Carbon black recovery from waste tire pyrolysis by demineralization: production and application in rubber compounding

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Abstract

Pyrolysis offers the possibility to convert waste tires into liquid and gaseous fractions as well as a carbon-rich solid (CBp), which contains the original carbon black (CB) and the inorganic compounds used in tire manufacture. Whilst both liquid and gaseous fractions can be valorized without further processing, there is a general consensus that CBp needs to be improved before it can be considered a commercial product, seriously penalizing the pyrolysis process profitability. In this work, the CBp produced in a continuous pyrolysis process was demineralized (chemical leaching) with the aim of recovering the CB trapped into the CBp and thus, producing a standardized CB product for commercial purposes. The demineralization process was conducted by using cheap and common reagents (HCl and NaOH). In this sense, the acid treatment removed most of the mineral matter contained in the CBp and concentration was the main parameter controlling the demineralization process. An ash content of 4.9 wt.% was obtained by using 60 min of soaking time, 60 °C of temperature, 10 mL/g of reagent/CBp ratio and HCl 4M. The demineralized CBp (dCBp) showed a carbon content of 92.9 wt.%, while the FRX analysis indicated that SiO₂ is the major component into the ash. The BET surface area was 76.3 m²/g, and textural characterizations (SEM/EDX and TEM) revealed that dCBp is composed by primary particles lower than 100 nm. Although dCBp showed a low structure, the surface chemistry was rich in surface acidic groups. Finally, dCBp was used in Styrene Butadiene Rubber (SBR) compounding, probing its technical feasibility as substitute of commercial CB N550.

Keywords: carbon black, carbon black recovery, demineralization, pyrolysis, waste tire

1. Introduction

Waste tires are considered a continuously growing environmental problem with negative impacts on economy and health matters (Zabaniotou et al., 2014). About 1.5 billion tires are sold worldwide each year, and 50% of that amount is estimated to be discarded without any treatment (Thomas and Gupta, 2016). Pyrolysis is an energy and material recovery process and could form part of the solution to this global issue, and is currently considered an effective and sustainable process able to deal with the waste tire disposal problem (Antoniou and Zabaniotou, 2013; Martínez et al., 2013c; Williams, 2013). However, one of the major issues behind this practice is the process economy and the value of the resulting products. Specifically, the profitability of the waste tire pyrolysis at industrial or semi-industrial scale depends on the market/application for the major products obtained, i.e. the liquid and the solid fraction.

In a good pyrolysis process, the liquid yield should be higher than 40% of the waste tire weight. This liquid shows the best possibilities for commercialization among the pyrolysis products, since it can be added to petroleum refinery feedstock, or to be used as: (i) a source of value-added products (for instance limonene (Danon et al., 2015), or as an alternative liquid fuel given its higher heating value (> 40 MJ/kg (Martínez et al., 2013a)). On the other hand, the solid yield should match the contents of fixed carbon and ash of the waste tire (approximately 35-40% of the waste tire weight). This carbonaceous material contains the carbon black (CB, between 80 and 90 wt.%) and the inorganic substances (between 10 and 20 wt.%) used in tire manufacture (Martínez et al., 2013c; Sagar et al., 2018) and for this reason, is commonly referred as pyrolytic carbon black (CBp). In addition, it can also contain extra carbonaceous residues onto the CBp surface as consequence of repolymerization reactions among the polymer-

derivates, mainly depending on the pyrolysis severity (Chaala et al., 1996; Murillo et al., 2006; Roy et al., 2005).

CB is essentially an amorphous carbon material of quasi-graphitic structure commonly used as reinforcing filler and pigment in rubber and plastic products and coatings. In rubber manufacture, CB is used to strengthen the rubber and aid abrasion resistance, being the major reinforcing filler in the rubber industry. The most popular CB by far for rubber manufacture is the one made by the furnace process, with grades ranging from N100 through N700 series (Liang, 2004). Given the high cost of CB, which can vary between 600 and 1000 €/ton (depending mainly of the CB grade and market fluctuations), the most straightforward CBp application is as substitute of commercial CB, i.e. to be used in rubber formulations. Besides the environmental advantages of this application, for instance that of CO₂ reduction, this market positively affects the economy feasibility of pyrolysis since this application forms a recycling loop for the CB recovered from waste tires.

CBp properties seem to be strongly dependent on both the pyrolysis conditions and technology. In addition, tire manufacture uses various grades of commercial CB depending on the end-use properties and the tire component (inner liner, sidewall, belt package, tread, cushion gum). Therefore, the CBp notably differs from a unique CB and for this reason does not show the same reinforcement properties than a commercial CB (Mastral et al., 1999). A compendium of CBp yields as well as some physical-chemical properties from different results reported in literature are shown elsewhere (Antoniou and Zabaniotou, 2013; Martínez et al., 2013c; Williams, 2013).

Physical properties such as surface area and structure are considered key factors in the CB industry. In fact, two ASTM standards are addressing these issues (D6556-17 and

D2414-17, respectively). Besides these properties, surface activity is also an important aspect for the application of CB as reinforcing filler. This property is defined by both surface area and surface chemistry (related to the chemical reactivity of chemical groups onto CB surface), since they determine the level of physical and chemical interaction, respectively, during compounding (Donnet, 1993). Although there are no standards involving surface activity (linked to oxygen-containing functional groups) and chemical composition (particularly ash content) to classify CBs and much less CBp; these two parameters seem to be the most important barriers to the CBp application in rubber compounding.

