Effect of empty fruit bunches microcrystalline cellulose (MCC) on the thermal, mechanical and morphological properties of biodegradable poly (lactic acid) (PLA) and polybutylene adipate terephthalate (PBAT) composites

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Abstract
Nowadays, awareness of the environment is rising among society. Thus, more researches on the utilization of biodegradable polymer as an alternative to non-biodegradable polymers have been published. Among various biopolymers, Poly (lactic acid) (PLA) and polybutylene adipate terephthalate (PBAT) have received a lot of attention because they can be processed using most of the conventional polymer processing methods. PLA is high in strength and modulus, but it is brittle while PBAT is flexible and tough. Thus, PBAT is a good candidate for the toughing of PLA. But when the PLA is blending with PBAT, a certain strength of PLA may be affected. Hence, the reinforcement material is required to improve weakened strength. In this study, PLA was blended with PBAT at various ratios (PLA: PBAT = 90: 10, 80: 20, 70: 30) with a melt-blending method. The PLA/PBAT blends at a blend ratio of 80: 20, exhibited optimum mechanical performance. Then, PLA/PBAT blends at a blend ratio of 80: 20 was reinforced with different content of EFB-MCC (1 wt%, 3 wt% and 5 wt%) using an internal mixer. The PLA/PBAT blends reinforced with EFB-MCC composites were produced using the compression moulding method. The mechanical, thermal and morphology properties of the composites were investigated. The impact strength of PLA/PBAT blend after addition of both C-MCC and EFB-MCC up to 5 wt% was reduced. The morphological observations from SEM proved the occurrence of the MCC agglomeration in PLA/PBAT blend. DSC results showed trivial changes between the Tg and Tm of PLA/PBAT blend with PLA/PBAT blend reinforced with both types of MCC. TGA results demonstrated that the PLA/PBAT blend reinforced with EFB-MCC has better thermal stability compared to C-MCC. However, further research is needed to improve the interfacial properties of the immiscible PLA/PBAT by compatibilization and enhance the properties of the MCC reinforced PLA/PBAT blend composites.

1. Introduction

Due to the increased demand for plastic usage in our daily life, plastic pollution is a serious issue in our environment. According to research by (Sherman et al 2015), the plastic pollution in the ocean already reached a very high level of concentration which is about 580,000 pieces per km². Thus, bio-based or cellulose-based composites have been growth and become popular in the market because these products are environmentally friendly and it can reduce the rate of pollution globally (Peças et al 2018). Another reason that bio-composites are highly recommended in the current market is due to its bio-degradable properties and can be recycled (Kumar et al 2018). According to reported work from literature (Johnson et al 2017) (Mitra 2014), biocomposites material can also be known as ‘green’ material due to its biodegradable properties.
Poly (lactic acid) (PLA) is one of the commonly used biodegradable polymers. It was first discovered in 1932 by Carothers and only able to produce a low molecular weight of PLA by heating lactic acid under vacuum condition. The high-molecular weight PLA that combine with polyglycolic acid (PGA) as stitching material was sold under the name Vicryl in US in 1974 (Jamshidian et al 2010). It is also considered as a thermoplastic that with high strength, high modulus polymer which can be derived from renewable resources such as corn starch, sugarcane, cassava toots, chips or starch. PLA is a material that good in tensile strength and high modulus, but it has its weakness of the brittleness and heat resistance that cause by slow crystallization. To overcome this weakness, PLA can be blend with others biopolymer such as polybutylene adipate terephthalate (PBAT) to improve the strengths such as impact strength (Hongdilokkul et al 2015) (Jiang et al 2006).

Polybutylene adipate terephthalate (PBAT) is also a well-known biodegradable plastic that synthesized from petroleum-based monomer (Muthuraj et al 2017). It is a flexible material and has a high elongation at break. PBAT has been widely used in blown film and membrane products (Weng et al 2013). Due to its high toughness and biodegradability, it is very suitable as the material to toughening PLA (Kumar et al 2018). PBAT cannot use on its own due to the shortcoming’s properties such as high cost, low heat resistance, and low stiffness (Muthuraj et al 2017). (Yang et al 2010) studied the compatibility, crystallization and tensile properties of PLA/PBAT blends in different proportions produced by melt-blending. The results showed that PBAT effectively improves the impact resistance of the PLA. However, after blending PLA with PBAT, several researchers reported that the impact strength will increase but the tensile strength will decrease compared to pure PLA (Al-Itry et al 2012) (Jiang et al 2006). Thus, the reinforcement is required to improve the shortcomings of PLA/PBAT blends.

Microcrystalline cellulose (MCC) is a naturally occurring substance obtained from the purified and partially depolymerised cellulose. It has a high potential to be used in several different areas such as pharmaceutical, cosmetic, food and polymer composites industries. In the powder form, it can be utilized as a binder and filler particularly as a reinforcement agent in the polymer composites industry (Haafiz et al 2013). In the previous study, Haafiz et al 2013 have successfully isolated the MCC from oil palm empty fruit bunches (EFB-MCC) fiber-total chlorine free (TCF) pulp using acid hydrolysis method. They investigated the potential of the EFB-MCC as reinforcement in pure PLA and found that the tensile strength (Haafiz et al 2013) of pure PLA has improved. Other researchers also have demonstrated that reinforcement of MCC in the polymers improve the crystallinity and storage modulus (Murphy and Collins (2018)) and However, limited research works have been published on the reinforcement of EFB-MCC in PLA/PBAT blends. It is interesting to investigate the potential of EFB-MCC to be used as reinforcement in PLA/PBAT blend as PLA normally blended with other biopolymers, especially PBAT to improve the functionality of PLA in many applications especially for packaging application.

