

EFFECT OF OIL PALM EFB-BIOCHAR ON PROPERTIES OF PP/EVA COMPOSITES

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Abstract

In recent years, the race for producing biodegradable products has increased tremendously. Different approaches have been attempted to utilise biomass as filler for the production of composites. In this work, biochar from oil palm empty fruit bunch fibre (EFB) was used as reinforcing filler. The biochar was produced by pyrolysis of EFB at 700°C under nitrogen environment. Later, the biochar was added in different ratios up to 40 wt% in PP/EVA/MAPP blend using internal mixer Brabender PL200 twin-screw extruder. The composition ratio of EVA and MAPP was kept constant to 20 wt% and 5wt% respectively. Effects of biochar on the mechanical and thermal properties of the composite were investigated. Results reveal that the addition of 30 wt% biochar enhances thermal properties whilst having no detrimental effect on any mechanical properties. Studies on the morphological properties have shown good compatibility between biochar and polymer matrix at moderate addition of MAPP.

Keywords: Biochar, Mechanical, Thermal, EFB.

1. Introduction

Polypropylene (PP) is one of the most widely used petrochemical products. It is a versatile polymer with various applications, both as a structural plastic and also as a fibre. Studies are done to yield the promise of exciting new types of composites with new compositions, which is expected to make significant differences from the neat version of PP that is currently available at present [1].

Abbreviations

EFB	Empty Fruit Bunches
EVA	Ethylene-Vinyl Acetate
MAPP	Maleic Anhydride-Polypropylene
PP	Polypropylene
SEM	Scanning Electron Microscope
TGA	Thermogravimetric Analysis

Malaysia, and surrounding South East Asian countries, generates a large amount of biomass. Empty Fruit Bunches (EFBs), an Oil-Palm mill by-product, are one of those main biomass productions. Oil palm industries generate an abundant amount of biomass, said to be in a range millions of tons per year [2, 3].

Environmental friendly, light weight and low cost have made biocomposites rapidly emerged as the perfect substitute to synthetic composites and traditional materials. Biocomposites have been utilized by automotive industry for several years in the production of non-structural components [4]. The demand is expected to be increased year by year. However, low thermal stability and low mechanical performance are greatly restricted their use to certain extend. Numerous studies have been done in order to improve the mechanical performance and thermal stability of biocomposites.

Pyrolysis is one of the most beneficial conversion processes of biomass materials [5 - 8]. Studies have been broadly converting solid fossil fuels and organic materials [9 - 11]. The quantity of lignocellulosic waste has increased proportionately with increases in oil palm cultivation acreage [12]. Many studies have been conducted to use this renewable resource as a raw material such as in polymer blended composite manufacturing [13 - 20].

Biochar produced at 700°C contains 68% of pure carbon [21, 22]. This temperature for pyrolysis has been proved to be an optimum temperature to yield the most biochar with the highest content of pure carbon. Recently, Shariff et al. [23] recommended EFBs as a suitable feedstock for the production of biochar. This was due to the high fixed carbon content of the biochar prepared from EFBs. Whilst comparing the results to other studies related to EFBs products, a conclusion can be drawn that EFBs have a higher percentage yield of biochar than rice-husks. The aim of this work is to study the feasibility of biochar in preparing the composites for structural applications.

2. Experimental procedure

2.1. Materials and sample preparation

2.1.1. Grinding and sieving of biochars

The dried EFB was obtained from a local supplier. Prior to pyrolysis the EFB were grinded using Ultra Centrifugal Mill ZM 200 with mesh size of 0.2 mm. The ground EBF were later sieved using ELE international laboratory sieve size of 125 micron to obtain a uniform size of the filler. They were then collected and kept in zip plastic bags to prevent any moisture adsorption. The ground EFBs were used to increase the amount of feedstock load per round in pyrolysis process.

2.1.2. Pyrolysis of EFB

It is well known that the various method of activation on the same raw material can yield significantly different characteristics for the carbon content [24]. The pyrolysis was done using a vertical furnace (Kanzen-Tetsu fluidized bed reactor, designed following ASTM A312 standards). During pyrolysis, nitrogen gas with a rate of 10 cm³/min was used to avoid any oxidation of the EFB fibres. The furnace was programmed to increase the temperature by 5°C/min up to a maximum of 700°C and then maintaining it for 3 hrs. After pyrolysis process is completed, the furnace was then cooled down to room temperature before removing the biochar. During the cooling process the nitrogen flow rate was maintained at 10 cm³/min.

