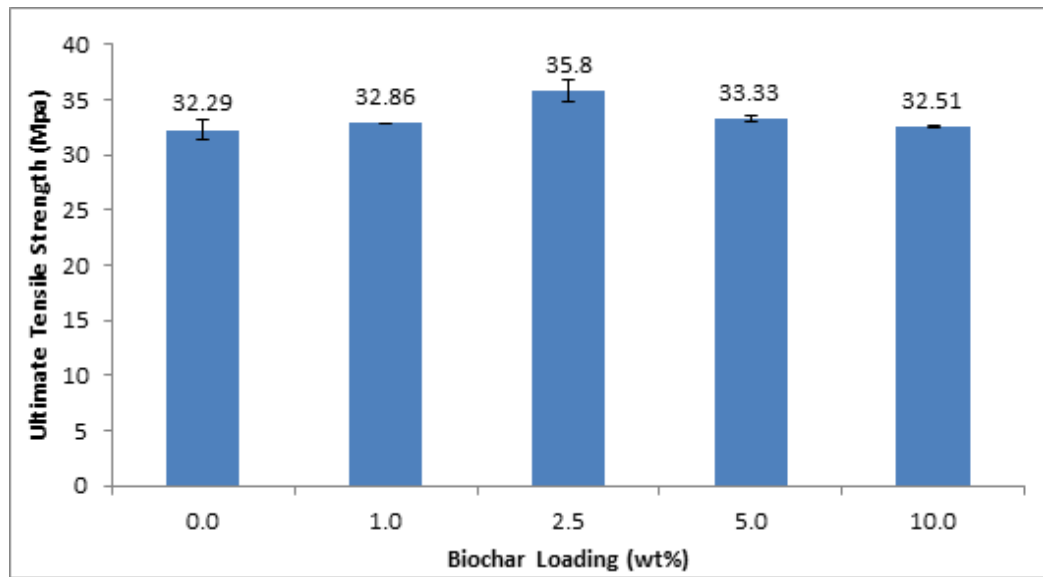


Figure 4.10: Ultimate Tensile Strength of HDPE/BC Composites at Different BC Loading

