



Cite this: *RSC Adv.*, 2022, **12**, 13938

## Emerging application of biochar as a renewable and superior filler in polymer composites

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Biochar is conventionally and widely used for soil amendment or as an adsorbent for water treatment. Nevertheless, the need for transition to renewable materials has resulted in an expansion of biochar for use as a filler for polymer composites. The aim is to enhance the physical, chemical, mechanical and rheological properties of the polymer composite. The reinforcement of biochar into a polymer matrix however is still new, and limited reports are focusing on the effects of biochar towards polymer composite properties. Hence, this review highlights the unique properties of biochar and its effect on the crystallization, thermal, flammability, electrical conductivity, and mechanical properties of polymer composites. This review does not solely summarize recent studies on biochar–polymer-based composites, but also offers insights into a new direction of biochar as a renewable and superior polymer filler in the future.

Received 24th March 2022

Accepted 25th April 2022

DOI: 10.1039/d2ra01897g

rsc.li/rsc-advances

### 1. Introduction

Given the high demand for smart materials, most materials such as metals, glass and ceramics have been replaced by polymer composites mainly due to their light weight, easy processing and low production cost.<sup>1</sup> Polymer composites have been used for various purposes ranging from low-cost household products to high-performance industrial products. According to the Plastics Market Size Share Industry Analysis Report released by Grand View Research in February 2020, the plastics market growth has been increased from USD 72.7 billion in 2016 to USD 568.7 billion by 2019 due to the high demand from various industrial sectors including the wind energy, aerospace, packaging, construction and automotive industries. This was highly attributed to the versatility of polymers as they are light in weight, have good strength, are corrosion-resistant, cheap and easy to produce and can be reused multiple times. Despite their diverse properties, polymers have some drawbacks associated with their components

such as low thermal stability, low conductivity and low flame retardancy. Research has been carried out to unfold such issues and one of the most effective solutions is by adding a filler to improve and modify the composite properties.<sup>2–7</sup> Since there is great interest in low-cost, sustainable and environmentally friendly materials, biochar has received great interest for use as a filler, as an alternative to the other non-environmentally and non-economically viable carbon fillers such as carbon black, carbon nanotubes and graphene.

In contrast to the other carbon fillers which require complex synthetic production methods, biochar which is a porous carbonaceous solid residue can be produced by slowly pyrolyzing the biomass at a high temperature ranging from 500 to 700 °C.<sup>8</sup> Similar to other carbon fillers, biochar is porous, thermally stable, has large specific surface area, and consists of several functional groups: hydroxyl, carboxyl, carbonyl and others.<sup>5,9,10</sup> The use of biomass for biochar production to be used as filler in polymer composites will not only solving the waste management issue, but it also promotes the potential of biomass for the production of high-value-added products.

Over the recent years, there has been an influx of research done to assess the potential of biochar to act as a cost-efficient, sustainable and renewable filler for polymers. The major aim of reinforcing biochar is to enhance the mechanical, thermal and electrical conductivity properties of polymer composites.<sup>11</sup> Based on the previous research, biochar has been proven as a superior filler compared to other fillers, especially natural fibers.<sup>12–16</sup> In contrast to the natural fibers, the properties of biochar can be altered by modifying the pyrolysis condition to achieve high hydrophobicity properties, which can help in

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enhancing the compatibility with the polymer matrix. In fact, the thermal stability of biochar composites was found to be higher than the composites reinforced with natural fibers, thus diversifying their usage for various purposes. For instance, Khan *et al.* (2017)<sup>14</sup> reported the use of biochar as a filler in epoxy composites and compared with carbon nanotubes (CNT). It was revealed that the ultimate tensile strength of epoxy composites reinforced with 2 wt% biochar was higher than that of epoxy composites reinforced with 2 wt% CNT. In the same report, tensile toughness was superior in the case of biochar as compared to CNT. In fact, the microwave permittivity and conductivity among epoxy/biochar and epoxy/CNT composites were comparable. This shows the potential of biochar to replace the expensive carbon nanotubes as a filler for polymer composites.

In general, biochar reinforced polymer composites have potential applications in various industries. Biochar reinforced polymer composites could be beneficial in the packaging industry and for the manufacturing of interior components for cars or aeroplanes, as it is light-weight and has fire-resistant property.<sup>17</sup> Nevertheless, there is still limited research published on biochar-polymer-based composites. This might be due to the lacking of understanding on the potential effect of biochar on the polymers. Hence, this review intends to highlight the unique properties of biochar, to explain its effect on the polymer matrix. Comparison on the properties, processing methods, and interaction with the polymers between biochar and other carbon fillers are also discussed, to provide the new insights of biochar as a potential renewable filler to enhance the properties of polymer composites.

## 2. Production and characterization of biochar

### 2.1. Biochar production

Thermochemical decomposition of biomass has been the most common and convenient conversion technique for biochar production. The thermochemical conversion refers to the controlled thermal treatment to activate and sustain decomposition and/or oxidation of biomass to produce energy carriers (biochar, bio-oil and syngas) or heat.<sup>18</sup> Several thermochemical schemes have been developed to produce biochar from biomass feedstock. Among the various thermochemical conversion technologies, pyrolysis and hydrothermal carbonization are the preferred methods for high carbon yield.<sup>19</sup>

**2.1.1 Pyrolysis.** Pyrolysis is one of the typical thermochemical conversion processes in which treatment temperature between 200 and 900 °C is employed to activate and sustain the decomposition of different biomass components to yield biochar, tars and syngas.<sup>20</sup> Depending on the operating conditions, pyrolysis conversion technology can be broadly classified to include slow pyrolysis, fast pyrolysis, flash pyrolysis, catalytic pyrolysis, microwave pyrolysis, torrefaction and hydrothermal carbonization; as illustrated in Fig. 1. The different pyrolysis modes are designed to produce biochar as the main product or co-product with different characteristics. Slow pyrolysis is the

most conventional thermal conversion method used to obtain high biochar yield. It involves heating biomass feedstock slowly from around ambient temperature to the treatment temperature, which is usually >400 °C in the presence of inert gas to avoid carbon oxidation. The long residence time in slow pyrolysis provides an opportunity for the condensable volatile compounds to continue to react (polymerization) to form biochar.<sup>21</sup> Fast and flash pyrolysis are carried out at a higher heating rate than slow pyrolysis, and shorter vapor residence time. Flash pyrolysis is considered a better process for producing biochar and syngas, whereas bio-oil is the major product obtained using fast pyrolysis.<sup>21</sup> During the flash pyrolysis, the condensable volatile compounds formed are further cracked or polymerized to produce syngas or biochar respectively due to the relatively higher treatment temperature and heating rate.<sup>22</sup> Residence time and biomass conditions are the key factors to be considered when selecting a suitable reactor. The fixed-bed reactor is the most common reactor used for slow, catalytic and microwave pyrolysis.<sup>23</sup> In addition to having a long residence time, the fixed-bed reactor is designed to handle biomass with various particle sizes. Entrained flow and fluidized-bed reactors are designed to perform the swift operating conditions of fast and flash pyrolysis. For the efficient performance of these reactors, biomass particles must be small enough to minimize resistance to heat and mass transfer processes.