Among others, rubber formulations using CB needs suitable surface activity since these properties determine the strength of the CB–rubber interaction (Chaala et al., 1996; Darmstadt et al., 2002; Roy et al., 2005). Some oxygenated functional groups, such as carboxyls, phenols and ketones (acidic functional groups) have been identified onto the CB surface, and they strengthen surface activity (Rodgers and Waddell, 2005). Likewise, ash content has been considered a major barrier for the CBp incorporation in rubber's market (Chaala et al., 1996; Roy et al., 2005). The inorganic matter presence into CBp represents an inert load and hence, does not contribute to the surface area. Consequently, it can cover active sites hindering the interaction between the CBp and the polymer.

Therefore, a post-treatment process able to reduce mineral matter, improving surface activity in the CBp during compounding is investigated in this work. Demineralization from acid and basic reagents has been extensively studied for coal deashing to obtain environmentally acceptable clean fuels (Önal and Ceylan, 1995; Bolat et al., 1998; Alam et al., 2009). It is well-known that mineral matter in coals has a marked and undesired effect on most coal utilization processes. Likewise, this process has been

explored by several authors in order to assess gasification/activation and combustion processes using demineralized CBp (dCBp) as a raw material (Ariyadejwanich et al., 2003; Ucar et al., 2005; Suuberg and Aarna, 2009; Alexandre-Franco et al., 2010). In addition, there are some works dealing with CBp demineralization as those conducted by Chaala et al., (1996); Roy et al., (2005) and Zhang et al., (2018). Iraola-Arregui et al., (2018) have been recently reviewed some of these works, where operating conditions for demineralization of waste tire and lignocellulosic wastes as well as their respective pyrolysis chars were highlighted. However, neither of them has showed a robust experience at semi pilot-scale as showed in this work.

Herein, the CBp produced in a continuous pyrolysis process was demineralized (chemical leaching) in order to recover the CB trapped into the CBp. The demineralization process was performed by using cheap and common reagents commonly used in the chemical industry (HCl and NaOH). To the best of authors' knowledge, this is a promising study investigating the recovery of the CB trapped in the CBp considering an easy and scalable process which has been operated with higher sample (150 g) than those reported in literature. Likewise, this is one of the first studies showing how a demineralization process improves the CBp for Styrene Butadiene Rubber (SBR) compounding, in order to assess its technical feasibility as a concept proof. From this work, the barriers regarding the recovery of CB from waste tires are expected to be reduced in order to improve the economic feasibility of the waste tire pyrolysis process.

2. Materials and methods

2.1 CBp production

The demineralization process was studied in a semi pilot-scale system. The CBp used in this work was produced in long-term pyrolysis experiments (more than 500 kg of shredded waste tires were pyrolyzed in 100 h of operation) by using a continuous auger reactor at 550 °C, as showed elsewhere (Martínez et al., 2013b). Liquid and gas yields were 42.6±0.1 and 16.9±0.3 wt.%, respectively. The CBp yield was 40.5±0.3 wt.%, which was slightly higher than the resulting sum between the ash and the fixed carbon contents present in the waste tire (≈35 wt.%). Before being demineralized, the CBp was submitted to an extra-heating at 700 °C under inert atmosphere (N₂) by using the same pyrolyzer reactor in order to decrease residual carbonaceous deposits as well as to reduce the strong unpleasant odor.

2.2 Semi pilot-scale facility for demineralization

The semi pilot-scale facility is depicted in **Fig. 1** and consisted of (1) a 2 L jacketed glass reactor AFORA 110 with (2) one mechanical stirrer. The reactor also incorporated a (3) thermocouple sensor and also a (4) reflux condenser to prevent possible water evaporation and changes in reagents concentration. Two heater/chiller units provide hot and cold water to both reactor and condenser. This experimental set-up was designed, assembly and operated for the dCBp production and allowed identifying the main variables involved in the demineralization process.

Fig. 1. General scheme of the semi pilot-scale facility

2.3 Experimental procedure for demineralization

Once concentration and volume of reagent were prepared and 150 g of CBp placed into the reactor, the temperature was settled at the value chosen to conduct the experiment. The liquid-solid mixture was mechanically stirred by the mechanical agitator. Different rotation velocities were tested in order to achieve a proper stirring process. In all cases, the rotation velocity of the mechanical stirrer was fixed at 400 rpm since this value showed to be the best condition to reach an intimate mix between the reagent and the CBp. Regardless of the experimental conditions, the residual solid obtained after conducting the demineralization process was successively washed with distilled water until the filtrate pH was neutral. Later, the washed solid was dried using an electric oven at 120 °C during 5 h. The variables studied in this work are listed in **Table 1**. The experimental campaign associated with the demineralization process started with a reproducibility study followed by the optimization of the process variables, as shown later. Demineralization experiments were conducted aimed at finding a CBp with the lowest ash content without remarkable losses of carbon.

Table 1. Parameters studied for CBp demineralization

2.4 Characterization techniques

Both CBp and dCBp were subjected to ultimate and proximate analyses, ash chemical composition, BET surface area (S_{BET}), Hg porosimetry, He picnometry, scanning electron microscopy/energy dispersive using X-ray (SEM/EDX), transmission electron microscopy (TEM) and temperature-programmed desorption (TPD) analyses. In addition, relevant properties of some commercial CBs (N234, N375, N550 and N772) were also determined for comparison purposes.

The ultimate analysis was carried out in a Carlo Erba-1108 instrument, the moisture and the ash contents were measured according to EN 14774-3 and EN 14775, respectively; while the volatile matter was determined according to EN 15148. Fixed carbon was calculated by difference. The ash composition was determined by inductively coupled plasma-optical emission spectroscopy using an ICP-OES JY 2000 Ultrace equipment.

