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ORIGINAL PAPER

Valorization of Biomass Gasification Char as Filler in Polymers and Comparison with Carbon Black

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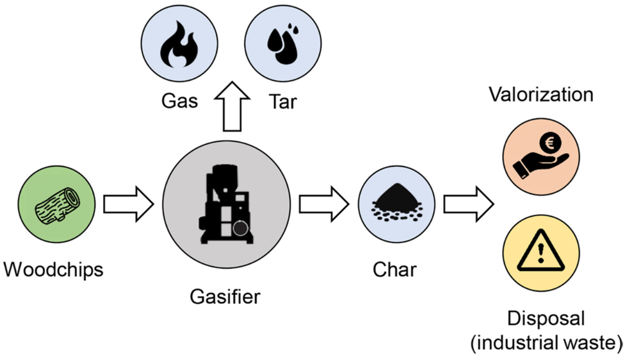
Abstract

Char, the solid residue produced during biomass gasification, is usually treated as a waste with high environmental and economic costs associated to its disposal. However, char shows remarkable properties that make it suitable for a plethora of different applications. In particular, this study aims at investigating the feasibility of using char as filler in polymers for boosting polymer thermal stability and electrical conductivity, and comparing its performances with carbon black (CB), a more traditional carbonaceous filler. Char residues were collected from a commercial biomass gasifier, thoroughly characterized, and compared with CB. Both materials were used in combination with a styrene–ethylene–butylene–styrene (SEBS) matrix for the production of two different compounds, deeply characterized as well. An addition of 44 wt% of char increases the thermal stability of the compound and its electrical conductivity up to 2×10^{-3} S cm^{-1}, without interfering with its structure and mechanical properties. Less CB (20 wt%) was needed for obtaining composites with the same electrical conductivity. The findings of this study pave the way for new valorization routes for large amounts of char in cutting-edge applications and present the opportunity to the polymer manufacturing to use a high-available and low-cost substitute for carbon-based fillers.

Graphic Abstract



Keywords Biomass gasification · Char · Carbon black · Polymer · Filler · Electrical conductivity

Statement of Novelty

Char derived from biomass gasification is still considered as a waste with high environmental and economic costs associated to its disposal. However, due to its remarkable properties, char has the potential to be further valorized in different applications. This pioneer study shows how commercial char could be employed as renewable, low-cost carbon-based filler in polymers and compares its performances with more

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traditional and high-cost fossil-based carbon black, already available on the market. This work demonstrates that char addition in a polymer matrix not only allows for reducing wastes, pollutants, chemicals utilization, costs, but also for obtaining polymeric compounds with enhanced thermal stability and electrical conductivity.

Introduction

Char is the solid residue obtained after the gasification of biomass, i.e. the thermochemical conversion of biomass in an oxygen-deficient atmosphere [1]. The main products of gasification are syngas, tar, and char. The desirable product is syngas, a mixture of gases such as CO, H_2, CH_4 and lighter hydrocarbons, that can be used in combined heat and power (CHP) engines for cogeneration of heat and electricity or for production of fuels (e.g. F-T diesel, methanol, hydrogen, etc.). On the other hand, tar, a black and highly viscous liquid residue similar to a bituminous oil, and char, a solid carbon based material with a highly porous structure, are the undesirable products of the process [2].

Particularly, char is currently treated as an industrial waste with high costs associated for its management and disposal.

Considering the Italian Region of South Tyrol as benchmark, 1300 tons of biomass gasification char are produced every year with a related disposal cost ranging from 140 to 150 €/ton [3]. However, char possesses remarkable properties, such as a high carbon content and well-developed porosity, that make it suitable for several applications. Therefore, char should be valorized in order to lower its economic, energetic, environmental impacts, and eventually allow for carbon sequestration [4]. Ideally, the same CO_2 amount emitted from the combustion of gas derived from biomass, is used by the plants for photosynthesis, leading to a carbon neutral cycle [5]. However, when part of the carbon in the plant is not converted into CO_2 but stored in the char, the theoretical maximum CO_2 emissions would be reduced and thus carbon sequestrated. In particular, char potential could be exploited in the field of polymers, as filler, for boosting their thermal stability and electrical conductivity. Fillers are the inorganic or organically modified materials added to polymers not only to strengthen the composite or improve/introduce other functional properties, but also to reduce the production cost and the environmental impacts of a high-cost fossil-based matrix [6]. Recently, the utilization of carbon-based materials as fillers in polymers has attracted the interest of the scientific community. In particular, carbon nanotubes (CNT) [7], carbon black (CB) [8], carbon fibers (CF) [9], graphite [10] and graphene [11] have been used for enhancing the tensile properties, thermal stability and electrical properties of the composites. Nevertheless, the high production-costs, the fossil fuel-based feedstocks and the need of chemicals for their synthesis, make carbonaceous materials less attractive in the view of minimizing the costs and increasing sustainability. As alternative, biochar obtained from the pyrolysis of biomass-derived waste has been employed and successful results have been obtained. Indeed, according to the literature, biochar composites showed improved thermal, electrical and mechanical properties [6, 12–16]. Moreover, the hydrophobic nature of biochar makes it more compatible with polymers, which are also hydrophobic, such as polyolefines (also bio-based). Different combinations of pyrolytic biochar and polymers have been studied in the last years (Table 1) and all the studies reported unique properties for the composites.

