EFFECTS OF BAMBOO CHARCOAL ADDITION ON THE MECHANICAL AND THERMAL PROPERTIES OF POLY(LACTIC ACID)/POLYPROPYLENE BLEND NANOCOMPOSITES

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Abstract. In this research the biodegradable composite was developed by blending of poly (lactic acid) (PLA), synthetic polymer (PP) and hybrid fillers of nanoclay and bamboo charcoal powder (BC). The effects of BC content (3, 6 and 9 % by weight) on the composite properties of PLA/PP nanocomposites were investigated. The matrix was processed by blending PLA/PP in a weight ratio of 75/25 wt.% and reinforced with 3 wt.% nanoclay and BC in the extruder. The tensile strength and strain results were decreased as increasing the BC loading from 3 to 9 wt.%. However, Young's modulus results increased from 983 MPa to 1855 MPa as increasing the BC loading to 9 wt.%. Increasing BC to 9 wt.% also resulting in slightly increased in Izod impact strength to 1.9 kJ/m^2. TGA analysis indicated that incorporation of 9 wt.% BC increased the thermal stability of PLA/PP nanocomposites. From DMA analysis, the storage modulus increased with increasing the BC content. Results also indicate that the glass transition temperature, T_g of the hybrid composites 3 and 6 wt.% BC shifted towards a higher temperature compared to the composites without addition of BC. Morphological observation under TEM shows, there were certain intercalation of the silicate layers for both samples of nanocomposites and hybrid with 3 wt.% BC. SEM analysis shows, the surface roughness was increased as BC loading increased. In conclusion, the results showed that for hybrid composites prepared with an addition of BC content of 3 wt% exhibited the best overall performance.

Keywords: poly(lactic acid), nanoclay, bamboo charcoal powder, dynamic mechanical analysis, thermal properties

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Introduction

Plastic packaging and composites from petrochemical-based polymer, contribute to the highest of the landfill since it is a necessary part of exchanging goods around the world. Due to the concern on the growth in environmental consciousness and unsustainable application of this man-made material, it is very important to find the solution in the production of plastics and their composites. Based on the statistics study by Condor Ferries [1], the industries had produced over 321 million tons of plastic which is will be double by the year of 2034. This pollution will affect the humans and wildlife by numerous chemicals used in the materials of plastics which are known to be carcinogenic tend to interfere with the body's hormone system then tend to affected the reproductive, neurological and immune disorders. Therefore, biodegradable polymer seems to be the best solution to this environmental problem. Poly(lactic acid) (PLA) is a biodegradable polymer produced from a renewable resource such as extract starch from corn to produce dextrose. It is then fermented, transforming into lactic acid. The lactic acid is altered into a polymer by a chemical process called condensation, thus forming long chain molecular compounds into polylactic acid [2]. However, PLA is a comparatively, brittle and stiff polymer with low deformation at break as compare with other flexible synthetic polymers such as polypropylene (PP) or polyethylene (PE).

Meanwhile, polypropylene (PP) is one of the most versatile synthetic thermoplastic polymers which is light in weight with low density which make it suited to be used in various industrial applications [3]. PP also among the type of plastics which has several potential properties such as low heat distortion temperature, flame retardant, transparency and good dimensional stability besides suitable to be used for filling with filler, reinforcing and also blending [4]. Fillers were added in the polymer composites to improve the performance of the composites. Filler can be divided into two types which are synthetic and natural filler. Synthetic filler was widely used in the composites industries [5-6]. Natural filler is gaining attention from industries due to its eco-friendly properties besides being low in weight as compared with synthetic filler. The examples of natural fillers are flax, hemp, jute, kenaf, pineapple, and many others are now quite well known of plant [7]. Bamboo charcoal (BC) is one of the natural fillers which derived from bamboo plant then carbonized to produce black powdered form. The advantages of BC filler are because this material has numerous pores in their structure. Therefore, BC can absorb the volatile chemicals, control the temperature, preventing the growth of bacteria and fungi besides avoiding static electricity build-up which otherwise causes electric shocks in dry conditions [8-10]. Meanwhile, at present nanoclay has gained attention from researchers and is widely used in the industry which acts as a nanofiller in the polymer matrix for the fabrication of nanocomposites [11]. Nanoclay are organophobic but can be changed into organophilic by replacing Na^{+} or Ca^{2+} cations which is content in the galleries with one organic cation such as alkylammonium ions through an ion-exchange reaction [12]. Hybrid composites were the other alternatives in composites industry in order to develop the good properties of composites. The method of blending polymeric materials of plastics matrix with more than one composition of fillers were used in this fabrication of hybrid composites. Several years of ongoing research on the improvement of new hybrid composites containing particles and fibrous shaped fillers, it is still a scientific problem to find a high-performance material with well-defined properties and at the same time to reduce the cost of product [13].

