Possibilities of carbon black recovery from waste tyre pyrolysis to be used as additive in rubber goods -a review-

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Abstract. This work deals with the literature review of the main carbon black (CB) properties required for reinforcing-filler rubber applications. Commercial CB is rich-carbon material widely used as reinforcing filler in rubber goods. When waste tyres are transformed by pyrolysis, the obtained solid fraction known as pyrolytic carbon black (CBp) contains the original CB (80-90 wt.%) added in tyre manufacturing process along with sulphur (1-3 wt.%) and a representative quantity of inorganics (10-15 wt.%). Taking this into account, it could be inferred that some physical-chemical properties of CBp are similar to those of the original CB. This fact has encouraged the use of CBp as an alternative substitute of CB in different rubber applications. However, it has been found that CBp can be used in certain rubber applications, some research works have also noted the detrimental of some mechanical properties. The inorganics presence in CBp limits some important properties such as tensile strength, tear strength, and hardness in the rubber composites. Also, these compounds as well as some carbonaceous deposits seem to affect the surface area and the surface chemistry, and therefore the active sites, affecting the reinforcing activity. To overcome these limitations, some post-treatments processes are proposed.

1. Introduction

The accelerate growth of the populations as well as the remarkable increase of vehicles worldwide have led to an environmental and public concern over the waste tyres (WTs) disposal in the last few years. It is forecasted that the growth of tyres demand all over the world is about 4.3% per year reaching 2.9 billion units in 2017 [1]. Tyres show several problems at the time to be disposed since they are designed to be extremely resistant to physical, chemical and even biological degradation. Moreover, their storage represents a big risk of fire that would cause severe environmental impacts due to uncontrolled toxic gaseous emissions as occurred in Madrid (Spain) in 2015 [2]. To overcome these issues, different recycling alternatives have been proposed over the years, including retreating, and material and energy recovery practices.

The progress made in recent years in the management of polymer wastes has made WTs to be perceived as valuable materials [3]. Considering that tyres are composed by natural and synthetic rubber (60-65 wt.%), carbon black (25-35 wt.%) and inorganic additives, it is reasonable to find routes for energy and materials recovery purposes[4]. In this sense, pyrolysis of WTs has been considered one of the most promising pathways over other possible valorisation methods such as combustion and
gasification. This is due to its less environmental impact and the possibility to recover liquid and solid compounds with a wide potential in the energy and material sectors [5–7].

In the WTs pyrolysis process, the solid fraction is, along the liquid fraction, the most abundant obtained fraction since it considers around 30-40 wt.% of the tyre weight [8]. This fraction, also known as pyrolytic carbon black (CBp), is composed of a mixture of commercial carbon blacks (CB) which were added in the tyre manufacturing process, carbonaceous deposits (as a result of secondary reactions) and some inorganics such as Zn, Ca, and Si added during tyre manufacture. This composition makes CBp to be different from the commercial CB which has limited its application and profitability in the current market. However, it has been argued that the careful control of the feedstock and pyrolysis processing conditions may lead to CBp grades specially tailored for certain applications [9]. For instance, one of the most immediate uses of CBp is the production of activated carbon as reviewed by Mui et al [10]. Similarly, low-grade rubber pieces and raw material for both pavements and pigments, among others, have been reported to be a technical and a feasible way to use this material. On the other hand, it is also possible use the CBp as a solid fuel despite its slow oxidation kinetics [11]. Besides, some demineralization processes have been also conducted to remove the inorganic material as well as the carbonaceous deposits in order to reach CBp with similar properties to those ones of commercial CBs [12, 13].

Conventionally, CB is usually produced by the partial oxidation of hydrocarbons leading to high CO₂ and polycyclic aromatic hydrocarbons (PAHs) emissions that not only affect the environment but also the human health [14, 15]. For instance, the incomplete combustion process carried out to obtain the commercial CB drives to a carbon footprint around 5.7 kg of equivalent CO₂ per kg of CB [16]. Indeed, it has been recognized that the carbonaceous particulate matter emitted to the environment during this process has a global warming potential between 330 and 2240 kg of equivalent CO₂ [17]. Likewise, the International Agency of Research on Cancer (IARC) has defined PAHs as carcinogenic substances [18]. These facts have motivated the idea of recovering CB from WTs through pyrolysis processes. In this sense, the obtained CBp could be reused in new rubber goods as well as be precursor of other carbonaceous materials [19]. In spite of the difference between CB and CBp mainly associated with the high concentration of inorganic impurities and carbonaceous deposits, the CBp could present a big potential for its application in rubber formulations as a partial substitute as will be shown later.

Taking this into account, the present work deals with the literature review of the CBp properties and some scientific results when it is used in different rubber goods. According to the best authors’ knowledge, there is not this kind of study in the scientific literature, which represents an important contribution not only to the problems associated with WTs disposal but also to substitute the commercial CB given the environmental concerns related to its production.