Not only pyrolytic biochar but also hydrochar from hydrothermal carbonization (HTC) was tested as filler for polymers. For instance, Nizamuddin et al. [27] incorporated hydrochar from rice husk in polylactide (5–10–15–20 wt%) by melt processing at 170 °C and reported the beneficial effects of hydrochar addition on the tensile modulus of the compound. Due to their characteristics and similarities with pyrolytic biochar, also char residues from biomass gasification could be included in the group of carbon-based fillers. However, char from biomass gasification has never been tested in such an application. Char exploitation in this field would be beneficial both from an environmental and economic point of view. Firstly, this application allows for consuming a large quantity of residues from biomass gasification minimizing the production of waste and the cost related to its disposal. Secondly, char could be seen

Table 1 Different combinations of pyrolytic biochars and polymers tested in the literature (*PBT* polybutylene terephtalate, *PTT* polytrimetheylene terepthalate, *HDPE* high-density polyethilene, *PVA* polyvinyl alcohol, *PP* polypropylene, *PLA* polylactic acid, *UPE* unsaturated polyester)

Biochar precursor	wt% biochar	Polymer	References
Oil palm sludge	2.5	HDPE	[6]
Pine wood	6–30	PP + wood	[13]
Mixed hardwood	2–10	PVA	[15]
Wheat straw	10	PBT (30%) + PTT (70%)	[17]
Wood shavings Pinecone Plastic waste	5–30	Epoxy resin	[18]
–	25	Epoxy resin	[19]
Maple tree	2	Epoxy resin	[20]
Date palm	5–15	PP	[21]
Rice husk	30–70	HDPE	[22]
Bamboo	2.5–10	PLA	[23]
Rice husk	0.5–2.5	UPE resin	[24]
Lignin	20	PTT	[25]
Mischantus	10	PTT + PLA	[26]

as a renewable low-cost alternative to more traditional fossil-based fillers alleviating all the critical issues associated to their high cost and polluting potential. For instance, compared to a fossil-based filler such as carbon black, char costs ten times less. Moreover, char-based polymers could find fertile ground in a great deal of applications, particularly applications where polymers with low electrical resistivity are desired e.g. automotive industry [28], aerospace [29, 30] and biomedical engineering [31], electrical and electronics industry [32–34], building sector [35].

It is worth noticing that unlike biochar, char is not produced on purpose, but it is a waste, obtained as a by-product and therefore, its properties should be investigated in detail before determining the best conditions for its utilization.

Furthermore, char might contain PAHs (polyaromatic hydrocarbons) in different concentrations depending on the starting feedstock, its moisture content, and the operating conditions of the gasification process [36]. However, the negative effect of char PAHs on the compound should be evaluated in relation to the final use of the polymer.

In this regard, the European Union issued several pieces of legislation about PAHs to limit their presence in certain food products, as well as in water and ambient air [37]. Specifically, an amendment of the REACH regulation (EC 1907/2006 Annex XVII, Entry 50), establishes content limits for eight selected PAHs of 0.5 mg kg^{-1} for plastic and rubber components of toys/childcare articles, and 1 mg kg^{-1} for all other consumer articles, in direct and prolonged, or short-term repetitive, contact with the skin or oral cavity. Although it can be assumed that the small amounts usually present in char [36], which is subsequently diluted in the polymer matrix, might not negatively affect the final products, further investigations would be needed to confirm this thesis.

In this study, in order to evaluate the implications of char valorization from and industrial and more practical point of view, char derived from a commercial biomass gasifier, currently operating in South Tyrol, Italy, has been selected for being characterized and used as filler in TPE (Thermoplastic Elastomer) compounds, mainly for improving polymer thermal stability and electrical conductivity. According to the authors' knowledge there are not published studies about biomass gasification char used as filler, especially if char directly collected from an industrial plant is considered. Moreover, a comparison between char and a more conventional fossil-based filler (carbon black, CB) already available on the market is presented to show the similarities between them and confirm the advantages of using char.

Materials and Methods

Materials

Char was collected from a dual-stage gasifier currently operating in the Italian region of South Tyrol. The gasifier was designed to operate in the temperature range of 200–700 °C and at atmospheric pressure, using spruce woodchips as feedstock and air as gasifying agent. This gasifier is characterized by a nominal thermal and electrical power output of 540 kW and 280 kW, respectively, from a throughput of about 230 kg h^{-1} of dry biomass. A more detailed description of the gasification plant can be found elsewhere [38].

As CB, Carbon Black IMERYS Ensaco 250 g was selected due to its very good conductivity and ability to be dispersed in polymeric matrix during melt compounding. Unlike char, CB is derived from fossil fuels and produced on purposes at the industrial level with consequent high environmental and economic costs associated to it.

As polymeric matrix, SEBS (styrene–ethylene–butylene–styrene) thermoplastic elastomer provided by Kriburg, was selected.

Composites Preparation

Composites were made by melt compounding technology by means of a lab-scale co-rotating twin-screw extruder installed at Nadir Laboratory (c/o University Ca' Foscari of Venice), with a screw diameter of 11 mm and a length-to-diameter ratio (*L*/*D*) of 40. The screw profile is composed of eight zones with three interposed kneading sections. This machine is optimized for the production of polymer composites with fine dispersion of filler inside the polymer bulk [39]. The process conditions have been selected in order to make the production less invasive as possible and thus not to modify the final morphology of the compound in an appreciable way. Polymer pellets together with the desired amount of char or CB, were fed in the main hopper with a volumetric feeder and a double inlet. The screw rotation speed and the barrel temperature were optimized during operation. At the exit of the extruder, composites wires were recovered, solidified in a water bath, and finally, cut in pellets by means of a pelletizer machine. From now on, char-based composite is called Green Polyohm™ (GP). Figure 1 shows a Green Polyohm™ wire and pellets. Char and SEBS matrix showed very good compatibility during the production of the compound. In particular, a strong interface bonding between the two phases was created due to the high wettability of char.