Therefore, the main objective of this research is to investigate the effect of EFB-MCC on the mechanical, thermal and morphology properties of the PLA/PBAT blends. The PLA/PBAT blends: 90 wt% PLA: 10 wt% PBAT, 80 wt% PLA: 20 wt% PBAT and 70 wt% PLA: 30 wt% PBAT was prepared by using an internal mixer. Blends of 80 wt% PLA: 20 wt% PBAT was then reinforced with various EFB-MCC content (1 wt%, 3 wt% and 5 wt%). The thermal, mechanical, and morphology properties of the composites were also tested.

2. Materials and methodology

2.1. Materials
PLA, Ingeo ™ Biopolymer 2003D manufactured by NatureWorks, USA, was obtained from Innovative Pultrusion Sdn Bhd, Negeri Sembilan, Malaysia. Polybutylene adipate terephthalate, PBAT (Ecoflex C1200), was supplied by BASF, Malaysia. MCC from oil palm empty fruit bunches (EFB-MCC) was prepared by using acid hydrolysis method according to the method by (Nasution et al 2017) and (Haafiz et al 2016). The particle size for EFB-MCC form EFB is in the range of 32 μm-75 μm. Commercial MCC will be used as a control. Commercial MCC Avicel® PH-101 with a particle size of 50 μm was supplied by Sigma-Aldrich.

2.2. PLA/PBAT blends preparation
PLA and PBAT were dried at 70 °C in a vacuum oven for 24 h before use. All the samples were prepared in a LABTECH twin screw extruder at screw speed of 60 rpm and the temperature range of 150 °C and 180 °C. Then, the blends were cut into pellets using the LABTECH strand pelletizer. Afterward, the pellets were compression moulded into a 3 cm thick sheets at 175 °C and 10 MPa for 13 min. The hot compression moulded samples were subsequently cooled down with room temperature compression plates under a pressure of 10 MPa. The compositions of the PLA/PBAT blends are as follows: 90/10, 80/20, 70/30 (weight ratio). The compression-moulded samples were then used for further testing and characterizations. Seven specimens have been tested for the mechanical characterizations. At this stage, only one composition of PLA/PBAT blends was be selected based on the mechanical properties, thermal and morphological analysis for further study and the selected composition of PLA/PBAT blend was reinforced with MCC. The weight ratio of PLA to PBAT is fixed at 80/20
in the blends. The mixing ratio of PLA and PBAT is fixed because the PLA/PBAT (80/20) blends showed balanced and promising properties as per discussion in section 3.1.

2.3. PLA/PBAT/MCC composites preparation
Prior to the compounding of PLA/PBAT blends with EFB-MCC, PLA/PBAT pellets were dried in a vacuum oven for 24 h at 70 °C and MCC were oven dried for 24 h at 40 °C. PLA/PBAT/EFB-MCC composites were prepared by melt-mixing PLA, PBAT and EFB-MCC by using a batch process of internal mixer (Extruder Torque Rheometer Mixer by HAAKE) at 180 °C for about 5 min total mixing time for each formulation at a rotor speed of about 40 rpm. The formulations of PLA/PBAT/MCC were prepared according to table 1.

The PLA/PBAT/MCC compounding was then compression moulded at a temperature of 175 °C and 10 MPa for 13 min. The hot compression molded samples were subsequently cooled down with room temperature compression plates under a pressure of 10 MPa.

2.4. Characterizations
2.4.1. Mechanical properties
2.4.1.1. Flexural test
A flexural test, Instron model 5582 universal tester was used to and conducted as per ASTM D790. Seven samples were cut according to the standard specification and the samples were loaded in three-point flexural with the recommendation span to depth ratio of 16:1. The testing was operated at a crosshead speed according to the standard.

2.4.1.2. Impact test
Impact test was conducted according to ASTM D256 using Izod GOTECH impact tester model GT-7045-MDL. The impact resistance of the composite was determined in vertical notched test samples according to the standard using a pendulum impact tester. The impact velocity used was 3.46 m s$^{-1}$ with hammer weight 1 Joule.

2.4.2. Morphological analysis

2.4.2.1. Scanning electron microscopy (SEM)
SEM (Quanta FEG 650 model) was used to study the morphology of samples and the fracture surfaces of specimens. The surfaces were coated with a thin gold layer before observation.