2. Commercial carbon black (CB)
Commercial CB is essentially elemental carbon (higher than 97 wt.%) in the form of extremely fine particles with amorphous molecular structure. It is produced by the incomplete combustion or thermal decomposition of gaseous or liquid hydrocarbons under controlled conditions. Even though CB is mainly used as reinforcing filler in the rubber industry (90%), it has also other important applications such as pigments for printing inks (9%) and as an additive in hundreds of diverse processes (1%) [20]. When this material is used in rubber goods (especially tyre manufacture), it is added to improve the processing, strength and durability of elastomer composites [21]. Some CB production processes include oil furnace, thermal, lamp, acetylene cracking, gas furnace and channel processes. Nevertheless, furnace and thermal accounts for about 90% and 10% of CB production in U.S., respectively. Besides, the lamp and acetylene processes are small-volume specialty black operations that constitute less than 1% of total production in U.S. Whereas, the gas process is being phased out and the last channel black plant in the U. S. was closed in 1976 [22].
2.1. Oil Furnace black process
The oil furnace black or simply furnace black process is based on the incomplete combustion of heavy hydrocarbons. This process is carried out in a closed reactor with atomizing nozzles [20]. The fuel is sprayed into a hot gas stream generated by burning a secondary feedstock and pre-heated [3, 20]. Then, the hydrocarbons drops are vaporized and then pyrolyzed to give rise to carbon particles. Finally, the cracking reaction is stopped by adding steam or liquid water sprays. The formed CB flows from the reactor through heat exchanger where it is cooled down and then collected in bag filters [20]. Process yields range from 35 to 65 percent, depending on the feed composition and the grade of CB desired. Generally, yields are highest for large particle blacks and lowest for small particle CB [22]. This process has become the predominant method for CB production since the hydrocarbons serve both as a source of heat and carbon [3].

2.2. Thermal black process
This process consist in a thermal decomposition of natural gas in the absence of air [18, 23]. The system consists in two refractory-line furnaces that alternate between furnace preheating and CB production approximately every five minutes. The natural gas is injected into one previously preheated refractory-line furnace (about 1300 °C [24]) in air absence, while the other furnace remains in the heating cycle. Then, the heat from the refractory material in the furnace decomposes the natural gas into CB and H₂. Finally, the aerosol material is cooled down with water sprays and collected in bags. The H₂ is burned using air to pre-heat the reactor in the heating cycle for later production cycle [20, 22]. In fact, more than enough H₂ is produced to make the thermal black process self-sustaining, and the excess H₂ is used to produce steam and electric power [22].

Generally speaking, commercial CB is classified by ASTM into different classes such as N120, N330, N550 and N660. Herein, the N is used to indicate a normal curing rate typical of furnace blacks that have received no special modification to alter their influence on the rate of cure of rubber. The next digits indicate the typical average particle size [18, 20]. Taking this into account, the higher the CB reference number, the lower the specific surface area (e.g. for reinforcing applications big surface areas are required). Moreover, thermal black is classified into the N900 series while furnace blacks fall within the N100 to N700 series [25]. The most common CBs used in tyre manufacturing are N330 and N550, which present a specific surface area of 78 and 40 m²g⁻¹, respectively. These references are used in low hysteresis tyre treads, inner liner tyres, carcass, sidewall, among others. In addition, due to their high dimensional stability, these CBs are also used in hoses, belts plastic piping, etc [18, 26]. Table 1 shows the classification as well as some properties and applications of commercial CBs.
Table 1. Properties and applications of some commercial carbon blacks, adapted from [18, 26]

| ASTM Classification | Iodine absorption (g kg⁻¹) | Area BET (m² g⁻¹) | STSA (m² g⁻¹) | DBPA (mL 100g⁻¹) | Ash (wt. %) | Sieve residue 45 μm (wt. %) | Density (kg m⁻³) | pH | Type | Production process | Average primary particle size (nm) | Reinforcing grade and applications |
|---------------------|---------------------------|------------------|----------------|------------------|-------------|-----------------------------|-----------------|-----|------|------------------|-------------------------------|----------------------------------|
| N110                | 145                       | 127              | 115            | 113              | n.r         | n.r                         | n.r             | 113 | SAF  | Furnace          | 17                            | High reinforcement; high abrasion resistance; used in special and off-road tyre products. |
| N220                | 121                       | 114              | 106            | 114              | <0.5        | <0.05                       | 355             | 9   | ISAF  | Furnace          | 21                            | High reinforcement and tear strength, good processing; used in passenger, off-road and special tyres. |
| N330                | 82                        | 78               | 75             | 102              | <0.5        | <0.05                       | 380             | 7   | HAF   | Furnace          | 31                            | Medium-high reinforcement, low modulus, high elongation, good flex, tear and fatigue resistance; used in tyre tread, carcass and sidewall compound, bicycle tyres. |
| N550                | 43                        | 40               | 39             | 121              | <1.5        | <0.05                       | 360             | n.r | FF    | Furnace          | 53                            | Medium-high reinforcement, high modulus and hardness, low die swell and smooth extrusion; used in tyre inner liners, carcass and sidewall compounds and hose and other extruded goods. |
| N660                | 36                        | 35               | 34             | 90               | <0.5        | <0.05                       | 440             | n.r | GPF   | Furnace          | 63                            | Medium reinforcement and modulus, good flex and fatigue resistance, low heat build-up; used in tyre inner liners, carcass and sidewall, sealing rings, cable jackets, hose and extruded goods. |
| N762                | 27                        | 29               | 28             | 65               | n.r         | n.r                         | n.r             | 110 | SRF   | Furnace          | 110                           | Medium reinforcement, high elongation and resilience, low compression set; used in mechanical goods, footwear, inner tubes and floor mats. |
| N774                | 29                        | 30               | 29             | 72               | <0.5        | <0.05                       | n.r             | n.r | Furnace | n.r                | Medium reinforcement, high loading capacity and low hysteresis. Easy extrusion black. Used in belts, hoses, molded goods, and footwear. Low reinforcement, low modulus, hardness, hysteresis and tensile strength, high elongation and loading capacity; used in wire insulation and jackets, mechanical goods, footwear, belts, hose, gaskets, O-rings and tyre inner liners. |
| N990                | n.r                       | 8                | 8              | 43               | <0.7        | <0.1-0.05                   | 355             | 7   | MT    | Thermal          | 320                           | Low reinforcement, low modulus, hardness, hysteresis and tensile strength, high elongation and loading capacity; used in wire insulation and jackets, mechanical goods, footwear, belts, hose, gaskets, O-rings and tyre inner liners. |