S_{BET} was determined by multi-point N_2 adsorption at 196 °C in a Micromeritics ASAP-2020 apparatus, whereas particle density and porosity were obtained from a Micromeritics AccuPyc II 1340 helium picnometer and from a Quantachrome PoreMaster 33 mercury porosimeter, respectively.

SEM/EDX analyses were conducted using a Hitachi S-3400 N instrument. This equipment was coupled to Röntec XFlash de Si(Li) for energy-dispersive X-ray (EDX) analysis, in order to determine the elemental microanalysis. The incident electron beam energy used was 15 keV. TEM images were acquired using a FEI Technai G² microscope operated at 200 kV. The samples were treated by sonicating in absolute ethanol for several minutes, and a few drops of the resulting suspension were deposited onto a holey-carbon film supported on a copper grid, which was subsequently dried.

TPD was also performed in order to quantify both CO and CO₂ concentration released when samples were submitted to a progressive heating in an inert atmosphere. Thus, 100 mg of sample was heated at 20 °C/min from 25 to 900 °C in a 20 cm³/min Ar flow to carry the desorbed gases during the reaction. A conventional flow-through reactor connected to a mass spectrometer Omnistar GSD30102 registered the m/z fragments 28 and 44 for CO and CO₂, respectively. Both CO and CO₂ concentrations were related to the presence of basic and acid functional groups, respectively.

2.5 Rubber processing

In order to test the practical ability of the upgraded CBp and identify the importance of the demineralization process, both CBp and dCBp were used in SBR formulations. Vulcanization curve, Mooney viscosity and some physical properties of the SBR vulcanizates such as tensile stress at 300% elongation (also known as modulus at 300%), tensile stress at break, elongation at break, tear resistance, hardness and abrasion loss were determined and compared with those obtained when using a commercial CB (N550).

Table 2 shows the components and the proportions used in each rubber formulation. All samples were based on parts per hundred (phr) of SBR. Firstly, activating agents (ZnO and stearic acid) were added into the rubber and then, after dispersion, fillers under study were included. At last, TBBS (n-tert-butyl-2-benzothiazolesulfenamide) and sulfur were added as vulcanization accelerators.

Table 2. Formulations for rubber processing using CBp, dCBp and CB N550

All blends were prepared in a mixing cylinder at 40°C and fixing a gear friction of 1:1.2 following the standard ASTM D-3182-16. After 24 hours, both viscosity and vulcanization curves were obtained according to the standards ASTM D-2084-17 and ASTM D-5289-17, respectively. Thus, some rheological parameters involved in the reaction and the Mooney viscosity (ML_{1+4}), were determined. The curing degree measurements were conducted in a Moving Rheometer, Model MDR 2000E, (Alpha Technologies) whereas the viscosity was determined from a viscometer MV 2000E (Alpha Technologies).

3. Results and discussion

3.1 Post-heating treatment of CBp

The formation of carbonaceous deposits during waste tire pyrolysis onto the CBp surface affects the surface activity and morphology. These carbonaceous deposits are likely located in the void space between the primary particles of the CB aggregate, blocking a portion of their surface (Pantea et al., 2003). Therefore, the original CB is trapped into the CBp and therefore, the reinforcement properties of CBp could not be the same than those of commercial CB. As showed in **Table 3**, the post-heating treatment decreased the volatile matter (from 4.7 to 2.4 wt.%,) and led to an increase of the S_{BET} (from 65.7 to 72.4 m²/g), as expected. Volatile matter in CBp produces agglomerated particles that are difficult to break.

Similarly, the strong odor was diminished leading to more practical handling of the CBp. Surface area is a very important property for CB utilization in rubber manufacturing since it is one of the parameters that determine the degree of interaction of the rubber within the CB (Tricás et al., 2002; Liang, 2004; Norris et al., 2014) and consequently, its reinforcement capacity. In fact, an increase of surface area suggests an increase in the concentration of active sites in the edges of graphite-like regions, which could provide higher interaction between the CB filler and the rubber matrix (Darmstadt et al., 2000).

Table 3. Ultimate and proximate analyses of the CBp before and after post-heating treatment and for the repeatability tests

3.2 Semi pilot-scale tests: demineralization process

As commented above, the CBp virtually contains all of the inorganic matter used in tire manufacture since they are not devolatilized at typical pyrolysis temperatures.

Consequently, the ash concentration in CBp is considerably higher (≈ 15 wt.%) as compared to that of commercial CBs (< 0.5 wt.%) (Roy et al., 2005). This section shows a reproducibility study and the effect of soaking time (t), temperature (T), reagent/CBp ratio (R), reagent concentration and sequential treatment acid/base on the demineralization process, according to levels showed in **Table 1**.

3.2.1 dCBp production: repeatability tests

In order to assess the reproducibility of the demineralization process, seven independent runs at equal conditions were conducted. The experimental conditions were 60 min, 60 °C, 3 mL/g and HCl 3M. As observed in **Table 3**, the demineralization conditions led to C, H, N and S contents of 91.5 ± 0.2 , 0.6 ± 0.0 , 0.3 ± 0.0 and 0.9 ± 0.0 wt.%, respectively. The demineralization process greatly increased the C content at expense of the ash content, indicating an ash reduction ratio around 50%. Taking into account the experimental facility scale and the experimental error associated, the results found suggest that demineralization shows a reasonable reproducibility.

