Chapter

Towards Traditional Carbon Fillers: Biochar-Based Reinforced Plastic

Mattia Bartoli, Mauro Giorcelli, Pravin Jagdale and Massimo Rovere

Abstract

The global market of carbon-reinforced plastic represents one of the largest economic platforms. This sector is dominated by carbon black (CB) produced from traditional oil industry. Recently, high technological fillers such as carbon fibres or nanostructured carbon (i.e. carbon nanotubes, graphene, graphene oxide) fillers have tried to exploit their potential but without economic success. So, in this chapter we are going to analyse the use of an unconventional carbon filler called biochar. Biochar is the solid residue of pyrolysis and can be a solid and sustainable replacement for traditional and expensive fillers. In this chapter, we will provide overview of the last advancement in the use of biochar as filler for the production of reinforced plastics.

Keywords: biochar, composites, sustainable production, carbon materials

1. Introduction

Carbon-based materials are a very well-established commodity generally used in materials science [1]. Nowadays, many commodities makes use of carbon fibres as they become an unavoidable asset for the global market [2]. Carbon fibres represent the most diffuse high-tech carbon materials, but carbon black played the main role in these materials. Carbon black (CB) harvests a great global carbon revenue due to its use for the production of plenty of composites but mainly for tyres [3]. Over the years, high-cost carbon materials such as carbon nanotubes (CNTs) and graphene-like materials have gained the attention of the scientific community with their amazing conductivity and optic and mechanical properties [4, 5]. Despite the expected revolution, nanosized allotropic carbon form did not have much progress in the research area. In a very optimistic report, Segal [6] dreamed that the world was ready for the industrial-scale production of graphene, but after a decade, single-layer graphene is still sold at 200 €/cm^2, while graphene oxide costs 100,000 €/kg [7]. On the other hand, CB is sold for around 1 €/kg [8]. New-generation high-tech carbon materials (i.e. CNT, graphene and graphene oxide) have not yet fulfilled the promise for a new carbon era. While the industry waits for large-scale commercialization of high-quality affordable carbon allotropes, new materials have been considered through engineered carbon for profitable business. In recent years, a new material has emerged as the most promising for the integration of carbon

production with waste management [9–11]. This material is biochar, the solid residue from pyrolytic conversion of biomass. Biomass waste stream is one of the most abundant worldwide, and it is generally disposed through incineration. This presents both an environmental issue and an economic loss due to the transformation of a high-quality material into heat. Accordingly, a more profitable advantage was found in their thermal conversion for the production of biofuels [12, 13], chemicals [14] and other materials [15]. Conversion of biomass into liquid fuels is challenging due to the high oxygen content compared with traditional oil-derived products (i.e. gasoline, virgin nafta, diesel). On the contrary, biochar production is a process full of opportunities with the emergence of carbonaceous material from both lignocellulosic and non-lignocellulosic biomasses. This bioderived carbon is used in many applications [16] due to its properties and low cost attested at around 1–2 €/kg [17–19]. Actually, biochar has found a large-scale application for soil health improvement [20–22] and as solid fuel with a heating content of around 40 kJ/mol [23]. Nonetheless, these applications are limited and unable to exploit the full potentiality of biochar due to their easy tunability with simple process adjustment [24].

In this book chapter, we report an overview of the composite applications of biochar to prove its feasibility as a replacement for traditional carbon materials and as a solid competitor with high-tech reinforced plastics.

2. Biochar: production ways

Biochar is produced through thermochemical routes such as torrefaction, pyrolysis and hydrothermal carbonisation and as residue of gasification.

Torrefaction is a low-temperature thermal conversion used to densify the biomasses for energy purposes [25]. The process temperature is in the range from 200–350°C, and the conversion requires long residence and processing times. Torrefaction is characterised by biochar and biochar-like yields [26]. The carbon percentage of solid residue is generally around 50–60 wt.% [27], but it can reach 72–80 wt.% using microwave process with the addition of microwave absorbers as reported in several studies [28–31]. Microwave use leads to the drastic reduction of process timescale from hours to minutes.

