Characterizations of poly-lactic acid/polypropylene filled with bamboo charcoal powder

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Abstract. In this study, polymer blend was prepared in the ratio of Polypropylene (PP) to Polylactic acid (PLA) of 70:30 by weight. Bamboo charcoal powder (BC), at different loading was added to identify its potential use as filler for the PP/PLA blend. The polymer blend and composites were prepared by using a twin screw extruder. The effects of BC content on the mechanical and thermal properties of the PP/PLA blend were investigated. The results of tensile strength and Izod impact strength show a significant decreased with the addition of BC content. The Young modulus of composites was significantly increased (80%) with the addition of 20 wt.% BC content. The SEM results of composites with 20 wt.% BC filler show a brittle fracture surface. TGA results revealed that, blending PP with PLA cause an increase in thermal stability of PLA. However, the incorporation of 20 wt.% BC has shifted the temperature of initial weight loss of PP/PLA blend towards lower temperature. DSC measurement indicates that the melting temperature (T_m) values of the PP/PLA blend decrease with the addition of 20 wt% BC content, from 169 to 164 °C.

1. Introduction
Blending of Polylactic acid (PLA) with petroleum-based synthetic polymers such as polystyrene (PS), polypropylene (PP) and polyethylene (PE) will be beneficial as synthetic polymers find extensive usage in plastic packaging [1,2]. Many techniques were studied to modify PLA such as copolymerization, the addition of plasticizers, the addition of nucleating agents, and the formation of composites with fibres and nanoparticles [3,4]. The interest in the utilization of biopolymers are associated with the factors of consumer demand for more environmentally sustainable products in order to reduce the use of polymers with high “carbon footprint” of petrochemical origin, particularly in the applications such as packaging, automotive, electrical and electronics industry, etc. [5]. Among them plastics packaging contributes to the highest of landfill. Therefore biodegradable polymer proposed to be the best solution to this environmental problem. PLA is a biodegradable polymer produced from a renewable resource such as extract starch from corn to produce dextrose.

However, PLA is comparatively a brittle and stiff polymer with low deformation at break (low toughness) than other flexible synthetic polymers such as PP or PE. These shortcomings limit the in certain applications where the deformation of plastic under high stress is compulsory [6]. In packaging applications, it is stated that PLA films have better mechanical properties than polyethylene terephthalate (PET), however, the lower glass transition temperature is considered as a disadvantage, especially in applications (e.g. hot packaging) where resistance at high temperature is a requirements
Besides that, cost of PLA is relatively higher; therefore it is not economically feasible to use it alone for daily usage as a packaging material without blending.

Reinforcing of PLA matrix with natural or synthetic fibers and the addition of micro and nanofillers considered as a powerful method to obtain specific end-use characteristics product [8,9]. Study shows that, incorporation of nanofiller into polymer matrix successfully improves the thermal stability of polymer [10]. The improvement in thermal stability due to the clay can hinder the permeability of volatile degradation products out of the materials. The dispersed clay generates a barrier which delays the release of thermal degradation products in comparison with the neat polymer. Therefore it is better if the filler can be replaced with material from the natural source such as bamboo charcoal (BC). The use of fillers from natural filler sources will further reduce the non-degradable component in the polymer composites system. Bamboo charcoal have a unique properties such as uniform composition, high porosity, anti-bacterial, anti-fungal, thermal regulation and odour control. In addition, BC possesses great absorption effect of microbes [11,12]. Walaikorn et al., [12] have studied Chitosan/bamboo charcoal composite films and they found that the tensile strength and Young’s modulus of these composite films were enhanced by the inclusion of modified bamboo charcoal at up to 1 wt%. Li et al., [11] utilize the bamboo charcoal as reinforcing filler of WPC to enhance the mechanical and thermal properties of wood plastic composites (WPC). The aim of this study is to investigate potential used of bio-filler, bamboo charcoal powder (BC) to reinforce the PP/PLA blend. The objective of this study is to examine the effect of BC powder content on the mechanical and thermal properties of the PP/PLA blend prepared by melt-compounding via the twin-screw extruder.