The other modes of high-temperature pyrolysis are microwave and catalytic pyrolysis. In microwave pyrolysis, the components of biomass are exposed to radiation respond by a sort of movement (dipole rotation or ion migration) and generates heat due to the friction between the molecules.<sup>24</sup> This *in situ* heating of the biomass components drastically limits the mass transfer of condensable volatile components within the biomass particle and encourages continuous reaction to form biochar. Biochar yield from microwave pyrolysis is comparable to slow pyrolysis. Depending on the type of catalyst used, catalytic pyrolysis can either favour the production of biochar or bio-oil. The research trend on catalytic pyrolysis is toward bio-oil production. Torrefaction and hydrothermal carbonization are types of biomass pyrolysis processes carried out at low-temperature (<350 °C) aiming to produce biochar as the main product.<sup>25</sup> For hydrothermal carbonization, yields of gas and liquid by-products are substantially low.<sup>26</sup> The degree of biochar carbonization is low compared to products of high-temperature pyrolysis and contains a high degree of oxygen functional groups. Autoclave reactors (pressure vessels) are used for hydrothermal carbonization of biomass. Autoclave reactors are designed to operate at elevated pressures and temperatures typical of the hydrothermal carbonization process and can efficiently convert wet biomass feedstock without extra energy input.

**2.1.2 Gasification.** Gasification refers to the thermochemical conversion process in which carbons of pyrolyzed biomass are partially oxidized with steam, carbon dioxide or air at temperature >700 °C to produce gas rich in carbon monoxide and hydrogen.<sup>20,27</sup> The partial oxidation of carbon during gasification process is an additional step following biomass drying



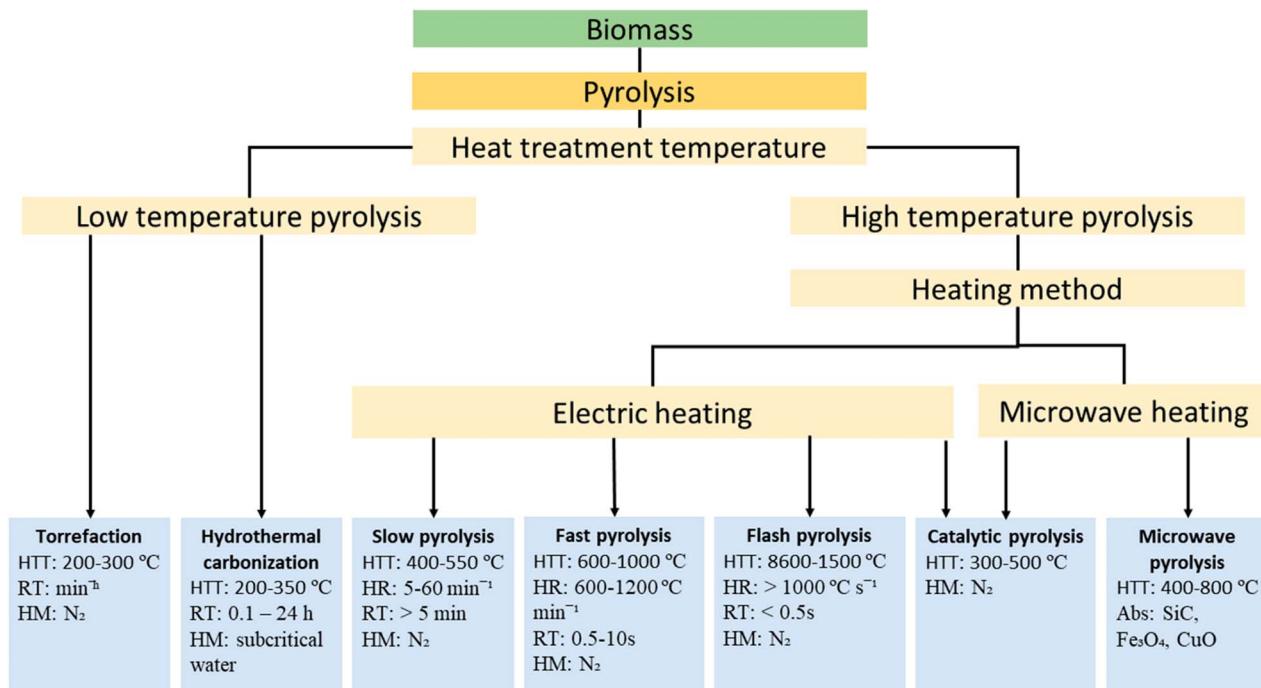


Fig. 1 Schematic of classification pyrolysis of biomass feedstock. HTT (heat treatment temperature), HR (heating rate), RT (residence time), HM (heating medium), and Abs (absorber).

and pyrolysis to produce high-energy syngas. Thus, biochar yield from the gasification process is generally lower than the yield obtained from pyrolysis.<sup>28</sup> Partial gasification of raw biochar (physical activation of biochar) is a well-established thermochemical modification process used to improve the porosity and surface chemistry of biochar. Both the biochar obtained from gasification processes that are intentionally restricted to produce syngas, or activate biochar are generally more porous than those obtained from the other thermochemical conversion processes.<sup>29</sup> Fixed-bed, fluidized-bed and entrained flow gasifiers are the common reactors used depending on gas–solid contact mode.<sup>30</sup>

**2.1.3 Other thermochemical technologies.** Direct combustion is the oldest biomass conversion technology typically employed to produce heat and biochar as a co-product. This conversion process involves igniting feedstock with flame in an open space or in a non-pressurized encloser under the flow of air. Temperature and airflow are difficult to control which leads to a vigorous conversion process and lower biochar yield. Self-sustained carbonization technology is developed to have a better-controlled conversion process and higher biochar yield. In the self-sustained carbonization process, biomass is combusted in an encloser under residual air and the conversion process takes a longer time.<sup>31</sup> Pilot and industrial-scale pools are common reactors used for the self-sustained carbonization process.