Pyrolysis is a high-temperature thermochemical conversion which induces the cracking of polymers with the formation of low-molecular-weight compounds in an oxygen-free or oxygen-poor atmosphere [12, 32]. Pyrolysis is run using different heating technologies [33] and apparatus design [34–37] at a temperature range from 450–700°C [38] with huge variations in product fraction yields. Pyrolysis of biomasses was deeply studied, and the main mechanisms can be rationalised in a few different steps. The first is the release of moisture from the feedstock, increasing the surface area and improving the pore structure, which favours a quick release of volatiles and minimizes char-catalysed secondary cracking. Lignocellulosic biomass behaviour during pyrolysis could be rationalised through the behaviour of the main components as cellulose, hemicellulose and lignin. The pyrolysis of cellulose takes place between 430 and 470°C and hemicellulose between 470 and 600°C while lignin between 600 and 800°C. During this process other reactions such as dehydration of the sample, pyrolysis of the volatiles present, formation of levoglucosan from cellulose [39] and formation of substituted aromatic rings from lignin [40] take place together with the formation of carbon.

Hydrothermal carbonisation is a thermal cracking used to produce crude-like oil and hydrochar under moderate temperature and high pressure [41] using aqueous solvent [42], nonaqueous solvent [43, 44] or subcritical/critical media [45].

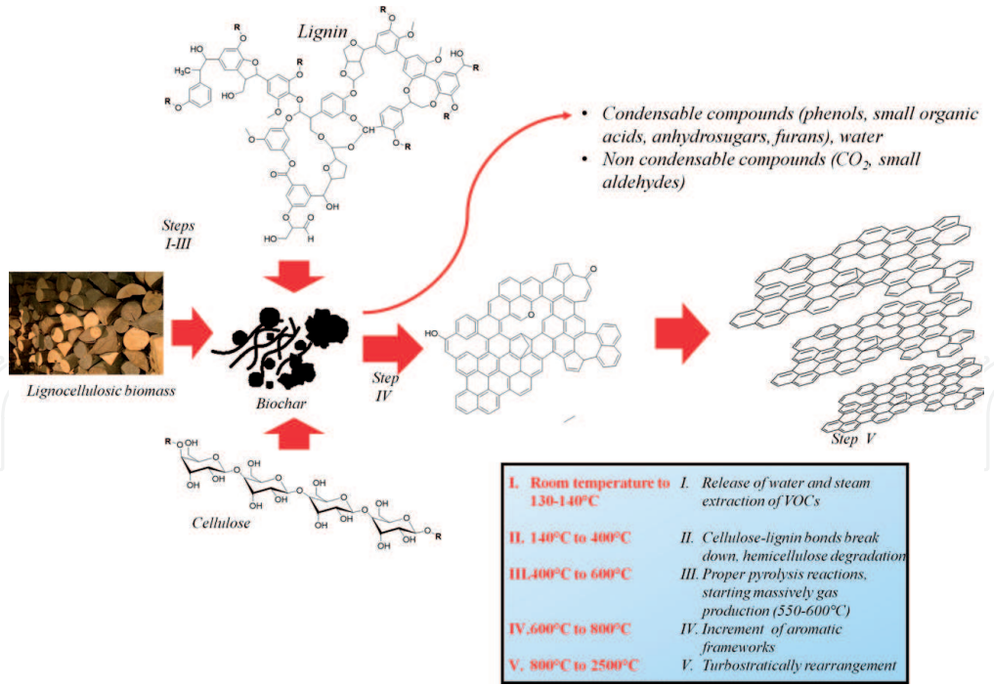

Figure 1.
Conversion of lignocellulosic biomasses to carbon structures.

Finally, gasification is the conversion of biomass into combustible gas by heating in air [46], pure oxygen or steam [47] at temperatures higher than 800°C with or without a catalyst [48]. Products from gasification are a mixture of carbon monoxide, carbon dioxide, methane, hydrogen and water vapour. Biochar is not the main product of gasification, but it is characterised by a simultaneous high carbon and ash content.

In summary, **Figure 1** shows the main stage of biomass conversion.

Furthermore, it is relevant to notice that leaves, stems, bark and roots are different lignin/cellulose ratio and mechanical properties. The same is true for different species.

Some of these differences could be retained into biochar and induce appreciable properties.

Also, the graphitic domains formed during pyrolytic treatment could undergo a stacking rearrangement leading to a graphitization of biochar with the increasing temperature.

3. Biochar-based reinforced plastics

Nowadays, reinforced plastic materials are one of the largest global markets in the polymer sector with an expected global revenue of up to 130 M$/year in 2024 as summarised in **Figure 2.**

Carbon-containing reinforced plastic is one of the most relevant materials with an annual production of up to 150 kton/y in 2018 [50]. As clearly reported in **Figure 3**, around 80% of the total carbon-containing reinforced plastic is represented by polymer host materials, 49% of which comes from thermoset resin and 30% from thermoplastic polymers. Among them, carbon fibre-reinforced epoxy polymers are the larger amount. This is due to their numerous applications in all-capital high-tech sectors ranging from aeronautics and aerospace industries [51] to automotive industries [52]. In this global scenario, biochar plays a minor role even if it could be used, and it is going to consolidate itself as a trustworthy commodity with its production flexibility and property tunability [53].

