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Tuning Sugarcane Bagasse Biochar into a Potential Carbon Black Substitute for Polyethylene Composites

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Abstract

One of the most used carbonaceous materials by industry are carbon blacks, which have technological applications in polymeric composites, coatings and paints, electric and electrochemical devices. One drawback is that they are produced from fossil fuels. Although biochars are also carbonaceous materials some disadvantages like their larger particles size, high ash content and highly oxygenated surface must be overcome to enable their use as substitute of carbon blacks in composites. Sugarcane bagasse biochar was used to produce carbonaceous materials to substitute carbon blacks. Milling of biochar decreased particle size from several hundreds of micrometers to 100–500 nm and narrowed its size distribution. Chemical leaching reduced the inorganic compounds and ash content by almost 20%. Great advance was achieved when biochar was thermally annealed in alcohol vapor atmosphere which resulted in biochar-based material with very low oxygenated carbon species at particles surface and turned them hydrophobic. Almost no C–O/C=O and O–C=O peaks components were observed at the X-ray photoelectron spectroscopy spectrum. Reactive thermal annealing of the biochar based additive was a key procedure to obtain polyethylene composites (5% loading) with mechanical, thermal and colorimetric properties very close to the ones prepared with the carbon black from fossil fuels.

Keywords Polyolefin · Composite · Pyrolysis · Filler · Nanomaterial

Introduction

Brazil's prominent position as a global leader in green fuels production is mainly related to its enormous ethanol from sugarcane industry. Around 650 Mtons of sugarcane were processed and converted into sugar and ethanol at mills during the 2017/2018 season [1]. However, this process leaves behind huge quantities of bagasse (~200 Mtons per year), which is the residue resulting from the sugarcane stalks milling for juice extraction. Currently, most of this residue is burned by sugarcane mills to produce heat that feeds their energy needs or is used in cogeneration plants for production of electricity [2]. At sugarcane industries the remaining part of sugarcane bagasse has found minimal uses in cellulosic ethanol generation [2], cattle feeding [3] or combustible pellets preparation [4]. Besides this, sugarcane bagasse has been studied as feedstock to produce other high-value products that could substitute for fossil-based materials which could be adopted by ethanol and sugar industries.

New proposals of use of this residue and other renewable resources, urge to be welcome in direction of sustainable development. Pyrolytic processing of biomass residues stand-out as a promising alternative [5–7]. Pyrolysis is a complex thermal process that happens when organic matter, like sugarcane bagasse, is heated at temperatures typically above 400 °C in absence or low concentrations of oxygen. During pyrolysis, organic matter undercomes degradation reactions that result in 3 different products: gases (bio-gas), liquids (bio-oil) and solids (biochar) [8, 9]. Bio-gas and bio-oil are used for heat and energy generation [10] or as feedstock for fine chemicals production [5]. On the other hand, biochar have been used as a carbon-based material for several applications [6, 7, 11–13]

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as for example to produce briquettes, pellets, activated carbon, or as soil conditioner.

Recently, biochar has been explored for the substitution of carbon black additives in polymeric composites [11, 14–22]. Carbon blacks are carbonaceous materials in powder form that are produced from incomplete combustion of aromatic and aliphatic hydrocarbons from natural gas or fractions of fossil fuels. Their particles are normally spherical and with sizes that range from a few nanometers to some hundred nanometers. Once in polymers carbon black particles are found in aggregates and bigger agglomerates with networks formation and percolation of particles within the matrix, which directly influence thermal, mechanical as colorimetric properties of carbon black filled polymeric composites. Carbon blacks are one of the most used additives in thermoplastics and elastomers, and are responsible for enhancing composites thermal and mechanical properties besides coloring them in black [23, 24].

Biochars are also carbonaceous materials but their larger particles size, higher ash content and highly oxygenated surface are some drawbacks to their use as substitutes to carbon blacks in most of polymeric composites. Despite this, this substitution seems to be a great alternative to replace, at least partially, fossil fuel based material by renewable feedstocks. To bring this into reality, there still the need for physicochemical procedures that tune specific properties of biochar closer to the ones found for carbon blacks. Use of biochar as carbon black substitute in polymeric composites will be enabled if proper particle size, surface chemistry and ash content are achieved with viable processing costs, and final product prices competitive with commercial additives. These characteristics must allow enhanced interaction between the biochar-based additive and the polymer matrix, so that adequate mechanical and thermal properties are found on the composite.

In this work, ball milling and chemical leaching procedures were used to reduce biochar particle sizes and inorganic compound content. For the very first time, a reactive thermal annealing treatment with alcohol vapor was used to diminish the oxygenated carbon species amount on the biochar-based particles surface. The particles hydrophobicity was drastically increased which imparted advantages at produced polyethylene composites properties. Biochar based carbon black filled composites presented very close thermal, mechanical and colorimetric characteristics to the one prepared with a fossil fuel-based additive due to better interaction between the additives particles and the polymeric matrix.

Experimental

Materials

Biochar used in this study was obtained at the Bioware Ltd (Campinas/SP, Brazil) and was produced from milled commercial sugarcane bagasse pellets (particle size distribution can be seen at Table S1, Supplementary material) as feedstock. The pyrolysis process was carried out on a fluidized bed reactor model SDB200 from the Bioware company on which fast pyrolysis was carried out at 480 °C. The feedstock was fed to the reactor at a rate of 100 kg h^{-1}. More details of this kind of pyrolysis plant were described before by Mesa-Pérez et al. [25, 26]. The physico-chemical biochar treatments have used sodium hydroxide (NaOH) solution 50 wt% and hydrochloric acid (HCl) solution 30 wt%, both from Quimitel, Brazil. During thermal annealing procedure 2-propanol from Merck (Germany) was used. Prepared biochar samples were compared to a fossil source carbon black (CB) from Cabot (VULCAN® XC72), Brazil. The composites were produced with low density polyethylene from Braskem, Brazil.