2.4.3. Thermal properties

2.4.3.1. Differential scanning electron (DSC)
DSC analysis was performed using Perkin-Elmer model DSC 6 to measure the glass transition temperature ($T_g$), melting temperature ($T_m$), and crystallization temperature ($T_c$) in an open aluminum pan under a nitrogen atmosphere at a 45 ml min$^{-1}$ flow rate in a heating range and rate of 5 °C min$^{-1}$. For monitoring DSC, the weight of the sample of ~10 mg were first heated from 25–250 °C and kept isothermal for 2 min to erase previous thermal history, then cooled to 25 °C with a cooling rate of 20 °C min$^{-1}$ and reheated again to 250 °C with the same heating rate to monitor calorimetric properties.

| Sample | Weight of PLA (wt%) | Weight of PBAT (wt%) | Commercial-MCC (Control) | EFB-MCC |
|--------|---------------------|---------------------|--------------------------|---------|
| 1      | 0                   | 0                   | 0                        | 0       |
| 2      | 1                   | —                   | 1                        | —       |
| 3      | 3                   | —                   | 3                        | —       |
| 4      | 80                  | 20                  | 5                        | —       |
| 5      | —                   | 1                   | 1                        | 1       |
| 6      | —                   | 3                   | 3                        | 1       |
| 7      | —                   | 5                   | 5                        | 1       |
2.4.3.2. Thermogravimetry analysis (TGA)

The thermal and degradation stability of the composite was analysed using TGA Model 2050 (TA Instrument, New Castle, DE) in an aluminum pan under a nitrogen atmosphere with a heating rate 10 °C min⁻¹ and the temperature range was scanned from 30–800 °C with a sample weight of ~10 mg. Then, the percentage of weight loss and the thermal stability of the compounds were estimated in accordance to METTLER. Degradation temperatures were determined from the DTG thermograms as the peak maximum.

3. Results and discussion

3.1. PLA/PBAT blends properties

3.1.1. Mechanical properties

3.1.1.1. Flexural properties

The results in figure 1 indicate that the flexural strength of pure PLA decreased with the addition of PBAT. The flexural modulus of PLA gradually reduced with the increased of PBAT amount. Similar observations can be seen for flexural modulus. The flexural modulus of the PLA/PBAT blends drops from 2400 MPa to 2038 MPa and 1927 MPa, respectively with increasing PBAT loading from 10 to 30 wt% as compared to pure PLA. The reduction in both flexural strength and modulus of PLA/PBAT blends was expected because PBAT has lower flexural strength and modulus than that of PLA as can be seen in figure 1. The results also in agreement with the finding from (Mohapatra et al (2014a)) and (Jiang et al 2006). (Jiang et al 2006) stated that the PBAT phase can act as stress concentrators in the blends due to the huge different elasticity of pure PLA and PBAT. PBAT also known as immiscible with PLA (Arruda et al 2015) that can also lead to poor interaction between both polymers and affecting their flexural properties.

3.1.1.2. Impact properties

Figure 2 demonstrates the impact strength of pure PLA, pure PBAT and PLA/PBAT blends of 10–30 wt% PBAT contents. The impact strength of PBAT shows no value because the samples were not broken during the impact test. Similar results can be seen from (Hongdilokkul et al 2015). The results shown in figure 2 indicate that the impact strength increased by about 53% and 394% with the addition of 10 wt% and 20 wt% PBAT, respectively. Thus, it can be concluded that the addition of PBAT into PLA can significantly improve the impact strength of PLA. In addition, the presence of PBAT reduced the brittleness characteristic of PLA, which was evident from an increase in impact strength. Figure 2 also displays that there is a sharp increase in the impact strength of PLA/PBAT blends when the content of PBAT is up to 20 wt%. This occurrence is an indication of brittle-to-tough transition as also reported by (Ren et al 2010). Further addition of PBAT up to 30 wt% still enhanced the impact strength of pure PLA about 352% as compared to pure PLA, however slightly lower as compared to impact strength exhibited by PLA/PBAT blend with 20 wt% PBAT content. According to (Jiang et al 2006) (Mohapatra et al 2014b), crazing, cavitation, shear banding, crack bridging, and shear yielding have been identified as main energy dissipation processes involved in the impact fracture of toughened polymer systems. The cavitation effect for PLA blends with 10 wt%, 20 wt% and 30 wt% PBAT content can be clearly seen from the scanning electron microscope images (SEM) in figures 3(a)–(c), respectively. The details of those phenomena will be discussed further in morphology analysis (section 3.1.2).

Figure 1. Flexural properties of pure PLA, pure PBAT, PLA/PBAT blends of 10%–30% PBAT contents.
3.1.2. Morphological analysis

3.1.2.1. Scanning electron microscopy (SEM)

Figures 3 (a)–(c) show SEM images of the PLA/PBAT blends samples with varying PBAT contents from 10–30 wt% PBAT content. In the two-phase system, PBAT dispersed in PLA matrix as round-shaped PBAT particles as can be seen in figures 3 (a)–(c). The cross-section images shown in figures 3 (a)–(c) also illustrate the presence of cavitation caused by debonding, which is a typical effect of a toughened system. Normally, the debonding of the round-shaped PBAT particles from the PLA matrix under tensile stress may cause oval cavities and these cavities were formed at the interface between the PLA matrix and PBAT. Debonding of the spherical inclusions of PBAT was clearly observed, suggesting there was very little adhesion between the two phases (Farsetti et al 2019). Since PBAT has different elastic properties compared to PLA matrix, its particles served as stress concentrators under tensile stress. The voids caused by debonding altered the stress state in the PLA matrix surrounding the voids, and triaxial tension was locally released and shear yielding was allowed. In the debonding progress, PLA matrix strands between PBAT particles deformed more easily to achieve the shear yielding (Ren et al 2010).