Furthermore, it was found a notably S reduction mainly due to sulfides solubilization with no apparent carbon reduction (see **Table 3** for comparison). This behavior is in agreement with results reported by Chaala et al., (1996) regarding the use of H_2SO_4 for CBp demineralization as well as those found by Alam et al., (2009) for coal de-ashing using HNO_3 and HCl. According to Loadman (1998), the S content in CBp does not play any part in the curing of vulcanizates and can be considered as inactive. The S content in commercial CBs mainly depends on the feedstock and contents around 0.6 wt.% are common in those obtained from furnace process (Donnet, 1993).

Similar results have been reported by using other chemical reagents in CBp demineralization, as showed in **Table 4**. As inferred, the demineralization conditions

used in the present work are less severe than those reported in **Table 4**. In addition, the ash content reduction is remarkable taking into account the higher amount of sample processed (150 g) as compared to those observed in literature. **Table 5** shows the ash composition analysis of both CBp and dCBp as well as the reduction ratio of each compound. As expected, the acid treatment favored the removal of Al, Ca, Fe Na and Zn, whereas Si was highly enriched.

Table 4. Demineralization conditions and results found in literature

Table 5. Ash composition analysis of CBp and dCBp

3.2.2 Soaking time influence

The soaking time influence was studied at 15, 30 and 60 min. Temperature, reagent/CBp ratio and reagent concentration were kept constant (60 °C, 5 mL/g and HCl 1 M, respectively). These experimental conditions were more demanding since they considered a very low reagent concentration and also a low reagent/CBp ratio. As seen in **Table 6**, the higher the soaking time, the lower the ash and the volatile matter contents. For this reason, 60 min has been chosen for performing the rest of the experiments. Even so, it is worth to point out that the demineralization results are not as good as those shown in **Table 3**. It seems that higher reagent concentration must be used.

Table 6. Variables effect on the demineralization process

3.2.3 Temperature influence

The reaction temperature is a key variable in solubilization processes. However, high temperatures lead to significant energy penalties and possible reagent losses by

evaporation. Three reaction temperatures (50, 60 and 70 °C) were tested while keeping constant the other process conditions (soaking time of 60 min, reagent/CBp ratio of 10 mL/g, and HCl 2M). As observed in **Table 6**, around 60% of ash reduction was achieved for all the samples, while the C content increased between 7 and 9 points (see **Table 3** for comparison). Also, these temperature levels did not seem to have a strong influence on the demineralization process since both the ash content and the S_{BET} differences were minimal and were within the experimental error found in **section 3.2.1**. The intermediate temperature of 60 °C was chosen for conducting the rest of experiments.

3.2.4 Reagent concentration influence

This experimental campaign was performed by varying four different HCl concentrations, as follows: 2, 4, 6 and 8 M. The soaking time was fixed at 60 min, while temperature and reagent/CBp ratio were 60 °C and 10 mL/g, respectively. **Table 6** also shows the results obtained for the different concentrations tested. As observed, HCl concentrations lower than 4 M produced a minor solubilization degree, whereas higher concentrations led to higher ash removal. However, it seems that HCl concentrations higher than 4 M start to affect the organic matter because both C and VM showed a trend to decrease. Hence, the optimal HCl concentration was fixed at 4 M. At this concentration, the S content was reduced around 57 % whereas the S_{BET} increased respect to the initial CBp.

3.2.5 Reagent/CBp ratio influence

The reagent/CBp ratio is an important variable because it is associated with the reagent consumption to carry out the demineralization process. Generally speaking, the higher the reagent volume and concentration, the higher the demineralization extent. However,

it could affect the C content. From this point of view, the goal to be achieved is to find a minimum reagent/CBp ratio in order to: (i) reduce operating costs and (ii) minimize the C reduction. Thus, three different reagent/CBp ratios (5, 10 and 15 mL/g) were tested while keeping the other process parameter constant (60 min of soaking time, 60 °C of temperature and HCl concentration of 4M). As shown in **Table 6**, the higher ash content was achieved using 5 mL/g in contrast to those obtained at 10 and 15 mL/g. However, 15 mL/g seems to attack the organic matter given the reduction of C, H and VM in comparison to the values found using 10 mL/g. Hence, 10 mL/g showed the most favorable value for conducting the demineralization process, even though S_{BET} was slightly lower than those obtained at 5 and 15 mL/g. At this condition a reduction ratio around 67% was reached.

3.2.6 Sequential acid/base treatment

Sequential treatment with HCl and NaOH was carried out in batch and alternately, i.e. the solid obtained in the first treatment (that obtained at 60 min of soaking time, 60 °C of temperature, 10 mL/g of reagent/CBp ratio and HCl 4 M) was used as raw material for the second one. From this sequence, removal of both acidic and basic compounds is expected. The experimental conditions used for the base treatment (NaOH) were the same utilized for the acid treatment but using a concentration of 5 M. As seen in **Table 7**, the ash content decreased from 4.9 to 3.1 wt.% ascribed to the SiO_2 solubilization. **Chaala et al., (1996)** also found an ash content around 3.0 wt.% after submitting the CBp to an acid-base treatment (H_2SO_4 1 N and NaOH 10 N) by using 5 g of CBp.

Table 7. Sequential acid/base treatment effect on the demineralization process

The acid treatment removes most of the mineral matter contained into the CBp, and excepting by the reagent concentration, no major effects of the process variables studied

were found. Generally speaking, an ash content of 4.9 wt.% was obtained by using 60 min of soaking time, 60 °C of temperature, 10 mL/g of reagent/CBp ratio and HCl 4M. Although the sequential acid/base treatment led to an ash content close to 3 wt.%, its implementation at industrial scale is environmentally unfriendly, costly and time consuming, and consequently unattractive. Looking for the industrial sector interest, only the acid treatment is proposed in this work to produce a dCBp aiming the substitution of commercial CBs.