Preparation of Sugarcane Bagasse Biochar Based Carbon Black

The as-prepared sugarcane bagasse biochar (SBB) was ground in a ball-mill (Quimis, Brazil) using a stainless-steel cylindrical milling vessel of 2.5 L volume and 13.5 cm of internal diameter rotating at ~ 60 rpm. Stainless-steel spheres of 6 mm diameter were used as milling elements. For each run, 200 g of biochar were processed using a mass ratio of 1:10 between biochar and balls. Milling times tested were 6, 24, 48, and 72 h which generated SBB-6 h, SBB-24 h, SBB-48 h, and SBB-72 h samples, respectively. The milling vessel was rotated 180º every 12 h to avoid dead volumes.

After ball-milling, SBB-72 h underwent base and acid aqueous leaching to reduce the quantity of inorganic compounds. For the base leaching, 100 g of ground biochar (SBB-72 h) was dispersed in 5 L of 5% (w/v) NaOH solution, heated to 80 °C and stirred for 3 h. Next, the solid was vacuum filtered and washed to neutral pH, then oven dried at 110 °C overnight. This procedure was repeated for the acid leaching using a 10% (w/v) HCl solution and heating at 50 °C. This procedure resulted in the acid and base leached milled biochar sample herein named SBB-72 h-ABL.

SBB-72 h-ABL sample was submitted to thermal annealing under isopropanol vapor atmosphere to reduce oxygenated carbon functional groups at the particles

surface. Isopropanol vapor were generated by bubbling N_2 at ambient temperature with a flow of 10 LPM in a flask containing isopropanol. The N_2 flow with alcohol vapor was then carried to a quartz tube containing 20 g of the sample in a Lindberg Blue M furnace. The reaction was carried out for 1 h at 900 °C, with heating rate of 10 °C min^{-1}. This procedure originated the sample rSBB-72 h-ABL. A sample annealed only with N_2 at 900 °C was also produced for further comparisions (SBB-72 h-ABL(900)).

Characterization

Particle size of ball-milled sugarcane bagasse biochar (SBB-6 h, SBB-24 h, SBB-48 h, and SBB-72 h) was evaluated by counting the mean size of 500 particles from scanning transmission electron microscopy (STEM) images. Images were acquired on FEI Inspect F50 microscope operating at 30 kV. Samples were deposited on Cu TEM grids with holey carbon after being dispersed in water using an ultrasound bath for 10 min. Particle size counting from the STEM images was done manually using the Image J software.

X-ray photoelectron spectroscopy (K-Alpha Thermo Scientific) using Al Kα X-rays charge compensation during measurements was used for surface analysis of milled and annealed biochars (SBB-72 h and rSBB-72 h-ABL respectively). Survey and high-resolution spectra were recorded using pass energy of 200 and 50 eV, respectively. High resolution carbon spectra were used to confirm oxygenated functional groups removal from particles surface of samples annealed under alcohol vapor. XPS spectra were collected at three areas per sample for statistical purposes. Data were analyzed using the Thermo Avantage software (Version 5.921).

To determine ash content and inorganic composition of the samples (SBB-72 h, SBB-72 h-BL, SBB-72 h-ABL, and rSBB-72 h-ABL), materials were ashed in a muffle furnace (Carbolite RWF 1100) using the following procedure: heating to 200 °C for 30 min (ramp of 2 °C min^{-1}), then heating to 700 °C for 1 h (ramp of 10 °C min^{-1}). This procedure was performed in triplicate for each sample. After this calcination step the remaining mass was considered as the samples ash content. Inorganic composition was estimated by energy dispersive X-ray spectroscopy EDS (X-Max, Oxford Instruments, SDD 80 mm^2) on a scanning electron microscope (Inspect F50 FEI), spectra were acquired in 5 different areas for each sample on ×1000 magnification.

Polyethylene/Carbon Black Composites Preparation and Characterization

Compounding of carbon black samples with polyethylene was conducted for CB, SBB-72 h, and rSBB-72 h-ABL. The additives were dried at 60 °C overnight and mixed with polyethylene, at loadings of 1 and 5 wt%. Extrusion of 200 g of each composite was performed in a double screw extruder (APV MPC/V30), with zone temperatures of 150, 200, 210, and 220 °C, from feeding zone to extrusion mold, and rotor screw speed of 20 rpm. Following extrusion, the material was chilled in a water bath, dried and pelletized.

Thermal gravimetric analyzer (Netzsch, STA 449 F3 Jupiter) was used to investigate thermal stability of composites. About 10 mg of composites and pure polyethylene samples were heated from 25 to 1000 °C under nitrogen and synthetic air at a heating rate of 10 °C min^{-1}. Differential scanning calorimeter (Netzsch, DSC 214 Polyma) was used under nitrogen atmosphere to determine fusion and glass transition temperatures of composites. Measurements were adapted from ASTM D3418-15 procedure, from room temperature to 150 °C at a heating rate of 10 °C min^{-1}, and following a cooling ramp to 60 °C with a rate of 10 °C min^{-1}. The samples were thermally treated twice by the same procedure to remove their thermal record. The DSC data were calculated from the second run.