Figure 2: Impact strength of pure PLA, pure PBAT and PLA/PBAT blends with varying PBAT contents.

Figure 3. SEM micrographs of fracture surface of PLA/PBAT blends with varying PBAT contents (a) 10 wt% PBAT, (b) 20 wt% PBAT and (c) 30 wt% PBAT.
In Figure 3(a), the size of PBAT particles and cavities for PLA blend with 10 wt% PBAT are bigger than that of PBAT particle sizes and cavities of PLA blends with 20 wt% and 30 wt% PBAT as shown in Figures 3(b) and (c), respectively. The difference in the particle and cavity sizes might be one of the factors that affect the impact strength of the PLA/PBAT blends. Besides, the distance between the particles also essential. (Deng et al 2018) has reported that when PBAT content less than 20 wt%, the PBAT disperses in PLA as droplets as can be seen in Figure 3(a). However, when the PBAT content more than 20 wt%, PBAT and PLA form a co-continuous phase. Figure 3(b) and 3(c) indicate that the distance between particles is closer, thus will likely form co-continuous phase. The sample at the composition of 20/80 PLA/PBAT has a fine structure with the PBAT well dispersed in the PLA as also displayed by (Deng et al 2018). They have predicted that a co-continuous phase structure should be formed at a PBAT concentration of 19 wt%. Figure 3(b) shows a typical of that of two interpenetrating phases, thereby giving credence to the co-continuous phase prediction. The impact strength of PLA blend begun to reduce with the addition of 30 wt% PBAT might be due to the particle and cavity sizes of PBAT became irregular as shown in figure 3(c), thus could be affecting the co-continuous phase structure. Therefore, the blends ratio of 80/20 PLA/PBAT can be indicated as the beginning point of inversion for the present PLA/PBAT blends system.

3.1.3. Thermal Properties

3.1.3.1. Differential scanning calorimetry (DSC)

Figure 4 displays the second heating DSC curves of pure PLA, pure PBAT and PLA/PBAT blends with varying PBAT contents. The second heating curves were chosen to remove previous thermal history and to make Tg clearer and more obvious as stated by (Jiang et al 2006, Gao and Qiang 2017). From the DSC curves in figure 4, Tg of PBAT was absent due to Tg of PBAT was reported at −37 °C (Signori et al 2015)(Carbonell-Verdu et al 2018). DSC test in the current study was conducted at a temperature between 25–250 °C, thus the Tg of PBAT cannot be detected. Figure 4 also shows that PBAT has a wide Tm peak unlike PLA. This is because PBAT is a random copolymer, thus it is not able to crystallize to a significant degree (Shahlari and Lee (2008)). The Tm peak of PLA shows the appearance of two peaks (melting temperature) and this might be due to the possibility of two different crystalline structures which are composed of α′ and α types for PLA as similar reported by (Fehri et al 2016)(Kmetty et al 2018)(Quero et al 2012)(Jiang et al 2006, Zhang et al 2012, Arruda et al 2015). (Fehri et al 2016) (Kmetty et al 2018) provided the explanation that the first peak refered to as α′-crystal type which fused at lower temperature correspond to the melting of thinner crystals and the second peak refered to as α-crystal type which fused at higher temperature correspond to the melting of more stable crystals. The addition of PBAT into PLA results in multiple Tm of PLA. As an example, at 10 wt% PBAT of PLA/PBAT blends samples, the Tm peaks are 127, 148 and 151 °C where Tm at 127 °C and 151 °C were referred to PBAT and PLA, respectively. As (Zhang et al 2012) and (Schick 2009) reported that double or multiple melting endothermic peaks often result from the melting of crystals are either of different stability (dual morphology mechanism) or the melting re-crystallization and re-melting process (reorganization mechanism).
PLA and PBAT are semi-crystalline polymers thus their mechanical properties of PLA/PBAT blends are strongly dependent on their crystallization behaviour. DSC heating curves from figure 4 display a decreasing temperature of cold crystallization exotherm of PLA/PBAT blends with the increasing amount of PBAT into PLA than pure PLA indicate that the addition of PBAT enhanced the crystalline ability of PLA as also reported by (Jiang et al 2006) (Teamsinsungvon et al 2013) and (Arruda et al 2015). Figure 4 shows that the addition of PBAT contents into PLA result in sharper crystallization peak however, at 20 wt% PBAT contents of PLA/PBAT blend their crystallization peak are wider and weaker compared to 10 wt% and 30 wt% PBAT. This suggested that the addition of 20 wt% PBAT contents has an influence on crystallization of PLA. Similar result reported by (Ren et al 2010).

