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Effect of Pyrolysis Temperature on Biochar Microstructural Evolution, Physicochemical Characteristics, and Its Influence on Biochar/Polypropylene Composites



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Abstract: Environmental management through effective utilization of biowastes has been a topic of intensive research in recent years. This study examines the effect of pyrolysis temperature on the physical and morphological characteristic of biochar (BC) derived from lignocellulosic wastes. The biochar was prepared by pyrolysing date palm biomass at various temperatures, i.e., 300, 400, 500, 600, and 700 °C. These pyrolysed biochars were then characterized for their carbon content, mineral compositions, chemical functionalities, and morphological structures, for understanding their physicochemical characteristics and microstructural evolution. It was revealed that the pyrolytic condition plays a key role in the formation of biochar microstructure. These biochar samples were then utilized without any further treatments/purifications for their practical application as reinforcement materials for polymer composites. They were blended with a polypropylene matrix by a melt mixing technique followed by injection molding process. The type of biochar was found to significantly affect the composites properties. Differences in microstructure, surface chemistry, and chemical compositions of BCs were observed to be determining factors affecting the compatibility and thermomechanical properties of resulted composites.

Keywords: biochar; environment; lignocellulosic biowaste; pyrolysis; polymer composites; mechanical properties

1. Introduction

Biochar (BC) is a low-cost, carbon-rich material derived from the thermochemical decomposition of lignocellulosic biomass in limited or absence of oxygen. Compared to other types of carbonaceous materials, biochar emerges as a new cost-effective and environmentally friendly carbon material with great potential of application in many different fields. In recent times, there has been a considerable shift in research interest toward the utilization of biochar in various advance applications, such as carbon fuel cells [1–3], energy storage [4–6], and catalysis [5,7–9], along with its traditional uses as an adsorbent and soil amendment agent to promote carbon sequestration [10].

The solid biochar can be obtained from biomass via various thermal decomposition processes such as pyrolysis, combustion, gasification, and liquefaction. Among these processes, pyrolysis is considered

a viable method that can rapidly convert biomass into solid biochar by thermal decomposition. However, the physicochemical properties of biochar are very complex and depend on several factors, like feedstock type, carbonization processes, pyrolysis temperature, heating rate, and residence time. In order to utilize this biochar for further applications; it is desirable to understand the most important pyrolysis indicator such as proximate analysis, i.e., information of moisture, ash content, mineral composition, and carbon contents, as well as ultimate analysis such as C, H, N, S, and O composition; H/C and O/C atomic rations; and surface area.

Polypropylene is a versatile commodity polymer and has excellent processing characteristics that allow it to be converted into film, extrusion, and injection molding parts. In one of the studies, suitable biomass has been attempted to find out the fire susceptibility of biochar-polypropylene composites [11]; similarly, bamboo particles and biochar have been used to reinforce polypropylene (PP) matrix. The mechanical and thermal properties of the composites were reported to improve through the addition of BC [12]. Moreover, biochar was produced from miscanthus grass by two different experimental pyrolysis conditions (i.e., 500 °C and 900 °C), and their physical and chemical properties were evaluated [13]. These biochars were then used to reinforce polypropylene/poly (octane-ethylene) copolymer system. It was reported that higher pyrolysis temperature eliminates the surface functional groups, thereby making it less polar. However, it increases the specific surface area and pore volume. The composite based on this biochar was analyzed by surface morphology (impact facture surface), and shown to exhibit higher impact strength than the lower temperature biochar. This higher impact property was attributed to superior physical interactions affinity of the nonpolar fillers with the nonpolar polymeric chains of matrix [14]. In another study, the same biochar was used for polypropylene composites and its properties were then compared with those of talc based composites. It was reported that biochar-based PP composites have lower density but comparable specific tensile and flexural properties to talc based composites [15].

In our previous work, we used biochar obtained by pyrolysing date palm biomass at relatively higher temperature and used as fillers for the polypropylene. An increase in electrical conductivity and mechanical properties was observed, but a decrease in crystallinity was also observed [16]. However, systematic studies investigating the effect of pyrolysis, specifically at lower temperature on the surface characteristics and physicochemical properties of biochar need to be analyzed in detail. Moreover, it assumed that the polar groups that formed or present on the biochar at lower pyrolysis temperature could help for better adhesion with the selected polymer matrix. It should also be note that all above studies were related to ternary composites system, and much attention has been given to performance of types of biomass used than the biochar itself. In the case of a polymer composite, the biochar used was produced at a relatively higher temperature; compatibilizers were also used. Therefore, this paper investigates the changes in the physicochemical properties of the date palm-based biochar towards pyrolysis at a lower temperature range. The objective of this work is to know how these experimental conditions affect the final composition and structure of the biochar in order to determine its suitability for use as functional filler for polypropylene composites.