3.3 dCBp characterization: comparison with commercial CBs

3.3.1 Surface area, porosity and real density

Table 8 shows the ultimate analysis, S_{BET} , porosimetry and real density of dCBp (produced at 60 min of soaking time, 60 °C of temperature, 10 mL/g of reagent/CBp ratio and HCl 4M) and different types of commercial CBs (N550, N772, N375 and N234). Firstly, it is worth to point out the slightly higher S_{BET} of dCBp (76.3 m²/g) respect to that found before demineralization (72.4 m²/g). This increase was expected taking into account the partial removal of mineral elements which were blocking the CBp porosity. Likewise, S_{BET} of dCBp is higher than those of N550 (44.8 m²/g) and N772 (26.8 m²/g) and lower than those of N234 (120.4 m²/g) and N375 (89.6 m²/g). This first comparison suggests that the dCBp could serve as substitute of medium/low-grade CBs such as N375 and N550, being closer to N550. The CB N550 is typically used in tire inner-liners, carcass, inner tubes, hoses, extruded goods and "V" belts whereas the CB N300 series are often used for standard tire treads, rail pads, solid wheels, mats, tire belts, sidewall, bushing, weather strips and hoses among others (Liang, 2004).

Table 8. Properties of dCBp and commercial CBs

Although results shown in **Table 8** are on a.r basis, the C content for dCBp (92.9 wt.%) was lower than all commercial CBs at expense of the higher ash content, whereas H (0.6 wt.%) and S (1.1 wt.%) contents were higher. N content (0.3 wt.%) compared well with all commercial CBs. Likewise, real density and porosity were also in the range between those of N375 and N550, as seen for the S_{BET} .

3.3.2 SEM/EDX analysis

SEM micrographs revealed some morphological characteristics of N550 (**Fig. 2**) and dCBp (**Fig. 3**). Although the appearance of dCBp (**Fig. 3d**) showed some similarities respect to that of N550 (**Fig. 2b**), the agglomerates of the former were less homogenous and much larger than that of N550. In this way, the N550 agglomerates seem to be finer and more homogenous than those of dCBp, which at first glance exhibit quasi-spherical and elongated shape. In addition, this commercial CB showed a smoother surface composed by a finer grain structure in contrast to the dCBp, although this fact did not seem to affect the surface area.

Size and bulkiness of both aggregates and agglomerates are described by the term structure. High structure indicates that there is a large number of primary particles per aggregate, whereas low structure is related to a weak level of aggregation (Donnet, 1993). Comparing **Fig. 2** and **Fig 3**, the structure of dCBp was lower than that of N550, which was rather moderate. This is not surprising since tire manufacturing uses different CBs grades and hence, the resulting CBp is a mixture of different CBs. In addition, the presence of both mineral matter and carbonaceous deposits, which were not removed after both the post-pyrolysis heating treatment and the demineralization process, could also contribute to the lower structure of dCBp. Structure plays an important role in the reinforcement properties of any CB (Chaala et al., 1996). Low structure CBs pack much

more tightly than high structure ones and are more difficult to disperse during the mixing stage (Boonstra, 1967; Wijayarathna et al., 1978).

Fig. 2. SEM micrographs of CB N550. a) magnification 1000x; b) magnification 10000x

Fig. 3. SEM micrographs of dCBp. a) magnification 500x (backscattering); b) magnification 1500x; c) magnification 2500x (backscattering); d) magnification 10000x

EDX characterization carried out at both CBp and N550 (Fig. 2a and 3b, respectively), is showed in Table 9 (area analyzed is marked in these Figs.). In contrast to the dCBp surface, the N550 surface showed the predominant presence of C, S and O and the absence of mineral matter, as expected. Si, Al, Mg, K, Na and Cl were more relevant than C onto the dCBp surface. This observation was also indicated by Chaala et al., (1996). The authors advised that after demineralization, salts and non-soluble oxides remain fixed onto the surface of the CBp aggregates.

Table 9. EDX characterization of both N550 CB and dCBp

3.3.3 TEM analysis

TEM micrographs showed that dCBp is mainly composed by nearly nano-size spherical particles lower than 100 nm, but with a wide range particle size distribution (Fig. 4a, 4b), in contrast to the high homogeneity found to the N550 (between 35 and 60 nm) (Fig. 4c, 4d). The mean primary particle size of commercial CBs is mostly in the nanometer range (from 8 to 100 nm) with particles often aggregating in grape-like clusters up to 500 nm (Rodat et al., 2011). Sometimes the term agglomerate is confused with aggregate. An agglomerate comprises of a large number of aggregates, which are physically held together as opposed to the continuous graphitic structure, which strongly links the particles in aggregates (Donnet, 1993). The ability to break up these

agglomerates into aggregates in order to ensure an adequate dispersion is crucial for achieving a desirable CB performance. Although significant literature has been developed on the CB dispersion in various medium (Pomchaitaward et al., 2003; Hanada et al., 2013); its practical application remains in experience practitioners who have the expertise, the technique and the trade secrets. However, high shear mixing in polymeric systems causes significant aggregate breakdown relative to the dry state (Donnet, 1993).