The DSC curve clearly shows two individual melting peaks of PLA with the addition of PBAT compared to melting peaks of pure PLA. (Jiang et al 2006) stated that the peaks at higher temperature correspond to the shoulder of the pure PLA while the lower peaks correspond to the presence of a new crystalline structure induced by PBAT. (Ibrahim and Kadum 2010) stated that the appearance single peak of $T_g$ has been used as an indicator to averm the state of miscibility of the polymer blend. Figure 4 and table 2 shows slight change in a $T_g$ of PLA with the addition of PBAT which corresponds to significant improvement of compatibilization between the immiscible PLA and PBAT. However, PLA and PBAT cannot be considered as thermodynamically compatible even though there is only one peak of $T_g$ shows at figure 4 since the test was conducted at a temperature between 25 to 250 °C. Thus the state of miscibility of the PLA/PBAT blends cannot be concluded based on $T_g$ value. Moreover, $T_g$ of PLA moves toward higher values and not towards the $T_g$ of PBAT which is lower than PLA indicated that both PLA and PBAT lacks of miscibility. The $T_m$ (see figure 4) peak of PLA/PBAT blends are sharper with varying PBAT contents from 10–30 wt% suggest that the addition of PBAT to PLA has an influence on the crystallization of PLA. However, all PLA/PBAT blends samples showed two distinct $T_m$ relative to the PLA and PBAT phases (see table 2). This indicated that the formed PLA/PBAT blends are not thermodynamically miscible. Similar results were reported by (Signori et al 2015) regarding PLA/PBAT blends containing 75 wt% of PLA.

The degree of crystallinity $X_c$ (%) of PLA was calculated by dividing the $\Delta H_m$ with $\Delta H_m^o$, where $\Delta H_m$ is the melting enthalpy (J/g) of the sample, $\Delta H_m^o$ is the melting enthalpy of the 100% crystalline PLA (93.7 J g$^{-1}$) (Kmetty et al 2018) and (Fehri et al 2016).

### Table 2. $T_g$, $T_m$, of pure PLA and PBAT, and PLA/PBAT blends with varying PBAT contents.

| Sample       | $T_g$ (°C) | $T_m$ (°C) | $T_c$ (°C) | $\Delta H_m (\text{J g}^{-1})$ | $X_c$ (%) |
|--------------|-----------|-----------|-----------|-------------------------------|-----------|
| Pure PLA     | 116.06    | 146.16    | —         | 31.00                         | 33.08     |
| Pure PBAT    | —         | 120.12    | —         | —                             | —         |
| 10 wt% PBAT  | 104.03    | 143.48    | 150.89    | 21.08                         | 22.49     |
| 20 wt% PBAT  | 111.16    | 145.48    | 151.52    | 14.43                         | 15.40     |
| 30 wt% PBAT  | 98.27     | 142.80    | 152.20    | 19.83                         | 21.16     |

3.1.3.2. Thermogravimetry analysis (TGA)

Figures 5(a) and (b) displays TGA and DTG curves of pure PLA, PBAT and PLA/PBAT blends, respectively. As shown in the figure 5(a), both pure PLA and pure PBAT exhibit single step degradation around 341.82 °C and 385.99 °C respectively. Thus pure PBAT possessed better thermal stability than pure PLA. Meanwhile, PLA/PBAT blends with varying PBAT contents take place in multiple degradation step and their initial degradation temperature are before pure PLA and PBAT. Basically, PLA in the blends decomposes at the first step meanwhile PBAT decomposes at the second degradation step. The initial degradation temperature of 10 wt%, 20 wt% and 30 wt% PBAT are 277.84 °C, 286.84 °C and 271.98 °C respectively. That is their initial degradation temperature of the PLA/PBAT blends slightly increases with increasing the addition of PBAT contents indicate that the PLA/PBAT blends have a good improvement in its thermal stability. However, their thermal stability is not comparable to pure PLA and pure PBAT. This might be due to the incompatibility of the immiscible PLA and PBAT in an agreement with the DSC result (see figure 4) and SEM result (see figure 3).

Figure 5(a) depicts that 20 wt% PBAT contents of PLA/PBAT blends had the highest decomposition temperature compared to 10 wt% and 30 wt% PBAT contents.

The derivative thermogravimetric (DTG) curves from figure 5(b) shows that PLA/PBAT blends take place in multiple degradation step. The 10 wt% and 20 wt% PBAT of PLA/PBAT blends degraded in two degradation step. The first and second step degradation attributed to the degradation of PLA and PBAT respectively.
3.2. PLA/PBAT/MCC composite properties

In this section, the properties of PLA/PBAT (80/20) blend reinforced with MCC were discussed. The mixing ratio of PLA and PBAT is fixed because the PLA/PBAT (80/20) blends showed balanced and promising properties as per discussion in section 3.1.

3.2.1. Mechanical properties

3.2.1.1. Flexural Properties

Figure 6 shows the flexural strength and flexural modulus of pure PLA, pure PBAT, PLA/PBAT blends of 80 wt% PLA and 20 wt% PBAT and PLA/PBAT/MCC composites.