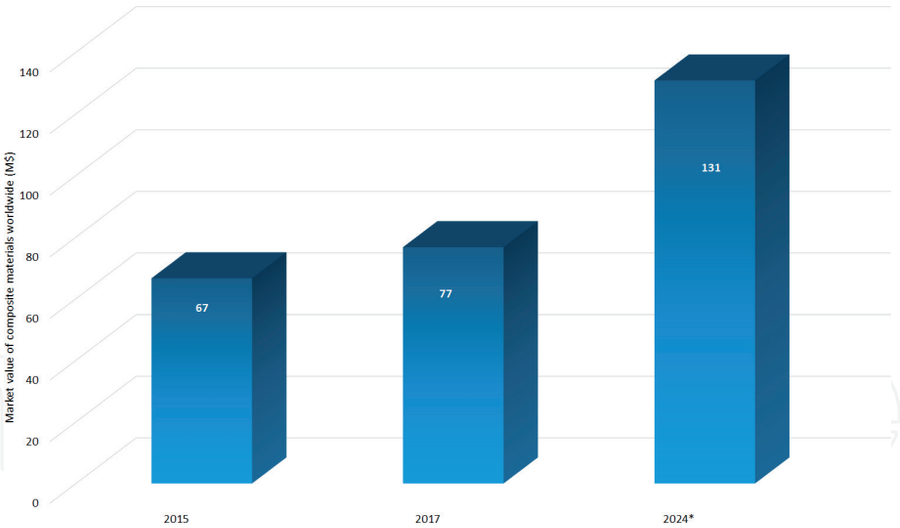

Figure 2.
Reinforced plastic worldwide revenue with a prediction for the year 2024 [49].

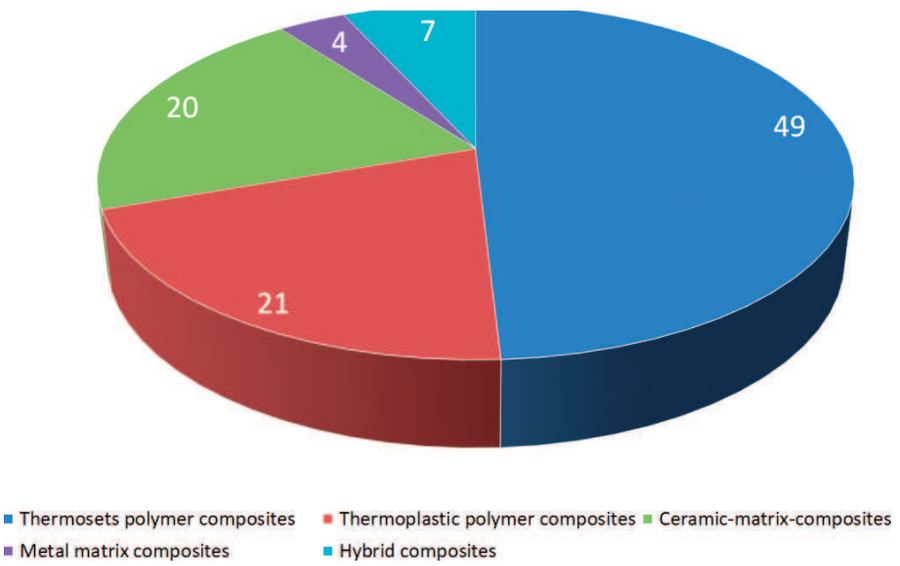

Figure 3.
World's carbon-based reinforced plastic production in 2018 [50].

Therefore, the main uses of biochar in both thermoset and thermoplastic matrices are overviewed.

Carbonaceous-reinforced thermoset resins are the most commonly used materials dispersed in plenty of different polymer hosts [54–56]. Epoxy resins are the most deeply applied and used around the world. Consequently, the replacement of carbon fibres and carbon black, carbon soot and anthracites with biochar has gained a great interest. Khan et al. [57] described the mechanical and dielectric properties of high-temperature-annealed maple-derived biochar dispersed into a two-component epoxy resin. Biochar filler was used in concentration ranging from 0.5 wt.% to 20 wt.%. The authors clearly showed the improvement of mechanical properties using filler loading of up to 4 wt.%. Regarding electric properties, Khan and co-workers found that a low loading of multiwalled CNTs induced the same effects of a 20 wt.% loading of biochar. Recently, Bartoli et al. [58] described the relationship between the biochar morphology and related composite mechanical properties using a biochar loading of 2 wt.%. The authors achieved a 40% increment of maximum elongation using a rhizomatous grass-derived biochar and Young's modulus increment using a wheat straw as a source for biochar production.