Pellets of pure polyethylene and extruded composites were injected in a mini injection molding machine (Thermo Scientific HAAKE MiniJet II) with mold temperature of 60 °C, cylinder temperature of 150 °C, injection pressure of 200 bar, holding pressure of 500 bar, and holdup time of 5 s. The injected samples were molded as type V specimens (ASTM D638). Tensile tests were performed in a universal testing machine (DL2000 EMIC, Brazil), with load cell of 5000 N, at an extension speed of 200 mm min^{-1} and 2.53 cm height between claws. The values reported are average of 10 specimens for each sample.

Plaques of polyethylene composites extruded with CB, SBB-72 h, and rSBB-72 h-ABL, with 1 and 5 wt% loadings, were produced in a heated hydraulic press (HM Equipamentos Ltd, Brazil) at 8 tons and temperature of 150 °C. They were made from approximately 30 g of pellets of the composites molded into a square-shaped plaques of 15 × 15 cm dimensions and 1 mm thickness.

Colorimetric analyses of these plaques were conducted in a Hunterlab UltraScan VIS spectrophotometer, operating in reflectance mode, analysis window with a diameter of 25 mm and diffuse/10° geometry. L * a * b values were used to compare the results of composites containing biochar-based carbon blacks and commercial carbon black. Color measurement was performed in triplicate of five different points on each plaque (at the four corners and on center).

Approximately 2 cm of extruded polymer composites filaments were analyzed by means of a high-resolution X-ray microtomograph (SkyScan 1272, Bruker), operating at X-ray source voltage and current of 20 kV and 175 μA, respectively. Samples were set perpendicular, in its longer dimension, to the X-ray source-detector axis. The nominal

resolution was 2 μm using the X-ray detector of 2452×1640 pixels. Images were reconstructed from microtomography projections to 3D images with NRecon software (v.1.6.9.8, Bruker MicroCT®) using Feldkamp algorithm. The same electronic density contrast limits were selected for all samples for comparisons purposes. 3D images visualizations are acquired in the CTVOX program (v.2.2.3.0, Bruker MicroCT®) using the same RGB and two different opacity profiles for each sample.

Scanning electron microscopy images were acquired for cryo cut polymeric composites samples surfaces on Inspect F50 FEI microscope using acceleration voltage of 5 kV. Cryo cut polymer pieces were mounted on stainless steel stubs and coated with a 16 nm thick Au conductive layer. Conductive carbon tape was used to improve the electrical contact between the gold coated sample and sample holder.

Results and Discussion

Sugarcane Bagasse Biochar Characteristics

Pristine sugarcane bagasse biochar sample present particles with sizes over several hundreds of micrometers (see Supplementary material Figure S1). Biochar is composed of 59.73% of carbonaceous materials and 40.27% of ash (see Supplementary material Table S2), and particles surface are composed mainly by C and O, while Si and Al can be found as constituents of the inorganic fraction.

Effects of Milling on Sugarcane Bagasse Biochar Particle Size

Particles size distribution for each of the milled sugarcane bagasse biochar samples is presented in Fig. 1a (values were obtained from STEM images like the ones presented in Figure S2). Increase of milling time resulted in reduction of the biochar particles size, as particles size distribution fitted curves shift to lower sizes and increases in intensity simultaneously. Cumulative particle size counting curves from 0 to 4000 nm (Fig. 1b) also corroborates with particles reduction due to increase of the milling time. The inset in Fig. 1b shows particle size values at cumulative counts equal 50%, where it is possible to confirm the lower mean particle size values for higher milling times. Furthermore, Table S3 (presented at Supplementary material) shows that particle's average size, standard deviation and median values decrease as milling time increases, which supports the particle size and size distribution reduction. It was also
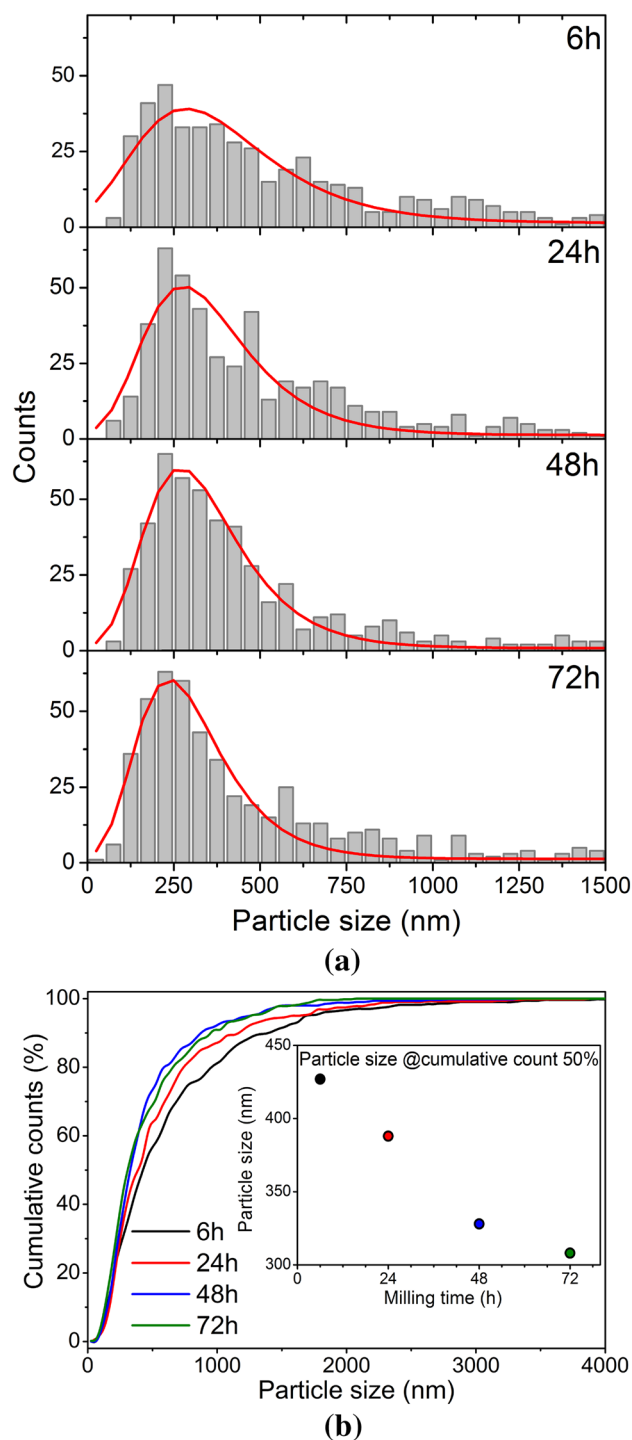