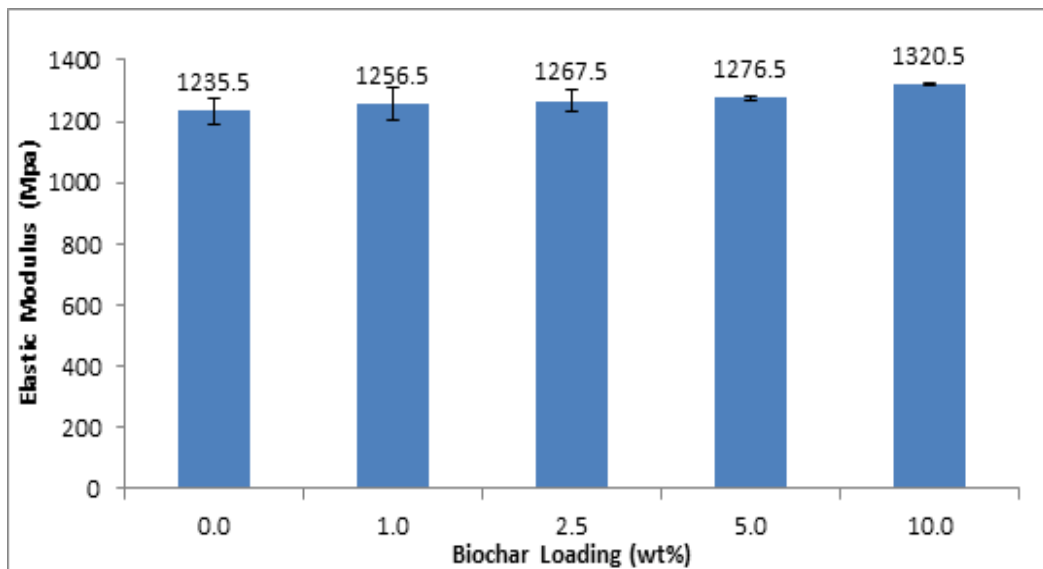


Figure 4.11: Tensile Modulus of HDPE/BC Composites at Different BC Loading

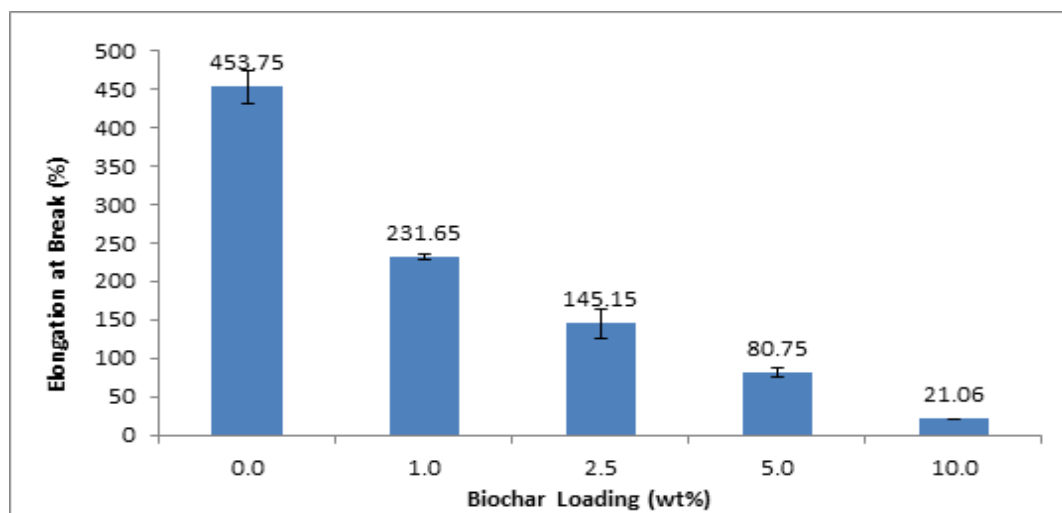


Figure 4.12: Elongations at Break of HDPE/BC Composites at Different BC Loading

4.3.7 Scanning Electron Microscopy (SEM)

The morphology of HDPE/BC composites at 0 wt%, 2.5 wt% and 10 wt% BC loading were analyzed by SEM. Figure 4.13 (a) illustrates the morphology of unfilled HDPE, whereas Figure 4.13 (b) and Figure 4.13 (c) shows the morphology of HDPE/2.5 BC and HDPE/10 BC respectively. In contrast, unfilled HDPE has flat and smoother surface compared to HDPE/2.5 BC and HDPE/10 BC. The smooth surface of unfilled HDPE indicated the high tensile modulus and lowest tensile strength on unfilled HDPE, which aligned with tensile test's results.

Besides, the smooth surface and less crack propagation path presented in the morphology also indicated the flexibility of HDPE and allowed high elongation at break of unfilled HDPE, which corroborated with the tensile test's results obtained. Comparatively, HDPE/2.5 BC has relatively smooth surface and less matrix tearing than HDPE/10BC. Apart from that, tearing of matrix can be clearly noted in Figure 4.13 (c). Matrix tearing happened due to the agglomeration of BC particles in matrix, where the agglomeration of BC particles can be seen in Figure 4.15 (c). Thus, the rough surface of HDPE/10 BC has the lowest elongation of break which is in line with the results obtained from tensile test.

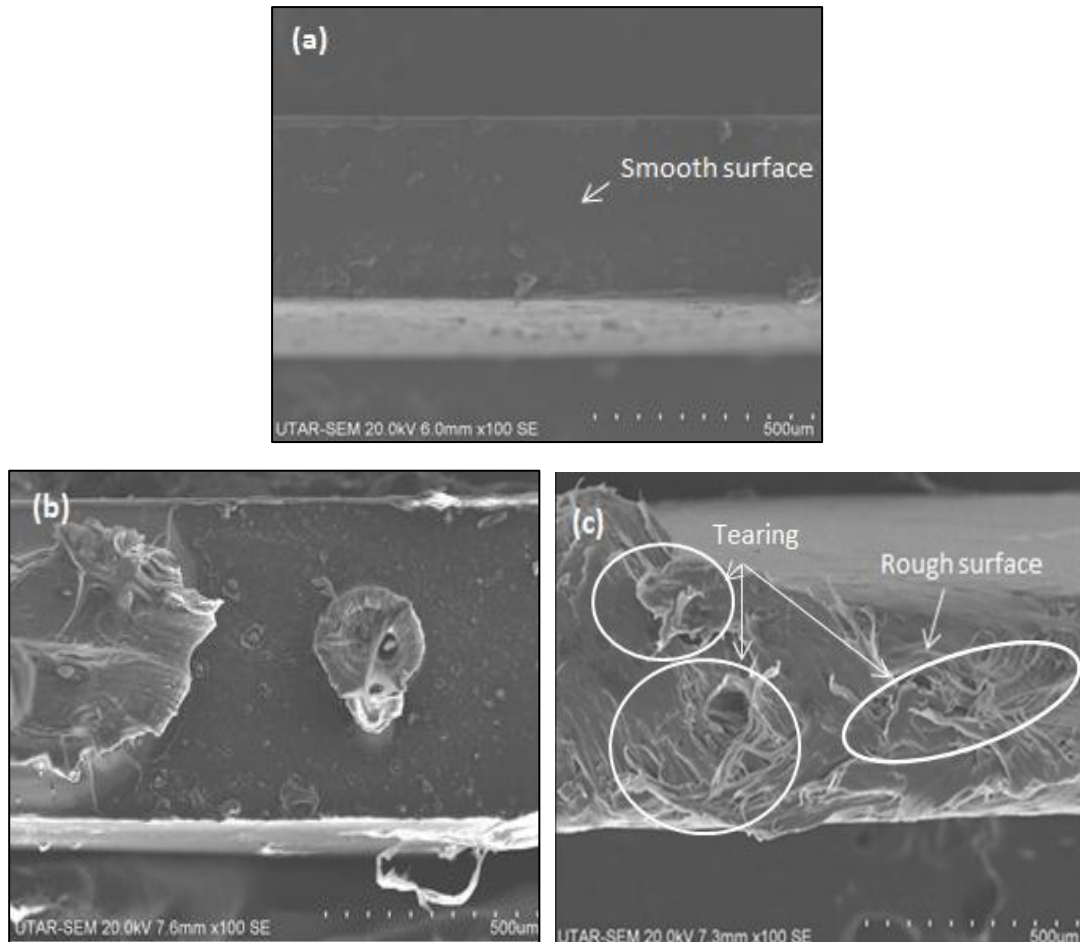


Figure 4.13: SEM Micrograph of Tensile Fracture of (a) Unfilled HDPE, (b) HDPE/2.5 BC and (c) HDPE/10 BC at 100x Magnification

Figure 4.14 (a) shows also smooth surface with a lot of micro-bubbles appeared in unfilled HDPE. The water moisture entrapped in HDPE caused the presence of micro-voids in the morphology of unfilled HDPE. In addition, Figure 4.14 (b) shows that HDPE/2.5 BC has relatively smooth but rougher surface than unfilled HDPE. Morphology with rougher surface at 2.5 wt% BC loading indicated good interaction between HDPE and BC in the composite as more penetration of HDPE matrix was allowed into the highly porous and cracked structure of BC. Besides, no clustering of BC particles was observed in the morphology of 2.5 wt% BC loading also represented good dispersion of BC particles in the HDPE/BC composite matrix.