SAF superabrasion furnace black, ISAF intermediate superabrasion furnace black, HAF high abrasion furnace black, FF fast extruding furnace black, GPF general purpose furnace black, SRF semi-reinforcing furnace black, MT medium thermal black, STAS statistical Surface area, DBPA: dibutyl phthalate absorption
3. Pyrolytic carbon black (CBp)

As mentioned before, CBp is a heterogeneous carbonaceous material obtained from the WTs pyrolysis process. Physically, CBp is visible as solid, black particles of varying size, depending on the WT size used during pyrolysis. CBp particles seem to be much coarser in size compared to their original CB counterparts present in tyres since CBp particles act as nuclei during pyrolysis favoring the growth of solid carbon structures by crosslinking or cyclisation [27]. This material typically contains a mixture of different commercial CBs (since each part of the tyre requires a specific CB reference), some carbonaceous deposits [28], and inorganics (SiO₂, ZnO, K₂O, Fe₂O₃, etc) coming from the tyre manufacturing process which are reflected in the ash content. The carbonaceous deposits are the consequence of repolymerization reactions (secondary reactions) that take place among the polymer-derivatives. In other words, some of the organic vapours released during pyrolysis are converted into coke by dealkylation and dehydrogenation reactions or absorbed onto the CBp surface reducing its activity and morphology [29]. For instance, Darmstadt et al. [28] reported that the average size of the aromatic compounds onto the CBp surface is around five condensed rings when it is obtained at atmospheric conditions. However, some studies have demonstrated that low pressure (~20 kPa) and high temperature (up to 700 °C) during pyrolysis can reduce these carbonaceous deposits resembling some commercial CB (N115 to N774) [30, 31]. Likewise, the inorganic compounds seem to be absorbed onto the active sides of the CB reducing surface activity.

On the other hand, CBp shows a heating value between 25 and 34 MJ/kg and may have composition of carbon and sulphur higher than 80 and 2 wt.%, respectively. During pyrolysis, approximately 70 wt.% of the sulphur contained in the tyre (added during vulcanization) remains into the solid fraction in the form of sulphides [32]. Moreover, CBp exhibits a specific surface area between 57 and 89 m²g⁻¹, which is comparable with the surface area of the commercial CBs N330 and N550, as showed in Table 1. In addition, Table 2 summarizes the elemental and proximate analyses as well as the higher heating value (HHV) and surface area (BET) of some CBp reported in the literature. The difference in ash content arises from the difference of tyre type (e.g. passenger, truck, bicycle, etc.) although it usually remains between 6 and 16 wt.% [33, 34]. Table 3 shows some CBp ashes composition reported in the literature. As observed, the main compounds are SiO₂ and ZnO which are used as filler and activating agent in tyre manufacturing process, respectively.