## 2.2 Factors influencing biochar properties

The properties of biochar are known to depend on the characteristics of its feedstock and production methods, and they were

summarised in Table 1. Biomass feedstocks are mostly composed of different proportions of cellulose, hemicellulose, lignin, extractives and inorganic compounds. These components decompose differently during thermal treatment and thus have a great influence on the properties of the biochar produced. Meanwhile, the dependence of biochar properties on lignin and ash contents could be related to their low volatility.

The properties of biochar are also significantly influenced by the production conditions such as temperature, residence time and heating rate. The peak temperature is an important and dominant process parameter in determining the stage of biomass degradation, which invariably has a significant effect on the yield and quality of biochar. Biochar prepared from biomass show the common trend of yield reduction with the rise in temperature. Antal and Grønli (2003)<sup>36</sup> and Weber and Quicker (2018)<sup>25</sup> have succinctly summarized the biochar properties with different carbonization temperatures. The drastic yield reduction at the initial stage of thermal treatment (<500 °C) followed by a slow decrease thereafter has been observed for lignocellulosic biomass feedstocks.<sup>37–41</sup> These trends of reduction in biochar yield reflect the devolatilization of organic polymers of the feedstock and the slow carbonization of the solid residue. Quality properties such as fixed carbon and volatile matter contents increase and decrease with temperature, respectively. A rise in carbonization temperature results in variations in the element composition and atomic ratios of the biomass by releasing oxygen and hydrogen groups resulting in carbon-rich and hydrophobic products.<sup>42</sup>

Changes in textural properties of biochar have been identified to correlate with carbonization temperature. Biomass



Table 1 Summary of factors influencing biochar properties

Factors	Descriptions
Proportion of biomass feedstocks composition	Influence of lignin: high yield of biochar and fixed carbon content, <sup>32</sup> low surface area, <sup>33</sup> high surface pH and functional groups, <sup>34</sup> high ion exchange capacity <sup>25</sup>
Production condition	Influence of inorganic constituent: <sup>35</sup> high biochar yield through bond dissociation energy alteration between organic and inorganic carbon, loss of volatile matter, high electrical conductivity of biochar correlated with potassium and sodium fractions of the total ash Influence of high temperature: low yield of biochar, <sup>37</sup> high fixed carbon and low volatile matter contents, <sup>42</sup> high specific surface area of biochar, <sup>43,44</sup> high total pore volume biochar, <sup>40</sup> high crushing and impact strengths of biochar, <sup>45</sup> high pH and electrical conductivity <sup>46</sup> Influence of low temperature: better cation exchange capacity <sup>25</sup>

pyrolysed at milder peak temperatures typically  $<400$  °C does not produce biochar with a relatively high specific surface area compared to its original biomass. However, a significant increase in the specific surface area between the production temperature range of 450 and 700 °C was observed.<sup>43,44</sup> Removal of volatile matter through destruction of aliphatic alkyl and ester groups, exposure of aromatic lignin core, and restructuring (re-polymerization and aromatization) of fixed carbons through higher production temperature could be responsible for the higher surface area.<sup>20</sup> As production temperature further increases from 700 to 1000 °C, the specific surface area starts to decline possibly due to softening and sintering of high molecular weight volatile matter which leads to shrinkage of biochar.<sup>40</sup> The pore volume is another textural property that is relevant in many biochar applications. The total pore volume increases with temperature which corresponds to a decrease in biochar particle density. Again, as the volatile matter is released from the biomass and solid carbons are re-polymerized and aromatized due to temperature rise, pores are gradually developed within the biochar matrix.

Crushing and impact strengths are relevant in the design of material handling and transportation systems. Both crushing and impact strengths of biochar exhibit a similar trend to the surface area with temperature rise. M. Kumar *et al.* (1999)<sup>45</sup> reported that both crushing and impact strengths of biochar produced from acacia and eucalyptus wood biochars increased with temperature and further decreased after the production temperature of 600 °C. Clear trends were also observed between temperature and changes in electrical conductivity and ion exchange capacities of biochar. Low-temperature biochar gives rise to a better cation exchange capacity due to the presence of a sufficient amount of negatively charged functional groups.<sup>25</sup> Biochar pH and electrical conductivity were reported to increase with production temperature due to loss of hydrogen : carbon ratio and volatile matter resulting in high ash content production.<sup>46</sup>

### 2.3 General applications of biochar

Biochar now becomes a more appealing carbon material owing to its features of being a sustainable, green, easy-produced and cost-effective alternative to other forms of carbon materials. The

high surface area, porosity and large amounts of surface functional groups are key properties influencing the suitability of biochar for various applications. Initially, soil improvement, waste management, climate change mitigation and energy production motivated the application of biochar on environmental management.<sup>47</sup> Currently, advancement in production, modification and characterization of biochar is motivating its application beyond environmental management services to emerging high-end applications. Biochar is identified as an adsorbent for the removal of contaminants and pollutants in liquid and gas phases.<sup>48–50</sup> Today, biochar is acknowledged to perform efficiently by accelerating the decomposition of substrates and improving compost quality,<sup>51</sup> having good specific capacitance and current density,<sup>52</sup> increasing catalytic removal of nitrogen oxides,<sup>53</sup> improving the stiffness and flame retardancy of glass-fiber reinforced composites,<sup>54</sup> and improving the mechanical properties of polypropylene composites.<sup>12</sup>

## 3. Effects of biochar addition on the characteristics of polymers composites

The porous structure of biochar is extremely advantageous for the purpose of filtration and soil remediation. Recently, researchers have found the potential of biochar to be used as a filler for polymer composites, owing to its porous structure, excellent thermal stability, low-cost production and minimal negative impact on the environment.<sup>55</sup> Theoretically, different kinds of fillers will act differently on polymer matrix, so does biochar. This section discusses the effect of biochar on the crystallization, thermal, flammability, electrical conductivity and mechanical properties of polymer composites.