As illustrated in Figure 4.14 (b), air gap was presented in morphology at BC loading 2.5 wt%. The presence of air gap indicated no chemical reaction between HDPE and BC in the HDPE/BC composites, which also act as the propagation path for cracking to occur when stress is applied. Therefore, rougher surface at 2.5 wt% BC provided high strength in HDPE/BC composite by allowing more crack propagation when stress was applied. The morphology analyzed for 2.5 wt% BC loading was similar to the findings conducted by Ahmetli et al. (2013) and Ho et al. (2015), where BC distributed uniformly in the matrix of HDPE/BC composite. On the other hand, the morphology of HDPE/10 BC shows the tearing-out matrix with clustering BC particles. Thus, it can be said that BC particles were not disperse well in HDPE matrix as BC particles tend to agglomerate in the matrix, hence, less interaction between HDPE and BC which resulted in low flexibility of HDPE/BC composite and led to low elongation break at 10 wt% BC loading.

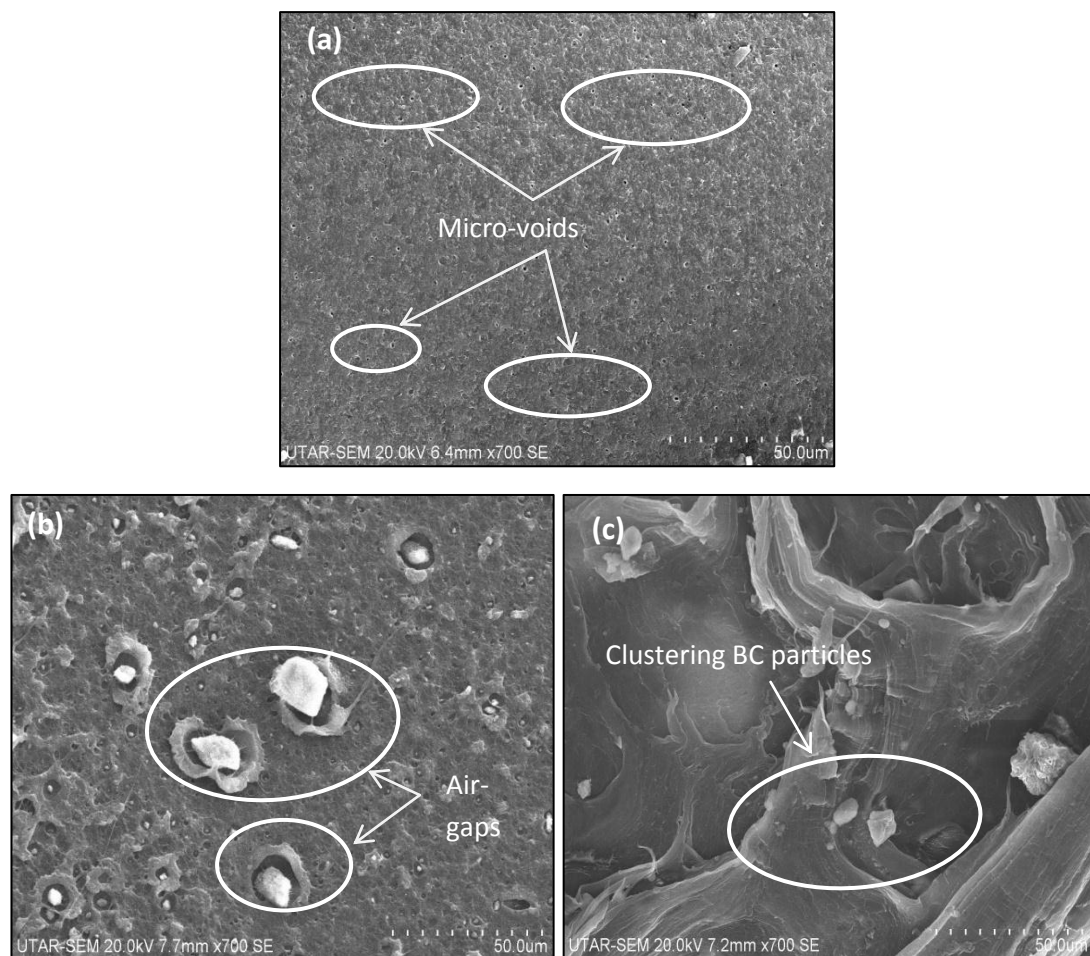


Figure 4.14: SEM Micrograph of Tensile Fracture (a) Unfilled HDPE, (b) HDPE/2.5 BC and (c) HDPE/10 BC at 700x Magnification

As shown in Figure 4.15, unfilled HDPE possess smooth and flat surface with micro-voids which leads to low tensile strength, whereas matrix string can be observed in HDPE/2.5 BC. Matrix strings linked between HDPE and BC as interlocking, thus, resulted in improved interaction between HDPE and BC and yielded high tensile strength in HDPE/BC composite. This observation is in line with the results obtained from tensile test, where HDPE/2.5 BC possessed the highest ultimate tensile strength amongst all. However, when BC loading was increased to 10 wt%, agglomeration started to happen in HDPE/BC composite matrix as BC has reached its optimum amount. This situation can be clearly noted in Figure 4.15 (c), where the distance between the BC particles becomes shorter and increased the tendency of higher interaction between BC particles as compared to BC and HDPE. The agglomeration of BC in the matrix of HDPE/BC composite has resulted matrix detachment and yielded low tensile strength in HDPE/BC composite at 10 wt% BC loading.