From figure 6, it indicates that the addition of both commercial MCC (C-MCC) and MCC from EFB (EFB-MCC) lead to the reduction in flexural strength of PLA/PBAT blend. This could be related to poor bonding between the MCC and the PLA/PBAT blend matrix because PLA and PBAT are hydrophobic; MCC is hydrophilic. However, the flexural modulus of PLA/PBAT blend was increased from 2038 MPa to 2583 MPa with the incorporation of 1 wt% C-MCC loading. The addition of more C-MCC loading into PLA/PBAT blend up to 3 wt% and 5 wt% reduced its flexural modulus. In contrast, the addition of 1 wt% EFB-MCC results in a
decreased of flexural modulus of PLA/PBAT blend to 677 MPa. Nevertheless, the addition of 3 wt% EFB-MCC into PLA/PBAT blend improved the flexural modulus to 2274 MPa with a slightly decreased with the addition of EFB-MCC up to 5 wt%. The irregular trend of flexural modulus most likely caused by aggregation of both types of MCC in PLA/PBAT due to Van der Waal’s forces and the presence of void or air bubbles after the fabrication that affect the strength of the composites due to stress transfer to the filler that lead to inefficient load bearing entity (Haafiz et al 2013). Thus, the results contradict with the theory where the flexural modulus was expected to increase with the increasing amount of MCC content. This is because the stiffness of PLA/PBAT was predicted to increase with the incorporation of high stiffness of MCC.

### 3.2.1.2. Impact Properties

The impact strength of the composites is usually depending on the amount of reinforced material added and types of testing used whether the sample is notched or unnotched. Figure 7 shows the results of impact strength obtained from the notched Izod impact testing.

The impact strength of PBAT shows no value because the samples were not broken during the impact test as mentioned in figure 2. Based on figure 7, the results show that the PLA is toughed by blending with PBAT. This is because of the outstanding properties of PBAT in terms of softness and ductility. In both types of MCC, it shows the same trend that when the content of MCC increased from 1 wt% to 3 wt%, the impact strength will be
increased; while, from 3 wt% to 5 wt% the impact strength will be decreased. This is proven that both types MCC are comparable as reinforcement material for PLA/PBAT composites.

The impact strength dropped after added 5 wt% of both types of MCC. This is because 5 wt% is already beyond the optimum level of the MCC content. Too much MCC content in the formulation of composites will lead to weak bonding of matrix and reinforcement due to the aggregation of MCC is easy to occur.

3.2.2. Morphological Analysis

3.2.2.1. Scanning Electron Microscopy (SEM)

To study the failure mechanisms and the interaction between matrix and reinforcement, SEM of the cross-sectional surface of the composites’ specimens was observed. Most of the mechanical properties depend on the interaction between matrix and reinforcement material. SEM of the fractured cross-sectional surfaces of the composites was shown in figure 8.

Figure 8(a) shows the SEM of the fractured cross-sectional surface of 20 wt% PBAT of PLA/PBAT blends as selected from 3.1 section. It shows that the PLA and PBAT are not chemically mixed but physically mixed since the round-shaped of PBAT still can be figured out by SEM (see figure 8(a)). This is because PLA/PBAT blends might be either immiscible or partially miscible due to the weak interfacial adhesion between both polymers (Teaminsungyon et al 2013) and (Hongdilokkul et al 2015). Similar observation also shown in figures 8(b)–(g) after the addition of MCC. However, the appearance of the PBAT round-shaped are hardly seen in figures 8(b)–(g) compared to PLA/PBAT blends in figure 8(a).

In figures 8(b)–(g), the composites structures showing that MCC still remains in aggregates form (red circle in the figure 8) and not evenly much distributed in the composites after fabrication. The aggregations of MCC may be due to the incompatibility of the hydrophilic polar MCC with the less polar PLA/PBAT matrix and the MCC is poorly dispersed in the composites; hence, the aggregation of MCC is easily formed in the composites. This probable aggregation and uneven distribution of MCC may leads to numerous voids formation at matrix-filler interaction. This might be the reason why the mechanical properties of PLA/PBAT blend reinforced with C-MCC result in poor properties with the increasing addition of C-MCC (see figure 6). This result is in agreement with (Haafiz et al 2016).

Figures 8(b), (d) (e) and (g), it clearly shows that there are spaces in between the MCC and matrix of PLA/PBAT blends for both PLA/PBAT blends with 1 wt% and 5 wt% C-MCC and EFB-MCC. This might be due to the incompatibility between MCC and PLA/PBAT blends. MCC may absorb moisture content from the environment before undergoes the fabrication process. Not only that, it is also might be due to the pulled out of MCC during the impact testing.

In figures 8(b), (c) and (f), (g), there are clearly showed there is an uneven surface on the fracture surface. This is considered as the ductile fracture that usually formed when composites mixed with small particle materials such as MCC (Gao and Qiang 2017). In addition, the fractured cross-sectional surface of figures 8(d), (e) and (g) could be considered as ductile fracture because the fibrils still can be seen from the fracture surface. By compared figures 8(f) and (g); figure 8(g) showed a more uneven surface than figure 8(f). This can be explained as more MCC added will form more ductile fracture in the composites (Gao and Qiang 2017).

3.2.3. Thermal properties

3.2.3.1. Differential scanning calorimetry (DSC)

Melting behaviours of composites investigated by using DSC are shown in figure 9. The melting temperature ($T_m$), glass transition temperatures ($T_g$) and heat of fusion ($\Delta H_m$) for the composites were determined by the DSC thermograms second heating and is summarised as shown in table 3.