Different composites were prepared with different amount of fillers in order to select the best weight

Fig. 1 Green Poyohm™ wire and pellets

Table 2 Extrusion parameters for Green Polyohm™

Char (wt%)	SEBS (wt%)	Torque (Nm)	*T* melt (°C)	*P* melt (bar)
41	59	1.9	178	16
43	57	1.9	178	18
44	56	1.6	177	16

Table 3 Extrusion parameters for CB composite

CB (wt%)	SEBS (wt%)	Torque (Nm)	*T* melt (°C)	*P* melt (bar)
20	80	1.6–1.9	179	23–24
23	77	1.9	179	26–28
24	76	1.8–2.0	179	27–28

percentage to ensure good mechanical and thermal properties and a high electrical conductivity. Tables 2 and 3 show the different weight percentages of char and CB tested, and the parameters used during the extrusion of the compounds: torque, pressure (P melt) and temperature (T melt) of melt.

The maximum amount of char to be added to avoid clogging was fixed at 44 wt%. Weight parentages of CB were selected in order to achieve electrical conductivity values similar to Green Polyohm™, loaded with maximum 44 wt% of char. At weight percentages lower than 38 and 20% for Green Polyohm™ and CB composite, respectively, the materials behave as insulating. In both cases, the rotation speed was fixed at 100 rpm. When char was used, temperature varied in the 170–200 °C range, while when CB was used, in the 180–200 °C range. The process data show a significant difference between the melt pressures of the two compounds: even if the percentage of char is significantly higher than CB, the melt pressures are much lower to indicate the better workability of this compound. This difference is probably due to the lamellar structure of char which favors the movement of the compound through the extrusion nozzle. Green Polyohm™ with 44 wt% of char and CB composite with 24 wt% of CB were selected for further characterization due to their higher electrical conductivity as explained later in the text.

Characterization Techniques

The elemental composition of carbonaceous fillers, polymeric matrix and composites was evaluated using a Vario MACRO cube (Elementar) elemental analyzer, yielding their carbon, hydrogen, nitrogen, and sulfur content. The ash content was measured according to UNI EN 14,775:2010. Both, measurements were repeated three times for each sample.

A 3Flex Surface Characterization Analyzer (Micromeritics Co.) operating with N_2 at -196.15 °C was employed for calculating the surface area, pore volume and pore size of the carbonaceous samples. Before analysis, samples were dried for 24 h and vacuum degassed at 300 °C for 3 h. The Brunauer–Emmett–Teller (BET) method [40] and the Barret-Joyner-Halenda (BJH) desorption analysis [41], were used for the calculation of the specific area and the pore size distribution, respectively.

True density of samples was measured by a helium pycnometer (Multivolume Pycnometer 1305, Micromeritics). Fillers were used as powder, while SEBS and composites as discs. Bulk density was evaluated for SEBS and composites as the ratio between the total mass of the sample and the total volume occupied. Measurements were performed three times for each sample.

The structural features of char, CB, SEBS, and composites were investigated by the X-ray diffraction (XRD) technique. X-ray powder diffraction patterns were collected at room temperature using a Philips X'Pert powder diffractometer (Bragg–Brentano parafocusing geometry) equipped with a focusing graphite monochromator on the diffracted beam and a proportional counter with electronic pulse height discrimination. A divergence slit of 0.5°, a receiving slit of 0.2 mm, an antiscatter slit of 0.5° were used, employing a nickel-filtered Cu Kα1 radiation ($\lambda = 0.15406$ nm) and a step-by-step technique (step of 0.05° for 20 s) with collection times of 10 s/step.

The particle structure and the surface topography of char, SEBS and Green Polyohm™ were investigated by Scanning Electron Microscopy (SEM) using a Jeol JSM-5600 LV, a variable pressure instrument (VP-SEM) equipped with an Oxford Instruments Isis Series 300 energy dispersive x-ray spectroscopy (EDS) system. On the contrary, CB and CB composite were characterized by a Zeiss Supra 40 VP field emission microscope (FE-SEM).

Table 4 Elemental analysis results and ash content of char, CB, SEBS and composites and the relative standard deviations (O calculated by difference)

($wt\%_{dry}$)	Char	CB	SEBS	GP	CB composite
C	91 ± 2	99.66 ± 0.03	86.5 ± 0.1	87.8 ± 0.3	89.6 ± 0.1
H	0.72 ± 0.05	0.09 ± 0.01	13.10 ± 0.05	8.2 ± 0.4	10.6 ± 0.2
N	0.26 ± 0.03	0.07 ± 0.01	0.05 ± 0.01	0.15 ± 0.06	0.05 ± 0.01
S	0.56 ± 0.07	0.20 ± 0.04	0.35 ± 0.08	0.20 ± 0.08	0.5 ± 0.1
O	2.89	–	–	2.18	–
Ash	4.20 ± 0.05	–	0.12 ± 0.10	1.55 ± 0.01	–

Thermal degradation profiles of samples (thermogravimetric/TG) and the corresponding derivative (DTG) were evaluated using a simultaneous thermogravimetric analyzer (Jupiter STA 449 F3, Netzsch). Approximately 10 mg of sample was placed in an alumina crucible and heated from 40 to 1000 °C at a constant heating rate of 10 °C min^{-1}. Both nitrogen and air were used as purge gases (20 mL min^{-1}) for studying the thermal behavior of samples under oxidative and inert atmosphere, while only nitrogen was used as protective gas (20 mL min^{-1}).