Besides, it also can be observed that the filler was not fully embedded into the matrix, which result the pulled out phenomenon and caused the HDPE/BC composite to be broken easily as voids increased in the matrix. Therefore, when BC loading was too high, the interactions between BC particles were stronger than the interaction between HDPE and BC. Consequently, BC particles agglomerates and clusters together to form bulk particles instead of being distributed homogeneously in the matrix of HDPE/BC composite. The bulk particles formed in the HDPE matrix has hindered the interlocking, thus, reduce the tensile strength of HDPE/BC composite and increase the water uptake tendency by HDPE/BC composite. The morphology analysis of HDPE/BC composite at 0 wt%, 2.5 wt% and 10 wt% BC loading is in line with the results obtained from tensile test. Thus, it can be said that the 2.5 wt% was the optimum BC loading as it possessed the highest tensile strength among other BC loadings and moderate elastic modulus and elongation percentage before breaking.

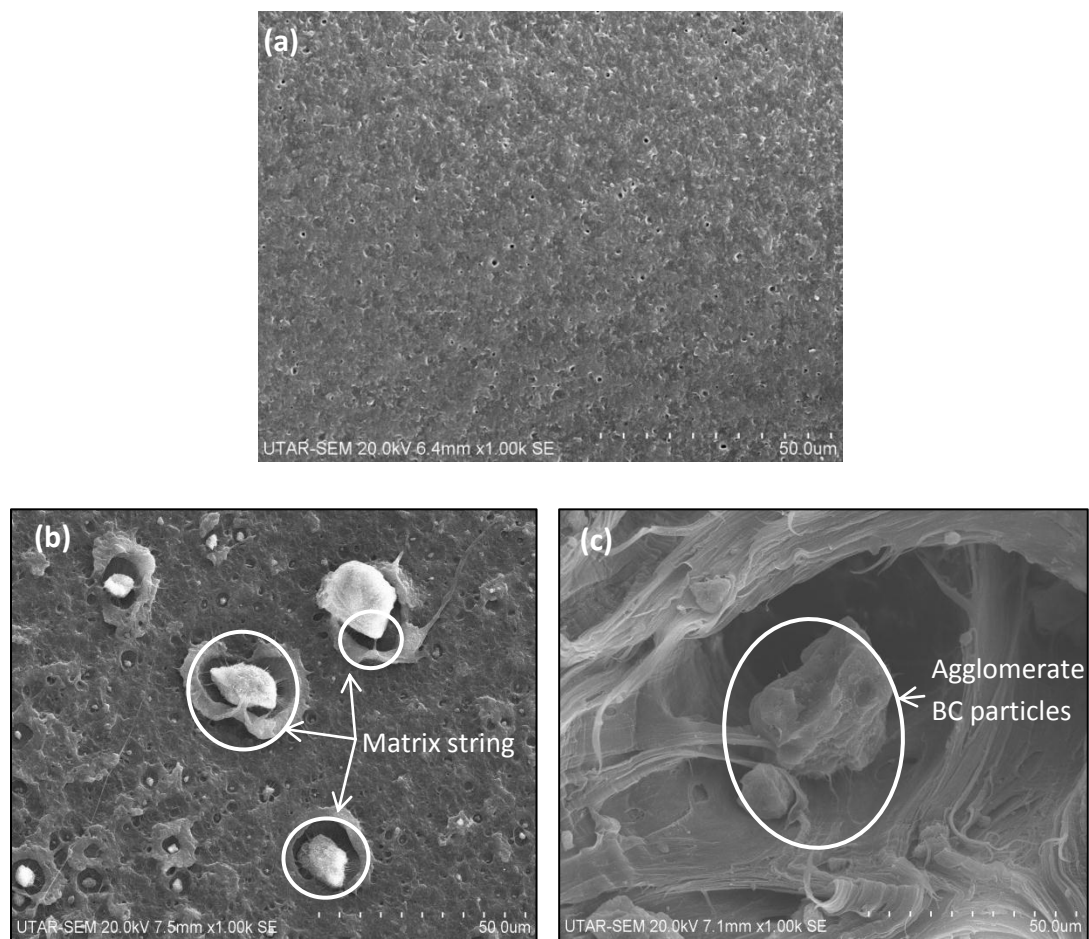


Figure 4.15: SEM Micrograph of Tensile Fracture (a) Unfilled HDPE, (b) HDPE/2.5 BC and (c) HDPE/10 BC at 1000x Magnification

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

BC filled HDPE composite has been successfully prepared through melt blending using a Brabender internal mixer with 8 min of processing time at 160 °C and 60 rpm.

Characterization of BC revealed that BC are highly potential as filler in HDPE due to the presence of surface porosity and cracks which may contribute to physical interaction via HDPE chain interlocking at BC surface. Particles of BC are irregular in shape with individual or small aggregate structure which suggests that it can be easily dispersed in HDPE matrix. Besides, particle size distribution of BC falls in the range of other commercial fillers. Furthermore, BC also has high thermal stability and does not contain any reactive hydrophilic groups, thus, it is compatible with HDPE.

Testing results also showed that the processing torque, melting temperature (T_m), crystallization temperature (T_c) and degree of crystallinity was not significantly affected with BC loading into HDPE which suggest comparable processing of HDPE/BC in comparison to neat HDPE. Apart from that, addition of BC has improved the chemical resistance, thermal stability, tensile strength and tensile modulus of HDPE/BC composite. However, elongations at break and resistance towards water of HDPE/BC composite have been decreased with the addition of BC.

The optimum loading of BC to produce the best HDPE/BC is 2.5 wt% which shows good BC dispersion in HDPE, and resulting in the highest tensile strength, high thermal stability, high toluene resistance and comparable processability as compared to unfilled HDPE. Further addition of BC above 2.5 wt% results in deterioration on tensile properties though the thermal, chemical and processability was improved. Besides, HDPE/BC composite with high BC loading has darker colour than low BC loading, thus, it limits the usage of HDPE/BC composite.