Therefore, in this study fabrication of hybrid composites with the usage of blending biopolymer and synthetic polymer materials reinforced with bio-filler and low loading of nanofiller is expected to contribute to addressing growing environmental issues. In this study, the effect of various concentrations of basio-filler bamboo charcoal (BC) and nanoclay (3 wt.%) in a polymer matrix of PLA/PP blend (75:25 wt.%) was investigated. This blend has bio-disintegration characteristics since PLA is a biodegradable polymer. The composites were melt compounded using an extruder. Mechanical, morphological and thermal testing was carried out to examine the effects of hybrid fillers of BC and nanoclay to PLA/PP blend nanocomposites.

Materials and Methods

Materials and Composites Preparation

Two types of polymers were used in this study. The poly(lactic acid) commercial grade PLA 2003D and the polypropylene resin (PP), with the density of 0.95 gcm^{-3} was manufactured by Lotte Chemical. The filler used were bamboo charcoal powder (BC) (about 3000 mesh in size), was purchased from local supplier and nanoclay (Nanomer, I.44P) manufactured by Nanocor.

To produce green polymers, composites must have a bio-polymer content of more than 50 %. Therefore, the PLA content was used at a higher ratio in this study. The polymer matrix for the composites was prepared from blending of PP and PLA in the ratios of 25 to75 wt.%. In order to produced nanocomposites, the polymer blend was then mixed with 3 wt.% nanoclay. Prior to the mixing, all the materials were dried in the oven to remove the moisture. For the nanocomposites which contained bamboo charcoal filler, amounts of 3, 6 and 9 wt.% BC was added to the nanocomposites. All composites were then melt compounded by using an extruder (Prism TSE 16TC). Table 1 shows the formulations of material used in this preparation of the hybrid nanocomposites. The barrel temperature was set from the feed section to the die head at 180/190/200/210 °C and the screw speed used was 80 rpm. Subsequently, the extrudate was palletized by using a palletizing machine to produce pallet shape materials. The test specimens such as dumbbell shape samples were fabricated using injection molding (Thermo Haake) according to the testing requirement.

Table 1: The formulations of nanocomposites and hybrid composites

Samples	Polyl(actic acid) (PLA, wt.%)	Polypropylene (PP, wt.%)	Nanoclay (NC, wt.%)	Bamboo Charcoal (BC, wt.%)
Matrix	75	25	0	0
N3BC0	75	25	3	0
N3BC3	75	25	3	3
N3BC6	75	25	3	6
N3BC9	75	25	3	9

Mechanical Testing

The tensile properties of hybrid nanocomposites were determined according to ASTM D638 using a Universal Tensile testing machine. Five replicate test specimens were used for each compound. A cross-head speed of 10 mm/min was used for testing. The Izod impact test was conducted by using a Ray Ran Impact tester. The test was performed according to ASTM D256 with a load of energy used 5.5 Joule. The testing was performed at room temperature. Ten specimens were used for each compound.

Dynamic Mechanical Analysis (DMA)

Dynamic Mechanical Analysis used in this study was DMA instrument (Perkin Elmer DMA8000). The test was conducted under the condition of a static force of 10 N and a dynamic force of 8 N. The test was performed by using 3 points bending mode at the temperature range of -40 °C to 140 °C and at the rate of 5 ºC min^{-1}. The sample was prepared with the dimensions of 4 mm thickness and 20 mm length.

Thermal Properties

Thermogravimetric analysis (TGA) of the samples was studied using a TGA (Netzsch TG209) in a nitrogen atmosphere. A mass sample of approximately 10 mg was used. The samples were heated from 25 ℃ to 600 ℃. The composites were tested under nitrogen gas flow at the heating rate of 10 ℃ min^{-1}.