The authors suggested that smooth surface could induce an improved mobility inside the epoxy matrix, while highly porous and channelled surfaces do not. Additionally, they suggested that the dispersion methodology adopted based on ultrasonication, summarised in **Figure 4**, reduced the size of biochar particles with a direct relation with the original morphology of the very same particles.

Furthermore, pyrolytic temperature is the main and critical parameter for tuning biochar properties with the goal of improving resin properties. The interactions between epoxy resin and biochar particles. Bartoli et al. [59] studied the effect of the heating rate and maximum pyrolytic temperature on biochar. Furthermore, cellulose templates could be used for the production of biochar fibres and balls using selected precursors. As a matter of fact, biochar produced from wasted cotton fibres could be recovered as carbon fibre shape showing a property enhancement of epoxy resin host matrix [60, 61], while the one produced from cellulose nanocrystals could be recovered as micrometrics ball or nanometric needles [62].

Authors showed the complex relationship of produced biochar with related containing epoxy composites. Sample prepared at different temperature and using different heating rate increment or the Young's modulus or the toughness of the reinforced plastics. Interestingly, the biochar produced at very high temperature of up to 1000°C generally induced a high increment of elongation probably due to the unpacking of the aromatic ring of epoxy host.

Similarly, Giorcelli et al. [63] proved the effectiveness of maple tree-derived biochar produced at 600°C and 1000°C, observing a drastic improvement of maximum elongation compared with neat resin.

Temperature also affected the electrical properties of biochar and biochar-containing composites. High thermal annealed biochar could represent a solid choice for the production of conductive epoxy composites. Giorcelli et al. [64] described that highly graphitic biochar induced better performances during DC electrical conductivity measurements. Temperature treatment and related graphitization processes lead to an improved ability of these materials to shield microwave radiation with similar outputs with respect to multiwalled CNTs [65] even under thin-film shape [66].

The other huge field of composite materials is represented by thermoplastic reinforced plastics. In this very same field, polyolefin represents the greater amount of worldwide production. Among them, biochar-containing polyethylene was studied by Arrigo et al. [67] using an exhausting coffee-derived biochar produced at 700°C. The authors described the rheological and thermal properties of biochar-related composites with a filler loading up to 7.5 wt. %, showing a decrement of the dynamics of polymer chains in the host matrix related to the confinement of the

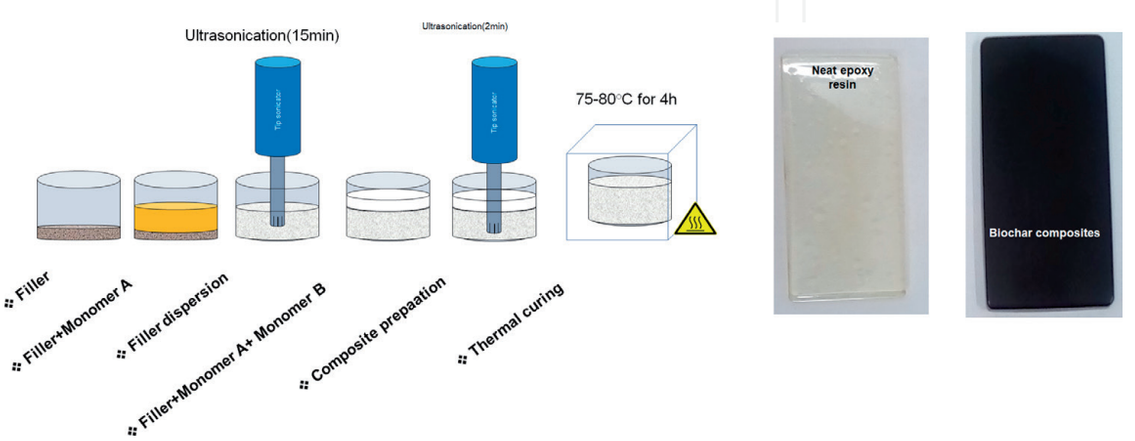

Figure 4.
Ultrasonication methodology for the effect dispersion of biochar inside the epoxy resin host.