Differential Scanning Calorimetry (DSC) measurements were carried out by a Maia 200 F3 heat flux DSC (Netzsch) using nitrogen as purge gas (20 mL min^{-1}). 10 mg ca of sample was placed in a closed aluminum crucible holed on the top. The samples were heated from 0 to 270 °C with a 5 °C/min ramp rate, followed by a 10 min isothermal step to erase the thermal history. Then, they were cooled down to 0 °C at 5 °C min^{-1}, and then heated up again to 270 °C at 5 °C min^{-1}.

Finally, electrical conductivity measurements were carried out by a Keithley Voltmeter using the four-point method according to ASTMD4496-87 and ASTMD991-89.

Results

Elemental Analysis

The elemental composition in terms of C, H, N, S, O and ash content of fillers, polymer and composites are reported in Table 4.

In comparison to other chars obtained from other biomass gasifiers operating in South Tyrol [4], the selected char shows a high carbon content (91 $wt\%_{dry}$) and a low ash content (4.20 $wt\%_{dry}$), that ensure a reduced brittleness of the material. CB shows the highest C content (99.66 $wt\%_{dry}$) among the samples and no ash, as expected from a carbonaceous material derived from fossil fuels and industrially prepared to reach high C content. Adding carbonaceous fillers to the polymeric matrix increases C content of the composites. The increment in C content is higher for CB composite than Green Polyohm™ due to the higher percentage of carbon in CB. Moreover, char addition to SEBS matrix increases the ash amount to 1.55%, while decreasing its H and S content. On the other hand, CB addition does not vary H, N, S, and ash content of the SEBS matrix appreciably.

Table 5 Physisorption analysis results obtained for char and CB

	Unit	Char	CB
S_{BET}	$m^2\ g^{-1}$	297	64
Pore volume	$cm^3\ g^{-1}$	0.26	0.06
Pore diameter	nm	4.5	6.8

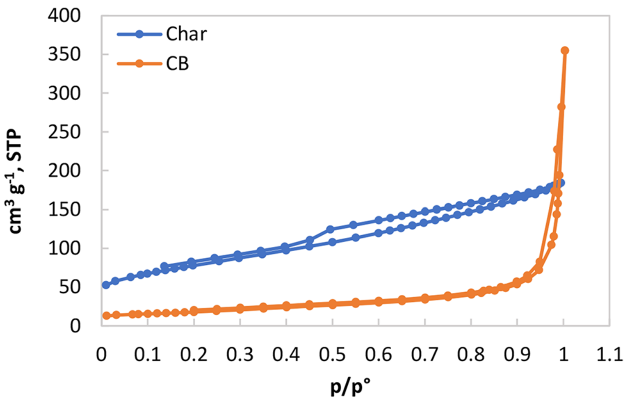

Fig. 2 Adsorption–desorption isotherm of char and CB (N_2, − 196.15 °C)

Physisorption Analysis

Physisorption analysis results obtained for both carbonaceous fillers in terms of BET surface area, pore volume and pore diameter are reported in Table 5.

Char shows a well-developed porosity ($S_{BET} = 297\ m^2\ g^{-1}$, $V_{pores} = 0.26\ m^3\ g^{-1}$, $d_{pores} = 4.5$ nm) compared to other chars obtained from other biomass gasifiers operating in South Tyrol [4]. A large surface area of the filler is beneficial since it enhances the wettability of the filler particle with the polymer matrix. CB has lower surface area ($S_{BET} = 64\ m^2\ g^{-1}$), pore volume ($V_{pores} = 0.06\ m^3\ g^{-1}$) and larger pore diameter ($d_{pores} = 6.8$ nm) than char. The adsorption–desorption isotherms for char and CB are shown in Fig. 2. According to the

BDDT (Brunnauer–Deming–Deming–Teller) classification [42], char isotherm can be classified as type IV isotherm, typical of mesoporous structures, while CB isotherm can be classified as type V isotherm, characteristic of weak gas–solid interactions given by macro-porous materials. At relative pressures higher than 0.45 and 0.9 for char and CB, respectively, both isotherms display a type III hysteresis loop indicative of the presence of slit pores. Moreover, CB isotherm takes on a hyperbolic shape close to $p/p° = 1$, due to the presence of macropores.

Bulk and True Density

From a comparison between bulk and true density, it is possible to retrieve information regarding the presence of open pores on the surface of the material. According to the results reported in Table 6, there are no differences between bulk and true density of each composite and therefore the presence of open pores must be excluded. This is due to the production process that occurs at high pressure (i.e. extrusion and injection molding). However, values differ from one composite to another. Indeed, bulk and true densities of SEBS (0.90 and 0.87 g mL^{-1}) increases with the addition of CB (1.00 and 0.97 g mL^{-1}) and even more with char (1.06 and 1.02 g mL^{-1}).

XRD

Figure 3 illustrates the XRD patterns obtained for char, CB, SEBS, Green Polyohm™ and CB composite where the XRD patterns have been shifted in order to improve the readability of the graph. For char, two phases can be distinguished: an amorphous phase related to the carbon structure and a crystalline phase related to the presence of calcite ($CaCO_3$) corresponding to the peak at $2\theta = 29.364°$ (JPDS 00–005-0586). In respect to other chars collected from other small scale-biomass gasifiers [4], less crystalline phases are present. This can be also related to the low amount of ash of the char under analysis (Table 4). On the other hand, CB does not display any crystalline phase due to the absence of ash (Table 4). SEBS spectrum shows peaks at 14°, 17°, 18.5°, 21°, 22° and 25.5° corresponding to monoclinic crystals (α-form) with the indexed planes of (110), (040), (130), (111), (041), (060) [43]. As expected, Green Polyohm™ and CB composite spectra are the result of the superimposition of the spectra related to the carbonaceous material and the SEBS matrix, and filler addition decreases peaks intensity. Moreover, the addition of amorphous char did not affect the crystalline nature of the composite.