5.2 RECOMMENDATIONS

In order to improve the outcome of this research, few recommendations are made such as:-

- Extrusion machine should be used to conduct the melt mixing of HDPE/BC. This would greatly provide homogenous mixing between HDPE and BC, hence, good dispersion of BC on HDPE can be achieved and better quality of HDPE/BC composite would be obtained.
- Biodegradability on HDPE/BC composite can be studied in the further research. BC is organic filler which may lead the composite to be biodegradable. Thus, weathering test and soil burial test can be conducted to determine the biodegradability of BC filled HDPE composite.

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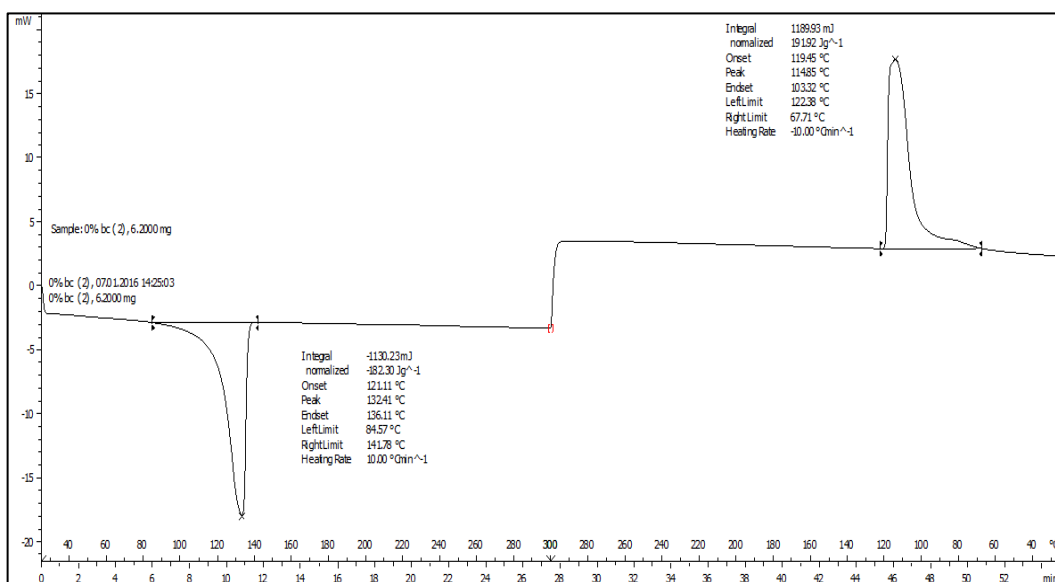
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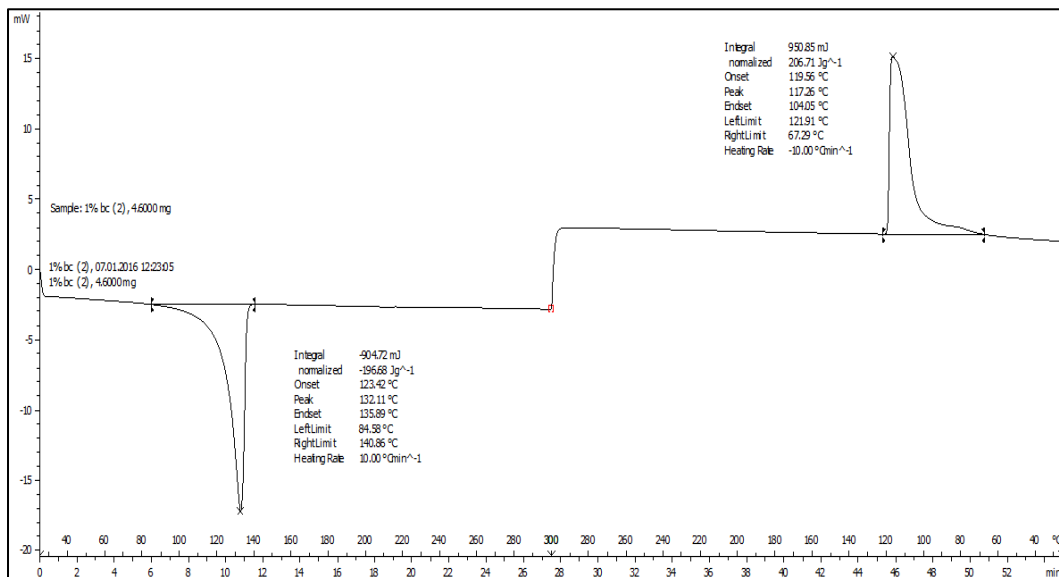
APPENDICES