2. Materials and Methods

2.1. Pyrolysis of Biomass

The lignocellulosic biomass from date palms was collected from a local farm in the Riyadh region of Saudi Arabia. It was cut into smaller pieces and dried at room temperature. The pyrolysis process was carried out at different temperatures ranging from 300 °C to 700 °C by using an electrical muffle furnace (Carbolite, UK) in the presence of the inert gas. The feedstock material was kept in a tubular reactor of stainless steel and tightly closed with the closing caps from both ends. The one end of closing cap has a gas inlet and the other end is used as a vent for pyrolytic vapors. The feedstock samples were then slowly pyrolysed to the desired temperature with heating rate of 10 °C min⁻¹ and residence time of 2 h. After completion of the residence time, the as-prepared samples were cooled down to

room temperature, stored and labeled as BC-300, BC-400, BC-500, BC-600, and BC-700, according to pyrolysis temperature.

2.2. Biochar Characterization

Fourier transform infrared spectroscopy (ATR-FTIR) analysis was carried out using a (Thermo Scientific, Winsford, UK) Nicolet iN10 FTIR microscope having a Germanium microtip accessory with wave number scanning range between 400 and 4000 cm⁻¹. The moisture and ash content in the BC samples were determined according to ASTM D1762-84. The elemental analysis (C, H, and N) was performed using a PerkinElmer 2400 CHNS/O series II analyzer (Norwalk, CT, USA). Acetanilide was used as a standard. Approximately 2 mg of BC was used for each measurement, and each measurement was carried out in triplicate. The percentage of oxygen content (O) was calculated by difference from the original dried sample and the sum of C, H, N, and ash content. The BET specific surface area of biochar samples were determined using N₂ adsorption isotherms in a Tristar-II 3020 (Micromeritics, Norcross, GA, USA) instrument at -196 °C. The surface morphology and elemental analysis of biochars were performed using SEM equipment coupled with an Energy Dispersive X-Ray (EDX) facility (JEOL, JSM-6360A, Tokyo, Japan)

2.3. Composites Preparation

The polypropylene pellets used in the current study were composed of a homopolymer polypropylene resin produced by the Saudi Basic Industries Corporation (SABIC), and commercialized under the brand name (LADENE PP570P), with melt flow index (MFI) of 8 g/10 min and density of 905 kg/m^3 .

The BC/PP composite BC samples were prepared through a melt mixing process followed by injection molding. Prior to the melt compounding process, both materials (BC and PP) were dried in an oven (at 110 °C for 24 h) to remove the moisture content. Afterward, 20 wt % of BC and 80 wt% of PP were premixed and the mixture was then introduced to the melt compounder (DSM Xplore microcompounder, 15 cm³, Sittard, The Netherlands). The melt mixing process was performed in speed-controlled mode at melting temperature of 190 °C, screw speed of 100 rpm, and mixing time of 5 min. After the specified mixing time was finished, the composites molten mass was collected in a preheated collector equipped with a cylindrical piston assembly. The collector temperature was kept the same as the compounder temperature, i.e., 190 °C. This melt was then subjected to a molding machine, (DSM Xplore microinjection molder, IM 12 cm³, Sittard, The Netherlands), for the preparation of the dumb-bell shape specimens for tensile testing (As per the ASTM standard, type 1, D 639). The mold temperature and holding pressure were kept at 35 °C and 6 bar, respectively, with 45 s of total injection time. The list of composites fabricated are presented in Table 1.

Sample ID	Composition (wt %)
Neat PP	PP (100)
BC300/PP	BC300 (20) + PP (80)
BC400/PP	BC400 (20) + PP (80)
BC500/PP	BC500 (20) + PP (80)
BC600/PP	BC600 (20) + PP (80)
BC700/PP	BC700 (20) + PP (80)

Table 1. List of biochar (BC)/polypropylene (PP) composites prepared in this study.