(a)

(b)

Fig. 1 **a** Particle size distribution and **b** cumulative particles size counts for sugarcane bagasse biochar (SBB) ball milled for 6, 24, 48 and 72 h. The inset in **b** presents particle size values at cumulative count of 50% for all samples

observed that for the highest milling time (72 h), minimum and maximum sizes are also by far the lowest values for all samples.

Ash and Main Inorganic Elements Content of Base and Acid Leached Biochar

Ash and main inorganic elements content of base and acid leached samples are presented in Table 1. Although the leaching procedures have not removed with high efficiency the inorganic compounds of SBB-72 h, a reduction of 20% of ash was observed with great removal of compounds containing iron (−63%) and silicon (−20%). Transition metal compounds and their ions, like Ti and Fe, are known to act on photo-oxidative degradation of polymeric materials [27–29], and therefore their removal from biochar-based additives is highly desirable. Similarly, incomplete removal of Si from samples may have some impact at the physico-chemical properties of the composites as silica is a common additive used in polymers. For the sample annealed under isopropanol vapor atmosphere (rSBB-72 h-ABL) an increase of ash content is observed, this is related to carbon losses due to the temperature used during this treatment. Biochar annealing at higher temperatures lead to carbonaceous structure rearrangement and loss of volatile and labile carbon containing molecules.

Effects of Annealing Under Alcohol Vapor on Biochar Surface Chemistry and Polarity

The procedure used to decrease of oxygenated carbon content at the particles surface and consequently reduce their polarity consisted in annealing the sample under alcohol vapor atmosphere (using N_2 as carrier gas) as suggested by Ching-Yuan Su et al. whose used this procedure to restore of graphitic structure in graphene oxide [30].

Figure 2a shows carbon high resolution XPS spectra of SBB-72 h, SBB-72 h-ABL and annealed samples at 900 °C under N_2 and isopropanol (SBB-72 h-ABL(900) and rSBB-72 h-ABL, respectively). Quantitative data of carbon species of each of these samples are presented in Fig. 2b. No significant changes are observed between milled (SBB-72 h) and acid/base leached (SBB-72 h-ABL) samples. This indicates that the leaching process removes inorganic compounds without altering the carbonaceous fraction. Therefore, it

is expected that SBB-72 h-ABL still a polar additive as SBB-72 h.

But significant changes can be observed for annealed samples. These spectra show an immense decrease of oxygenated carbon content after annealing as significant decrease of the peaks related to oxygenated functionalities (C–O, C=O and O=C–O) is observed. This is accompanied by decrease on the Coxi/(Csp2 + Csp3) ratio, which is the atomic abundance ratio between oxygenated and non-oxygenated carbon species. This indicates that annealing procedures are able to remove oxygenated species from the carbonaceous material surface, which might impact their polarity turning them more apolar. This removal of oxygenated functionalities from biochar is well-known to happen due to increased annealing temperatures under inert atmosphere, and was previously used to tune biochar particles surface chemistry used to produce nylon-6 bicomposites [22].

But XPS spectra highlight changes at the carbonaceous materials caused by annealing under isopropanol vapor. rSBB-72 h-ABL sample presented a relative increase of 22% of sp2 carbon species when compared to SBB-72 h-ABL(900). Additionally, annealing under isopropanol vapor promoted a decrease of the Coxi/(Csp2 + Csp3) ratio from 0.35 to 0.20, resulting from its lower oxygenated carbon species content. Those two outcomes underline that annealing with isopropanol has promoted enrichment on aromatic or graphitic carbon species and a substantive decrease on the quantity of oxygenated functionalities at this additive when compared to the sample annealed only under N_2. Thus, it is expected that this procedure renders a more apolar additive with closer properties to carbon black. We suggest that the annealing under isopropanol vapor promoted an improved removal of superficial oxygenated carbon groups from particles surface due to: (i) chemical reduction of oxygen containing functionalities by oxidation of the alcohol molecules, as well as (ii) carbon deposition (mainly aromatic and graphitic carbon) at particles surface originated from alcohol molecules under high temperature during the annealing process, such as a low-pressure chemical vapor deposition (LPCVD) procedure.