2.1.3. Sample preparation and mixing

After the production of biochars, the raw materials were then ready to be dry mixed with polymers. Polypropylene, grade G452 from Propilenas, Ethylene-vinyl acetate and Maleic anhydrid (MAPP) grade of TPW104 from Structol was obtained from SIRIM Sdn. Bhd., Malaysia. 5 wt% of MAPP (based on the PP weight) as a compatibilizer was added to all compositions. The composition of the composites is given in Table 1. The preparation of for each batch was based on 1kg. Additionally, the PP/EVA without the Biochar was used as a control sample.

Table 1. Compounding name tags of different composites.

Sample	Char (wt%)	EVA (wt%)	PP (wt%)
PP1	0	20	80
PP2	10	20	70
PP3	20	20	60
PP4	30	20	50
PP5	40	20	40

2.1.4. Compounding and injection moulding of components

Melt mixing of the raw materials for the preparation of the composites was carried out in an internal mixer Brabender PL200 twin screw extruder at SIRIM Sdn. Bhd., equipped with a pair of roller-type blades. The screw speed was set to 30 RPM. The extruder had three heating zones and the temperatures were set to 170°C (near hopper), 185°C and 190°C (near die) respectively. The extruded filaments were cut into small pellets using a pelletizer. According to the ASTM standards, these pellets were then injection moulded into tensile type 4 and a bar shape for charpy test. The pressure of and temperature of injection moulding was maintained at 8 Bars and 195°C respectively. Figure 1 presents a schematic diagram of this process. At this stage, the specimens were ready to undergo further analysis and studies.

2.2. Thermal analysis

The TGA measurements were carried out using ~7 mg of the composites at a heating rate of 10°C/min from room temperature to 600°C in a N₂ atmosphere, using a thermogravimetric analyser (Mettler Toledo). The TGA was conducted with the composite material placed in high quality nitrogen (99.5% nitrogen, 0.5%

oxygen content) atmosphere with a constant flow rate of 50 mL/min, in order to avoid unwanted oxidation.

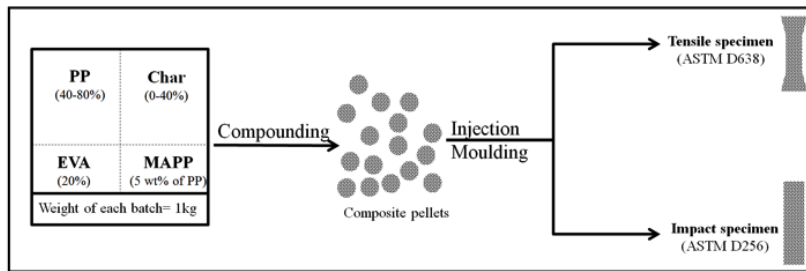


Fig. 1. Schematic diagram of biocomposite preparation stages.

2.3. Mechanical analysis

2.3.1. Tensile strength test

To evaluate the composite mechanical properties, tensile test (also known as tension test) was carried out using the specific ASTM D638 standards. The tensile testing machine LR50KPlus, controlled with a microprocessor, was used to pull the sample from the top end whilst measuring the force required to pull the specimen apart and the extent that the sample stretches before breaking. Data for yield strength, elastic modulus and elongation at break of specimens were digitally obtained at a crosshead speed of 5 mm/min, with gauge length of 12.5 mm (± 0.5 mm) and thickness of 3.3 mm. Seven specimens were tested and at least five replicate specimens were presented as an average of tested specimens.

2.3.2. Impact strength test

In order to determine the response of specimens to sudden impact, the procedure of Charpy impact test had been utilized. This involved performing a striking of a fixed sample of composite with a pendulum, utilizing a measured amount of force. The sample specimens had been notched following ASTM D256 (Izod impact test), located directly behind the point of impact. This notch is required to provide an area of stress concentration for the test. Seven specimens were tested and at least five replicate specimens were presented as an average of tested specimens.

2.4. Morphological studies

The samples were cryo fractured by soaking them into liquid nitrogen for 2 minutes. The fractured edges were studied at different magnification using scanning electron microscope (Model FEI Quanta 400F) under a voltage of 20 kV.

3. Results and Discussion

3.1. Thermal analysis results

As also observed by Xiao et al. [1], while the volatiles leave the biochars at high temperature, the carbon walls become stronger and more stable and as a result the pyrolysis has been done at 700°C which has brought a good thermal stability to the carbons at that temperature. This stability was observed through TGA results.