The pattern found for the dCBp is ascribed to the several types and brands of waste tires pyrolyzed, which are incorporating different CBs grades, as previously stated. In this sense, Helleur et al., (2001) showed similar TEM micrographs for the CBp produced in an ablative pyrolysis process. Huang and Tang, (2009) also found a wider CBp particle size distribution in comparison to that found for commercial CBs. This heterogeneity reduces the space availability for a proper filler-rubber interaction. Roughly speaking, the larger the particle size, the lower the surface area and the poorer the reinforcement potential (Liang, 2004). The loss of reinforcement is translated by a reduction in modulus, tensile strength, abrasion resistance and other mechanical properties (Barlow, 1993)

Fig. 4. TEM images of dCBp (a, b) and CB N550 (c, d)

3.3.4 TPD analysis

Besides porosity, surface functional groups also affect the interfacial adhesion characteristics of the CB with the rubber polymer (Boonstra, 1967; Darmstadt et al., 2000). According to Chaala et al., (1996), the surface effect is a key CB parameter to be considered more than just a filler. The surface chemistry is a very important property which influence some physico-chemical properties of CB such as wettability, catalytic,

electrical and chemical reactivity. Hence, the presence of oxygen-containing acidic functional groups on the CB surface determines their practical application in the rubber and plastic sector (Donnet, 1993). As stated by Mathew et al., (2009), the CB surface consists of graphitic planes, amorphous carbon, crystallite edges and slit shaped cavities. Particularly, the crystallite edges and the slit shaped cavities are the most important sites with respect to rubber filler and filler–filler interaction, since the acidic functional groups are preferably located at the edges of the graphitic basal planes or at the crystallite edges. These acidic functional groups are altered when the CB is submitted to heat treatment under vacuum or inert atmosphere in the temperature range 300-800 °C, and are linked to the evolved CO₂ (Donnet, 1993; Shen et al., 2008). These acidic functional groups have been suggested to be carboxylic, anhydride, lactonic and phenolic among others (Donnet, 1993; Burg and Cagniant, 2008).

Fig. 5 shows the TPD for both dCBp and N550. Functional groups can be quantified according to the decomposition temperature and type of gas released (CO₂ and CO). In this sense, carboxyl groups decompose between 200 and 400 °C, whereas phenolic or quinone groups decompose at higher temperatures (Shen et al., 2008). As seen in **Fig. 5**, the CO₂ evolved by dCBp (0.074 mmol/g) was higher than that obtained by N550 (0.035 mmol/g) while the CO was negligible for both samples and for this reason was not shown.

Fig. 5. TPD result for dCBp and CB N550

Therefore, the surface of dCBp is covered with higher acidic groups than that of N550, which could be related to the HCl treatment since it favors the formation of acidic functional groups in demineralization processes (Önal and Ceylan, 1995; Lou et al., 2011). Treatments with oxidizing agents are common procedures in CB technology in

order to increase the concentration of acidic functional groups considerably (Donnet, 1993). The interaction between rubber and filler is mainly determined by the polymer molecules adsorption onto the filler surface either chemically or physically (Donnet, 1993; Fröhlich et al., 2005). This adsorption is governed by many properties such as structure, surface area and surface chemistry, being the last two gathered by the term surface activity (Fröhlich et al., 2005; Tricàs Rosell, 2007). Even so, surface chemistry seems to play an important role in rubber-filler interaction since it exerts a notable influence in the adhesion ability and physical contact (Gessler, 1969; Dannenberg, 1986). Because of the higher CO₂ evolved, dCBp has much higher acidic surface groups than N550; and hence, a good polymer-filler interaction is expected, which could balance the detriment role of other factors such as ash content. According to Bhadra et al., (2003), CBs with high amount of surface acidic functional groups influence positively the rubber-filler interaction.

3.4 Rubber compounding

Rubber formulations were carried out by using (i) the CBp after post-pyrolysis heating-treatment, (ii) the dCBp obtained at 60 min of soaking time, 60 °C of temperature, 10 mL/g of reagent/CBp ratio and HCl 4M, i.e. that with 4.9 wt.% of ash content and 76.3 m²/g of surface area, and (iii) the commercial CB N550. The aim of these tests was to identify the effect of replacing CB N550 with both CBp and dCBp on SBR processing, as well as to observe the response on some mechanical properties.

Fig 6 shows the Mooney viscosity and the Mooney relaxation curve according to the formulations prepared (see **Table 2**). Likewise, **Table 10** shows the rheological parameters involved in the rubber compounding such as Mooney viscosity at 100 °C, minimum torque (M_L), highest torque (M_H), scorch torque (M_S) and torque increment

(ΔM). Also, different cure times (t_c) and scorch times (t_s) are showed. Mooney viscosity gives information just for one point of the flow curve and is the most used property for rubber characterization since it determines the mechanical processing ability. The higher the viscosity, the higher the shearing force during mixing and therefore, a higher frictional heat and mixing temperature.

Fig. 6. Viscosity curve of the rubber fillers used

As seen in **Fig. 6**, the SBR vulcanizate with N550 led to the lowest Mooney viscosity (80.6 MU) followed by that one with dCBp (91.8 MU) and CBp (98.0 MU). Although the resulting Mooney viscosity of the dCBp was not as good as that of the N550, it is worth noting that is better than that found using the CBp. The higher Mooney viscosity for the vulcanizate with both CBp and dCBp in comparison to that N550 is ascribed, besides the mineral matter, to the influence of both surface area and rubber-filler interaction (given the surface activity) since it has been reported that these parameters increase the viscosity (Sae-Oui et al., 2002). Likewise, it is not ruled out the possible worst dispersion of these fillers. Both CBp and dCBp showed a wider size distribution, in terms of aggregates, which negatively influences the dispersion ability (Donnet, 1993).