### 3.1 Crystallization behavior

Crystallization behaviour is important due to the role they play in the mechanical properties of the polymer composites. Knowing the crystallization kinetics of a polymer or composite is also vital when it comes to assessing the processability of these plastics during downstream manufacturing. The crystallization kinetics of materials can be observed through



a combination of differential scanning calorimetry (DSC) and X-ray diffraction (XRD). The effect of biochar on the crystallinity of the different polymers is mixed. There are multiple explanations for the fluctuations in crystallinity of the polymers due to the addition of biochar. Poulose *et al.*, (2018)<sup>13</sup> and Zhang *et al.*, (2018)<sup>56</sup> explained that the decrease in crystallinity and the slower crystallization rates were due to the hindrance of mobility of the polymer chains caused by biochar. However, although the crystallinity of the composite was reduced, the crystallization onset temperature ( $T_c$ ) of the composites was slightly higher than the neat polypropylene (PP).<sup>13</sup> This suggested that biochar was able to act as a nucleating agent triggering nucleation at a higher temperature as compared to neat PP. This is in agreement with the report by Li *et al.*, (2018),<sup>57</sup> which stated that well distribution of biochar in the polymer matrix has contributed to the functionality of the biochar as nucleating agent to initiate the crystallization of the polymer. This was supported by their findings on the decrease of crystallinity at higher loadings of biochar, which caused mobility restrictions of the molecular chains. In another study involving polyethylene terephthalate (PET)/biochar composites, the addition of biochar caused a decrease in the cold-crystallization temperature and a significant increase in the crystallization rate as well as the crystallinity of the composite when compared to the neat PET.<sup>58</sup> Zhang *et al.*, (2019),<sup>59</sup> experienced similar effect where the addition of poplar biochar caused the crystallization of high-density polyethylene (HDPE) to occur earlier. They explained that the poplar biochar acted as a nucleating agent to decrease the amount of energy required for the crystallization of the composites.

### 3.2 Thermal properties and thermal stability

The thermal properties of polymers are typically assessed with the help of DSC. The DSC curves will provide information on the melting temperatures, glass transition temperatures as well as the various enthalpies that are required to induce the phase transitions in the polymers or composites. According to Poulose *et al.*, (2018),<sup>13</sup> the melting temperature ( $T_m$ ) of PP was not affected by the addition of biochar. Additionally, Das *et al.*, (2016a)<sup>12</sup> discovered that while the addition of biochar did not give an effect on the  $T_m$  of PP, the melting enthalpy ( $\Delta H_m$ ), however, was increased and attributed. Also in agreement with the previous two studies, Zhang *et al.*, (2019)<sup>59</sup> revealed that the addition of poplar biochar to the HDPE had no effect on the composite's  $T_m$  but also no change in  $\Delta H_m$ .

Thermal stability is essentially the resistance of a certain molecule to high levels of heat. The thermal stability of polymers is usually determined using thermogravimetric analysis (TGA). Depending on the raw material, biochar by itself has extremely high thermal stability as proven by numerous studies by Das *et al.*, (2015a),<sup>62</sup> Nan *et al.*, (2015)<sup>60</sup> and Jeon *et al.*, (2019).<sup>61</sup> This was especially true for biochar that has undergone pyrolysis at very high temperatures as it was found that biochar seems to be thermally stable below their pyrolysis temperatures. Therefore, the higher the temperature at which the biochar is produced, the more thermally stable it will be due to a higher

degree of carbonization.<sup>63</sup> The addition of biochar seems to consistently improve the thermal stability of various polymers. Nan *et al.*, (2015)<sup>60</sup> reported that both thermal degradation and weight loss of polyvinyl alcohol (PVA) were delayed due to the addition of biochar into the matrix and this was highly attributed to the superior thermal stability of biochar particles. Li *et al.*, (2018)<sup>57</sup> also reported similar results where the increasing content of biochar in the ultrahigh molecular weight polyethylene (UHMWPE)/linear low-density polyethylene (LLDPE) matrix delayed the onset of thermal degradation even further. The authors attributed this to the faster heat transfer from the polymer matrix to the filler due to higher biochar content. However, they also noted that the maximum degradation temperatures of the composites were below that of the neat polymer blend. This was due to the higher thermal conductivity of biochar.

Another study done on biochar/PET composites suggested that the improvement in thermal stability could be due to the biochar acting as a barrier to volatiles and that the oxygen permeation into the polymer matrix could have been affected by the presence of biochar.<sup>58</sup> They found that the addition of biochar to recycled PET increased the onset degradation temperature from 381.8 °C of neat PET to 387.2 °C with the addition of 5 wt% of biochar. Das *et al.*, (2015a)<sup>12</sup> conducted their research on the addition of biochar to conventional PP. Yet again, biochar has proved to be significantly advantageous to the thermal properties of polymers. In this case, the authors recorded a clear increase of residual mass after thermal degradation as the biochar content in the PP/biochar composites increased.

### 3.3 Flammability and flame retardancy

Flammability or combustibility, unlike thermal stability, is the ability of a substance or chemical to combust or ignite, causing a fire. Flame retardancy, on the other hand, is the ability of a substance to prevent combustion. Combustion of materials can only occur in the presence of fuel and sufficient heat and oxygen. The absence of one of these requirements will prevent a fire from starting. Logically, most applications of polymers would benefit from a material with low flammability and high flame retardancy. Zhang *et al.*, (2017),<sup>64</sup> did a study where they tested the effects of biochar on the flammability properties of Al(OH)<sub>3</sub>/HDPE/wood composites where Al(OH)<sub>3</sub> is used as a flame retardant. They found that the addition of biochar to the composite yielded a limiting oxygen index (LOI) of up to 30% with flame retardant content of 40 wt%. This is an improvement to the LOI of the composite without biochar at about 27.1%. It was explained that the addition of biochar helped to delay the heat degradation velocity which in turn, boosted the flame retardancy of the overall material.<sup>64</sup> Another study tested the flammability properties of PP/biochar.<sup>12</sup> From their research, they stated that while the time to ignition (TTI) of the composites decreased when compared to neat PP, the peak heat release rate (PHRR) decreased significantly with the addition of biochar to PP. In another study by the same principal researcher, they found that the LOI of PP was increased from 18% to 22.08% with the addition of 25 wt% biochar.<sup>16</sup>