Roughly speaking, when CBp is considered as alternative to commercial CB, the main properties to take into account are particle size, structure, surface area and surface chemistry. The reinforcement mechanism between the CBp and the polymer is mainly influenced by the size of CBp aggregates (formed by primary particles strong linked), and the surface morphology and chemistry. Chemical and physical interactions lead to adsorption of polymer chains onto the CBp surface. These interactions restrict the segmental movement of the polymer molecules, giving place to different reinforcement grades. Increasing surface area and activity will increase polymer-filler interactions [9]. Taking this into account, it is a fundamental step to establish these CBp properties and compare them with those of the commercial CB in order to define further applications.
Table 2. Proximate and elemental analyses of CBp reported in literature

| η (wt.%) | Elemental analysis wt.% (a.r) | Proximate analysis wt.% (a.r) | HHV (MJ kg⁻¹) | BET area (m² g⁻¹) | Temp. pyrolysis (°C) | Reactor type | Ref. |
|---|---|---|---|---|---|---|---|
| 40.5 | 84.2 | 1.1 | 0.3 | 2.1 | 3.6 | 12.4 | 4.7 | 79.3 | 30.0 | 65.7 | 550 | AR | [29] |
| 37.9 | 82.7 | 0.4 | <1 | 2.2 | n.r | n.r | 2.2 | 16.1 | 5.5 | 78.4 | 27.9 | n.r | 69.5 | 500 | FBR | [35] |
| 37.6 | n.r | n.r | n.r | 0.0 | 16.1 | 5.5 | 78.4 | 27.9 | n.r | 69.5 | 500 | FBR | [35] |
| 39.9 | 80.8 | 1.5 | 0.5 | 2.4 | 1.3 | 14.6 | 6.9 | 77.2 | 30.0 | 89.1 | 550 | FBR | [37] |
| 36.1 | 85.2 | 1.2 | 0.6 | 2.0 | n.r | n.r | 13.3 | n.r | n.r | 68.0 | 500 | FBR | [38] |
| 38.0 | 90.3 | 0.3 | 0.2 | 1.2 | 0.1 | 8.4 | 0.7 | 90.8 | n.r | 63.0 | 500 | FBR | [6] |
| 40.0 | 86.3 | 0.3 | 0.3 | 2.8 | 0.4 | 12.5 | 1.8 | 91.3 | 29.7 | 64.0 | 500 | FBR | [39] |
| 33.0 | 80.1 | 0.4 | 0.2 | 2.8 | 1.0 | 16.5 | 1.2 | 81.3 | 28.6 | n.r | 550 | FBR | [34] |
| 41.7 | n.r | n.r | n.r | 1.0 | n.r | 40.8 | n.r | 55.9 | 15.7 | 60.5 | 650 | FBR | [40] |
| 33.8 | n.r | n.r | n.r | 2.3 | n.r | 14.8 | n.r | 82.6 | 33.4 | 63.5 | 550 | FBR | [29] |
| 49.1 | 85.3 | 0.3 | 0.3 | 2.1 | 3.6 | 15.3 | 12.8 | 71.9 | 30.7 | n.r | 550 | RKR | [41] |
| 35.0 | 89.4 | 1.8 | 1.8 | 0.9 | n.r | 7.7 | n.r | n.r | 30.9 | n.r | 550 | FBR | [42] |
| 52.5 | 0.0 | 0.0 | 0.0 | 0.0 | n.r | n.r | n.r | n.r | n.r | 550 | FBR | [43] |
| 34.1 | 86.6 | 0.8 | 0.8 | 2.2 | n.r | n.r | n.r | n.r | n.r | 65.2 | 500 | CSBR | [44] |
| 36.9 | 87.4 | 0.4 | 0.4 | 3.3 | n.r | n.r | n.r | n.r | n.r | 77.9 | 500 | FBR | [45] |
| 38.0 | 81.1 | 0.4 | 0.4 | 3.4 | 1.2 | 13.2 | 3.5 | 82.1 | n.r | n.r | 600 | AR | [46] |
| 38.0 | 81.8 | 0.3 | 0.3 | 3.0 | 0.3 | 13.8 | 2.5 | 83.4 | n.r | n.r | 500 | PDU | [28] |
| 35.0 | 80.7 | 0.4 | 0.7 | 3.6 | n.r | 14.4 | n.r | n.r | n.r | 500 | PDU | [28] |
| 35.0 | 87.2 | 0.4 | 0.5 | 2.0 | n.r | 9.9 | n.r | n.r | n.r | n.r | 500 | PDU | [28] |
| 35.0 | 85.7 | 1.0 | 0.4 | 1.3 | n.r | 9.1 | n.r | n.r | n.r | n.r | 500 | AR | [47] |

n.r: not reported; M: moisture; A: ash; VM: volatile matter; FC: fixed carbon; C: elemental carbon; H: hydrogen; N: nitrogen; S: sulphur; HHV: Higher Heating value; η: CBp yield; FBR: Fixed Bed Reactor; AR: Auger Reactor; PDU: Process Development Unit, CSBR: Conical Spouted Bed Reactor, MBR: Moving Bed Reactor. RKR: Rotary Kiln Reactor.