According to previous research, the transition glass temperature ($T_g$) of pure PLA is about 57°C–58°C. The results determined by DSC shows that the $T_g$ decreased when PLA blends with PBAT. According to the research by (Carbonell-Verdu et al 2018), the $T_g$ of PBAT is not shown in the DSC system due to the $T_g$ of PBAT is below room temperature. This might be the reason that $T_g$ of PLA will drop after blending with PBAT. Also, after added MCC in the formula, most of the composites had a negligible dropped in $T_g$ compared to PLA/PBAT blends. This can be described as a weak interfacial adhesion due to poor compatibility between the matrices and the fillers in agreement with (Tao et al 2017).

For the melting temperature ($T_m$), from the previous research on PLA-MCC composites (Abdulkhani et al 2015), it showed that $T_m$ slightly affected after MCC is added. The trend also can be found in this PLA/PBAT/MCC composite research. Most of the composites with C-MCC slightly decreased and most of the composites with EFB-MCC slightly increased in $T_m$. Thus, the results are still considered as comparable on both MCC due to less effect of addition MCC toward the melting temperature of the composites. The melting temperature of 1 wt% EFB-MCC slightly decrease might be due to a negative effect on the mobility of PLA/PBAT blends chains.
which hindering the crystallization process. The melting temperature peak is slowly increased with more addition of EFB-MCC and sample with 3 wt% EFB-MCC displays the highest melting temperature peak compared to PLA/PBAT blends and PLA/PBAT blends with the use of C-MCC. The increasing melting temperature indicated the enhanced crystalline ability of PLA/PBAT blends also as reported by (Murphy and Collins (2018)). Further evidence on the thermal stability of PLA/PBAT blends with the addition of EFB-MCC is given in the TGA analysis in figure 10 which will be discussed in detail in the next section.

From the figure 9, the cold crystallization temperature peak of PLA/PBAT blends become sharper and slightly shifted to lower temperature with the addition of 1 wt% and 5 wt% EFB-MCC when compared to PLA/PBAT blends. This indicates that the crystallization occurs faster with cellulose as a nucleating agent for

**Figure 8.** SEM fractured cross section of (a) PLA/PBAT blends and PLA/PBAT/MCC composites with varying MCC contents and sources (b) 1 wt% C-MCC, (c) 3 wt% C-MCC, (d) 5 wt% C-MCC, (e) 1 wt% EFB-MCC, (f) 3 wt% EFB-MCC, (g) 5 wt% EFB-MCC.
PLA/PBAT blends crystallization. This is an agreement with what was reported previously by Murphy and Collins (2018). However, for a sample containing 3 wt% EFB-MCC it can be seen that cold crystallization temperature peaks become broad and move slightly to higher temperature indicating an increase in crystallinity.

3 wt% EFB-MCC in PLA/PBAT/EFB-MCC composites shows an improvement in agreement with the mechanical testing in 3.2.1.

3.2.3. Thermogravimetric analysis (TGA)

Thermal stabilities of the PLA/PBAT blends and PLA/PBAT/MCC composites were investigated by using thermogravimetry analysis (TGA). The thermal degradation of polymer and polymer composite occurs when the heat is applied. This will lead the composites’ material to experience major uncoverable changes in physical and chemical properties. It will influence the chemical compositions and physical parameters such as chain conformation, molecular weight, cross-linking, etc (Ray & Cooney, 2018). Figure 10 shows the TGA curves and DTG curves for all the composites. The TGA and DTG curve of PLA/PBAT blends and PLA/PBAT/EFB-MCC exhibited similar decomposition patterns of a two-step degradation process presented by two peaks as displayed in figure 10. Figure 10 shows that the initial degradation temperature of PLA/PBAT blend reinforced with 1 wt%, 3 wt% and 5 wt% of C-MCC are 300.68 °C, 319.30 °C to 319.66 °C, respectively. These temperatures are slightly higher compared to PLA/PBAT blend initial temperature which is 312.14 °C except for 1 wt% C-MCC. This demonstrates that the addition of C-MCC increases the thermal stability of the PLA/PBAT blend. On the other hand, figure 10 indicates that the initial degradation temperature of PLA/PBAT blends composites reinforced with 1 wt%, 3 wt%, 5 wt% of EFB-MCC are 332.59 °C, 330.44 °C, 358.32 °C, respectively. These temperature are greater than PLA/PBAT blend and PLA/PBAT blends reinforced with C-MCC composite. This shows that the reinforcement of EFB-MCC to PLA/PBAT blends have better thermal stability than C-MCC.

According to the research by Azubuike and Okhamafe (2012), the peak temperature of C-MCC from Avicel is about 280 °C which means it is lower than EFB-MCC (317.86 °C). This might be the reason of PLA/PBAT blend reinforced with C-MCC and EFB-MCC had a different property in their thermal degradation. This phenomenon proved that the origin of the MCC obtained affect the properties of its thermal stability. (Haafiz et al 2013) found that thermal stability of PLA was increased after 1 wt% and 3 wt% EFB-MCC was added into the PLA. However, they found that the addition of 5 wt% MCC into PLA reduced the thermal stability of the PLA.