Removal of oxygenated carbon functionalities from biochar-based carbon black samples surface is expected

	SBB-72 h	SBB-72 h-BL	SBB-72 h-ABL	RSBB-72 h-ABL
Ash (wt%)	41.22	36.16	33.30	41.84
Si (wt%)	10.64	10.02	8.72	10.55
Fe (wt%)	5.24	4.31	1.91	2.5
Al (wt%)	2.39	1.69	1.92	2.3
Ti (wt%)	0.87	0.91	0.74	0.93
K (wt%)	0.76	0.39	0.13	0.16
Other (wt%)	1.29	1.18	0.87	1.1

Table 1 Ash content and inorganic compounds composition for SBB-72 h, SBB-72 h-BL (sample leached with base), SBB-72 h-ABL (sample leached with base followed by acid leaching) and rSBB-72 h-ABL (sample thermally annealed under isopropanol vapor)

to reduce their polarity and may impart advantages when compounding them with polyolefins and other low polarity matrices. Interaction between biocarbon particles and polymers play pivotal roles for example on mechanical properties of composites [22]. SBB-72 h and rSBB-72 h-ABL samples hydrophobicity was evaluated testing its affinity to water (polar, $\gamma LV(p) = 51.0$ mN/m) or toluene (apolar, $\gamma LV(p) = 0$ mN/m) in a bi-component system as shown in Fig. 2b. It is observed that after reactive annealing biochar particles get less polar and therefore present greater affinity to toluene as also observed for commercial carbon black (CB) sample. By our knowledge so far, such kind of thermal annealing was used for the very first time for biochar based polymer additives in this work, and the achieved results encourage the use of this materials as polyolefins additives. Biochar particles that are more hydrophobic are expected to have enhanced affinity with low polarity polyolefins such as polyethylene and polypropylene, which might have a positive effect over mechanical properties of the final composites [19, 22, 24].

Polyethylene Composites Containing Sugarcane Bagasse Biochar Additive

Until this point all physico-chemical procedures were used to tune the sugarcane bagasse biochar properties. This tuning was necessary overcome some of the identified drawbacks of use of biochars as additives for thermoplastics with potential to act like carbon blacks. Reduction of particles size, ash content and surface polarity enable the use of sugarcane bagasse biochar as a renewable resource for production of carbon black-like materials which meets some of the demands of green chemistry in direction of sustainability.

Thermal and Mechanical Properties

Polyethylene composites containing 1 and 5% of commercial carbon black (CB), milled biochar (SSB-72 h) and annealed biochar (rSBB-72 h-ABL) were compared concerning their thermal, mechanical and colorimetric properties. Table 2 shows the decomposition off-set temperature (T_d) obtained by thermogravimetric analyses (TGA), as well as fusion and crystallization temperatures and enthalpies obtained from differential scanning calorimetry (DSC) data. Addition of the carbon blacks to polyolefin results in an improvement of composites thermal stability when compared to pure polyethylene. Moreover, comparison between the materials with higher carbon black loading show that the biochar based
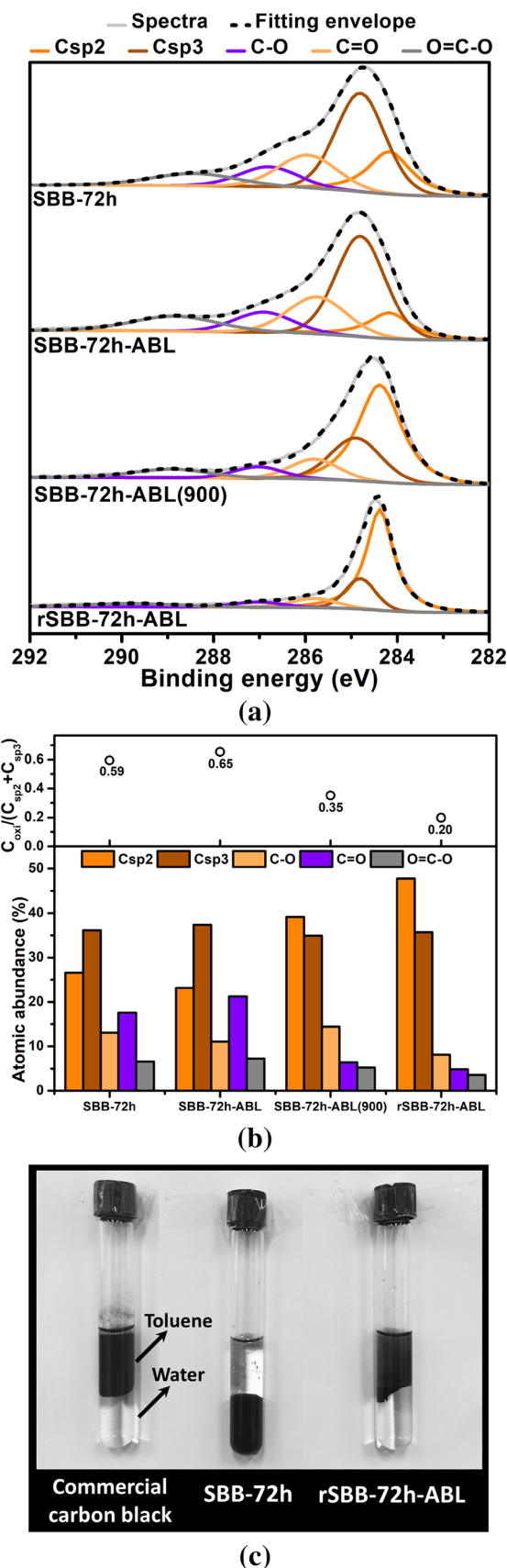
(a)

(b)

(c)

Table 2 Degradation (T_d), fusion (T_f) and crystallization (T_c) temperatures, and fusion (ΔH_f) and crystallization (ΔH_c) enthalpies of pure polyethylene (PE) and its composites with carbon blacks