Table 3. Ash composition of pyrolytic carbon black

| Ash composition wt.% | Al₂O₃ | CaO | Fe₂O₃ | K₂O | MgO | Na₂O | SiO₂ | TiO₂ | ZnO | Total |
|---|---|---|---|---|---|---|---|---|---|---|
| 1.9 | 4.9 | 1.2 | 1.3 | 0.7 | 39 | 0.1 | 31.7 | 81.8 |
| 11.5 | 10.2 | 2.7 | 0.1 | 1 | 2.4 | 27 | 29.6 | 84.5 |
| 5.0 | 3.1 | 26 | 1.4 | 1.3 | 0.8 | 1 | 2.6 | 48.1 | 84.2 |
| 0.2 | 0.4 | 0.1 | 0.2 | 0.1 | n.r | 2.7 | n.r | 2.5 | 6.2 |

n.r: not reported

4. Main properties of both CB and CBp for rubber formulations

As aforementioned, the characteristics of CB and in this case of CBp are determined by some fundamental physical-chemical properties. The size, shape and distribution of aggregates are generally termed CBp structure. Likewise, CBp surface activity is described in terms of the oxygen containing chemical groups onto the surface (e.g. carboxyl, quinone, phenol and lactone) and delocalized π electron [50]. The smaller the particle sizes (<50 nm), the higher the surface area and hence, the higher the reinforcement grade [18, 51, 52]. Generally, the higher the surface area, the surface activity and the structure, the higher the CB reinforcing potential.
4.1. Particle, aggregate and agglomerate

CB exhibits hierarchy morphological features: (i) particles (that is, primary particles), (ii) aggregates, and (iii) agglomerates, as shown in Figure 1. Even though the fundamental building block is based on primary particles, they tend to strongly linked by covalent bonds forming aggregates. Thereafter, individual aggregates get together by van der Waals forces to form agglomerates. These agglomerates do not break down into smaller components unless adequate forces are applied [20]. Particle size is an important property since it contributes to strength and blackness in rubber goods [53]. The average primary particle size of commercial rubber type CB grades ranges from about 10 to 500 nm [18, 54]. The thermal CB has the largest particle size (mean diameters of 240 – 320 nm) [18]. In contrast, the furnace CB shows particle sizes approximately three to twenty times smaller (mean diameters of 15 – 80 nm) [18, 25]. In the case of CBp, there is an irregular distribution of particle size given the several CB grades used in tyre manufacture. Huang et al. [31] reported that commercial CB aggregates have a Gaussian distribution. They found three different aggregates distribution for the CBp produced at 500°C in a tubular reactor: (i) 80-115 nm, (ii) 212-253 nm, and (iii) 418-474 nm, which is far from a single commercial CB reference. Likewise, Du et al. [55] noticed by scanning electron microscopy (SEM) that the aggregation size of CBp (~10 μm) is larger than that of commercial CB N774 (~2 μm) and similar to Huang et al., they observed wider aggregate distributions for CBp.

4.2. Structure

The reinforcement potential of any CB is governed, in some extent, by its structural level (aggregation degree). Herein, structure is determined by the size and shape of the aggregated primary particles [18]. A high structure in a CB indicates a high number of primary particles per aggregate, while low structure degree is related to a weak aggregation level [29]. It is important to highlight that different CBs could have similar particle size but no equal structures [56]. Higher structure is manifested in many ways in the rubber compound. For instance, higher viscosity, stiffness or elastic modulus, hardness, conductivity and easier dispersion, while low tear strength and swell [52, 54]. Figure 2 illustrates the structure of three different commercial CB where N990 exhibits low structure (low aggregation degree), whilst N121 shows a high one (high aggregation degree).
The CBp structure seems to be low since it commonly shows wider aggregates size distribution. In this way, Berki et al. [57] compared the CBp to the commercial CB N330 through SEM images, finding that CBp is less homogeneous than N330 and contains many large aggregates. This result is not surprising since, as mentioned previously, CBp is a mixture of different CBs. The CB structure is commonly determined by the Oil Adsorption Analysis (OAN). Herein, the greater the volume of oil absorbed by the CB, the greater its structure [58]. The OAN value of commercial CB ranges from 58 to 105 mL100g⁻¹, while in the case of CBp this value has been found to be around 80 mL100g⁻¹ [9].

4.3. Surface area
Surface area is an important parameter for CB classification and also helps for predicting the rubber reinforcement potential. As mentioned before, surface area is related to particle size. In this sense, CBs with small particle size have more external surface ability for rubber interactions. In addition, CB pores also influence the surface area and promote the interaction between CB and rubber, although it depends on the pore opening size. Conventionally, pores are divided into three types according to size: (i) macropores (> 50 nm), (ii) mesopores (between 2 and 50 nm), and (iii) micropores (< 2 nm) [59]. San Miguel et al. [60] reported that the CBp obtained from the WTs pyrolysis at 700°C was limited in surface area and micropore volume but it exhibited a relatively large mesopores structure which can be helpful for large molecules size absorption. The common and accurate technique to determine the specific surface area is the N₂ adsorption known as Brunauer, Emmett, and Teller (BET), as described by the ASTM D6556. However, this analysis requires specific and qualified equipment, which makes it very expensive. For this reason, the CB industry commonly use cheaper techniques as the iodine adsorption (ASTM D1510) and the methylene blue adsorption (ASTM C1777). Typically, commercial CBs have surface areas (BET) between 40 and 155 m²g⁻¹ [59], whilst for CBp this property ranges between 57 and 89 m²g⁻¹ as reported in Table 2. It means that CBp surface area could be compared to the commercial CBs between references N774 and N330 (Table 1). BET surface area and iodine adsorption have a direct relation, although the proportionality constant depends on each CB type [61].