Scanning Electron Microscopy (SEM)

SEM was used to evaluate the morphological properties of the hybrid nanocomposites from PLA/PP blends. The morphology was observed on the tensile fractured surface of the samples. Hitachi TM3030Plus Scanning Electron Microscope was used in this study. The samples were sputtered coating with gold layers in order to avoid charging and white spot on the micrograph.

Transmission Electron Microscopy (TEM)

TEM was among preferred method in study of nanofiller. The samples were cut by an ultra-microtome technique into 60-80 nm thickness. The sample was observed under TEM, (JEM100CX, Nihon Denshi) at the accelerating voltage of 100 kV.

Results and Discussion

Tensile Properties

Tensile properties were studied to investigate the effects of various loading of bamboo charcoal (3, 6 and 9 wt.%) in the nanocomposites of PLA/PP blends reinforced with 3 wt% nanoclay. Table 2 shows the tensile properties and Izod impact strength results of nanocomposites and hybrid nanocomposites. It is shown that nanocomposites of 3 wt.% nanoclay indicate higher tensile strength compare to hybrid nanocomposites. The addition of 3 wt.% of BC in the nanocomposites (N3BC3) has decreased tensile strength to 8.0 % of nanocomposites without BC. For the hybrid nanocomposite system with 3 and 6 wt. % of BC powder shows about the same values of tensile strength among the three hybrid nanocomposites. This was probably due to the good interfacial bonding between BC particles at low loading with the matrices [14]. Increasing the BC loading to 9 wt.% has decreased the tensile strength of hybrid nanocomposites up to 40.9 %. This could be due to the formation of agglomerations in the system of composites at high loading of BC then tend to reduce their strength. As can be seen under SEM observation, the addition of BC increases the surface roughness at tensile fracture. This is because BC is a brittle material, therefore when BC content is too high, so there is insufficient polymer matrix to effectively transmit failure stress to BC filler. Thus, the composite has poor mechanical properties. From a previous study, increase the loading of BC, would increase the tensile strength, but when the loading reached 7.5 % and above the tensile strength will be decreased [15].

Meanwhile for the Young's modulus results, the hybrid nanocomposites with the addition of 9 wt.% of BC (N3/BC9) show the highest modulus which is 1855 MPa. The Young's modulus was increased about 88.6 % as compared to nanocomposites without BC fillers. The trend of Young's modulus seems increased as increasing the loading of bamboo charcoal from 3 to 9 wt.%. This indicates the potential of BC fillers to transmit greater stiffness to PLA/PP blend. The concentration of BC did not affect tensile strength properties. This might be due to poor stress transfer between PLA and BC particles [9]. The elongation results of PLA/PP with 3 wt.% nanoclay shows the highest percentage elongation as compared to the other composites. But for the hybrid nanocomposites, the percentage elongation slightly decreased with increasing the BC concentration up to 2 % for N3BC6 sample. The trend seems decreased when the addition of BC increased to 9 wt.% because BC dispersed unevenly and form agglomeration which leading to induce stress concentration during tensile deformation and breakage [14].

Table 2: The tensile and Izod impact test results of PLA/PP:(75/25) nanocomposites of 3 wt.% nanoclay (N3) with various content of BC filler (hybrid nanocomposites)

Sample	Tensile Strength (MPa)	Young's Modulus (MPa)	Elongation (%)	Impact Strength (kJ/m^2)
PLA75/PP25 (matrix)	47.76 ± 1.16	956.66 ± 24	6.02 ± 0.07	1.71 ± 0.41
N3BC0	46.19 ± 1.18	983.45 ± 34	5.88 ± 0.09	2.83 ±0.52
N3BC3	42.46 ± 0.74	1547.33 ± 42	3.40 ± 0.05	1.58 ± 0.18
N3BC6	42.86 ± 1.51	1751.00 ± 83	3.58 ± 0.07	1.85 ± 0.27
N3BC9	25.31 ± 2.01	1855.33 ± 99	1.97 ± 0.07	1.95 ± 0.33