### 3.4 Electrical conductivity

Poulose *et al.*, 2018,<sup>13</sup> measured the surface resistivity of PP upon the addition of date palm biochar. They tested the effects of biochar produced at two different pyrolysis temperatures (700 and 900 °C) on the properties of PP. They found that as the biochar content increased, the surface resistivity of the composites decreased. A decrease in surface resistivity means that the electrical conductivity of the composites increased by up to 4 orders of magnitude with the incorporation of 15% w/w biochar. It was also found that biochar pyrolyzed at a higher temperature (900 °C) lead to a more drastic decrease in surface resistivity. However, it is noted that the improvement to the electrical conductivity of PP with the addition of biochar is not to the level of other carbonaceous materials such as carbon black.<sup>65</sup> This could be due to the agglomeration of biochar or the presence of impurities and high ash content which could lead to the disruption of the conductive carbon network.<sup>13</sup>

Another study by Nan *et al.*, (2015)<sup>60</sup> on the electrical conductivity of PVA/biochar composites revealed that PVA by itself has no electrical conductivity properties and the addition of small amounts of biochar to PVA (2% w/w) did little to improve the electrical conductivity of PVA. This could be explained by the same reasoning used by Poulose *et al.*, (2018),<sup>13</sup> where there was not enough biochar to form a conductive network. However, upon higher loadings of biochar (6% and 10% w/w), the conductivity of the composite seemed to increase together with the biochar load. This is because an increase in biochar content provided enough biochar to reduce the insulated space in the matrix, forming a conductive network of carbon. The results from this study are in agreement with a study by Li *et al.*, (2018)<sup>57</sup> who combined UHMWPE/LLDPE with biochar to increase the electrical conductivity of the polymer. They also found that the electrical conductivity of a polymer would increase with higher loadings of biochar. It was also noted that at 80% w/w of biochar, they achieved one of the highest electrical conductivity ( $107.6 \text{ S m}^{-1}$ ) of a composite fabricated *via* melt processing. Interestingly, to further prove the electrical conductivity properties of the UHMWPE/LLDPE/biochar composite, they successfully lit a blue LED bulb using the composite as part of the circuit.<sup>57</sup> In short, this proves that the addition of biochar in a polymer matrix is beneficial for the production of high electrical conductivity composites including electromagnetic interference shielding.<sup>57</sup>

### 3.5 Mechanical properties

Out of all the properties of materials, the mechanical properties of materials are perhaps the ones that have garnered the most interest from researchers. Depending on the application, a material has to be strong and stiff or even flexible and stretchable. Researchers are always on the hunt for additives that could improve the mechanical properties of polymers. Biochar, among other green, environmentally friendly materials, has been the center of focus among material scientists to be used as a reinforcing material for various polymers.

The tensile strength of a material is the ability of the material to resist breaking under tension. A material of high tensile

strength would be able to undergo a higher degree of tensile stress without breaking as compared to a material with weaker tensile strength. Poulose *et al.*, (2018)<sup>13</sup> found that the addition of biochar to PP seemed to decrease its tensile strength. It was implied that the decrease in tensile properties could be due to poor interaction between the biochar particles and the PP matrix. Das *et al.*, (2015a)<sup>62</sup> who experienced a similar decrease in tensile strength with the addition of biochar to PP/wood, suggested that the presence of voids, which are empty spaces within the blend caused by biochar, could have contributed to the lower tensile strength of the polymer. Nevertheless, in another paper by the same author, they found that the addition of biochar to PP without the presence of wood did not cause any significant negative effects on the tensile strength of PP, so it could be that the reduction in tensile strength was caused by the presence of wood particles instead of biochar.<sup>12</sup>

Nan *et al.*, (2015)<sup>60</sup> added that a drop in tensile strength is theorized to be due to the particle size and dispersion into the matrix. It is said that the addition of biochar could have interfered with the cross-linking of the polymer network.<sup>60</sup> Upon higher loadings of biochar, the drop in mechanical properties can be attributed to aggregations formed by the biochar particles. Therefore, biochar of a smaller scale could have the potential to form proper interfacial bonding with the polymer matrix and in turn, improve the tensile strength of the resulting composite. Interestingly, while biochar may have negative effects on the tensile strength of some polymers, they have been found to be beneficial to the tensile strength of other polymers. Idrees *et al.*, (2018)<sup>58</sup> found that PET with biochar content up to 5% w/w had higher tensile strength when compared to the neat PET. This was attributed to the good interfacial bonding between the two components due to the porous structure of biochar which allows for mechanical interlocking of the matrix to the biochar additive. However, it was also noted that lower loadings of biochar (0.5% w/w) lead to a higher tensile strength as compared to higher loadings of biochar (1, 3, 5% w/w). This is because the lower content of biochar allowed for a more well dispersed composite mixture with less agglomeration. The addition of biochar to UHMWPE/LLDPE also seemed to increase the tensile strength of the polymer mixture.<sup>57</sup> They found that there was good homogenous dispersion of the additive even with biochar content of up to 60% w/w.

The elongation at break of a material is the ratio of the difference between the length of the sample at break and the initial length of the sample before tensile stress is applied. The elongation at break is a useful parameter to assess the ductility of a material. Poulose *et al.*, (2018)<sup>13</sup> reported a general decrease in elongation at break as a function of increased biochar load. This is caused by an increase in the toughness due to the incorporation of biochar with PP which led to the composite being more resistant to deformation. Nan *et al.*, (2015)<sup>60</sup> also found a decrease in ductility of PVA upon the addition of biochar. However, they found an increase in the tensile modulus which is a measure of polymer toughness, due to the biochar's naturally higher rigidity as compared to PVA. Das *et al.*, (2015b)<sup>66</sup> also discovered that the PP/wood composites had



a higher elongation at break as compared to PP/wood/biochar composites.