2. Methodology

2.1. Material

The material used for this study were Polylactic acid (PLA) resin, 3001D grade (pellet form) product of NatureWorks LLC, Polypropylene resin (PP), density of 0.95gcm$^{-3}$ and bamboo charcoal (BC) was obtained from Lancang Edible Garden, Malaysia.

2.2. Preparation of PP/PLA composites

The Blending of PP, PLA (70/30) and BC was carried out using the twin screw extruder. Prior to melt blending, all materials were predried at 80°C for 8 hours. The extrudate was then cut by using grinder machine to produce granule form. The(compounded) granule was compressed by using a compression moulding machine to produce plates in order to prepare test specimens. The temperature was set at 200°C for 7 minutes followed by cold press for 5 minutes. The tensile test specimens were prepared using Thermo Haake Mini Jet injection molding.

2.3. Testing and characterization

Tensile measurement was conducted based on the ASTM D638 using a Testometric 500, tensile testing machine with the cross-head speed of 50 mm/min. At least five specimens of each composition were tested for the tensile measurements and the average values were recorded. Samples for Izod impact test were cut from compression moulded sheets. Izod impact measurement was conducted based on the ASTM D256 with a V-notch cut into the samples. The test was conducted using a Ray Ran Izod impact testing machine with 5.5 Joule hammer. The test result was obtained from the average of 10 specimens.

The morphology of polymer composites was examined by scanning electron microscope (SEM) using Hitachi TM3030Plus SEM at an acceleration voltage of 15 kV to evaluate the possible differences in fracture surfaces. Samples for morphological analysis were observed from the tensile-fractured surfaces, which were coated with gold to avoid charging under the electron beam.

Differential scanning calorimetry (DSC) was carried out using a Netzsch DSC 200 F3. The samples were heated from 30 to 250°C at heating rate of 10°C/min, held for 3 min to remove the thermal history. Subsequently, the samples were cooled to 30°C at a cooling rate of 10°C/min and heated again
to 250°C at 10°C/min for the second heating scans. Thermogravimetric Analysis (TGA) was carried out using Netzsch TG209 TGA analyzer. The sample was scanned from 30 to 600°C at a heating rate of 10°C/min.

3. Results
3.1. Mechanical properties
The tensile test was conducted in order to determine the effect of the BC concentration on mechanical properties of PP/PLA blends. It can be seen in figure 1 that, the tensile strength of blend decreased with an increasing BC content from 5 to 20 wt%. The tensile strength decreased by 29.7% from 41.21 MPa for neat PP/PLA (70/30) blend to 28.95 MPa for PP/PLA composites with 5% BC. The results show that the higher the filler content of BC, the lower the tensile strength of the composites. This may arise from the agglomerates of BC particle in PP/PLA-blend composites. However, in figure 2, the Young modulus values of PP/PLA blend increased as the addition of BC filler increased.

The reduction in tensile strength was obvious at the BC content of 10% and above. This may be due to the agglomeration of BC filler. This may also contribute by a weak interface between BC filler and matrix. BC particles may restrict the motion of polymer blend chains and BC particles become unevenly dispersed and form the agglomeration in the composites system.

![Figure 1](image1.png)  ![Figure 2](image2.png)

**Figure 1.** The tensile strength for PP/PLA blend and composites.

**Figure 2.** The Young modulus for the PP/PLA blend and composites.

The results of tensile strain and Izod impact strength for the PP/PLA blend and composites with different BC content are presented in table 1.

| Samples composite | Tensile strain (%) | Impact strength (kJ/m²) |
|-------------------|-------------------|------------------------|
| BC-0%             | 16.60             | 1.76                   |
| BC-5%             | 1.68              | 1.65                   |
| BC-10%            | 0.88              | 1.13                   |
| BC-15%            | 0.92              | 1.10                   |
| BC-20%            | 0.84              | 0.90                   |