Impact Strength

The results of impact strength for the PLA/PP blend with 3 wt.% nanoclay as shown Table 2 exhibit the highest impact strength (2.8 kJ/m^2). It also indicates that the hybrid composites with the addition of 9 wt.% BC possessed the highest impact strength 1.9 kJ/m^2 among hybrid composites compositions. Based on a previous study by other researcher, total fracture energy of polymer matrix was increased when the BC loading increased up to 7.5 wt.%. This was due to the increasing BC content having improved the molecular chain self-arranged to a regular way and forming a large crystalline region. Hence increasing resistance towards the crack development [14]. However, in this study it can be observed that the impact strength of nanocomposites of was slightly decreased by addition on 3 wt.% BC and then was gradually increased when the BC loading increased from 3 to 9 wt.% in the hybrid composites. A previous study also showed that the same result when the combinations of two fillers nanoclay and wood flour reduced the impact strength as compared to single filler in composites [16].

Thermogravimetric Analysis (TGA)

The TGA analysis of PLA, matrix (PLA/PP blend), nanocomposites (N3BC0) and hybrid nanocomposites are shown in Figure 1. The results for composites system indicate two degradations steps which the first step (260-360 ºC) belongs to PLA 75 wt.% and the second degradation steps (360-460 ºC) belong to PP at 25 wt.%. The first degradation step where the T_d onset was 339 °C for PLA and 448 °C for PP. It can be observed that the nanocomposite PLA/PP with 3 wt.% nanocalay increased the thermal stability of PLA/PP blend. The presence of silicate clay layers from nanoclay may exhibit the tortuosity phase in the system which delayed the diffusion of volatile decomposition in the nanocomposites [17]. The results also indicate that the inclusion small amount of BC (3 wt.%) decreased the thermal stability of the nanocomposites. However, its gradually increased with increased of the BC content in nanocomposites. The results also indicate the starting and ending temperatures of thermal weight loss of the hybrid nanocomposites developed later than that of pure PLA. In conclusion, for the hybrid nanocomposites of nanoclay and BC fillers, the sample of 9 wt.% BC (N3BC9) was the most thermally stable than the others hybrid nanocomposites.

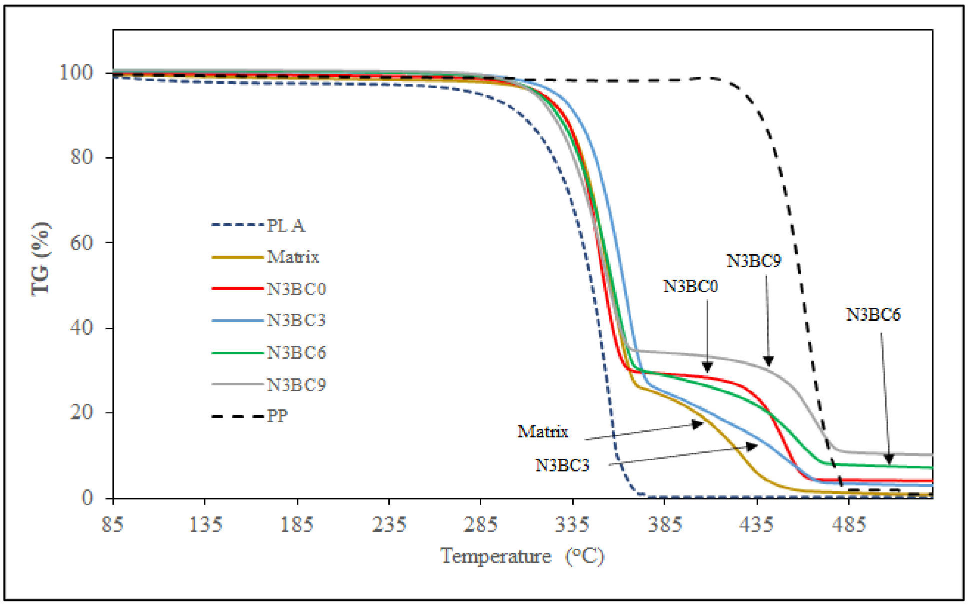

Figure 1: Thermal degradation curves of nanocomposites and the hybrid nanocomposites

Dynamic Thermomechanical Analysis (DMA)