Table 3. Tg and Tm of PLA/PBAT blend and PLA/PBAT blend with varying C-MCC and EFB-MCC.

| Samples                        | Glass transition temperature (Tg) (°C) | Melting temperature (Tm) (°C) |
|-------------------------------|--------------------------------------|------------------------------|
| PLA/PBAT blend                | 55.49                                | 147.04                       |
| PLA/PBAT/1 wt% C-MCC          | 54.30                                | 146.10                       |
| PLA/PBAT/3 wt% C-MCC          | 54.67                                | 147.76                       |
| PLA/PBAT/5 wt% C-MCC          | 53.76                                | 145.39                       |
| PLA/PBAT/1 wt% EFB-MCC        | 54.02                                | 146.28                       |
| PLA/PBAT/3 wt% EFB-MCC        | 55.65                                | 149.67                       |
| PLA/PBAT/5 wt% EFB-MCC        | 54.77                                | 148.85                       |
In contrast, in the current study, the thermal stability of PLA/PBAT blend reinforced with 5 wt% EFB-MCC exhibited greater thermal stability as compared to PLA/PBAT blend reinforced with 1 wt% and 3 wt% EFB-MCC. This occurrence indicates that the matrix system also affects the thermal stability of the composite. 

Figure 10. (a) TGA and (b) DTG curves of pure PLA, pure PBAT, PLA/PBAT blends and PLA/PBAT/MCC composites with varying MCC sources and contents.

Table 4. Residues of PLA/PBAT blend, EFB-MCC and PLA/PBAT reinforced with varying MCC contents from different sources.

| Samples                        | Residues at 800 °C (%) |
|--------------------------------|------------------------|
| PLA/PBAT blend                | 0.35                   |
| EFB-MCC                       | 10.44                  |
| PLA/PBAT/1 wt% C-MCC          | 1.10                   |
| PLA/PBAT/3 wt% C-MCC          | 1.28                   |
| PLA/PBAT/5 wt% C-MCC          | 1.29                   |
| PLA/PBAT/1 wt% EFB-MCC        | 1.29                   |
| PLA/PBAT/3 wt% EFB-MCC        | 1.37                   |
| PLA/PBAT/5 wt% EFB-MCC        | 1.51                   |

film. In contrast, in the current study, the thermal stability of PLA/PBAT blend reinforced with 5 wt% EFB-MCC exhibited greater thermal stability as compared to PLA/PBAT blend reinforced with 1 wt% and 3 wt% EFB-MCC. This occurrence indicates that the matrix system also affects the thermal stability of the composite.
film. Figure 10 displays that the initial and final degradation temperatures of pure PBAT are higher compared to pure PLA. This might be the reason of PLA/PBAT blend reinforced with EFB-MCC has better thermal stability than PLA reinforced EFB-MCC reported by (Haafiz et al. 2013). Table 4 displays an increasing amount of char residue with the increasing addition amount of EFB-MCC into PLA/PBAT blends compared to PLA/PBAT blends and PLA/PBAT blends reinforced with EFB-MCC. This is also an agreement with the DSC result shown in figure 9 and as reported by (Haafiz et al. 2013). It is might be due to the presence of a higher amount of crystalline cellulose I from EFB-MCC produced which has an inherently flame resistance property.

4. Conclusion

The biodegradable blends of PLA/PBAT were prepared in a twin screw extruder before being compressed. The PLA/PBAT blends were prepared with varying PBAT contents. Incorporation of PBAT contents up to 20 wt% in PLA improved the ductility, thus increased the impact strength of PLA with only a slight reduction of the flexural strength compared to pure PLA. The SEM micrographs show that 20 wt% PBAT has a fine structure with PBAT well dispersed in PLA. DSC results indicate that the addition of PBAT into PLA able to accelerate and enhance the crystalline ability of PLA which corresponds to significant improvement of compatibilization of immiscible PLA and PBAT. This can be indicated as the beginning point of inversion for the present PLA/PBAT blends. Thus, 20 wt% PBAT has been selected to be reinforced with MCC. The flexural strength of PLA/PBAT blend reinforced with C-MCC and EFB-MCC are lower compared to PLA/PBAT blend due to poor adhesion between both MCC with the PLA and PBAT matrices. While irregular trend of flexural modulus of PLA/PBAT blend reinforced with C-MCC and EFB-MCC are due to agglomeration of MCC in the PLA/PBAT blend system. A better dispersion method is required to reduce the agglomeration effect in composite system. However, the impact strength of PLA/PBAT blend after addition of both C-MCC and EFB-MCC up to 5 wt% was reduced. This is because of a poor dispersion of MCC in PLA/PBAT blend matrix. The morphological observations from SEM proved the occurrence of the MCC agglomeration in PLA/PBAT blend. DSC results showed trivial changes between the $T_g$ and $T_m$ of PLA/PBAT blend with PLA/PBAT blend reinforced with both types of MCC. TGA results demonstrated that the PLA/PBAT blend reinforced with EFB-MCC has better thermal stability compared to C-MCC. The results also proved that the better thermal stability of PBAT played a role for higher thermal stability of PLA/PBAT reinforced with EFB-MCC as compared to PLA reinforced EFB-MCC reported in literature. However, further research is needed to improve the compatibilization between immiscible PLA/PBAT and enhance the properties between the blends and cellulose with the increasing addition of EFB-MCC into PLA/PBAT blends.

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