As shown in table 1, the reduction trend was observed in both results with an increase of BC content. These indicating that, the BC filler had obvious influence on impact strength of the system. This might be contributed by the brittle nature of the BC filler, thus reducing the ductility of polymer matrix [13]. Besides that, the agglomerations of BC particle in PP/PLA-blend may generate as local stress concentrations in the composites, so that cracks tend to grow and spread and caused failure.
during the impact force. Therefore, the impact strength of composites decreased. The results of this study are contrary to the findings of the study by other researcher [14].

3.2. Thermal properties

Differential scanning calorimetry (DSC) measurements were carried out to investigate the thermal behavior of PP/PLA-BC composites. DSC heating curves of PLA, PP/PLA and the PP/PLA-BC composites are presented in figure 3 and 4 respectively. Thermal properties of these materials such as glass transition temperature (T_g), crystallization temperature (T_c), melting temperature (T_m), are summarize in table 2. The results shows, polymer blending and addition of filler had lowering the T_m as compare to pure PLA. This might be due to PLA continuous phase was disrupted by the filler.

| Sample              | T_g (°C) | First heating T_m(1) (°C) | Second heating T_m(2) (°C) | T_c (°C) |
|---------------------|----------|---------------------------|----------------------------|----------|
| PLA                 | 60.0     | 171.2                     | 154.0/161.4                | -        |
| PP/PLA              | 62.4     | 169.4                     | 161.6                      | 115.3    |
| PP/PLA-BC 5%        | 61.4     | 168.7                     | 160.5                      | 118.1    |
| PP/PLA-BC 20%       | 58.1     | 164.4                     | 157.3                      | 119.2    |

Figure 4 shows the DSC second heating curves of PLA, PP/PLA and the PP/PLA-BC composites. As shown in figure 4, pure PLA exhibits the clear T_g at 48.1 °C, T_c at 105 °C (cold crystallization temperature) and T_m at 171.2 °C. The T_c of PLA phase in the blend and composites disappears, which may be due to the high efficiency nucleating effect from PP for the PLA phase. It was observed that, during the second heating the T_g for pure PLA was shifted to lower temperature from 60 °C to 48.1 °C. T_m for second melting peak also decreased, and shifted to lower temperatures with increasing the BC content. This indicates that the immobilization effect became more dominant.

Figure 4 also shows, there were double melting peaks for the curve of pure PLA. This shows that PLA have two different crystal morphologies. The imperfect crystals of PLA in the samples recrystallize during the first heating process, thus double melting peaks appeared. The peak at lower temperature resulted from the original crystals, while the peak at higher temperature was attributed to the recrystallize ones of the original crystals [15].
DSC cooling curves of PLA, PP/PLA and the PP/PLA-BC composites are shown in figure 5. The results show that, the $T_c$ for polymer blend shifted to increase the $T_c$ but lowering the peak height with the increasing of BC content. The BC had restricted the mobility of the polymer chains. The crystallization peak of PP/PLA blend was very sharp located at 115.3 °C. Meanwhile the cooling curve for pure PLA is not show obvious crystallization peak in the temperature range. This is because the crystallization rate of the pure PLA was very slow at this cooling rate [15].

![DSC cooling curves of PLA, PP/PLA and the PP/PLA-BC composites.](image)

**Figure 5.** DSC cooling curves of PLA, PP/PLA and the PP/PLA-BC composites.

Thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) for PLA, PP/PLA and the PP/PLA-BC composites samples are shown in figure 6 and 7, respectively. The TGA and DTG curves of PLA showed only a single decomposition step. The degradation of the polymer blend and composites shows two degradation steps of mass loss during heating. The first step corresponds to the degradation of PLA and the second steps correspond to degradation of PP.