2.4. Composites Characterization

The composites surface morphology was investigated using scanning electron microscopy. The morphological analysis was performed on the specimens taken from injection molded bars of the composites. The tensile fractured surface of composites was scanned to observe dispersion of the fillers in the composites. All samples were sputter-coated with gold in a vacuum chamber prior to examination. Fourier transform infrared spectroscopy (ATR-FTIR) analysis was carried as described above. The thermogravimetric analysis (TGA) was performed in a DTG-60H (Shimadzu, Kyoto, Japan) apparatus with simultaneous DTA-TGA thermal analyzer. The aluminum pan was filled with approximately 10–15 mg of the prepared composite sample and the sample was heated from the ambient temperature up to 600 °C with heating rate of 10 °C/min. The analysis was done under nitrogen atmosphere with flow rate of $(50 \text{ cm}^3/\text{min})$ and, accordingly, the corresponding weight loss was recorded. The differential scanning calorimetry analyses were carried out using Shimadzu DSC-60 (Shimadzu, Japan). The heating and cooling program was from 30 °C to 220 °C and from 220 °C to 30 °C, respectively, at a rate of 10 °C/min and holding time of 3 min. The degree of crystallinity (X_c) was calculated by using equation,

$$X_{c} = \frac{\Delta H_{m}}{(1 - \Phi) \Delta H_{m}^{0}} \times 100 \%$$
⁽¹⁾

where ΔH_m is the calculated enthalpy of melting for the composite, Φ is the weight portion of the filler, and ΔH_m^0 is the theoretical enthalpy of melting for 100% crystalline PP which is reported to be 209 J/g [17]. The composites mechanical properties were estimated by using a Tinius Olsen (Hounsfield H100 KS Series, Salfords, UK) universal testing machine, tests were performed under ambient conditions according to the ASTM D 628 M. The reported values are an average of three measurements.

3. Results and Discussion

3.1. Biochar Characterization

3.1.1. Fourier Transform Infrared Spectroscopy (FTIR)

The changes of biochar surface functionalities with pyrolysis temperature are illustrated in Figure 1. In general, the FTIR analysis shows that the functional groups of biochar samples decrease with increased pyrolysis temperature. This is due to the rapid removal of volatile compounds as a result of the accelerated and intensified degree of carbonization at higher pyrolysis temperatures [18–20]. The FTIR spectra of biochar samples shows a broad peak at 3394 cm⁻¹ which corresponds to the O–H bond stretching of the alcoholic and phenolic hydroxyl groups. The intensity of this peak was found to be very strong at lower pyrolysis temperature; however, it becomes negligible at higher temperature. The characteristic C–H stretching vibration of alkyl structure of aliphatic group can be seen at 2927 cm⁻¹. The peak at 1693 cm⁻¹ represents the stretching of carbonyl bonds (C=O) of the carboxylic groups or conjugated ketone. The stretching vibrations of the aliphatic –C=C– appears at 1597 cm⁻¹ [21].

It can be seen from Figure 1 that the intensity of all these peaks decreases with increased pyrolysis temperature, as compared to the FTIR spectra of the date palm feedstock (see Figure S1 in the Supplementary Materials), and becomes negligible for the biochar produced at 700 °C. It is well known fact that the breakage of hydroxyl groups of aliphatic chain of biomass takes place between 120 °C and 200 °C. The cracking of aliphatic methyl, methylene, methoxyl groups, and reformation of other functional groups such as carbonyl and carboxyl occurs at ~400 °C. However, stable heteroaromatic and aromatic compounds will not be affected at this temperature. At higher temperatures, i.e., more than 600 °C, almost no aliphatic functional groups will be present in the biochar. These aliphatic structures are known to reform into aromatic structures, resulting in the increased presence of phenolic and ether groups. Moreover, at high temperatures many C=C bond breakages take place due to availability of adequate energy. Therefore, at higher temperature, due to extensive carbonization, formation of graphite-like structures of the biochar occurs which shows less intense peaks [22]. It was also reported that the biochar prepared at higher temperatures exhibited lower (O/C) and (H/C)

ratios, corresponding to the absence or limited presence of functional groups on surface and high percentages of carbon content [23].



Figure 1. Fourier-transform infrared spectroscopy (FTIR) of biochar samples.