polymer chains on the biochar surface. Additionally, the well-embedded biochar particles improved the thermo-oxidative stability of polyethylene composites produced. Zhang et al. [68] studied the temperature influence on biochar production from poplar and its use as filler for high-density polyethylene. Curiously, the microcrystalline structure of the polymer was not affected by the presence of biochar according to the thermal data collected. A different trend was reported for the mechanical properties that were appreciable different in the comparison between neat and biochar-loaded poly(ethylene) with an improvement of flexural strength and a decrement of the impact strength. Zhang et al. [69] valourized agricultural waste streams through pyrolysis, and the resulting biochar was used as filler for ultra-high-density poly(ethylene). The authors observed improvement in their mechanical properties and improvement in the flame retardancy of the high filler loading materials. Similar results were achieved by Sundarakannan et al. [70] using biochar derived from cashew nuts. Also Li et al. [71] investigated the high loads of biochar in ultra-high-molecular-weight poly(ethylene), achieving a remarkable electromagnetic interference shielding properties using an 80 wt.% of bamboo biochar pyrolysed at 1100°C. This material showed a very high conductivity of up to 107.6 S/m. Furthermore, Bajwa et al. [72] described the use of biochar for the production of a composite blend based on high-density poly(ethylene), poly(lactic acid) and wood flour with superior thermal stability.

The other largely used polyolefins is poly(propylene). Poly(propylene) is widely applied for the realisation of biochar-based composites due its workability. The main application of poly(propylene)-related composites is in the automotive sector. Tadele et al. [73] published an interesting comparative study on life cycle assessment of biochar used in automotive, showing the feasibility of its use. Das et al. [74] reached the same conclusions about the economic feasibility of the use of biochar instead of traditional carbonaceous fillers. The authors showed the appreciable cost reduction of a biochar-containing composites achieving the same properties of carbon black-based ones due to the sensible reduction of compatibilizer down to a maximum of 3 wt.%. The affordability of the cost of biochar was the core of the research proposed by Behazin et al. [75]. In this study, a pyrolysed perennial cane was used as filler of a polymer blend based on poly(propylene)/poly(octene-ethylene). The produced composite contained a filler loading ranging from 10 to 20 wt.% and showed the very strong interactions between polymer matrix and biochar particles. The most detailed and comprehensive set of studies about poly(propylene) and biochar interactions was conducted by Bhattacharyya research group and his co-workers as attested by many papers [76–78]. During this pluri-annual research, the authors investigated the kind and magnitude of interactions between filler and poly(propylene). They conclude that the addition of several types of biochars lead to a general improvement of the mechanical and thermal properties of related poly(propylene) composites together with the induction of flame retardancy properties. Additionally, Elnour et al. [79] studied the relationship between biochar properties and related poly(propylene) composites showing an increment of stiffness together with unaffected tensile strength. In the same period, Poulose et al. [80] mixed date palm-derived biochar with poly(propylene) showing the negligible effect of biochar on the storage modulus in a range of concentration of up to 15 wt.%. Poly(ethylene) and poly(propylene) are not the only polyolefins used for the production of carbon-based composites. Other largely used polyolefin matrices were poly(vinyl alcohol) and its derivatives [81, 82] and poly(acrylonitrile) [83]. Both of those two polymeric hosts are used for the realisation of piezo sensors due to their elastic properties.

Furthermore, polyesters were used for the realisation of carbon-based reinforced materials. As an example, polyamides were impregnated with biochar as

described by Ogunsona et al. [84]. The authors mixed nylon 6 with the biochar produced from the pyrolysis of *Miscanthus* canes. The biochar used was produced using a process temperature ranging from 500–900°C. The different temperatures used affected the output of the composites with a beneficial effect on only the high-temperature-treated biochar and a detrimental effect on the others. In 2019, Sheng et al. [85] modified bamboo biochar through the addition of silyl groups on the particle surface for the production of poly(lactic acid) composites. Surface functionalization showing an appreciable enhancement of maximum elongation of up to 93% was compared with neat polymer matrix.

Recently, biochar was used for the realisation of biopolymer composites based on polysaccharides such as cellulose [86], starch [87] or gluten [88] under the vision of blue and green economy for a total bio- and sustainable productive line.

4. Conclusions

In this chapter, we provided overview of the most recent applications of biochar in the field of polymer composite production with a focus on more useful and unusual ones. We also described in detail the possibility of using biochars as a sound replacement for traditional fillers in both thermoset and thermoplastic composite materials. The researches herein described the feasibility of biochar used in different industrial sectors as a solid alternative to traditional and nanostructured materials. The adaptive nature of biochar presents a very strong point of advantage for spreading its use across the field of materials science.

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