APPENDIX A: Differential Scanning Calorimetry

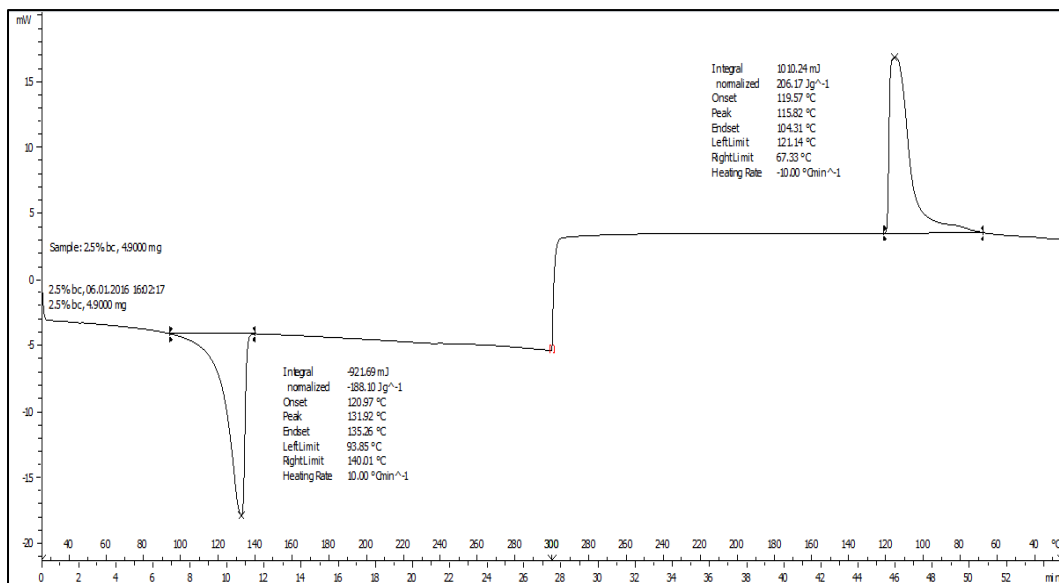
(a) Unfilled HDPE



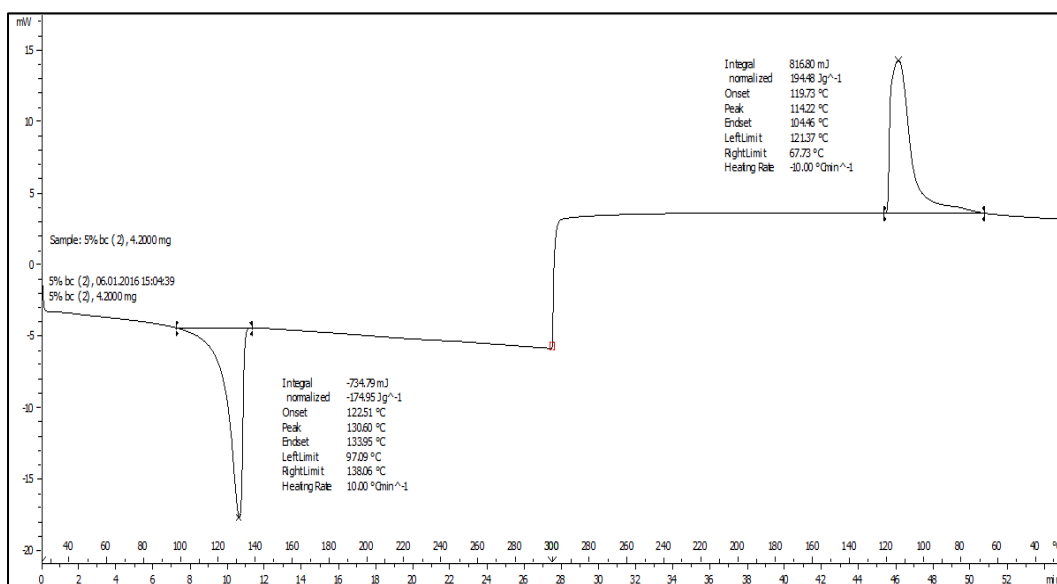
(b) HDPE/1.0 BC



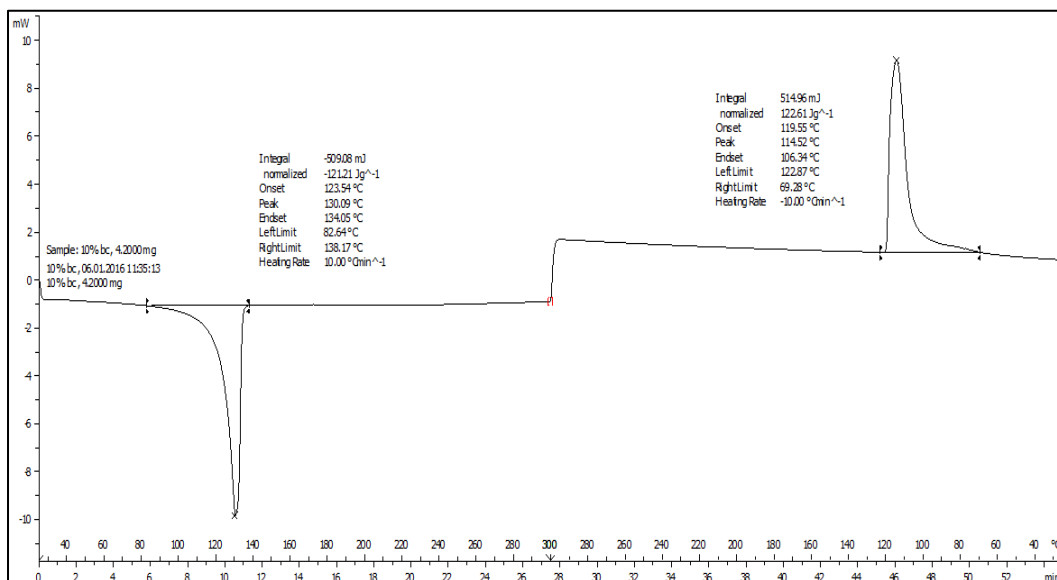
(c) HDPE/2.5 BC