During the TGA test, there was less weight loss in the composites with higher content of biochars (Fig. 2.). This could be referred to the stability of carbon structure in polymer matrix.

Through the work done by Jia et al. [25] addition of various fillers with different shapes, particle size and different sources into the epoxy matrix has resulted in different microstructures and has brought different effects on the properties of the polymer composites. As found by Clemons [26], compatibilizers such as maleated polyethylene (MAPE) and maleated polypropylene (MAPP) play an important role in improving the compatibility and bonding strength between hydrophilic wood flour and hydrophobic thermoplastics. Filler is known as an inert substance that gives little effect to the properties of the plastic, alongside lowering the costs.

Figure 2 depicts a comparison between samples at a temperature of 465°C. This point was found suitable for comparison, as PP1 had lost about 54% of its weight. In comparison, lower thermal stability is observed for the sample PP1 which could be related to the EVA content. Therefore, EVA could be as an additive to increase the weight loss of PP at high temperatures, which could be useful for applications where recyclability of composite is a priority/desirable characteristic. On the other hand, at the same temperature, PP1 experienced roughly 54% of weight loss whilst PP5 had the highest amount of filler, which was subjected to only 34% of weight loss. The decrease in weight loss can be observed at PP2, PP3, PP4, and PP5 where they all contain filler, resulting in a decrease of weight loss; this could be due to the addition of biochars and the property of the filler. This could be useful when the composites are being used at high temperatures and need to maintain their structure such as food containers, especially those meant to be dishwasher safe. In summary, it is observed that PP5, containing the highest amount of fillers, had the highest thermal stability which can be either a benefit or a drawback, depending on its desired uses.

The extent of heat conductivity properties achieved from different compositions can either be a positive or negative characteristic, depending on the situation and applications. Therefore, if the composite is going to be used as a base material of a container and its purpose is to keep the contents warm, it is suggested to use biochars at the maximum amount of 40%. On the other hand, where heat transfer is needed for cooling of the content, less biochar amount is recommended, so the heat transfer through the surrounding atmosphere is achieved with lower resistance.

According to the composites thermal behaviours through the works done by Li et al. [27], composites are either endothermic (absorbing the energy from the surrounding atmosphere) or release the energy in the form of heat which are called exothermic. Regarding the results achieved through TGA test, the composites have shown an endothermic behaviour, which is due to the need of energy for decomposition of composites.

Biochar has been known highly recalcitrant against decomposition and moreover regarding the achieved heat stability of composites in this investigation, with the idea of recyclability of composites. Less biochar usage is suggested, so less energy will be required for decomposition, with the idea of recycling. As a result, the uppermost addition of 20% of biochar is recommended, and as mentioned earlier, more than this amount provides higher decomposition resistant to the composite. Overall it can be believed that by using lower amount of biochar, in addition of improving the recyclability of composites, softer composite and better moulding properties can be achieved.

With the idea of helping the green world and using less petrochemical materials, in addition of enhancing the recyclability of composites, recycled PP can be a potential feed material in this composition.

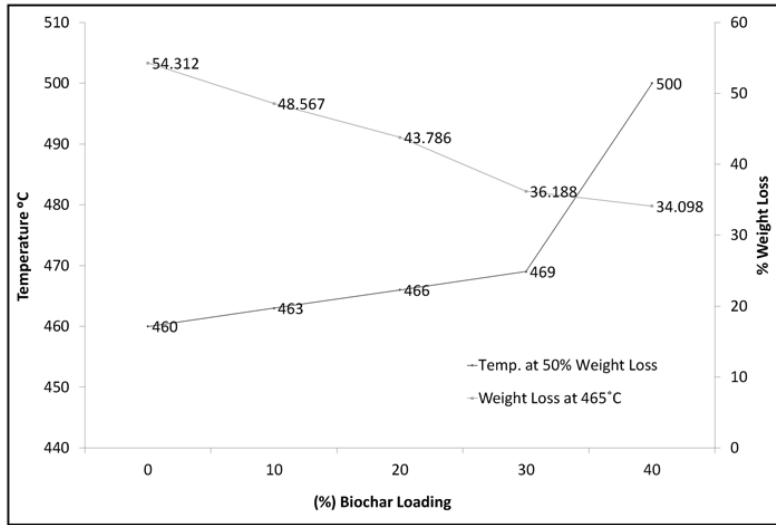


Fig. 2. Temperature and weight loss percentage comparison of prepared composites.