3.1.2. Elemental Analysis and Molar Ratios

The proximate analysis, ultimate composition, and molar ratios of biochars samples are presented in Table 2, and confirmed with the EDS elemental composition which is illustrated in Table 3. The ultimate and proximate analyses of the date palm feedstock are also given in Table S1 in the Supplementary Materials. The yield of produced biochar decreased with increased pyrolysis temperature from 43% for BC300 and reached 32% for BC700. It was found that the carbon content and ash content of all biochar samples increased with increasing pyrolysis temperature, whereas the elemental composition (H, N, and O) decreased with increased carbonization temperature. However, these trends are expected and known in the literature, and occur as a result of the accelerated and intensified degree carbonization with increasing of pyrolysis temperature [18–20]. This higher pyrolysis temperature induce more cleavage and cracking of the functional groups of within the biomass structure that consists of hydrogen, oxygen, and nitrogen [24]. Also, the moisture content of biochar samples was found to decrease with increased pyrolysis temperature. These results are consistent with those obtained by other researchers who used the same type of biomass feedstock for the production of biochar [25]. On the other hand, elemental molar ratios, i.e., H/C, O/C, and (O+N)/C, were found to sharply decrease with increasing of charring temperature. In general, the decrease in the (H/C) ratio means less original organic matter, such as polymeric CH₂ and fatty acid, lignin, and some cellulose is preserved, and more biomass has been pyrolysed. While the declining trend of the (O/C) ratio suggests that the surfaces of biochars produced at high temperatures become less hydrophilic. Also, the decrease in the ((O+N)/C) ratio, which is known as the polarity index, indicates a reduction of the biochars surface polar functional groups with increased pyrolytic temperatures [26]. The H/C ratio of biochar samples is more specifically related to the degree of aromaticity, while the (O/C) and (O+N)/Cratios are related to hydrophilicity and polarity, respectively. These molar ratios are known to be very important factors, and can play a major role in the interface compatibility between the biochar surface and the polymer matrixes (filler-matrix interactions).

Samala N/ 1	N/ 110/		Ultimate Analysis			Proximate Analysis		Molar Ratio		
Sample	Yield %	С %	С% Н%		O % (*)	Moisture %	Ash %	H/C	O/C	(O+N)/C
BC300	43	63.65 (4.44)	3.82 (0.33)	1.01 (0.06)	18.78 (4.83)	4.47 (0.26)	12.74 (0.02)	0.72 (0.01)	0.22 (0.07)	0.24 (0.07)
BC400	38	64.95 (0.84)	2.96 (0.04)	0.89 (0.01)	17.04 (0.80)	3.80 (0.12)	14.16 (0.12)	0.55 (0.01)	0.20 (0.01)	0.22 (0.01)
BC500	35	70.75 (1.24)	2.33 (0.06)	0.86 (0.01)	9.85 (1.29)	3.20 (0.09)	16.21 (0.20)	0.40 (0.00)	0.10 (0.01)	0.12 (0.02)
BC600	33	74.76 (0.88)	1.60 (0.04)	0.71 (0.00)	7.13 (1.94)	2.43 (0.10)	17.8 (0.04)	0.26 (0.00)	0.05 (0.01)	0.06 (0.01)
BC700	32	72.76 (1.95)	0.90 (0.01)	0.65 (0.01)	5.32 (0.91)	2.87 (0.05)	18.37 (0.18)	0.14 (0.01)	0.08 (0.02)	0.09 (0.02)

Table 2. Chemical characteristics of biochar samples.

(*) Oxygen determined by difference (100% – (C + H + N + ash %)). All analyses were conducted in triplicate (*n* = 3), values between brackets represent the standard deviation.

Table 3. Elemental composition of biochar samples.

Mass %	C	0	Mg	A1	Si	S	Cl	к	Ca	0/C
Sample	- C	Ũ	8	711	51	0	CI	K	Cu	0,0
BC300	57.00	32.72	0.86	0.24	1.71	0.63	1.83	3.47	1.54	0.57
BC400	59.62	29.70	0.26	-	1.42	0.53	2.48	4.56	1.43	0.50
BC500	66.41	15.52	0.97	-	1.21	0.89	5.43	6.80	2.77	0.23
BC600	69.19	11.88	0.94	-	1.21	0.75	5.84	7.04	3.16	0.17
BC700	69.32	12.47	1.05	-	1.18	0.79	5.34	6.34	3.52	0.18

3.1.3. BET Surface Area

The surface area and pore volume of biochar are very important factors when BC is considered as a potential filler for polymer composites. The higher surface area along with the increased pore volume of BC samples might induce a good mechanical interlocking between the filler and matrix. It can be achieved by the infiltration of the molten matrix into BC pores during the melt mixing process which, consequently, improves the mechanical properties of the composites [12,27].