Table 10. Rheological parameters obtained in rubber processing

Furthermore, no major differences were found for M_L and M_S and hence, the vulcanization reaction must follow the same pattern regardless the filler used. M_L gives information on the processing ability of the rubber (Nabil et al., 2013). This result indicated that both CBp and dCBp have a little negative impact on the rubber processability (Dick, 2003). On the other hand, M_H increased slightly for CBp and notably for dCBp respect to the value found to the N550. This parameter relates to the

ultimate reticulation density that results from the vulcanization process (Dick, 2003). Thus, dCBp seems to contribute favorably with the vulcanizate network. The increase of the crosslink density could be ascribed to the acidic chemical surface and surface area which favor the chemical links formation between polymer chains and the filler according to the results found by Rajeev and De, (2002). These functional groups should increase the polarity on the dCBp surface, and consequently increase the final reinforcement (Yehia et al., 2004). In addition, the higher the ΔM , the higher the chemical cross-linking due to the mobility reduction of the rubber chains (Sagar et al., 2018). Hence, the dCBp seems to show a great interaction with the SBR.

On the other hand, **Fig. 7** shows the vulcanization curve at 160 °C for all SBR formulations. As observed, three different regions can be identified (Sui et al., 2008). The first region is the scorch time or induction period that provided a safe processing time. The second region is the curing or vulcanization reaction period, during this stage the crosslinking network is formed in the SBR and the stiffness of rubber is increased. In the third period, the crosslinking network in the SBR is mature and some over-curing reversion, equilibrium, or additional but slower crosslinking may occur for the different rubber materials (Sui et al., 2008). The scorch time at different torque levels (t_{s1} and t_{s2}) and all the vulcanization times (t_{c10} , t_{c50} , t_{c90} and t_{c97}) were determined from **Fig. 7** and are also listed in **Table 10**. t_{si} means the time required for the increase of 1 (t_{s1}) or 2 (t_{s2}) points from M_L . These parameters are indicators of the time required for the beginning of the crosslinking process. Likewise, t_{ci} means the time taken to achieve different vulcanization levels. These parameters, specifically t_{s2} and t_{c90} , are indicators of the time at which vulcanization begins and reaches completion, respectively (Nabil et al., 2013).

Fig. 7. Vulcanization curve of the fillers blends used

All these reference times were shortened when dCBp is used in comparison to both CBp and N550, indicating that the vulcanization reaction was completed earlier. Thus, dCBp seems to behave as an effective catalyst agent for rubber compounding. However, if the t_s is not sufficient to enable for instance, a proper mixing before the beginning of vulcanization, different inhibitors can be used (Kruželák et al., 2015). Generally speaking, the filler addition in rubber compounding reduces both the scorch and the vulcanization time. The higher the filler loading, the lower the curing time (Sae-Oui et al., 2002). However, given the mineral matter presence in both CBp and dCBp their respective load contributions as net CB were lower than that of N550. The decrease in both scorch and vulcanization time may be attributed again to the higher surface acidity of dCBp. Accelerators used in rubber formulation are generally basic compounds and hence, their activity is faster in presence of acidic groups decreasing these rheological parameters (Bhadra et al., 2003). Also, it is worth to point out that the presence of ZnO and SiO₂, as well as other minor metal oxides, can cause an increase in the rate of the early reactions (Coran, 2005).

Some key mechanical properties of the SBR vulcanizates are shown in **Table 11**. As seen, the incorporation of dCBp only led to a reduction of both the modulus at 300% and the tear strength at break, in comparison to the vulcanizate with N550. Conversely, tensile strength, elongation at break, and abrasion loss were higher for dCBp than those for N550, while hardness remained practically unaltered. Likewise, it is worth to highlight that all properties were enhanced by using dCBp instead of CBp and so, the demineralization process proved to be a useful treatment for improving the CBp properties as a reinforcement filler.

Table 11. Mechanical properties obtained in rubber compounding

This randomness in the mechanical properties is ascribed to the combined effect of mineral matter presence, structure, specific surface area and chemical surface which play an important role in reinforcement (Boonstra, 1967; Donnet, 1993). There are trade-offs in rubber compounding regarding some properties of the resulting material. The use of a particular reinforcement to improve a particular property may have a negative effect on other properties (Donnet, 1993; Donnet and Custodero, 2005). Despite these facts, dCBp proved to have reinforcing effects on SBR formulations comparable with medium-grade CB such as N550 and therefore, it could be used for rubber compounding.

4. Conclusions

Reagent concentration showed the major effect on demineralization. The optimal conditions using only one step of demineralization are 60 min, 60 °C, 10 mL/g and HCl 4M. After demineralization, the ash content in CBp was reduced in 67% since the ash content decreased from 15.0 wt.% to 4.9 wt.%.

The S_{BET} of the dCBp slightly increased (76.3 m²/g) respect to the CBp (72.4 m²/g) and is higher than that for N550 (44.8 m²/g). dCBp is mainly composed by primary particles lower than 100 nm with a wide range particle size distribution. This behavior is related to the presence of several tires (types and brands) and CB grades used in the different parts of the pyrolyzed tires. Additionally, dCBp showed a low structure whereas the N550 presented a moderate structure. The surface chemistry of dCBp showed a higher amount of surface acidic groups than N550.

Although the SBR vulcanized with dCBp showed a reduction in both the tensile modulus at 300% and the tear strength in comparison to the vulcanized with N550, some other important mechanical properties were comparable and even better. This

randomness in the evolution of the mechanical properties is ascribed to the counterbalance effect of a higher mineral matter presence and poorer structure versus a higher specific surface area and richer chemical surface. Despite these negative properties, it was demonstrated that dCBp shows relevant reinforcing effects and can be used for rubber formulations.