3.2. Tensile modulus

Modulus (stiffness) is another basic property of composites; the primary intention of filler incorporation is usually to increase the stiffness of the resultant material. However, Fig. 3 shows a complete opposite behaviour. The modulus of pure PP is about 700 MPa and with the addition of 20 wt% EVA the modulus declined sharply. This is expected, because PP and EVA form a totally immiscible blend and the blend will have a modulus to which both polymers contribute equally. Moreover, a further decrease in the modulus was experienced with increasing biochar content.

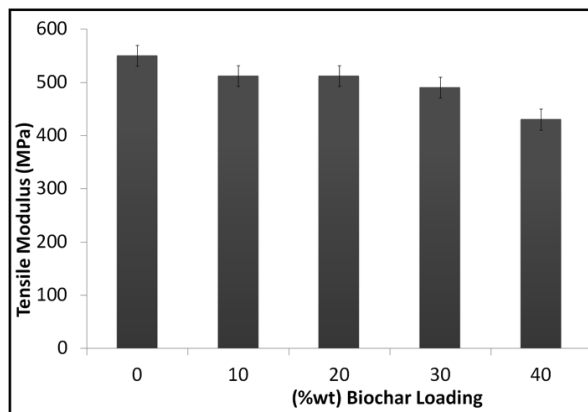


Fig. 3. Effect of biochar on the tensile modulus of PP composites.

This is probably the result of biochar particles physical bonding with the EVA phase (Fig. 6). Although the biochar has a greater affinity for EVA, and seems to preferably locate itself inside the EVA phase, there will not be enough EVA in the blends with high biochar contents, and as a result a fair amount of biochar particles may locate themselves at the EVA-PP interface. The modulus of these composites will therefore decrease because of the weak interaction between biochar and PP. Moreover, it is evident at higher biochar loading low compatibility between the hydrophilic biochar and hydrophobic PP reduced the modulus significantly.

3.3. Impact strength

Figure 4 depicts impact strength of the biochar composite. The addition of EVA clearly improved the impact strength of the blend. This initial improvement is due to the ability of EVA to act as an impact modifier [28]. Similar observations on EVA as an impact modifier were reported by McEvoy et al. [29] and Martins et al. [30]. Moreover, with addition up to 40 wt% of the biochar the impact strength slightly improved. This behaviour could be attributed to continuity of EVA phase in the PP matrix and adhesion of biochar with PP matrix, which tends to have improved energy absorption.

For the composite to be tough and to have high impact strength, there should be a mechanism for dissipating the absorbed energy throughout the volume of the material. If the energy is concentrated in a small volume, the material fails in a brittle manner, and the impact strength is low.

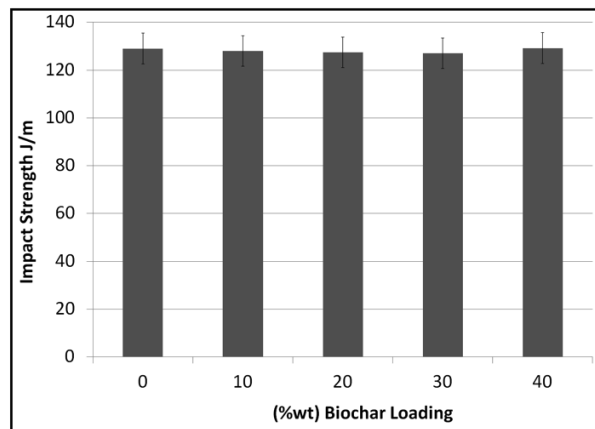


Fig. 4. Effect of biochar on the impact strength of PP composites.

3.4. Morphological results

Whilst using the SEM machine, as mentioned earlier, there had been three magnifications used to obtain a clear view of composites morphology. With the magnification of 1200X, a brief change in structure of composite can be clearly seen. Following the studies done earlier, addition of impact modifier brings circular morphology to the structure, as illustrated in Fig. 5. (white arrows). The

biochars have a porous structure and since the pores are in micron size, they are called macropores (according to IUPAC nomenclature), which were clearly observed in SEM pictures of PP2 to PP5 (Fig. 6).