The results show that, blending of PLA with PP lead to increase of thermal degradation ($T_{d,\text{onset}}$) of PLA. The $T_{d,\text{onset}}$ for PLA was 288.3 °C, whereas $T_{d,\text{onset}}$ of polymer blend was 336.0 °C. However, the addition of BC fillers has decreased the thermal stability of the polymer blend. The polymer composites with 5 wt% BC loading start to decompose at about 312.7 °C. This finding is similar to the findings by Zhu et al. [16] for the HDPE matrix composites. Meanwhile the composites with 20 wt% BC start degraded earlier than the pure PLA. This might be contributed by the poorly dispersed of BC filler in the matrix at higher loading. However, the second decomposition temperature remains unchanged at 50% weight loss ($T_{50}$). Therefore it can be concluded that the presence of BC in the PP/PLA blend significantly changes the decomposition profile of the PP/PLA composites.

TGA results in figure 7 shows, blending of 70 wt.% PP with 30 wt.% PLA increased the thermal stability of PLA but there also no changes in the thermal stability of PP was observed from previous study [17]. The presence of 20 wt.% BC has decreased the initial weight loss of PP component in the polymer blend, $T_{\text{onset}}$ from 445 °C to 432 °C.
3.3. Morphology

Figure 8 shows tensile fractured surface morphology of PP/PLA blend (a) and composites filled with 5% (b) and 20% BC filler (c). The micrographs of tensile fractured surface of the PP/PLA blend showed ductile fracture, evident from rough fracture surface and the presence of longer fibrils and cavitations, indicating matrix deformation. The morphology of undulated fracture surface with the introduction of BC was clearly exhibited in figure 8(b). Meanwhile PP/PLA composites with 20 wt.% BC composites show brittle fracture. This is confirmed by the results of tensile strain and impact strength. It is also noticeable, at low magnification (100x), the composites with 5% BC showed a homogenous system and with 20% BC showed heterogeneous system.

Figure 9(a & b) show the morphology of PP/PLA-BC (5 wt.%). It was found that phase separation occurred. PLA dispersed as small particles in the PP matrix. The tensile force applied to the sample resulted in pulling PLA particles out of the PP matrix and small holes could be observed. At 1k magnification, it is hardly to observe the BC filler in the polymer blend. This indicates that the BC filler was dispersed evenly in the matrix. Meanwhile in figure 9(c) SEM image shows, at 20 wt.% of BC loading the blend has shown a rough surface due to the presence of the BC filler. At higher magnification as shown in figure 9(d), the fracture surface of sample with addition of 20 wt.% of BC to the polymer blend clearly show the structures of the BC fillers. These indicate there are agglomerations of BC filler in the polymers matrix.
Figure 9. SEM image of PP/PLA-BC composites with 5% BC (a & b) and 20% BC (c & d) at the magnification of 300 and 1000 X.

4. Conclusions
In this study, the effects of bamboo charcoal powder (BC) on the tensile, Izod impact and thermal properties of the PP/PLA blends with different amount of BC content were investigated. From the results it was observed that the addition of the 5 to 20 wt.% of BC led to a clear promotion of Young modulus. However, tensile strength, strain and impact properties of PP/PLA-BC composites decrease with increasing the BC content above 5 wt.%. DSC measurement indicated that the melting temperature ($T_m$) values of the PP/PLA blend decrease with increasing of 20 wt% BC content, from 169 to 164 °C. TGA result shows, blending 70 wt.% PP with 30 wt.% PLA cause increased the thermal stability of PLA. However t h e presence of 20 wt.% BC has decreased the initial temperature of weight loss for polymer blend, from 336 °C to 279 °C. SEM image shows, at 20 wt.% of BC loading the blend has shown a rough surface due to the presence of the BC filler. From the tensile strength results, it is suggested that the optimum amount of the BC filler for this polymer blend is 5 wt.%.