Figure 2 shows DMA plots of storage modulus vs. temperature for PLA/PP blend, nanocomposites and hybrid nanocomposites at different amount of BC. From the analysis it can be observed that the storage modulus increased as the percentage of BC loading increased from 0 to 9 wt.%. The polymer matrix of PLA/PP blend was the lowest of storage modulus. The increased of storage modulus with the addition of BC show that BC contributes to the enhanced rigidity of the nanocomposites at lower temperature below T_g. The results also indicate the glass transition temperature, T_g of the hybrid nanocomposites of 3 and 6 wt.% BC shifted towards a higher temperature as compare to the nanocomposites. The T_g temperature range within 50 to 60 °C, are belongs to PLA (as shows by matrix). Previous study by other researcher indicates that the addition of inorganic filler causes an increased in thermal stability of the PLA matrix [18]. Other study on the effect of BC in PVA matrix indicates that, there was an improvement in their thermal properties as increasing the BC content [19]. This is because the high content of BC particles contributes to higher hardness and rigidity at low temperature. Meanwhile in this study there was no change can be observed in the Tg of 9 wt.% BC hybrid nanocomposites as compare to 3 and 6 wt.% BC content. The distribution of the filler in the matrix, (formation of agglomeration) at higher BC content might influence the mobility of the polymer molecules.

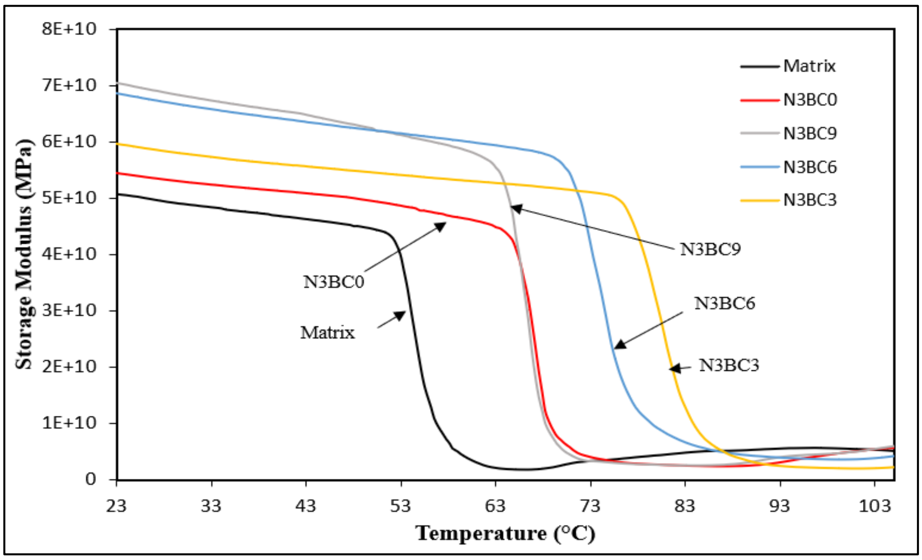

Figure 2: The storage modulus of nanocomposites and hybrid nanocomposites

Transmission Electron Microscopy (TEM)

Figure 3(a) exhibit the TEM image for the PLA/PP blend nanocomposites with 3 wt.% nanoclay. As can be observed in the micrographs, there were an exfoliated platelets of silicate layers exist in the polymer composites and also the partially exfoliated.