Another important aspect of the mechanical properties of a material is its flexural strength. In other words, flexural strength is the ability of the material to be bent without fracturing. Zhang *et al.*, (2018)<sup>56</sup> compared the flexural strength of HDPE/rice husk (RH) and HDPE/rice husk biochar (RHB). They found that although both RH and RHB had positive effects on the flexural strength of HDPE, at higher loadings, RHB continued to strengthen the flexural properties of the polymer whereas, RH started to cause a decline in tensile strength. With a maximum flexural strength of 53.7% at 70% w/w RHB, they attributed this to the fact that RHB limited the mobility of the polymer chains leading to less deformation of the matrix in its elastic zone.<sup>56</sup>

A similar study combined poplar biochar with HDPE and found that the addition of biochar up to 50% w/w significantly improved the flexural strength of HDPE.<sup>59</sup> However, further loading of biochar at 70% w/w caused the flexural strength of the composite to drop below that of neat HDPE. This was because, at 70% w/w biochar, there was not enough polymer matrix to properly bond with the biochar particles. Additionally, higher biochar content would lead to a higher degree of agglomeration which could be detrimental to the mechanical properties of the composites.<sup>59</sup> Das *et al.*, (2016b)<sup>67</sup> also had positive results in terms of flexural properties with the addition of biochar to PP. They found that the flexural strength of neat PP increased from 51.08 MPa to 58.26 MPa with the addition of 35% w/w biochar.

The ability to withstand a sudden force applied to the surface of a material is called impact strength. The impact strength is also one of the key properties of materials when referring to mechanical strength. The effect of biochar on the impact strength of polymers varies. In one study, it was found that the addition of biochar to HDPE had a negative effect on the impact strength of the composite.<sup>56</sup> The decline in impact strength increased with further addition of biochar content. It was explained that the high rigidity of the biochar fillers resulted in increased brittleness and decreased toughness in the composite. However, the authors also compared the results to those of wood/HDPE and found that biochar/HDPE had significantly higher impact strength than wood/HDPE, especially at higher filler loadings. This is attributed to the presence of pores in the biochar which allows a more uniform dispersion of filler due to HDPE being embedded into the pores.<sup>56</sup> In a similar study, Zhang *et al.*, (2019)<sup>59</sup> also found that biochar addition worsened the impact strength of the composite. While the presence of pores within the biochar structure may prove beneficial for filler-polymer dispersion and interaction, it also limits the mobility of the polymer chains resulting in a weakened ability to absorb the energy of an impact force. Nagarajan *et al.*, (2016)<sup>3</sup> stated that the size of the biochar particles had a profound effect on the impact strength of the composite. The authors found that by decreasing the size of the biochar particles, they were able to slightly increase the impact strength of poly(trimethylene terephthalate) (PTT) and PLA blends.

## 4. Comparison of biochar with other carbon materials as a reinforcement material in polymer composites

Besides biochar, other carbon materials especially carbon nanotubes (CNT) and graphene have been of great interest to be used as a reinforcement material as they can effectively enhance the properties of polymer matrices as well as their utilities to a large extent.<sup>68</sup> In this sub-topic, the effect of reinforcing CNTs and graphene for composite production will be discussed and compared with biochar.

### 4.1 Carbon nanotubes

Carbon nanotubes (CNTs) are cylindrical molecules that consist of graphite sheets, with a diameter size of about 100 nm, and their length can reach several micrometers.<sup>69</sup> In general, there are two types of CNTs which are single-walled (SWCNT) and multi-walled (MWCNT).<sup>70</sup> The major difference between these two types is their graphene layer. SWCNT can be described as a single hexagonal graphene layer with an approximate diameter between 0.4–3 nm. While MWCNT consists of a number of rolled-up hexagonal graphene sheets, and the diameter was around 1–3 nm.<sup>71</sup>

Unlike biochar which can be produced by a simple carbonization process, CNTs require a complicated process to be produced. Arc discharge, laser ablation, and chemical vapor deposition methods are among the common methods used to produce CNT from graphite. Nevertheless, these methods are costly and only able to produce a limited amount of CNTs. In fact, those produced CNTs need to be further purified prior to being used as a reinforcement material due to the presence of impurities associated with the catalyst that is needed during the production process as well as due to the presence of amorphous carbon and non-tubular fullerene structures in them.<sup>71</sup>

Despite their costly and complex production process, CNTs have been proven as a superior nanomaterial that can enhance the electrical and thermo-mechanical properties of matrices owing to their unique structure, outstanding thermal conductivity, and high aspect ratio.<sup>58,72</sup> Findings by Thi *et al.* (2020)<sup>68</sup> revealed that by incorporating only 1–3 wt% SWCNT in polycarbonate (PC) is enough in enhancing both electrical and mechanical properties of polymer matrix. Similarly, Liu *et al.* (2019)<sup>72</sup> also discovered that the incorporation of CNTs in microcapsules with dodecanol core and melamine-formaldehyde (MF) resin shell was able to enhance the thermal conductivity of the microcapsules by 35.2%.

On the other hand, the increase of CNTs loading in the polymer matrix may lead to a heterogeneous dispersion by forming clusters and agglomeration within the polymer matrix, thus reducing the mechanical properties. Hence, a high shear force is needed to disperse high CNTs loading into the polymer matrix.<sup>73</sup> In this particular scenario, pre-compounding is necessary to de-agglomerate CNTs by sonication or/and mechanical stirring, where the shearing force is higher than a typical screw-extruder used during compounding. However,



too high of shearing severity may likely cause CNTs degradation.

#### 4.2 Graphene

Graphene is a single atomic sheet composed of  $sp^2$  carbon atoms arranged in a honeycomb pattern.<sup>74</sup> It has high mechanical strength and modulus of elasticity, has unparalleled electronic properties, and a large surface area that can be chemically functionalized.<sup>75</sup> In general, graphene has two derivatives, namely graphene oxide (GO) and reduced graphene oxide (rGO).<sup>76</sup> Like any other carbon filler, the underlying reinforcement mechanisms of graphene in polymer composites are dependent on filler concentration, aspect ratio (interfacial area), homogeneous dispersion, and interfacial adhesion.<sup>73</sup>

Nevertheless, graphene is often chemically modified to either GO or rGO before being incorporated into the matrix. This might be because of their larger surface area, layered structure, and oxygen-containing functional groups compared to graphene. For example, epoxy composites with GO inclusion demonstrate improvement in tensile strength, Young's modulus, and fracture resistance over pure epoxy composites. The covalent bonds formation along with GO interface within polymer matrix attributes to effective load transfer.<sup>77</sup> Also, with a strong interfacial interaction it provides, the behavioral polymer chains mobility at a high temperature can be impeded, hence increasing the resulting composites' glass transition temperature ( $T_g$ ).<sup>78</sup>