Table 6 Bulk and true density of char, CB, SEBS, Green Polyohm™ and CB composite

g mL^{-1}	Char	CB	SEBS	GP	CB composite
Bulk density	–	–	0.90 ± 0.02	1.06 ± 0.02	1.00 ± 0.02
True density	1.69 ± 0.01	1.51 ± 0.01	0.87 ± 0.01	1.02 ± 0.01	0.97 ± 0.01

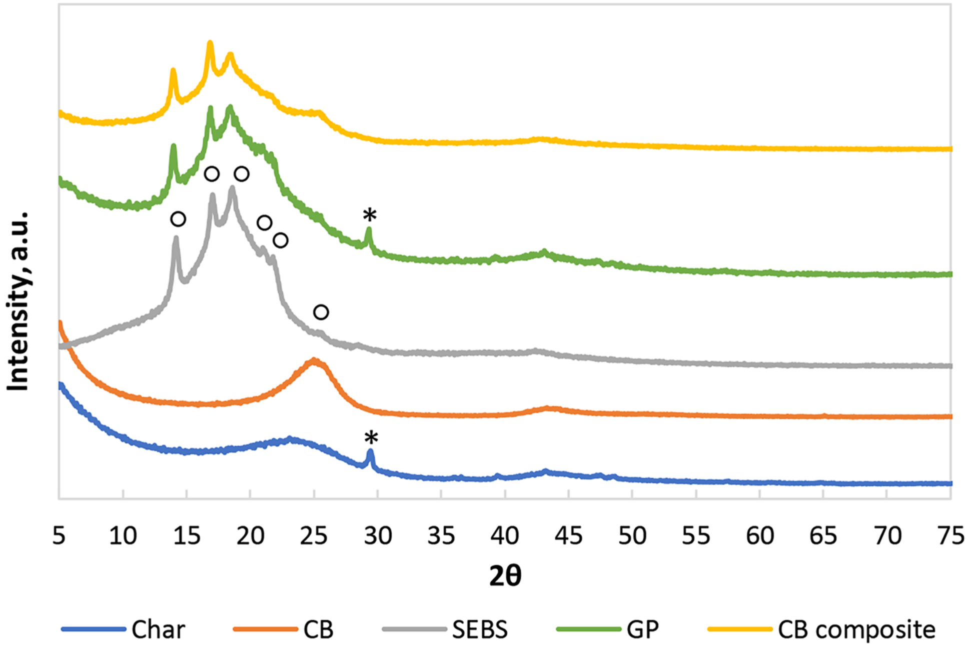

Fig. 3 XRD spectra for char, SEBS used as matrix, Green Poyohm™ and CB composite. *: $CaCO_3$, **o**: monoclinic crystals (α-form) with the indexed planes of (110), (040), (130), (111), (041), (060)

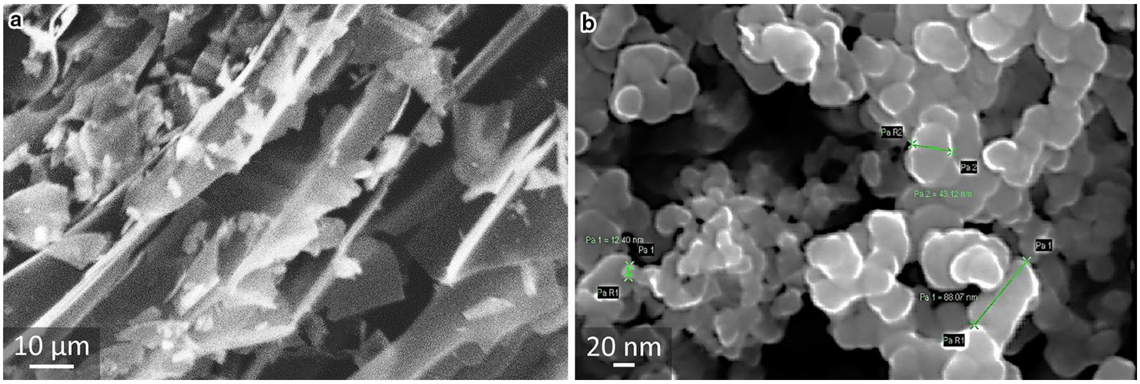

Fig. 4 SEM images for char (**a**) and CB (**b**)