Sample	T_d (°C)	T_f (°C)	T_c (°C)	ΔH_f (kJ kg^{-1})	ΔH_c (kJ kg^{-1})
Pure PE	421.3	109.29	86.17	78.30	− 74.96
PE + CB 1%	426.9	111.45	87.19	77.19	− 71.81
PE + SBB-72 h 1%	426.5	112.05	86.19	72.03	− 69.90
PE + rSBB-72 h-ABL 1%	426.2	111.45	85.59	74.15	− 71.64
PE + CB 5%	435.1	112.06	88.02	73.12	− 64.12
PE + SBB-72 h 5%	439.2	110.91	87.38	71.29	− 63.05
PE + rSBB-72 h-ABL 5%	441.9	113.05	87.75	73.20	− 66.30
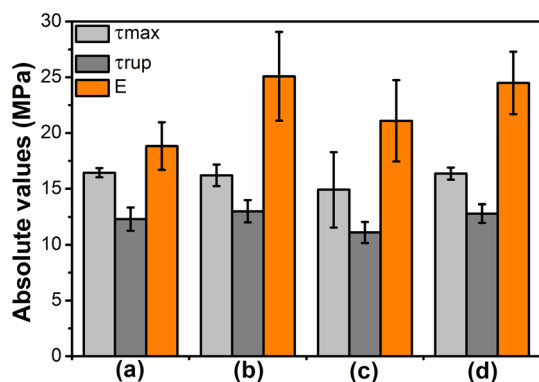
Fig. 3 Mechanical tests for the PE samples compounded with: **a** pure (no carbon black), **b** CB 5%, **c** SBB-72 h 5%, **d** rSBB-72 h-ABL 5%. Presented values are the average for 10 different specimens

additive performance is superior in relation to the commercial analogue, since the thermal decomposition temperature of its composite is at least 15 °C higher. Such kind of thermal degradation stabilization was observed before on the addition of carbon black to polypropylene and is attributed on changes on the degradation mechanisms and kinetics [31, 32].

DSC results show that the transition states temperatures remain approximately constant despite the additive type or loading. Enthalpies values, in turn, indicate that carbon black additives in the composites can slightly alter thermodinamic properties of polyethylene, once both fusion and crystallization enthalpies decrease. This behavior can be explained because of preferred formation of nucleation sites in these composites as nanofillers can act as heterogeneous nucleation sites [33–35]. It is important to highlight that results of the polymer prepared with annealed biochar additive (rSBB-72 h-ABL) are closer to values of the composite containing CB than the material extruded only with milled biochar (SBB-72 h). This is an evidence that reactive annealing is an important step to produce biocarbon additives with closer properties to commercial carbon blacks.

In addition to the thermal properties of the polymeric composites their mechanical properties are also affected by additives like carbon black. Polarity difference between polymer matrix and fillers, particle size and morphology of additives are some factors that affect mechanical behavior of polymers composites [19, 22, 24]. Figure 3 shows the results of mechanical tensile test for composites containing 5% (wt%) of the carbon blacks, emphasizing three properties: maximum tension (τ_{max}), rupture tension (τ_{rup}), and elastic modulus (E), also known as Young's modulus.

Similar Young modulus values within the standard deviation is observed for all composites. But, a decreased tendency of this value is observed for the composite containing SBB-72 h when compared to samples with CB and rSBB-72 h-ABL. This result confirms the expected better affinity between the polyethylene matrix and biocarbon black particles after reactive thermal annealing due to hindering of oxygenated carbon groups. Furthermore, maximum and rupture tensions (τ_{max} and τ_{rup}) did not vary significantly along the different composite samples, implicating that some mechanical properties of pure polyethylene are conserved. Is must be underlined that the mechanical properties of composites prepared with commercial carbon black and rSBB-72 h-ABL are very close, which reinforces again that sugarcane bagasse biochar-based additive after reactive annealing is a potential substitute for the fossil fuel based material.

Colorimetric Properties

Color properties of polyethylene composites with CB, SBB- 72 h and rSBB-72 h-ABL with 1% and 5% (%wt) loadings were measured in function of L * a * b color space (Fig. 4). In such color analysis, materials have their colors represented in three dimensions were L is used for lightness and a and b for green–red and blue–yellow color components, respectively. All samples presented very low L values (below 20) which indicate that they are dark. Lower L values are observed for the composites with higher additives loading.

Concerning the color components, a and b, composites prepared with rSBB-72 h-ABL present much closer values to commercial carbon black composites than the ones prepared only with milled sugarcane bagasse (SBB-72 h).
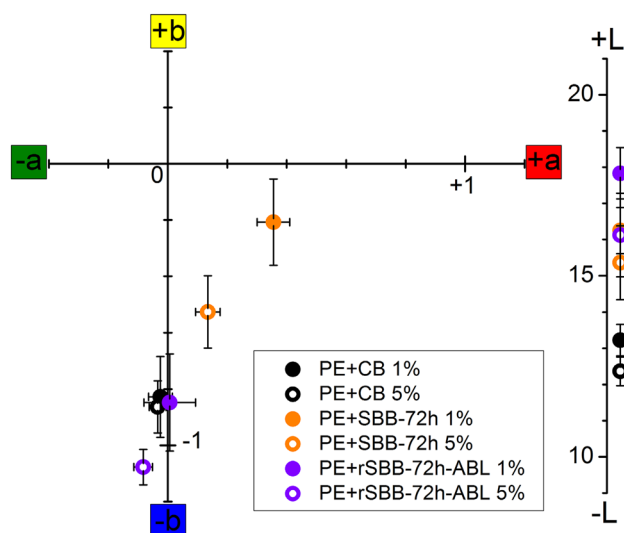
Fig. 4 L*a*b color values of composites prepared with 1% and 5% (%wt) of commercial carbon black (CB), SBB-72 h and rSBB-72 h-ABL

This indicates that reactive thermal annealing of the sugarcane bagasse biochar additive has induced not only better mechanical and thermal characteristics to the composites but also improved its coloring properties with very close characteristics to commercial carbon black.