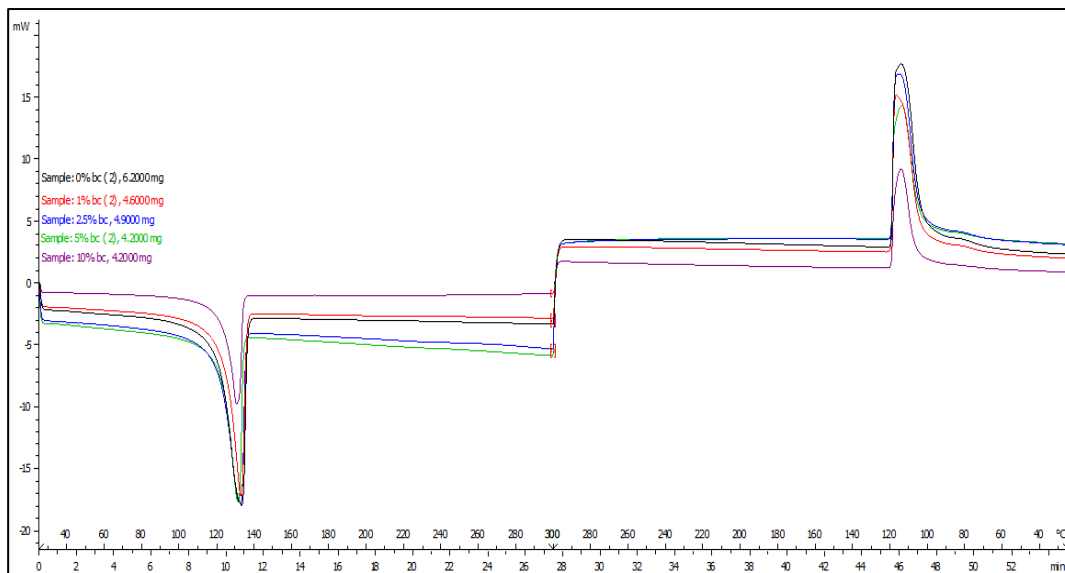


(d) HDPE/5.0 BC



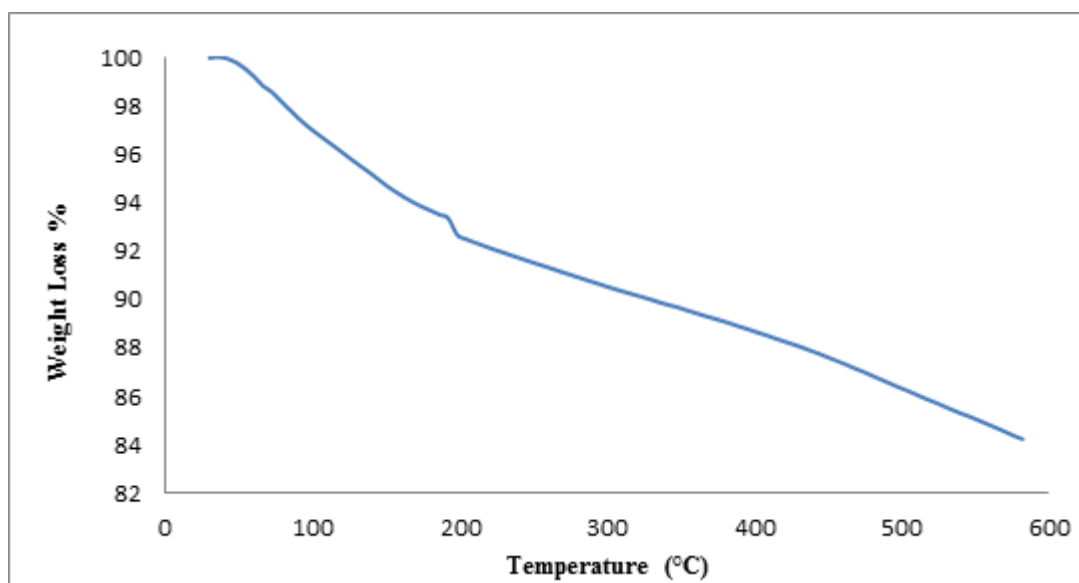
(e) HDPE/10 BC



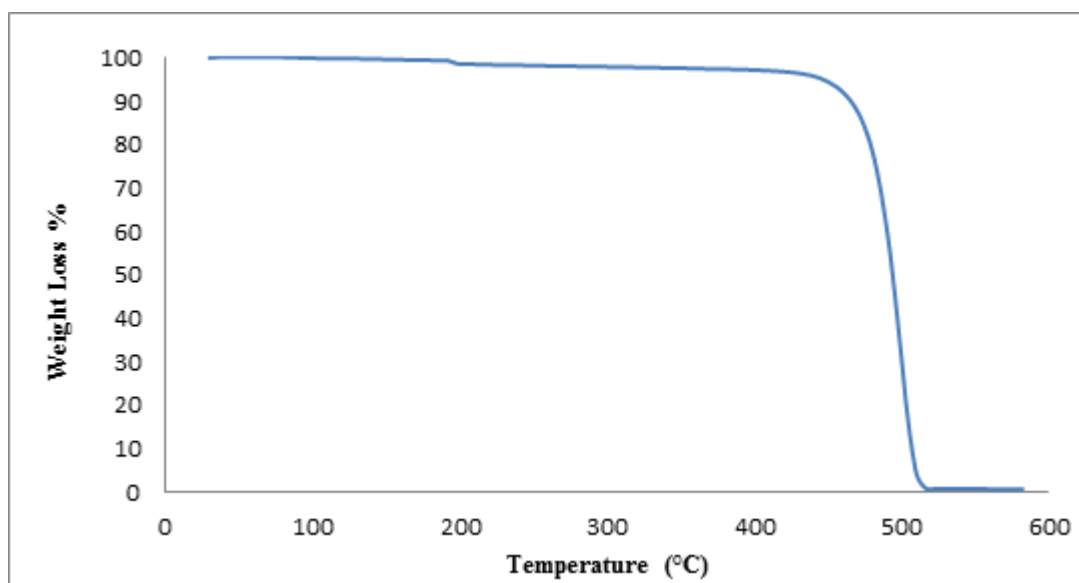
(f) Combined DSC Curve

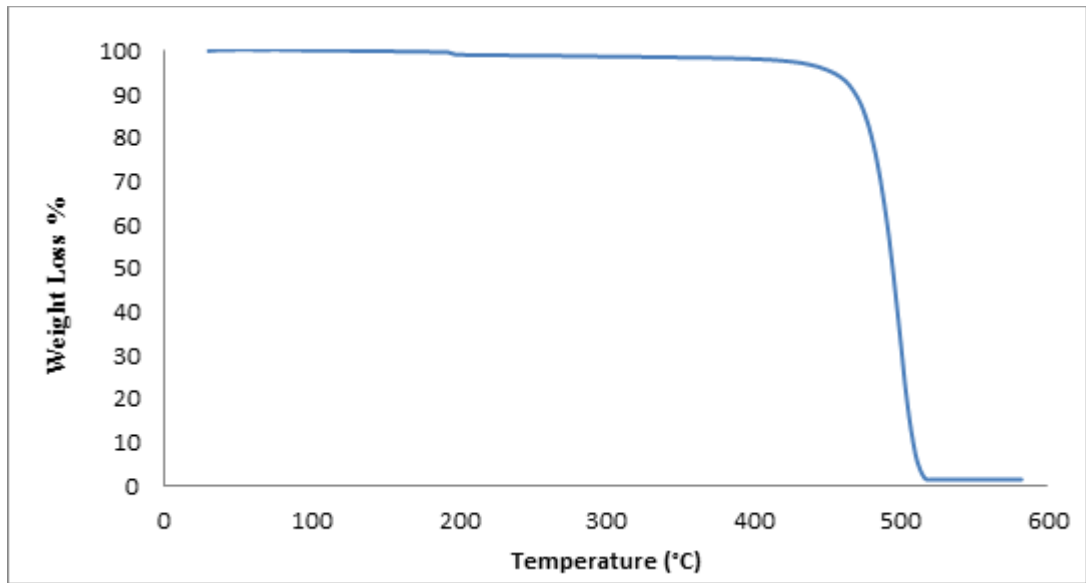