The BET surface area and pore volume of biochar samples are illustrated in Figure 2. It can be seen that both the BET surface areas and pore volumes of biochars were significantly increased with pyrolytic temperature. The surface area and pore volume of biochar produced at 700 °C was found to 249.13 m²/g and 0.031 cm³/g, respectively. On the other hand, biochar made at 300 °C exhibits a surface area of 2.04 m²/g and pore volume of 0.0057 cm³/g. This increase of surface area is due to the removal of carbon mass as volatile matters from the biomass surface which creates pores in the resulting biochars structure.



Figure 2. BET specific surface area and pore volumes of biochar samples.

3.1.4. Morphological Analysis

The scanning electron microscopy (SEM) images of the prepared biochar samples are shown in Figure 3. The SEM images shows that BC samples have random shape structures with sharp-edged particles. It can be observed that the BC average particle size distribution is in the range of 2 to $20 \mu m$ (Figure 3a); however, some bigger particles of larger size are also observed. On the other hand, high magnification images (Figure 3b) displays clearly the porous structures in the biochar samples. The appearance of deep channels and pores became more prominent with pyrolysis temperature caused by organic materials volatilization. However, destruction of the porous structure is also observed at higher temperature and can be seen in the BC-700 sample. This can be due to the accelerated and intensified degree of carbonization. The porous structure in biochar is vital aspect, because of the fact that these pores on the BC might enable the molten polymer chains to flow into this pores, which will lead to better mechanical interlocking and formation of stronger BC–PP interface [28,29].



Figure 3. Cont.



Figure 3. SEM images of biochar samples prepared at different temperatures. (**A**,**B**) for BC300, (**C**,**D**) for BC400, (**E**,**F**) for BC500, (**G**,**H**) for BC600 and (**I**,**J**) for BC700.

3.2. Composites Characterization

3.2.1. Morphological Characterization

The dispersion state of BC particles and the BC–PP interfacial interaction are two important factors that influence the properties of the composites. The SEM images of BC/PP composite systems prepared with different types of biochar are shown in Figure 4. It can be seen that the majority of BC particles are distributed uniformly in the PP matrix, however, the composites also show an agglomeration. It should be note that the BC/PP composites interface properties is highly dependent on the type of BC. The composites samples made with BC prepared at relatively higher temperatures, especially BC500, BC600, and BC700 show relatively better interfacial adhesion between the filler and matrix as compared to other composites prepared with BC obtained at lower temperatures. This improved interface quality can be attributed to the large surface area and porous structure of BC prepared at higher temperatures. The molten PP matrix, during processing, penetrates into BC pores, which results in better filler–matrix interlocking [29]. Nevertheless, filler pull-out effects, as indicated by the debonding of BC particles, are also observed. It is important to note that good mechanical strength can only be achieved if there is an excellent interfacial bond between the filler and matrix, and ultimately it must lead to a uniform and efficient transfer of applied stress. The fillers can pull out from the matrix in the lack of interfacial bond and results in an annulment of the reinforcing effect [30].



Figure 4. Cont.



Figure 4. SEM images of BC/PP composites. (**A**,**B**) for BC300/PP, (**C**,**D**) for BC400/PP, (**E**,**F**) for BC500/PP, (**G**,**H**) for BC600/PP and (**I**,**J**) for BC700/PP.

3.2.2. Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectrums of neat PP and BC/PP composites are shown in Figure 5. The FTIR of composites shows mainly the characteristics peaks of the neat PP. The strong peak at $3000-2800 \text{ cm}^{-1}$ is contributed by the C–H stretching vibrations of PP chains. The peaks at 1457 cm^{-1} and 1376 cm^{-1} are assigned to $-CH_2$ and $-CH_3$ bending vibrations, respectively. Moreover, small peaks at 1167 cm^{-1} , 998 cm⁻¹, and 973 cm⁻¹ are attributed to $-CH_3$ symmetric deformation and $-CH_3$ rocking vibrations, receptively [31]. The biochar peaks with very small intensity at 1693 cm⁻¹ and 760 cm⁻¹, due to stretching vibrations of the carbon double bond (C=C–), were also present in the composites. This indicates that biochar are well present in the composites.