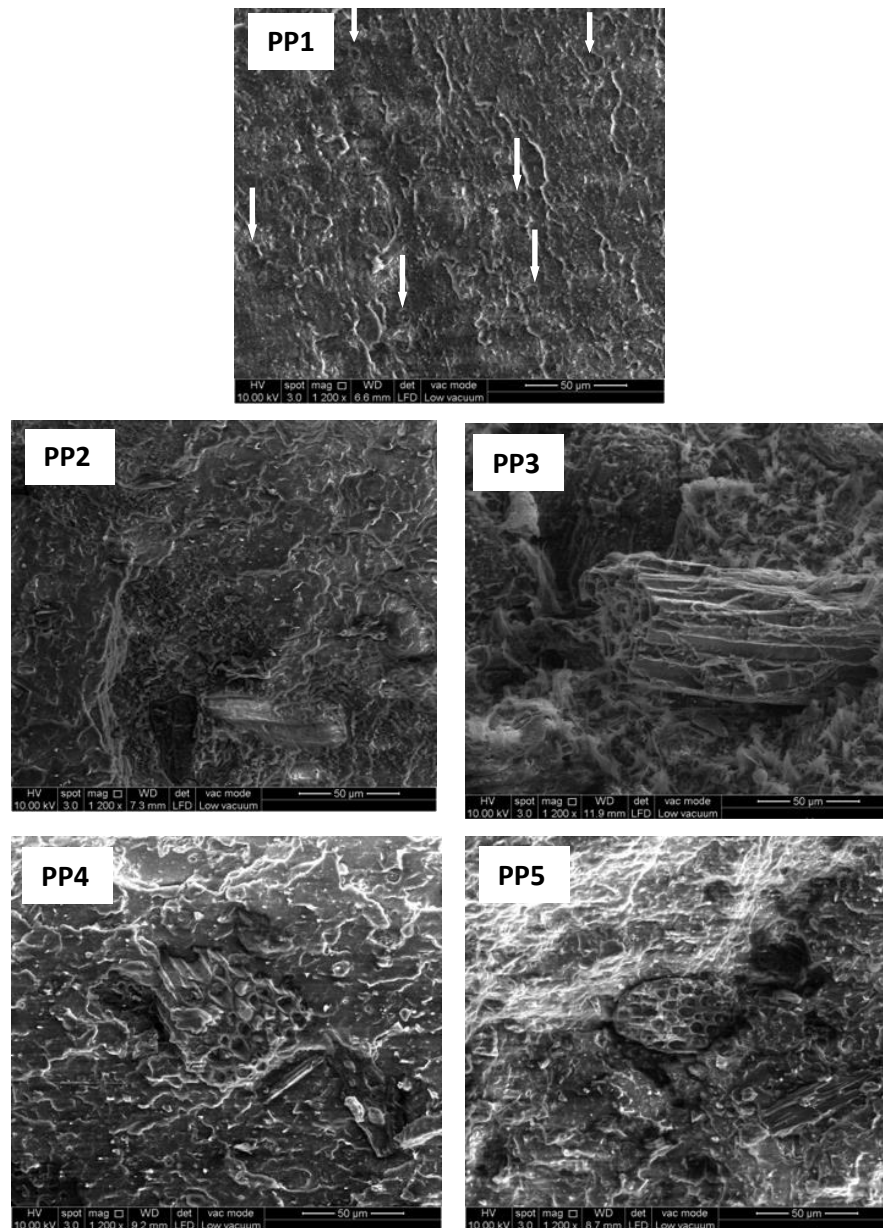


Fig. 5. SEM images of PP1-PP5 tensile test specimens (1200X magnification).

The biochars appeared to have a porous structure and as observed, the grafting is also present inside the pores, in a way that the polymers have settled inside the pores and have filled the hollow pores (Fig. 6.). This has resulted in a stronger composite structure, as seen in the mechanical properties. It was observed that the biochars haven't had any role in changing the morphology of the composites.