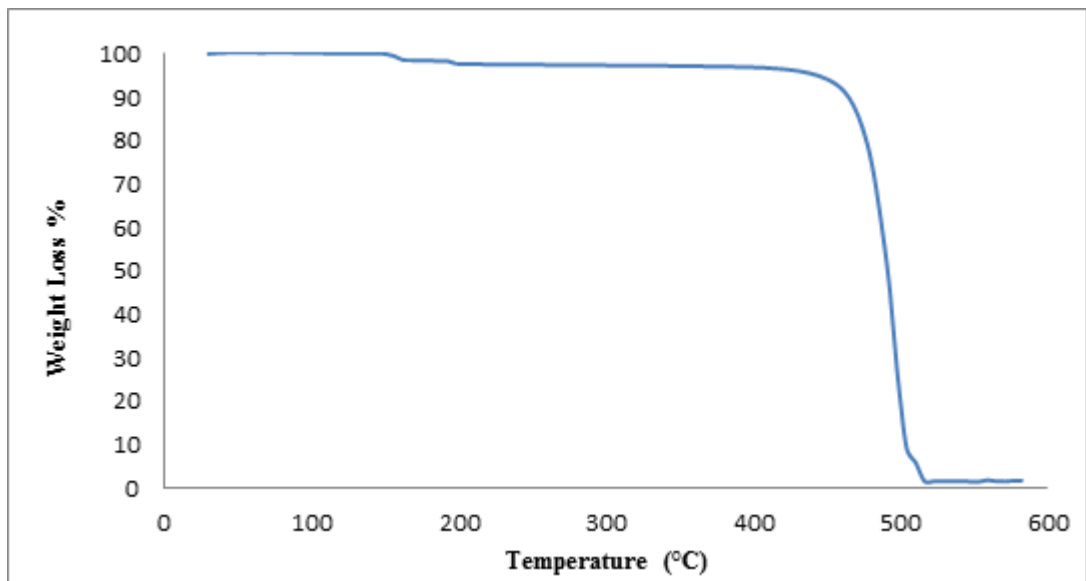
APPENDIX B: Thermogravimetric Analysis

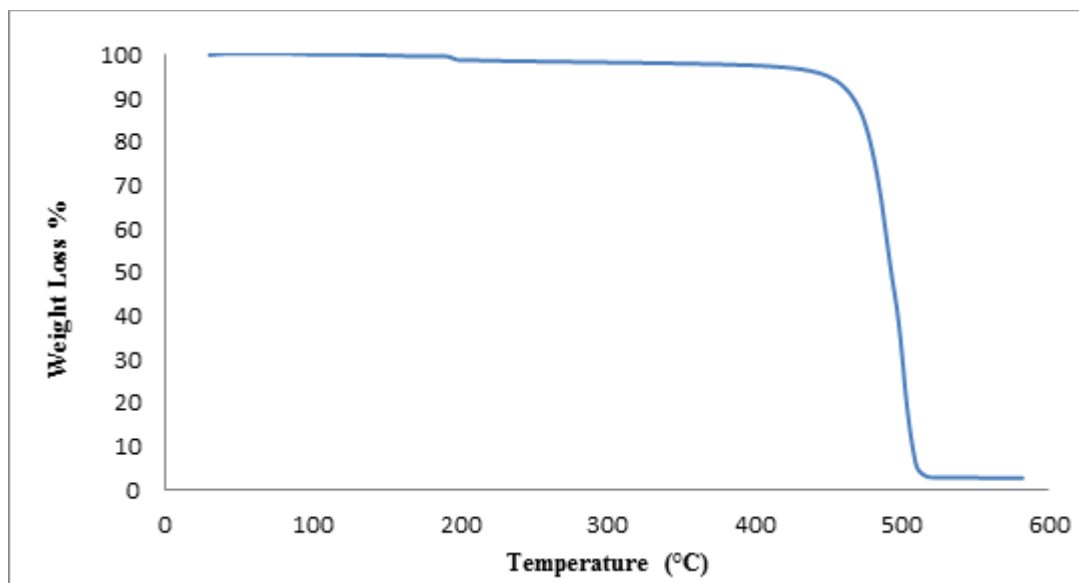
(a) Raw Biochar



(b) Unfilled HDPE



(c) HDPE/1.0 BC**(d) HDPE/2.5 BC**

(e) HDPE/5.0 BC**(f) HDPE/10 BC**