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References

[1] Su H Xue J Cai P Li J and Guo S 2015 Structure and oxygen-barrier properties of (linear low-density polyethylene/ethylene–vinyl alcohol copolymer)/linear low-density polyethylene composite films prepared by microlayer coextrusion Journal Appl. Polym. Sci. 132, 27 p. 42211 (1-7).

[2] Ghozali M Sinaga P D B Maranata S and Rohmah E N 2016 Study and development of linear low density polyethylene (LLDPE) and poly lactid acid (PLA) biodegradable compounds using compatibilizer LLDPE-g-MA World Chemical Engineering Journal 1, 2 p. 11-16.

[3] Montes W M C Sánchez G G and Gallardo S G F 2016 Poly-Lactide/exfoliated C30B interactions and influence on thermo-mechanical properties due to artificial weathering Polymers 8, 4 p. 154 (1-14).

[4] Ho M Lau K Wang H and Hui D 2015 Improvement on the properties of polylactic acid (PLA) using bamboo charcoal particles Composites Part B: Engineering 81, p.14-25.

[5] Chen J 2014 Global markets and technologies for bioplastics (BCC Research report PLS050C)

[6] Rasal R M Janorkar A V and Hirt D E 2010 Poly(lactic acid) modifications Prog. Polym. Sci. 35, 3 p. 338-356.

[7] Notta-Cuvié D Denot J Delille R Murariu M Lauro F Raquez J M Bennani B and Dubois P 2014 Tailoring polylactide (PLA) properties for automotive applications: effect of addition of designed additives on main mechanical properties Polym. Test. 36, p. 1-9.

[8] Sommai P-A Jutamas K Weraupon P Rutchanekorn W Narongchai O-C Sorapong P and Hirohiko H 2016 Effect of compatibilizer on PLA/PP blend for injection molding Energy Procedia 89, p. 353-360.

[9] Nalin P Panuwat S Duangduen A and Chiravoot P 2014 Blend of polypropylene/poly(lactic acid) for medical packaging application: physicochemical, thermal, mechanical, and barrier properties Energy Procedia 56, p. 201-210.

[10] Chern C E Nor A I Norhaizlin Z Hidayah A Wan Md Z W Yoon Y T and Cher C T 2013 Enhancement of mechanical and thermal properties of polyactic acid/polycaprolactone blends by hydrophilic nanoclay Indian Journal of Materials Science 2013, p. 1-11.

[11] Li X Lei B L Lin Z Huang L and Tan S 2014 The utilization of bamboo charcoal enhances wood plastic composites with excellent mechanical and thermal properties Materials & Design 53, p. 419-424.

[12] Walaikorn N Nantana J Sireerat C and Siriwan K 2009 Mechanical properties of chitosan/bamboo charcoal composite films made with normal and surface oxidized charcoal Carbohydrate Polymers 78, 3 p. 444-448.

[13] Chen Q Zhang R Wang Y Wen X and Qin D 2016 The effect of bamboo charcoal on water absorption,contact angle and physical-mechanical properties of bamboo/ low density polyethylene composites BioResources 11, 4 p. 9986-10001.

[14] Ho M and Lau K 2014 Enhancement of impact resistance of biodegradable polymer using bamboo charcoal particles Materials Letters 136, p. 122-125.

[15] Bai Z and Dou Q 2015 Melting and crystallization behaviors of poly(lactic acid)/polypropylene blends Proceedings of the 2015 International Conference on Material Science and Application (ICMSA 2015) p. 282-286.

[16] Zhu S Guo Y Chen Y Su N Zhang K and Liu S 2016 Effects of the incorporation of nano-bamboo charcoal on the mechanical properties and thermal behavior of bamboo-plastic composites BioRes 11, 1 p. 2684-2697.

[17] Engku Zawawi E Z Romli A Z Mat Suli S F and Amirrudin M I 2018 The effect of MAPP compatibilizing agent on the mechanical and thermal properties of polypropylene/PLA blends International Journal of Engineering & Technology 7, 14 p. 361-364.