The addition of graphene also shows an improvement in electrical conductivity and this was proven by Wang *et al.* (2012).<sup>73</sup> The author revealed that graphene is capable of providing electrical conductivity to the insulating polymer matrix. It has high intrinsic conductivity which leads to a lower electrical percolation threshold. With the addition of graphene, it promotes the formation of a percolating network within the matrix which reduces the electron conduction resistance. The conductivity output of nanocomposites is influenced by filler dispersion and alignment, as well as the intrinsic characteristics of the filler such as aspect ratio, morphology (defects), and inter-spacing between graphene sheets.<sup>73</sup>

A highly disperse graphene, however, has not necessarily promoted the onset of electrical percolation as it barely formed a continuous graphene-graphene conductive network within the matrix so that the electron can be percolated from one's end to another end of the nanocomposites.<sup>79</sup> The 2D geometry of graphene also offers a lower interfacial thermal resistance (high thermal conductivity) in the nanocomposites.<sup>80</sup> Similar to CNTs, high loading of graphene may also lead to the reduction of mechanical properties as graphene tends to agglomerate. In order to overcome this issue, a high shear force is needed to break the agglomeration. Nevertheless, this method is unsuitable for GO and rGO. Byrne and Guin Ko (2010)<sup>81</sup> reported that the poor thermal resilience and the small mass density of chemically modified graphene make it unsuitable for this method. The use of high shear force during mixing may result in graphene sheets shortening, thus reducing its aspect ratio.

Besides that, this technique often leads to unintended oxidative depolymerization at high temperatures.

#### 4.3 Comparison of biochar, carbon nanotubes and graphene-based composites

Overall, Table 2 summarises the comparison of composites reinforced with biochar, CNTs and graphene.

### 5. Challenges in the preparation of biochar-based polymer composites

The incorporation of biochar in polymers leads to the creation of new polymer composites with improved structural and functional properties due to the synergistic effects of the biochar and polymers. Nevertheless, there are challenges in utilizing biochar in the polymers such as the possibility of ash formation during polymer composite melt-compounding, and the appropriate methods to maintain the safe and environmentally friendly production.

In the context of polymer composites preparation, three common processes namely compounding, blending, and mixing are usually applied. Compounding is a process in which polymers are softened, melted, and intermingled with fillers to produce a composite. Blending is referring to a process in which two or more materials are physically intermingled without causing any physical changes to the materials. While mixing describes both compounding and blending processing, which involves the intermingling of polymers with fillers or other additional materials without any specific restrictions, to produce composite.<sup>92</sup>

These three processes play big roles in ensuring polymers, fillers, and other materials are homogeneously mixed to produce a desirable composite with superior properties. In the case of biochar-based composites, the major challenge comes from the varied properties of biochar itself. According to Bartoli *et al.*, (2019),<sup>93</sup> biochar from different biomass acts differently when being used as a filler for epoxy resin. In his findings, wheat straw (WS) and oilseed rape (OSR) derived biochars were able to increase tensile strength and Young's modulus of epoxy resin by approximately 35–50%, mainly due to the presence of pores that can act as anchoring sites for the resin to create high tensioned structures. Miscanthus straw (MS) and mixed soft-woods (SW) derived biochars, however, showed a different behavior, as they were only able to increase elongation of the epoxy resin while reducing Young's modulus. These differences could be attributed to the chemical composition of the biomass itself, especially cellulose.

According to Das *et al.*, (2018),<sup>94</sup> biomass that contains a high amount of cellulose such as wood resulted in better mechanical properties. As the main constituent of biomass, the strong and stiff cellulose remains aligned with the longitudinal axis of the fibers which is responsible for the resistance towards stress and indirectly helps to increase the composite's mechanical properties after being reinforced into the polymer matrix. Besides the properties of biomass or feedstock, the amount of biochar to be reinforced into the polymer matrix need to be identified as



Table 2 The comparison of composites reinforced with biochar, CNTs and graphene

	Biochar-based composites	CNTs-based composites	Graphene-based composites
<b>Raw materials and their production method</b>	Biochar can be produced by pyrolysed any biomass at a very high temperature ( $>500\text{ }^{\circ}\text{C}$ ) <sup>82</sup>	CNTs is produced by separating it from graphite by either: <sup>83-85</sup> catalytic chemical vapor disposition (CCVD), laser ablation, arc discharge	Graphene is produced by separating it from graphite by either: micromechanical exfoliation, liquid exfoliation, chemical vapor deposition, flame synthesis, pulsed laser deposition
<b>Advantages of filler as a reinforcement material</b>	Biochar is a renewable material and the use of it to replace non-renewable carbon materials would reduce the ubiquitous dependency on fossil fuels, minimise wastes and promote sustainability. The addition of biochar in the composites may improve their thermal stability. <i>E.g.</i> the addition of 20 and 30 wt% biochar to epoxy composites have increased the $T_{d10\%}$ by 7–20%. Overall, the thermal degradation of the epoxy/biochar composites was delayed. <sup>86</sup> Biochar exhibits aliphatic functional groups on its surface, which make it hydrophobic. Due to this, when biochar is incorporated in wood and polymer composites, it may lower the resulting moisture absorption of the entire composite. <sup>66</sup>	CNTs possess excellent adsorption ability, owing to its ability in creating a strong interaction with other molecules. <i>E.g.</i> CNTs has been used as an adsorbent for various heavy metal ions such as copper, nickel, cobalt, vanadium, silver, cadmium and other earth elements. <sup>87</sup>	Graphene recorded the highest thermal conductivity than biochar and CNTs which is about $5300\text{ W mK}^{-1}$ . <sup>72</sup> <i>E.g.</i> the incorporation of rGO into <i>n</i> -eicosane/silica microcapsules increased the thermal conductivity by 83–193% and decreased the latent heat by 6–15%. <sup>88</sup>
<b>Disadvantages of filler as a reinforcement material</b>	The properties of biochar are mainly dependent on the properties of biomass (raw material) and thermal conditions during pyrolysis. <sup>9</sup> Modification is needed to increase the properties of biochar, <i>i.e.</i> by increasing the specific surface area and pore fraction, forming functional groups, <i>etc.</i> <sup>89</sup> The different feedstock used to produce biochar will produce biochar with different properties. <i>E.g.</i> the percentage of biochar loading at which best mechanical properties obtained was inconsistent for epoxy composites with three different biochars; plastic waste char, wood shavings char, and pine cone char. <sup>86</sup>	Homogenous dispersion of CNTs especially at high loading is difficult to achieve. Modification is needed to reduce the aggregation and improve the dispersion of CNTs caused by the inactive surface of CNTs. <sup>70</sup> The high cost of CNTs does not compensate for the enhancement of properties on numerous occasions, unless for premium end-products. <sup>87</sup>	Graphene may cause a reduction in the mechanical strength of composites, mainly due to poor interface with matrices. Hence, it needs to be modified to GO or rGO. <i>E.g.</i> the mechanical strength and deformation at break of epoxy/graphene composites are much lower than the neat epoxy resin due to the poor interface between the nanofiller and matrix. <sup>90</sup> Similar to CNTs, graphene is expensive and considering the cost, it can only be used for premium end-products. <sup>87</sup> The cohesive energy between graphene layers is around $2\text{ eV nm}^{-2}$ which is considered very high, and this causes graphene to irreversibly agglomerate or restack when compounded with molten polymer or when solvents evaporate from graphene dispersion. <sup>91</sup>