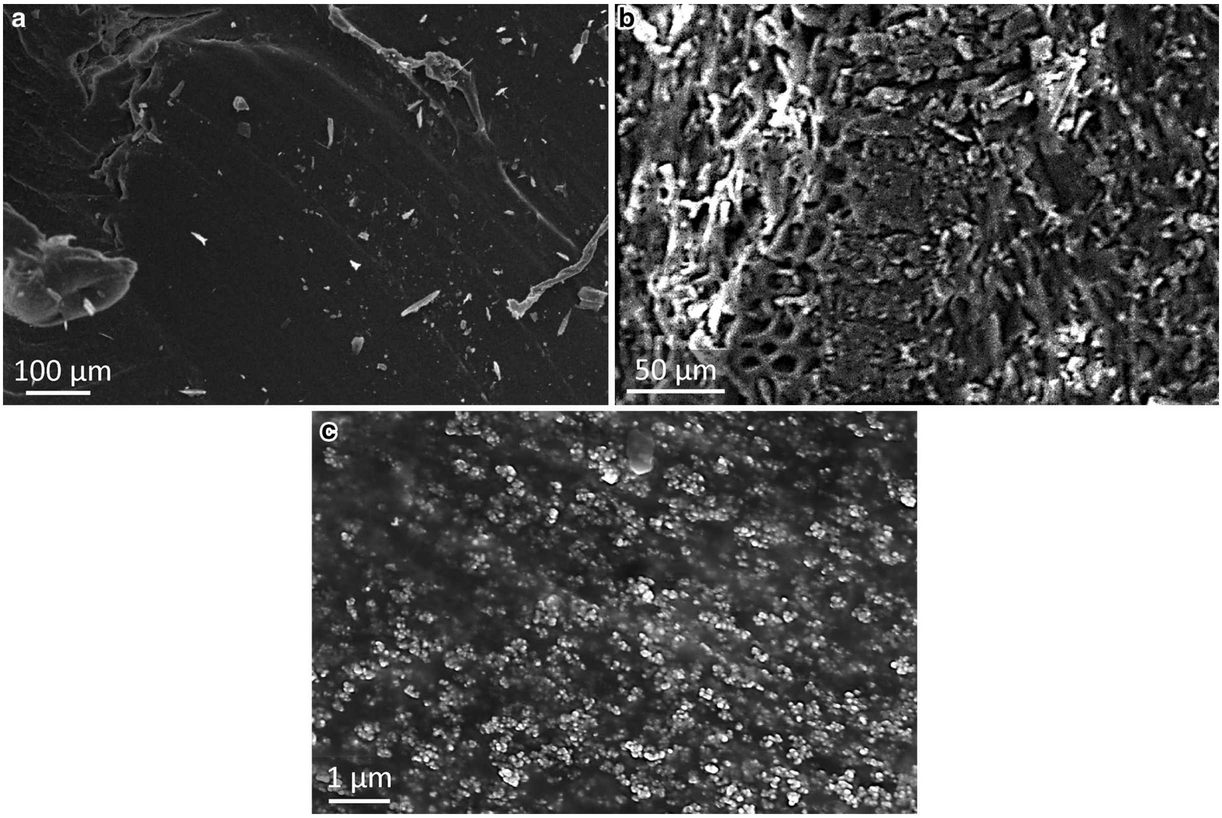

Fig. 5 SEM images for SEBS (**a**), Green Poyohm™ (**b**) and CB composite (**c**)

SEM

SEM results show the morphology of fillers, polymeric matrix, and composites (Figs. 4, 5). Char structure is irregularly shaped, and the external surfaces are quite rough. The lamellar structure is typical of char derived from woody biomass (spruce woodchips, in this case). The irregular structure of char and the presence of cracks and porosity on its surface may contribute to the physical interaction between char an SEBS and consequently favor the dispersion of the filler in the polymer matrix [6]. CB instead shows a wide distribution of irregularly shaped agglomerates with particles in the range of 12–88 nm. Pure SEBS (Fig. 5a) shows a more even and flat surface than composites. Green Polyohm™ morphology (Fig. 5b) reveals a good adherence between char and SEBS. Moreover, the composite shows cavities typical of the wooden structure of the char precursors. The good adherence of char on SEBS is also demonstrated at the macroscopic level. Indeed, no powder migration to the surface could be detected and the material was found very homogeneous to touch. Figure 5c displays that the filler is well dispersed in CB composite and no agglomerates are observed.

Thermo-gravimetric Analysis

The results of thermal degradation in inert atmosphere are shown in Fig. 6a, b. For all samples, the first degradation step, observed in the temperature range of 40–100 °C, is associated to the loss of physisorbed water and the evaporation of the residual moisture. Char shows the most relevant degradation in this range. Moreover, unlike CB with high thermal stability, char displays a continuous mass loss related to the incomplete degradation of the organic matter under heating [44]. Unlike other samples, Green Polyohm™ shows a degradation peak at 150 °C (both in inert and oxidative atmosphere). This can be associated to the release of water physisorbed on char walls during operation. Indeed, due to char larger porosity than CB, water is more likely to be retain inside Green Polyohm™ than CB composite.

SEBS, Green Polyohm™ and CB composite show a sharp mass loss associated to the polymer chain degradation. It occurs at 427 °C for pristine SEBS, 464 °C for Green Polyohm™ and 453 °C for CB composite, indicating that the addition of a carbonaceous filler in the polymer matrix increases its thermal stability. At higher temperatures, only Green Polyohm™ shows a continuous mass loss due to the effect of char addition.

Figure 7a, b shows the results obtained under an oxidative atmosphere. Char and CB exhibit a similar trend. However, char degrades at temperature (580 °C) lower than CB (800 °C) and it shows a residual mass related to the presence of inorganic materials completely absent in CB (ash, see Table 4). Pristine SEBS shows two degradation steps occurring at 365 and 430 °C related to the chain scission, and oxidation, which occur primarily at the boundary of styrene–olefin phase, with the consequent formation of acetone end-groups on the styrene units and carboxylic acids on the olefin chain ends [45]. Both Green Polyohm™ and CB composite show two main degradation steps related to the subsequent degradations of the polymer and the filler. Indeed,