Particles Dispersion and Interaction with the Polymeric Matrix

Micro X-ray tomography analysis were performed for the various composite samples and for pure polyethylene. Two different images processing profiles (shown in Fig. 5, Images information box) were used to highlight additive particles and agglomerates in the polymeric matrixes. At the right images for each sample it is possible to observe, that particles dispersed at the composites containing sugarcane bagasse-based carbon blacks present higher X-ray attenuation (lighter colors). This may be related to their bigger particles and agglomerates sizes and/or to its chemical composition which may contain some inorganic elements like silicon. This observation gets clearer when comparing left and right images of PE + CB 5% sample. In this case, although particles agglomerates are observed at the left image, they have enough low X-ray attenuation values so that their visualization is almost hindered at the right image. Despite the observed variations in particle size/agglomerates and their X-ray attenuation values the additives are relatively well dispersed along the polymer matrix, although some bigger aggregates are observed at composites prepared with biocarbon black. The presence in some extend of aggregates

is probably related to not fully efficient mixing of PE/additive during extrusion compounding as well as interparticle interaction due to surface chemistry affinity. Particles agglomeration can bring some drawbacks on mechanical properties of composites as it acts as a fracture point due to stress concentration effect. These drawbacks can be hindered by processing PE/additive mixture under higher energy or using compatibilizers.

Scanning electron microscopy images of cryo-cut surfaces of polyethylene composites prepared with 5% (wt%) of commercial carbon black (CB), SBB-72 h and rSBB-72 h-ABL are presented in Fig. 6. Carbon black particles prepared with the commercial additive present good dispersion and great affinity with the polyethylene matrix. At the composite prepared with milled sugarcane bagasse biochar (SBB-72 h) particles aggregation is observed and poor particles-polymer adhesion is also evidenced as can be seen in Fig. 6d.

For composite prepared with the reactive thermal annealed sample (rSBB-72 h-ABL) better particles dispersion is observed and there is also an improvement in the interaction between additive particles and polyethylene (Fig. 6e). Such behavior is clearly explained due to rSBB-72 h-ABL higher hydrophobicity which is induced by decrease in the amount of oxygenated carbon on particles surface.

Perspectives of Sugarcane Bagasse Biochar as a Carbon-Based Additive for Polyolefins

Achieved lab-scale results on the use of these carbon black-like materials as additives for thermoplastics stand-out as a promising sustainable alternative in comparison to conventional carbon blacks. The outlook on use of these additives in light weight composites move one step further in direction of green chemistry and engineering concepts as renewable resources are used as feedstock to their production. Moreover, preparation of carbon blacks from fossil fuels usually involve very high temperature processes (typically above 1500 °C) which demand huge amounts of energy. Although the proposed conversion processes of sugarcane bagasse (biomass preparation, pyrolysis, milling, chemical treatments) into carbon black-like materials demand also considerable amount of energy, scaled-up processes should take advantage from the biogas and bio-oil generated during pyrolysis to close energy balance. The presented proof-of-concept in this study encourage scale-up and optimization of this process to support techno-economic and environmental risks assessments toward full sustainability comparisons between this alternative materials and commercial carbon blacks.
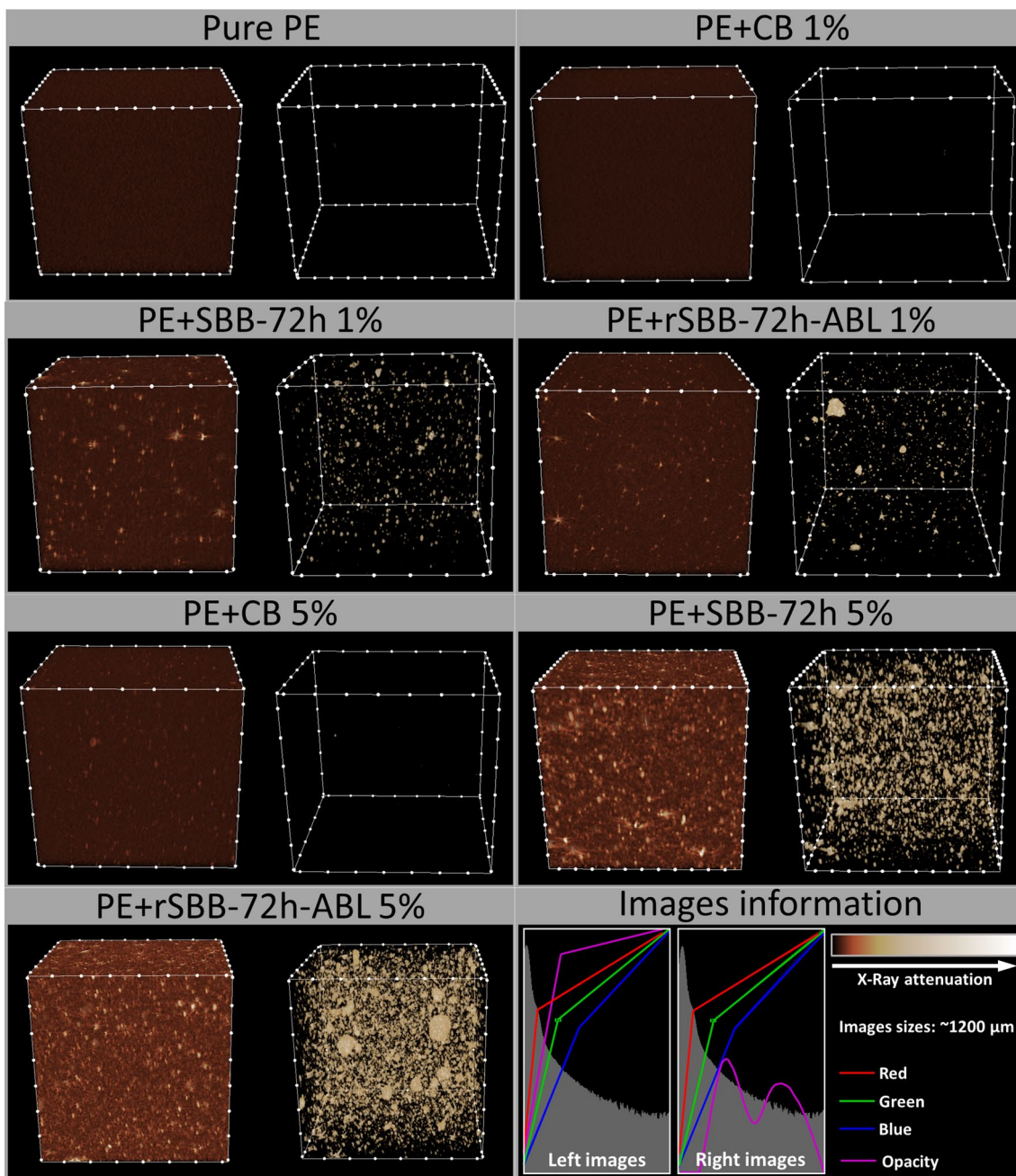
Fig. 5 X-ray microtomography images of pure polyethylene and composites prepared with 1% and 5% (%wt) of commercial carbon black (CB), SBB-72 h and rSBB-72 h-ABL