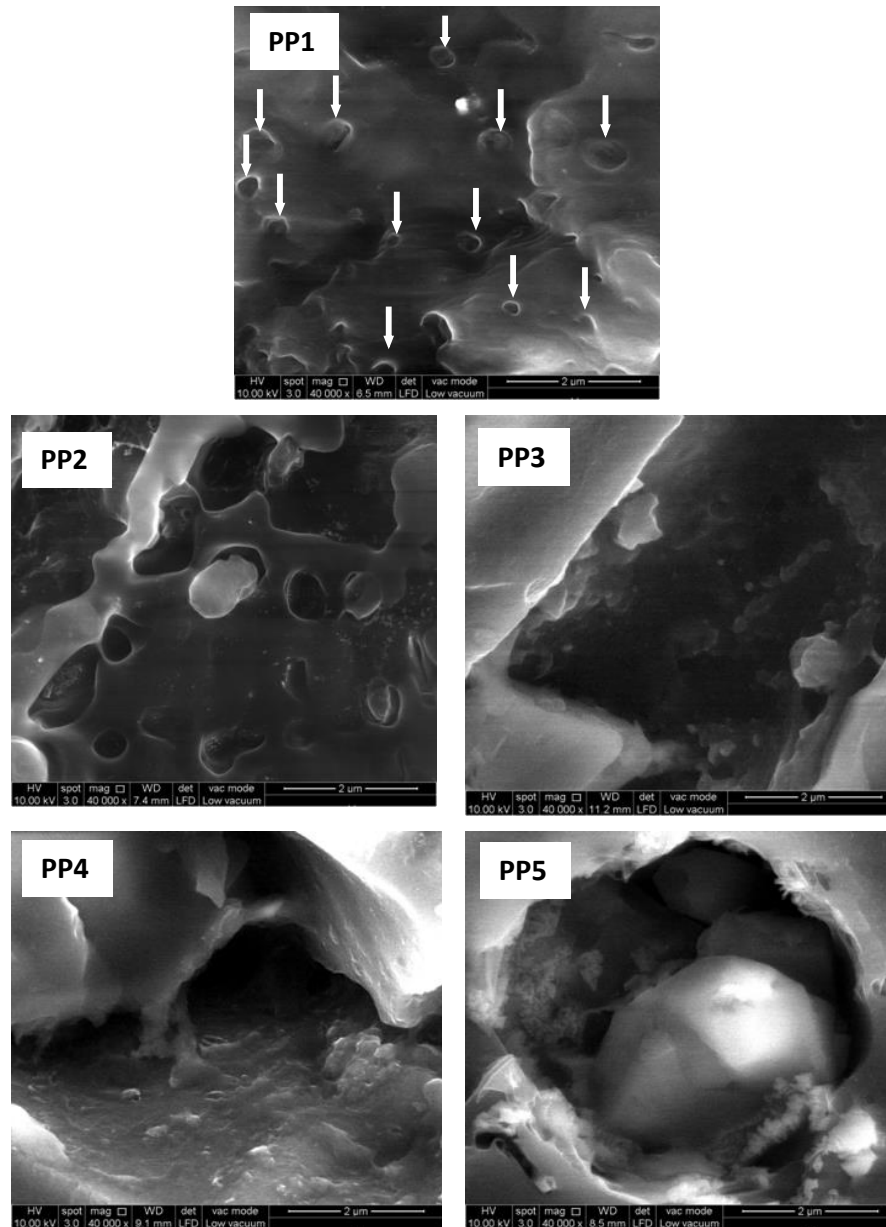


Fig. 6. SEM images of PP1-PP5 tensile test specimens (40000X magnification).

From PP1 to PP5, the amount of PP decreases as the amount of bio-char increases. The increase in impact properties can be linked to the structure of composites being enhanced by the settling of polymers inside the biochars.

The tensile properties decreased throughout all samples respectively and this can be directly linked to the addition of biochar and EVA, which has been also concluded by Shariff et al. [23]. The SEM results in this investigation showed that the pyrolysis process made the carbon walls very thin, since a notable amount of volatiles was discharged. Contrary to this, it has made the carbons to become more stable, which has helped with the enhancement of thermal stability with a reduction in tensile strength. In addition of filling the gaps within the components, it can also be known as an additive, as there has been a good compatibility between bio-chars and polymers due to the porous structure.

4. Conclusion

Polypropylene has been investigated as to whether the bio-char derived from empty oil palm fruit bunches (EFBs) can enhance its thermal and mechanical properties. According to the results, it can be concluded that for purposes of higher thermal conductivity, addition of lower amount of additive is recommended and vice versa for a lower heat transfer. Using a lower amount of bio-char lowers the energy required for sequestration of compound, which leads to a better recyclability property.

Concluding from the mechanical analysis, EVA was identified as an affective impact modifier for pure PP. PP4 can be introduced for the applications where the material is going to be under impact forces, since it can supply a better condition comparing to the neat PP, whilst saving the environment by using less petrochemical materials. Ultimately, PP4 incorporated with 30% of bio-char showed to have the best impact resistance, as well as having the optimum thermal stability. This conclusion approves that the optimum bio-char level for enhancing thermal properties without unacceptable deterioration of mechanical characteristics is 30%.

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