4.4. Surface chemistry
Surface chemistry in CB is usually related to oxygen surface functional groups (SFG), which improves the pigment wetting and dispersion, among others. Although it plays an important role in the polymer-filler interaction, no direct correlation has been demonstrated between the chemical groups present onto the CB surface and the related properties of rubber. Indeed, it has been stated that the filler polymer interaction in commercial CBs is mainly of physical nature (physisorption) [51]. For CBp, has been reported that functional groups can be obstructed by the inorganic matter, which have been promoted demineralization processes to remove these impurities to improve the filler-rubber interactions [13, 32, 48].
Generally speaking, some functional groups can appear at the edges of graphene layers usually formed by the presence of heteroatoms (H, O, N, S, halogens) which constitutes active sites [62]. These groups could have either acid or basic character. The acid groups are carboxylic acid, carboxylic anhydride, lactone, lactols, phenol, and hydroxyl. Whereas the basic character is related to the nitrogenous groups such as pyridine, nitrile, pyrrole, amine, amide, etc [62]. In general, high oxygen content is associated with the presence of more acid groups while low oxygen content with basic groups [63].

There are different methods, either qualitative or quantitative, to characterize the SFG. For instance, infrared spectra is commonly used as a qualitative technique and the volumetric analysis, developed by P. H. Boehm (known as the Boehm method), is used as a quantitative tool. The latter method consists in a selective neutralization of the acid or basic SFG. The acid groups quantified by this method are carboxylic (acid and anhydride), lactonic (lactone and lactols) and phenolic including hydroxyls. Figure 3 shows a schematic representation of these SFG. Boehm method consider that NaOH neutralizes carboxylic, lactonic and phenolic; Na₂CO₃ reacts with carboxylic and lactonic; and NaHCO₃ reacts only with carboxylic groups. Regarding basic groups, they are quantified as total basic groups and are neutralizes by HCl [63–68].

On the other hand, in the infrared spectroscopy, carbonaceous materials can exhibit characteristic peaks around 3300-3600 cm⁻¹ and 3100-3200 cm⁻¹ which correspond to carboxylic acid vibration COOH and hydrogen bond due to the OH stretching. The peak near to 3400 cm⁻¹ is characteristic from alcohol and phenol. Other important peaks are located around 1110, 1600 and 1500 cm⁻¹ and are related to C-O vibration, carbonate bond (C=O) and the carbonyl-carbonate group, respectively [69]. In addition, is possible to find a peak near to 1200 cm⁻¹, which is characteristic of aromatic alcohols. Also, peaks around 2900 cm⁻¹, representing the symmetric and asymmetric C-H bond, indicating some residual organic matter onto the CBp surface [70]. Furthermore, peaks in the range of 1200-1300 cm⁻¹ could also be found. They are linked to the vibration of C-O and C-OH molecules that represent phenolic or carboxylic compounds [71]. Table 4 shows the wavelength of some SFG commonly found in carbonaceous materials. The infrared spectra of CBp has been analysed by Li et al [70]. The authors reported that this CBp has similar absorption peaks as N330, but with weaker intensities for peaks at around 3435 and 1084 cm⁻¹, which are attributed to the stretching vibration of OH and CO, respectively.
Table 4. Infrared functional groups

| Wavelength (cm⁻¹) | Molecule or functional group                      | Ref. |
|------------------|---------------------------------------------------|------|
| 3440             | O-H de hydroxyl, phenol y/o carboxylic            | [71] |
| 3200-3640        | 1049-1276 Alcohols and absorbed water             | [69, 72] |
| 2500-3620        | 1160-1200 O-H de phenols                          |      |
| 2854 y 2920      | -CH₃, CH₂ y CH₄                                   |      |
| 2600-3000        | C-H                                              |      |
| 2500-3300        | 1665-1760 Carboxylic acids                        |      |
|                  | 1740-1880 Carboxylic anhydride                    |      |
|                  | 1675-1790 Lactones                                | [71] |
|                  | 1585-1600 C=C aromatic                            |      |
|                  | 1590-1600 Carboxylic-carbonate                    |      |
|                  | 1000-1220 C-OH de phenols                         |      |
|                  | 1000-1300 C-O ether                               | [69, 71] |
| 1723-1735        | C=O Carbonyl                                      | [19, 71] |
| 2250-2400        | C=O                                              |      |
| 1000-1200        | C-O                                              | [72] |

Throughout the years, efforts have been made to understand how the SFG reacts chemically with rubber molecules. However, no important results have been found. Instead, it is well-known that surface activity (related to surface chemistry) should be high in order to achieve a high interaction between the CB and the rubber matrix [73].