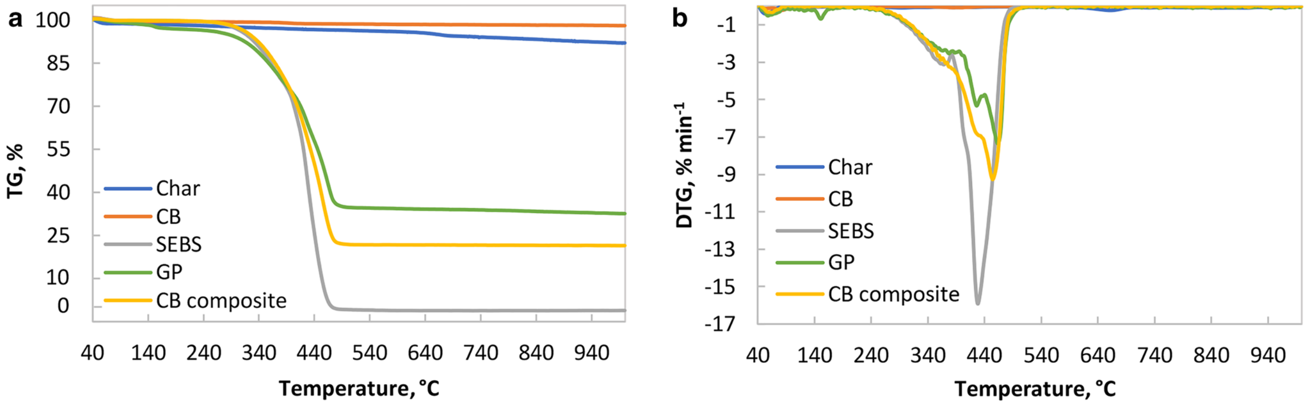

Fig. 6 TGA (**a**) and DTG (**b**) results in inert atmosphere obtained for fillers, pristine polymer and composites

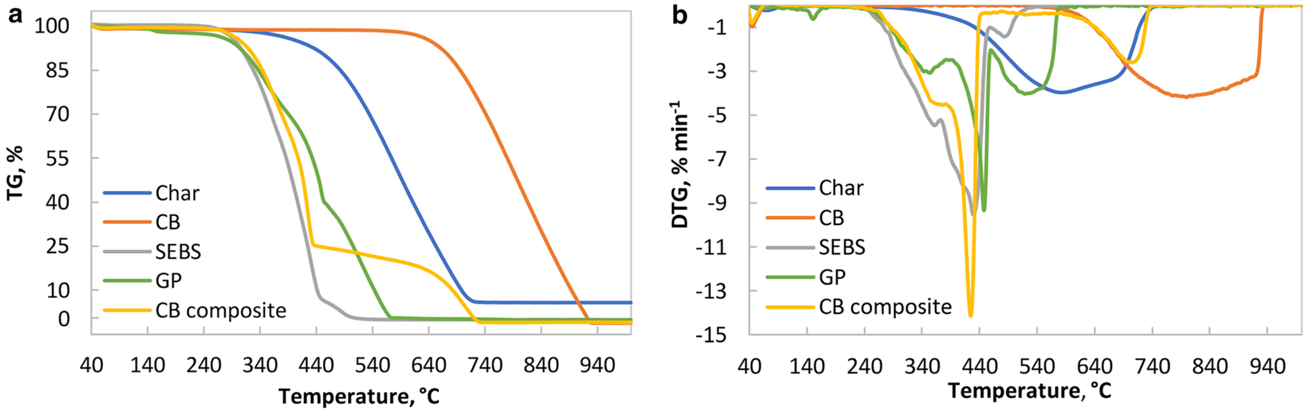

Fig. 7 TGA (**a**) and DTG (**b**) results in oxidative atmosphere obtained for fillers, pristine polymer and composites

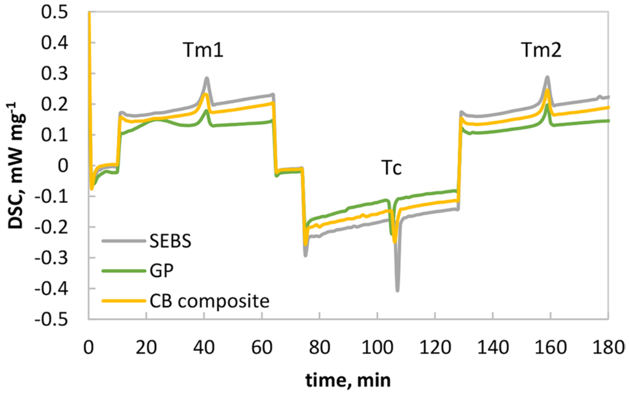

Fig. 8 DSC results obtained for pristine polymer and composites

Table 7 Temperature and enthalpy of melting (m) and crystallization (c) obtained through DSC for pristine polymer, Green Polyohm™ (GP) and CB composite

	Unit	SEBS	GP	CB composite
T_{m1}	°C	157	155	152
T_c	°C	104	114	108
T_{m2}	°C	156	155	155
ΔH_{m1}	J/g	13.95	7.51	10.69
ΔH_c	J/g	15.46	8.75	12.36
ΔH_{m2}	J/g	14.12	8.01	11.37

Table 8 Resistivity and conductivity values for Green Polyohm™

Char (wt%)	ρ (Ω cm)	σ (S cm^{-1})
41	2×10^5	5×10^{-6}
43	9×10^4	1×10^{-5}
44	6×10^2	2×10^{-3}

Table 9 Resistivity and conductivity values for CB composite

CB (wt%)	ρ (Ω cm)	σ (S cm^{-1})
20	3×10^2	4×10^{-3}
23	2×10^2	5×10^{-3}
24	1×10^2	7×10^{-3}

the first degradation step leads to mass percentage losses equal to the amount of polymer inside the composites (56% for Green Polyohm™ and 80% for CB composite) implying that this first step is related mainly to SEBS degradation. Not only CB but also char addition improved the thermal stability of the polymer shifting SEBS degradation peaks (365 and 420 °C) to higher temperatures, namely 425 and 709 °C for CB, and 448 and 540 °C for char. However, the improvement of thermal stability is not only related to filler properties, but also to the properties of polymer matrix, the processing methods, the filler dispersion, the interactions between phases, etc.[45].