Conclusion

In this work, sugarcane bagasse biochar was used to produce polymer additives with potential to substitute carbon blacks, which may be successfully applied to other abundant renewable resources. Different physico-chemical procedures were used to tune specific properties of biochar. Higher ball milling times have resulted in materials with particles sizes below 500 nm and narrower particle size distribution. Base and acid leaching reduced inorganic compounds and ash content in about 20%. Annealing under isopropanol vapor at 900 °C has shown to be efficient to remove oxygenated carbon functionalities from particles surface and to drastically reduce their polarity.
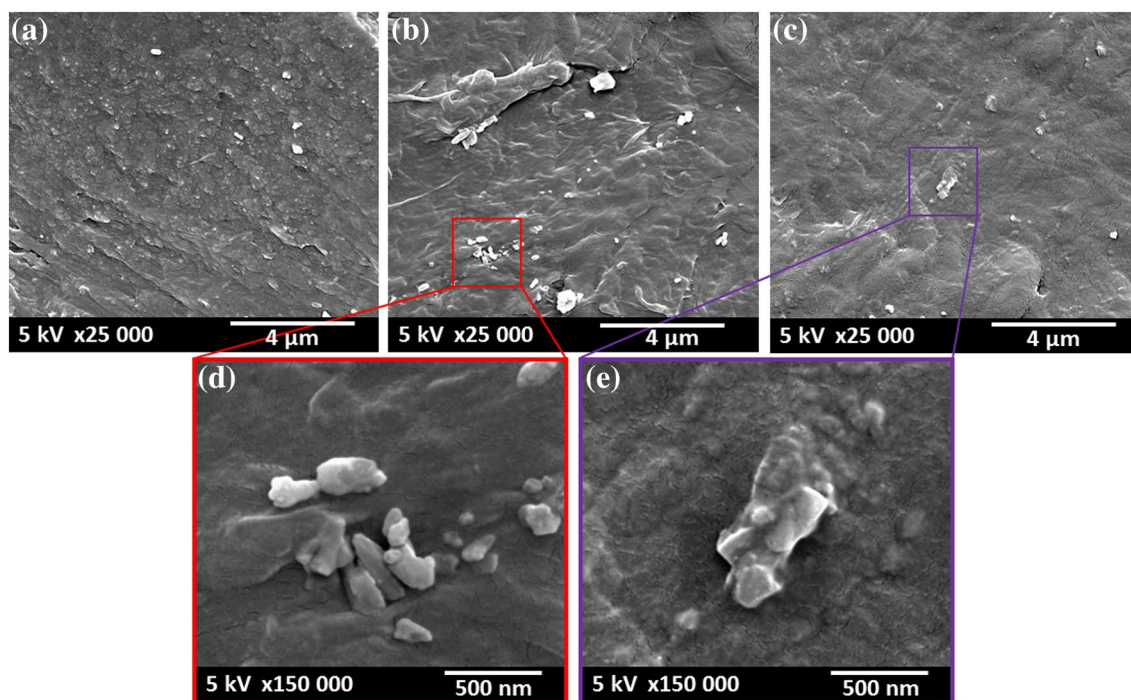
Fig. 6 Scanning electron microscopy images of composites with 5% (%wt) of **a** commercial carbon black (CB), **b** SBB-72 h and **c** rSBB-72 h-ABL; and higher magnification images at selected areas for the **d** SBB-72 h and **e** rSBB-72 h-ABL

Polyethylene composites (5% loading) prepared with annealed samples presented mechanical, thermal and colorimetric properties closer to the one prepared with commercial carbon black due to drastic changes on the particles surface chemistry which enhanced its interaction with the polymer matrix and improved composites quality.

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