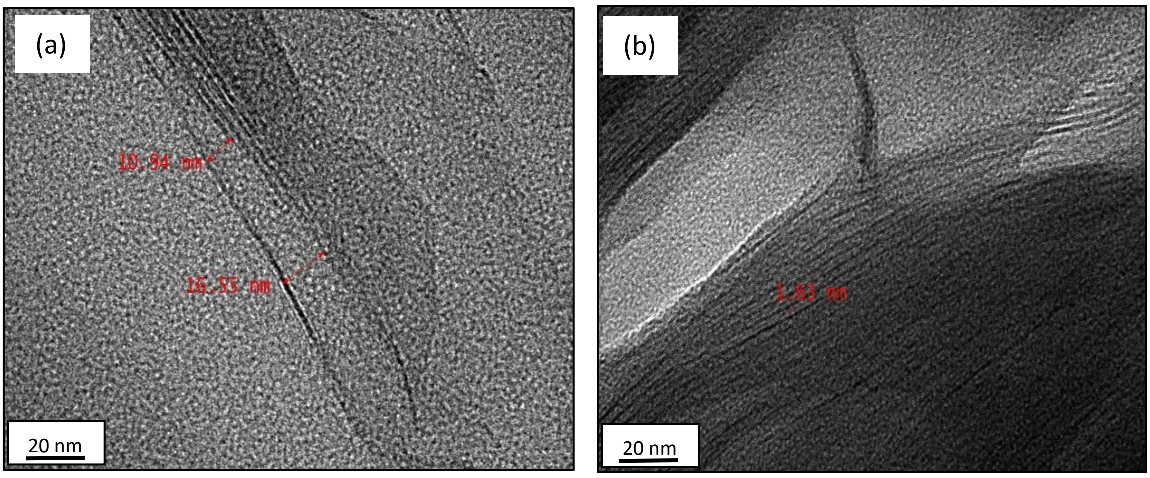

Figure 3: TEM micrographs of (a) PLA/PP with 3 % nanoclay and (b) PLA/PP N3BC3

The light region in the micrographs of TEM was matrix of PLA/PP. A good affinity between the nanoclay and polymer matrix is significant toward to achieved a good spreading of the silicate layers in the polymer matrix which is known as exfoliated structure [20]. It also can be seen that the intercalated structure existed as the clay layers can be observed under

TEM micrograph in Figure 3(b) which contain 3 wt% BC. Intercalated of the nanoclay is mostly observed in Figure 3(b) compared to Figure 3(a). This indicates that nanoclay and BC did not represent good synergistic effect therefore exfoliated structure is hardly seen in the hybrid nanocomposite.

Scanning Electron Microscopy (SEM)

Figure 4(a) shows the tensile test fractured micrographs of nanocomposites for PLA/PP blends with 3 wt.% nanoclay (N3BC0). Figure 4(b) to (d) shows the micrograph of hybrid composites of 3, 6 and 9 wt.% BC (N3BC3, N3BC6 and N3BC9). Based on the micrographs for the samples contain BC filler, it can be clearly observed that the present of bamboo charcoal (indicate as circle in the (b) and (c) micrographs). The surface roughness was clearly increased as the concentration of bamboo charcoal increased. This observation is consistent with the tensile test results, where the addition of BC into the nanocomposite has decreased the tensile strength, especially at 9 wt.% BC content. This is similar to others studies [15,21]. As the loading of bamboo charcoal increased, the distribution of BC particles in the composites system becomes larger and produced more agglomeration [22].