5. The potential used of CBp in reinforcing rubber
The incorporation of CB into rubber composites enhances the mechanical behaviour of the rubber good, from both physical and chemical interactions [59]. Physical interactions are related to the adsorption of free radicals coming from polymers onto the CB surface; while chemical interactions are associated with chemical reactions between these free radicals and the SFG of the CB. In this sense, that interaction is mainly related to the chemical surface, structure, particle size and surface area [74].

In general terms, the research works about the incorporation of CBp into styrene butadiene rubber (SBR) and/or natural rubber (NR), have concluded that commercial CBs (e.g. N660, N330, N550, N339, etc.) show higher reinforcing activity than CBp [57, 75–78]. Moreover, these research works have reported and compared the mechanical, dynamic mechanical thermal and the fracture mechanical behaviour when using different CBp in rubber formulations, as shown below.

5.1. Mechanical behaviour
The incorporation of CBp (with ~80 wt.% carbon content, ~20 wt.% ash and 75 m²g⁻¹ BET surface area) into SBR, resulted in the increase of both hardness (shore A) and tensile strength, as increasing the amount of CBp. The commercial reference N330 (80 m²g⁻¹ BET surface area -similar to CBp) has shown the same tendency but presented higher values of both properties as compared to CBp [57]. In addition, the same authors in other two papers, also found higher hardness and tensile strength in SBR formulations filled with N660 (BET of 35 m²g⁻¹) at 60 phr than with CBp (the same used in ref. [57]) [75, 76]. This fact could be attributed to the inorganic compounds and carbonaceous deposits presented in CBp [75, 76].

Du et al [55] also evaluated the mechanical properties of SBR formulations with CBp (with 85.8 wt% of C and 13.3 wt.% of ash) and compared it to SBR filled with N330 and N774 at different loadings. They noticed that the increase of each filler content greatly improved the tensile strength, tear strength and modulus at 100% of strain, as compared to the unfilled rubber. For instance, when the CBp amount
increased from 10 to 50 phr, the tensile strength of SBR composites increased by 9 times, while the tear strength increased by 3 times. However, the CBp led to a decrease of these properties, as compared to N774 and N330. Even though the authors stated that N774 can be partly replaced by CBp in some rubbers formulations.

The partial substitution of CB by CBp at a given amount, have resulted in different behaviours. For instance, Karabork et al [77] replaced partially the N550 at 50 phr by the CBp produced at 500-550°C in a fixed bed reactor (FBR) and evaluated its performance in NR-SBR blends. They found a decrease in hardness (shore A), tear strength and the tensile strength, as increasing CBp amount. On the other hand, Berki et al [57] found a decrease in the tensile strength and hardness when increase the amount of CBp in the partial substitution of N330 by CBp at different loads (30, 45 and 60 phr), although the tear strength increased. Likewise, Cataldo [78] evaluated the partial substitution of N339 (90 m²g⁻¹ BET surface area) by a CBp (produced at 700°C with 81 m²g⁻¹ BET surface area and about 10 wt.% ash) into NR-SBR composites. Similar to Karabork et al [77] and Berki et al [57], the author also observed a decrease of tensile strength and hardness IRHD with the increase of CBp content in the blends.

Another important property affected by the incorporation of CBp is the tensile strain at break. By increasing the filler amount, either CB or CBp as well as combinations of both, the tensile strain decreases. That phenomenon occurred because during filler dispersion in rubber, part of the elastomer fills the void volume of the CB aggregates. The elastomer portion located within the irregular contours of the aggregates is unable to participate fully in the deformation. If the CB presents high structure, the elastomer filled into the filler void volume shows lower deformation which means low tensile strain value [59]. Tensile strain was lower in N330 – SBR composites than composites filled with CBp [57]. SBR composites filled with N660 showed also lower tensile strain than those filled with CBp [75, 76].

Due to the low performance of CBp in rubber composites, different treatments have been tested to improve the CBp quality such as acid treatments and the use of coupling agents [12, 13]. For instance, Zhou et al [12] evaluated a washing process of CBp with HNO₃ (5wt.%) and the use of titanate coupling reagent into the washed CBp. Those modifications resulted in an increase of the tensile strength compared to the untreated CBp.

5.2. Dynamic mechanical thermal behaviour

The dynamic mechanical thermal analysis (DMTA) leads to obtain the storage modulus (E’') and the mechanical loss factor (tan δ). The maximum tan δ peak is found in a marginal change in glass transition temperature (Tg) [57]. In general terms, the tan δ at 0°C is related to the tyre performance, high value is associated with good skid resistance in wet or cold road conditions and low tan δ value at 60°C is correlating with low rolling resistance. However, it is difficult to obtain both high tan δ at 0°C and low tan δ at 60°C at the same time, therefore, a balance between those values may suggest a suitable rubber compound [79]. Furthermore, the DMTA also reports the E', specifically the rubber and glassy modules which are read at T=Tg+30°C and T=Tg-30°C, respectively. Both modules increase as increasing filler content, while a decrease in tan δ is shown as increase filler amount as well [57, 75, 76]. That decrease in tan δ is associated with the increasing of filler-rubber interaction (reinforcing effectiveness) due to the reduction of rubber chains mobility in the filler-rubber interphase caused by the increase of filler amount [77]. In addition, the rubber modulus is used to calculate the apparent crosslink density (Mₐ) (also known as apparent mean molecular weight). Although the Mₐ is an apparent value because it is affected not only by the filled rubber crosslinking but also by the rubber-filler and filler-filler interactions, lower Mₐ values indicates high crosslink [57, 75].