DSC

Figure 8 shows the DSC curves obtained for SEBS, Green Polyohm™ and CB composite. Information about temperature and enthalpy of melting (m) and crystallization (c) are reported in Table 7.

Char addition did not affect the melting temperature (Tm) of the pristine polymer, but increased its crystallization temperature (T_c) from 104 to 114 °C. This might be related to the nucleation effect of the char particles, which act as nucleation sites that initiate the crystal growth [21, 46, 47]. Moreover, the presence of fillers decreases both enthalpy of melting (ΔH_m) and crystallization (ΔH_c) of the two compounds, due to the lower content of polymer. The effect of char addition is more noticeable than the effect of CB. Indeed, char displays lower $\Delta H_{m,c}$ and higher T_c than CB. Only T_{m1} is lower for CB composites than pure SEBS and Green Polyohm™.

Electrical Conductivity

Tables 8 and 9 report the most frequent values obtained for resistivity and conductivity of Green Polyohm™ and CB composite, respectively.

Results show that char addition effectively increases the electrical conductivity of the polymer. Moreover, higher filler percentages lead to lower resistivity and therefore, higher conductivity, due to the reduced insulated space between biochar particles [15]. Conductive polymer composites are preferable than metallic conductors since they can be shaped more easily and at lower costs, they weigh less, provide corrosion resistance and their electrical conductivities vary in a wide range [18]. The lowest resistivity measured for Green Polyohm™ (44 wt%$_{char}$) was 600 Ω cm and the corresponding electrical conductivity was of 2×10^{-3} S cm^{-1}, in good agreement with what reported in the literature [21, 48]. Indeed, according to the data reported in Table 10, the electrical conductivity of Green Polyohm™, loaded with char obtained at ~ 700 °C, is in accordance with the values reported for other composites made with different chars carbonized at 700 °C (1.2–2.9 $\times$ 10^{-3} S cm^{-1}). However, it should be noticed that char loading and polymer matrix are different in the two studies. For achieving values of electrical conductivity similar to Green Polyohm™, 20% by weight of CB has to be added to the SEBS matrix. Thus, more char (44 wt%) than CB (20 wt%) would be needed for obtaining composites with the same electrical conductivity. This might

Table 10 Literature data for the electrical conductivity/surface resistivity of different char/polymer matrix combinations (*PWC* plastic waste char, *WSC* wood shavings char, *PC* pine char, *ER* epoxy resin, *MHC* mixed hardwood char, *PVA* polyvinyl alcohol, *CT* carbonization temperature of chars, *UHMWPE* ultra-high molecular weight polyethylene, *AC* apple char, *BC* bamboo char)

Sample	wt% filler	Electrical conductivity of char-based composites (S cm^{-1})				References
GP	44	2×10^{-3}				This study
CB composite	24	7×10^{-3}				This study
MHC/PVA	6–10	$0.2–1.8\times10^{-6}$				[15]
PWC/ER	30	2.8×10^{-3}				[18]
WSC/ER	30	5.4×10^{-4}				[18]
PC/ER	30	3.9×10^{-3}				[18]
Sample		CT 500 °C	CT 700 °C	CT 900 °C	CT 1100 °C	References
PC/UHMWPE	70	/	2.9×10^{-3}	5.7×10^{-2}	3.0×10^{-1}	[48]
AC/UHMWPE	70	/	1.7×10^{-3}	8.2×10^{-2}	3.7×10^{-1}	[48]
BC/UHMWPE	70	/	1.2×10^{-3}	1.0×10^{-1}	3.9×10^{-1}	[48]

be related to the higher presence of carbon in CB than in char and the lower fraction of inorganics. The carbon network in CB is supposed to be continuous and therefore more keen to conduct electrons. Moreover, char structure is more heterogeneous than the CB one, which is made of agglomerates of more regular spherical particles. However, it should be pointed out that char is a waste available in large amounts and at low cost. Therefore, its utilization in big quantities does not represent an issue but an advantage since in this way, more of it could be consumed and not disposed of as a mere waste.

Conclusion

According to the results of this study, char residues from biomass gasification could improve the properties of polymeric compounds when used as fillers. Particularly, SEBS polymers loaded with char and more traditional CB were synthetized, characterized in detail, and compared to prove char advantages. Char exhibits a high carbon content (91%) and a low ash content (4.20%) closer to CB values if compared to other chars derived from commercial biomass gasifiers. In addition, char porosity is well developed leading to a good adherence of the SEBS matrix to the char walls. SEM images proved that no structural modifications took place through filler addition. Not only CB, but also char improved the thermal stability of the composite increasing the degradation temperatures. Although melting temperature (Tm) of pristine polymer was not affected by fillers addition, crystallization temperature (Tc) increased due to the nucleation effect of the char particles, which act as nucleation sites that initiate the crystal growth. As far as electrical properties are concerned, an electrical conductivity of 2×10^{-3} S cm^{-1} was measured when 44% by weight of char was added to a SEBS matrix. Values in the same range were obtained adding 20% by weight of CB. Therefore, less CB would be needed for reach specific electrical conductivity values. However, char is a waste highly available at a low cost and its exploitation in big quantities would only be advantageous leading to the reduction of waste, environmental impacts, and polymer production costs. Indeed, the addition of a highly carbonaceous material like char would not only limit the need of fossil-based fillers but also promote carbon sequestration.

In conclusion, recycling char as filler for polymeric compounds could enhance its overall value, open up innovative horizons for its valorization, offer a sustainable way for its management, and mitigate waste generation while producing materials with improved properties suitable for a big variety of industrial applications in the field of automotive, aerospace and biomedical engineering, electronics and building construction.

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