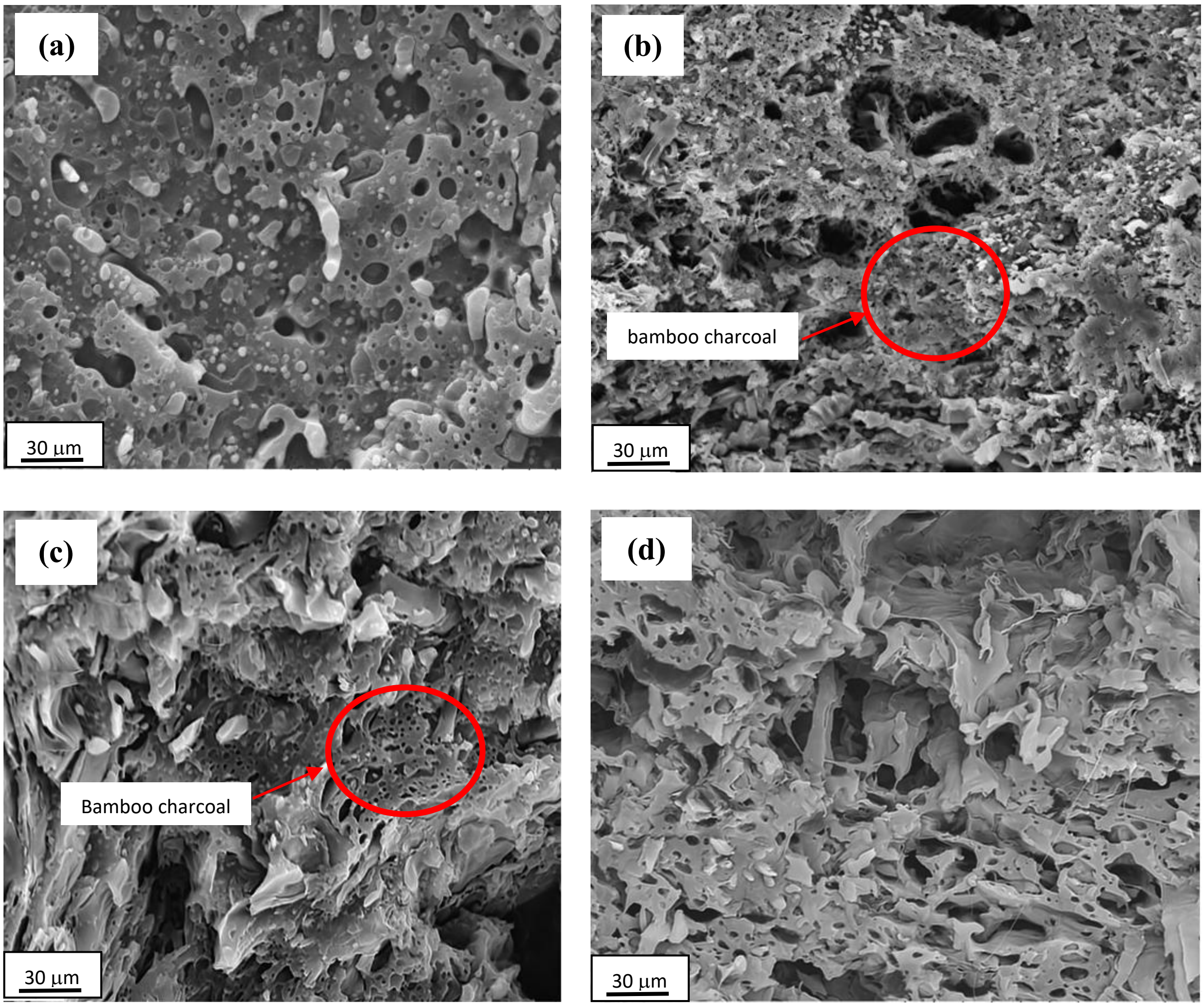

Figure 4: SEM micrographs of PLA75 PP25 nanocomposites (a) and nanocomposites with (b) 3 wt.% BC, (c) 6 wt.% BC and (d) 9 wt.% BC

Conclusions

The results of effect of adding bamboo charcoal on mechanical, thermal and morphological behaviors of PLA/PP nanocomposites was successfully obtained. The PLA/PP blend (75/25 wt.%) with incorporation of nanoclay and bamboo charcoal was successfully compound by melt blending. The addition of different BC concentration had affected the thermal and mechanical behaviors of the nanocomposites. In overall, the mechanical properties of nanocomposites decreased with increasing the BC content. The addition of BC increased stiffness of nanocomposites from 983 to 1855 MPa. The tensile strength decreased from 46 to 25 MPa, meanwhile the elongation at break from 5.9 to 1.9 %, and the impact strength from 2.8 to 1.9 kJ/m^2. This study demonstrates that the BC filler has adverse effect on the tensile strength properties of the PLA/PP nanocomposites. The TGA analysis indicated that the thermal stability of the nanocomposites increased as increasing the BC loading in the PLA/PP nanocomposites. DMA analysis indicated the storage modulus increased with increasing the percentage loading of BC to 9 wt.%. The results also exhibit that the T_g of the hybrid nanocomposites contained of 3 and 6 wt.% BC shifted towards a higher temperature as compare to the nanocomposites. The dark spot was noticed as nanoclay region and the silicate layers can be observed at this region as shown in micrograph under TEM study. Meanwhile under SEM analysis, the surface roughness was increased as BC loading increased. This observation is consistent with the tensile test results, where the addition of BC into the nanocomposite has decreased the tensile strength especially at 9 wt.% BC content. In conclusion, results showed that for hybrid nanocomposites prepared with an addition of BC content of 3 wt% exhibited the best mechanical performance and 9 wt.% BC the best thermal stability performance.

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Author Contributions

All authors contributed toward data analysis, drafting and critically revising the paper and agree to be accountable for all aspects of the work.

Disclosure of Conflict of Interest

The authors have no disclosures to declare.

Compliance with Ethical Standards

The work is compliant with ethical standards.

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