Figure 5. FTIR of BC/PP composites.

3.2.3. Thermogravimetric Analysis (TGA)

The thermal stability of polymeric materials is an important parameter, since the thermal stability of polymer materials can be a limiting factor in both processing and end-use applications [32]. Thermal degradation of the PP and BC/PP composites was determined from the weight loss during heating. The weight loss (TGA) and the derivative weight loss (DTG) curves are shown in Figure 6a,b, respectively. The values of temperatures for 5% and 15% weight loss ($T_{5\%}$ and $T_{15\%}$), and also the maximum decomposition temperature (T_{max}) are summarized in Table 4. It can be observed from Figure 6a that the thermal degradation of the neat PP and its BC/PP composites takes place in a single step. The maximum temperature of decomposition (T_{max}) for the neat PP was found to be around 477 °C, while the temperatures for 5% and 15% weight losses were observed at 395 °C and 433 °C, respectively.



Figure 6. TGA (a) and derivative weight loss (DTG) (b) curves of BC/PP composites.

Table 4. Summarized results of TGA analysis of PP and BC/PP composites.

Samm1a		DTG		
Sample	T _{5wt%.} ^a (°C)	T _{15wt%} . ^b (°C)	Residual wt %	$T_{max} c (^{\circ}C)$
Neat PP	395	433	0	477
BC300/PP	416	456	14.80	485
BC400/PP	457	473	15.47	489
BC500/PP	465	478	18.69	490
BC600/PP	467	478	17.02	491
BC700/PP	466	478	20.03	490

^a $T_{5wt\%}$ represents the temperature at which 5 wt % weight loss rate occurred, ^b $T_{15wt\%}$ represents the temperature at which 10 wt % weight loss rate occurred, and ^c T_{max} represents the temperature at which the maximum weight loss rate occurred.

Figure 6a also indicates that all BC/PP composite samples show a delayed onset degradation temperature compared to the neat PP. This delayed in degradation process is an indication of improved thermal stability of the composites, which is due to the addition of the thermally stable biochar.

This improvement in the resistance to thermal degradation can be attributed to the hindered diffusion of volatile decomposition products within the BC/PP composites. It also due to the barrier effect of the addition of BC to the PP matrix, causing mass transfer limitations of volatile gases produced during thermal transformation. The biochar is considered to be an amorphous material that is structurally disordered in nature. However, some rearrangement of molecular layers takes place between chains of carbon or/and carbon molecules depending on the temperature of pyrolysis and residence time [33]. Such type of carbon network transformation into the turbostratic stack-like structure of the biochar has already been reported [33,34]. It is concluded, therefore, that this biochar can act as a barrier element in the composites. Amongst the composites samples, it can be observed that the BC700/PP sample shows higher thermal stability than the others.

3.2.4. Differential Scanning Calorimetry (DSC)

The DSC thermal behaviors (heating and cooling) of the neat PP and the BC/PP composite systems are presented in Figure 7a,b. The heat of melting (ΔH_m) and crystallization heat (ΔH_c) were determined from the areas of melting and crystallization peaks, and the results are summarized in Table 5. The melting temperature (T_m) of all the samples was found to be ~163 °C, corresponding to the typical melting of PP. The type of BC was observed to have negligible effect on the melting temperature of BC/PP composites. However, the crystallization temperature (T_c) of neat PP appeared at 109 °C and was found to significantly increase with BC incorporation into BC/PP composites. The crystallization temperature of the composites was also found to increases proportionally with the BC pyrolysis temperature. This could be attributed to the increased number of BC particles and which in turn increases the number of nucleation sites available for crystallization. Furthermore, the overall degree of crystallinity was found to increase in BC/PP composites. This is attributed to the nucleation effect of the biochar particles in the PP matrix. It means the biochar particles acted as points from where crystal growth initiated. Similar nucleating effects through incorporation of other carbonaceous fillers into PP matrix has also been reported [35,36].



Figure 7. Cont.



Figure 7. DSC of BC/PP composites: (a) Melting and (b) crystallization curve.