well. Ho *et al.* (2015)<sup>95</sup> revealed that biochar composition gave significant improvement to both tensile and flexural modulus. This was highly attributed to the reduction of intra-particle distances by the incorporation of a higher amount of biochar. Nevertheless, an excess amount of incorporated biochar may as well lead to the reduction of mechanical properties, mainly due to aggregation. The aggregated biochar may enhance the brittleness of composites, thus reducing the elongation at break and this limits the composite's usage.

As a biomaterial produced by pyrolysis process which involves extremely high temperature, biochar consists of high carbon content which may cause health deterioration if being inhaled. Direct exposure to carbon especially during polymer composite compounding may lead to respiratory problems and skin inflammation, while chronic inhalation exposure may raise the risk of cancer and permanent damage to the lungs. Hence, protective equipment which may offer protection to the wearer as stipulated under the Occupational Safety and Health (Use



and Standard of Exposure to Chemical Hazardous to Health Regulations 2000 need to be worn throughout the processing. The aim is to eliminate, minimize and prevent hazards from being in contact with the worker.

## 6. Future recommendations and summary

A wide range of biomass have been explored as the potential feedstock for biochar production, and their effectiveness as filler for various polymer matrices were also reported. Despite of using various feedstock, all of them are facing similar issues after being reinforced into the polymer matrices, aggregation and heterogeneous dispersion of biochar. In regards to this matter, biochar properties need to be modified to ensure it can be used commercially as a polymer filler.

Reducing its size from macro/microsize into nanosize particles could be an interesting approach to further understand its potential as a filler. Nanosized biochar can be obtained by subjecting the biochar to physical treatment such as ball milling as illustrated in Fig. 2.<sup>96</sup> Biochar in its microsize has been found to improve the mechanical properties of polymer composites as mentioned earlier. It is expected that nanosized biochar would provide a better mechanical property due to the fact that the interfacial area of nanomaterial is higher as compared to the microsize material. The stress transfer from the polymer matrix to the nanomaterials is greater at a higher interfacial area and this leads to the improved mechanical properties when nanomaterial is used as a filler.<sup>97</sup> Nevertheless, agglomeration tends to occur for nanomaterial at high concentrations, it is, therefore, important to optimize the nanosized biochar loading into the polymer matrix, which could be the study of interest in the future.

The interaction of biochar and polymer matrices may also be enhanced by the addition of compatibilizers. Compatibilizers can help in modifying the interfacial properties of a blend of immiscible materials including biochar–polymer blends, making them bind tightly to each other. This will indirectly enhance the interfacial adhesion between biochar–polymer, thus increase the mechanical properties of the composite afterward. Besides physical modification by using a compatibilizer, biochar can also be modified using a chemical

treatment. The use of chemicals such as  $\text{HNO}_3$  and  $\text{NaOH}$  for surface modification of biochar can improve the biochar/polymer composite properties due to the introduction of amino and carbonyl/carboxyl groups on biochar surface.<sup>98</sup>

Despite some pointed difficulties that have to be overcome, the utilization of biochar as a renewable filler is seen as one of the alternatives to replace non-renewable filler. In fact, the use of biochar as a filler for biocomposite production fulfilled several principles of green chemistry, which are the 1st principle: prevention, 3rd principle: less hazardous chemical syntheses, 7th principle: use of renewable feedstocks and 10th principle: design for degradation.<sup>99</sup> The rationale behind the fulfillment of the 1st and 7th principles is since biochar is mostly produced from agricultural biomass, its usage as an alternative filler is seen to be able to reduce and prevent biomass accumulation, which if not efficiently managed, might cause environmental issues. This indirectly maximizes the utilization of biomass for high-value-added products. In terms of the risk of chemical synthesis, the overall biochar and biocomposite process do not generate toxic substances that may be harmful to humans and the environment, and biochar will also be degraded on its own over time, thus fulfilling the requirement of the 3rd and 10th principles.

## 7. Conclusion

Biochar from biomass is indeed potentially viable in terms of its performance and commercial value to be utilized as a renewable and superior filler for polymer composite. Further studies will be needed to determine the toxicity, rheology, and stability of the biochar/polymer composites in order to evaluate the potential applications of this material.

## Conflicts of interest

The authors have no conflict of interest to declare.

## Acknowledgements

The authors would like to thank the Ministry of Higher Education (MOHE), Malaysia for financial support through Fundamental Research Grant Scheme, FRGS/1/2019/TK05/UPM/02/1 (vote no. 5540321).

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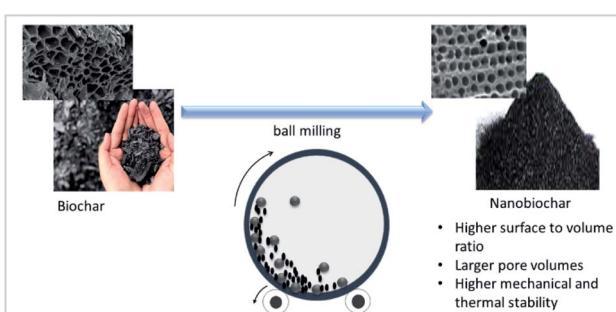


Fig. 2 Schematic diagram of nanobiochar production (modified from Naghdi et al., (2017)<sup>96</sup>).



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