In this sense, SBR-CBp composites (mentioned in section 5.1. ref. [57]) showed an increase of both rubber and glassy modules, a decrease of tan δ and a decrease of Mₐ by increasing the CBp content. In all filler loadings (30, 45 and 60 phr), the Mₐ and tan δ properties were lower, while the rubber and
glassy modules were higher in the N330 composites compared to the CBp ones [57]. In the case of the comparison of the CBp with the N660, which is a lower reinforcing grade CB respect to N330, the SBR filled at 60 phr showed similar $M_c$ and rubber modulus, while the glassy modulus was higher and the $\tan \delta$ was lower in the N660 composites compared to the CBp ones [75].

As well as the mechanical behaviour, in the partial substitution of CB by CBp, Karabork et al found in the composites mentioned before in section 5.1. that the $\tan \delta$ first increased and then decreased by increasing the CBp amount. However, all samples with CBp showed higher $\tan \delta$ than the N550 composites due to CBp caused a decrease in the elastic behaviour which is reflected in the greater $\tan \delta$ value. Respect to the $E''$, the same samples showed a decrease in this property by the CBp increase, as expected. This fact means a weaker reinforcing effect of CBp than the commercial N550 which is attributed to the difference in morphology, structure and surface area between those two fillers [77].

Another important parameter from the DMTA is the Payne effect which reflects the agglomeration tendency or the filler reinforcing activity. The higher this value, the more active the filler is. The Payne effect is read in the plot of $E''$ as a function of the strain and is measured by the difference in the $E''$ modulus at 0.01 and 10% tensile strain [57, 75]. The SBR-CBp composites of ref. [57] (mentioned in section 5.1. ), showed grater Payne effect value by the increasing CBp filled, but it was lower than the CB N330 at all loadings (30, 45 and 60 phr) [57]. Contrary, the SBR composites filled at 60 phr of CBp (the same used in ref. [57]) was higher than the ones filled with CB N660 at 60 phr as well. Furthermore, the combines filler (30 phr CBp and 30 phr N660), yields the same Payne effect that the ones of N660 alone [75].

5.3. Fracture mechanical behaviour
The fracture mechanical test is used to investigate the crack propagation and the failure process. Generally, it is applied the crack tip opening displacement (CTOD) to study the crack propagation by analysing a sequence of images to detect the point where fracture started to propagate. This test leads to calculate the energy dissipated during fracture per unit of newly created fracture surface area ($J$-integral). The critical value of $J$-integral ($J_c$) is found on the crack onset. Due to it is hardly to find optically, some authors settle the $J_c$ value at CTOD of 0.5 mm [75, 76] as well as 0.1 mm [57].

The SBR with CBp composites (mentioned in section 5.1. ref. [57]) showed slightly higher $J_c$ values compared to SBR with N330 [57]. However, the SBR with CBp (the same used in ref. [57]) at 60 phr filling showed the same value of $J_c$ at CTOD of 0.5 mm to SBR with N660 at 60 phr filling as well. The difference between CBp and N330 is attributed to the dispersion state. The wide range of particle sizes as well as the large particle agglomerates of the CBp hinder crack propagation [57].

6. Conclusions
This work considered the literature review not only of the CBp properties but also its potential as a reinforcing-filler in rubber applications. The main differences between CBp and CB is the inorganic content, the carbonaceous deposits on the CBp surface and the heterogeneous morphology. These factors affect structure, surface area and particle size, among others, and are the main responsible for the mechanical properties detrimental when CBp is used in rubber formulations. Hence, some post treatments to the CBp can overcome these challenges. For instance, a demineralization process can remove the inorganic compounds as well as the carbonaceous deposits. A thermal treatment is also useful to remove residual volatile matter. Other treatment is a milling process to reduce and homogenize the aggregate size of CBp. Those post treatments have been suggested in order to improve the CBp quality and enhance its performance in rubber composites. Despite of the weak performance of rubber formulations using CBp reported in literature, it is possible its partial substitution in rubber goods that not require high mechanical properties.
On the other hand, CBp quality seems to depend on both pyrolysis conditions (temperature, pressure, particle size, heating rate, residence time (solid and vapours)) and pyrolysis reactor technology (rotary kiln, fixed bed, fluidized bed and auger). All the parameters influence the CBp properties and hence, their performance in rubber formulations. Also, tyre type seems to affect the pyrolysis products yields and properties. In addition, a proper selection of waste tyres can enhance the CBp properties, as the CBp is more homogeneous as compared with that obtained when different types of waste tyres are pyrolyzed.

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