Samm1a	DSC Parameters							
Sample	Τ _c (°C)	ΔH_c (J/g)	Т _т (°С)	ΔH _m (J/g)	X _r (%)			
Neat PP	109.24	-91.25	163.05	76.2	36.46			
BC300/PP	119.83	-76.64	163.60	62.75	37.53			
BC400/PP	122.19	-76.26	164.58	64.13	38.36			
BC500/PP	124.06	-83.76	165.35	71.47	42.75			
BC600/PP	124.86	-82.03	165.52	69.9	41.81			
BC700/PP	124.65	-80.97	165.60	68.23	40.81			

Table 5. Summarized results of DSC analysis of PP and its BC/PP composites.

3.2.5. Mechanical Characteristics

The incorporation of particulate fillers can modify the mechanical properties of polymers in many ways depending on the particle size, loading, particle–matrix interfacial adhesion, and the composites microstructure [37]. Similarly, the maximum strength sustained by composites under uniaxial tensile loading depends on the effective stress transfer between the matrix and fillers [38]. The results of stress–strain curve of the BC/PP composites are shown in Figure 8. It can be observed that the addition of BC considerably affects the deformation behavior of the composites compared to the neat PP. The PP demonstrates a typical yielding process and ductile nature followed by strain hardening at the low strain rate. Contrarily, BC/PP composites exhibit a quasi-brittle behavior under tensile deformation. In other words, neat PP shows highly ductile fracturing behavior, while the ductility of BC/PP composites decreases considerably. The inset image in Figure 8 shows that the composites' deformation to rupture decreases with increased pyrolysis temperature, except for BC300/PP composite sample. The area under the stress–strain curve, which represents the amount of energy that the material can absorb until rupture, decreased compared to the neat PP.

The tensile modulus and strength of the neat PP and BC/PP composites are illustrated in Figure 9 and their numerical values along with their statistical significance analysis are summarized Table S2 (see the Supplementary Materials). It can be noticed that incorporation of the biochar into the polypropylene matrix leads to an increase in composites stiffness. This improved stiffness is due to the fact that the BC particles leads to hindered molecular mobility of the PP chain segments. The modulus of elasticity of the composites was found to increases gradually with pyrolysis temperature. It has been shown that the biochar derived from different sources has increased hardness and modulus at higher

temperatures [39,40]. Therefore, enhancements of these properties can be attributed to an increase in carbon content with higher pyrolysis temperature.



Figure 9. Tensile strength and tensile modulus of BC/PP composites.

The tensile strength of BC/PP composites was found to slightly decrease compared to neat PP. This is due to weak adhesion between the fillers and matrix. However, this property can be enhanced by using suitable compatibilizers, as evident in the literature [40]. Similarly, the elongation at break is a measure of materials ductility and expresses the capability of material to resist changes of shape under deformation without crack formation. The percentage elongation at break and percentage elongation at yield of neat PP and BC/PP composite systems are presented in Figure 10. It is observed that the addition of BC particles results in an abrupt decrease in both elongation at break and at yield as

compared to that of the neat PP. This reduction is due to the induced mechanical restrains as a result of the addition of filler that leads to restricted mobility of the PP chains. These results are in good accordance with the previously reported studies [11,40].



Figure 10. Elongation at break of BC/PP composites.

4. Conclusions

Low-temperature biochars from waste biomass have been prepared and their microstructure was studied. The pyrolysis conditions were found to have significant impact on biochar structure. The carbon and ash content, surface area, and pore volume are increased, while H/C, O/C, and (O+N)/C ratios decreased with pyrolyzing temperature. These biochars were then used as carbon fillers for the polypropylene composites without purification and use of compatibilizers. The biochar-filled PP composites have been formulated by melt mixing process to study its compatibility. These composites show significant changes in physical and mechanical properties compared to neat PP. These biochar-based PP composites enhance thermal stability by delaying both composite decomposition onset as well as the maximum degradation temperature. The DSC results revealed that biochar acts as nucleating agent and enhances the overall crystallization process. Enhancement of the stiffness of the composites has been observed due to rigid nature of the BC particles, while tensile strength and ductility remained unaffected. However, these properties can be improved with the further functionalization of BC particles or by using suitable compatibilizers. This study therefore suggests that biochar can be used as reinforcing filler for polypropylene and other polymer systems.

Supplementary Materials: The following are available online at http://www.mdpi.com/2076-3417/9/6/1149/s1, Figure S1: FTIR spectra of raw date palm feedstock, Table S1: Ultimate and proximate analyses of the date palm feedstock, Table S2: Mechanical characteristics of neat PP and BC/PP composites.

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