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Fig. 1. General scheme of the semi pilot-scale facility

Fig. 2. SEM micrographs of CB N550. a) magnification 1000x; b) magnification 10000x

Fig. 3. SEM micrographs of dCBp. a) magnification 500x (backscattering); b) magnification 1500x; c) magnification 2500x (backscattering); d) magnification 10000x

Fig. 4. TEM images of dCBp (a, b) and CB N550 (c,d)

Fig. 5. TPD result for dCBp and CB N550

Fig. 6. Viscosity curve of the rubber fillers used

Fig. 7. Vulcanization curve of the fillers blends used

Table 1. Parameters studied for CBp demineralization

Parameter	Values
Temperature (T, °C)	50, 60 and 70
Reagent/CBp ratio (R, mL/g)	5, 10 and 15
Soaking time (t, min)	15, 30 and 60
Reagent concentration (HCl and NaOH, M)	2, 4, 6 and 8

Table 2. Formulations for rubber processing using CBp, dCBp and CB N550

Component (phr)	Vulcanized		
	CBp	dCBp	N550
SBR 1500	100	100	100
CBp	50	0	0
dCBp	0	50	0
N550	0	0	50
ZnO	5	5	5
Stearic acid	1.2	1.2	1.2
TBBS	1	1	1
Sulfur	1.7	1.7	1.7

Table 3. Ultimate and proximate analyses of the CBp before and after post-heating treatment and for the repeatability tests

Sample/Run	Ultimate analysis wt.% (a.r)				Proximate analysis wt.% (d.b)			S_{BET} (m ² /g)
	C	H	N	S	A	VM	FC	
CBp before treatment	88.0	1.5	0.4	2.5	13.2	4.7	82.1	65.7
CBp after treatment	83.0	0.5	0.3	2.7	15.0	2.4	82.6	72.4
1	90.3	0.6	0.3	0.9	7.1	2.9	90.0	---
2	91.7	0.6	0.3	0.9	8.2	2.1	89.6	---
3	92.0	0.6	0.3	0.9	6.7	1.9	91.3	---
4	92.1	0.5	0.3	1.0	7.1	2.3	90.6	---
5	91.4	0.6	0.3	1.0	9.1	2.6	88.3	---
6	90.9	0.5	0.3	0.8	9.0	2.7	88.3	---
7	91.8	0.5	0.3	0.9	6.6	2.5	90.9	---
Mean Value	91.5	0.6	0.3	0.9	7.7	2.4	89.9	---
Std. Desv.	0.7	0.0	0.0	0.0	1.0	0.3	1.2	---
Abs. Error ±	0.2	0.0	0.0	0.0	0.4	0.1	0.5	---

(a.r): as received; (d.b): dry basis; C: carbon; H: hydrogen; N: nitrogen; S: sulfur; A: ash; VM: volatile matter; FC: fixed carbon; S_{BET} : BET surface area.

Table 4. Demineralization conditions and results found in literature

CBp ash content		Demineralization conditions					Ref.
Initial (wt.%)	Final (wt.%)	Reagent and concentration	Time (min)	Temp. (°C)	CBp (g)	R (mL/g)	
14.8	6.8	H ₂ SO ₄ 1N	30	60	5	10	Chaala et al., (1996)
14.7	6.2	HCl 1M	1440	25 ^a	2	40	Ariyadejwanich et al., (2003)
14.0-15.0 ^b	4.0-5.0	HCl 10 wt.%	120	100	43-46	n.r	Ucar et al., (2005)
15.0	5.6	HCl 12M ^c	270 ^c	25 ^a	n.r	n.r	Suuberg and Aarna, (2009)
14.0	1.2	HCl 4M ^d	360	60	11	10	Zhang et al., (2018)

a: room temperature; b: CBp from truck tire; c: four washing cycles using fresh acid, the time showed here included that took it in the four cycles; d: demineralization using ultrasonic conditions; n.r: not reported.

Table 5. Ash composition analysis of CBp and dCBp

Compound	CBp (wt.%)	dCBp ^a (wt.%)	Reduction ratio (%)
Al ₂ O ₃	1.9	0.2	89.9
CaO	4.9	0.3	93.1
Fe ₂ O ₃	1.2	0.2	80.7
K ₂ O	1.0	1.5	---
MgO	1.3	1.7	---
Na ₂ O	0.7	0.3	49.1
SiO ₂	39.0	85.8	---
TiO ₂	0.1	0.4	---
ZnO	31.7	5.4	83.1
Total	81.7	96.0	---

a: a mixture of all runs (HCl 3M, 60 min, 3 mL/g and 60 °C)

Table 6. Variables effect on the demineralization process

Parameter	Ultimate analysis wt.% (d.b)				Proximate analysis wt.% (d.b)			S_{BET} (m ² /g)
	C	H	N	S	A	VM	FC	
Soaking time (min)								
15	88.2	0.6	0.3	2.0	9.1	2.2	88.7	74.5
30	88.2	0.6	0.3	1.8	8.9	2.5	88.6	77.1
60	89.8	0.6	0.3	2.0	8.1	2.3	89.6	76.0
Temperature (°C)								
50	90.6	0.6	0.3	1.3	6.1	2.2	91.7	77.8
60	91.8	0.6	0.3	1.1	6.1	2.2	91.7	76.5
70	92.0	0.6	0.3	1.2	6.0	2.4	91.7	77.4
HCl concentration (M)								
2	91.8	0.6	0.3	1.1	6.1	2.2	91.7	76.5
4	92.9	0.6	0.3	1.1	4.9	2.5	92.6	76.3
6	92.0	0.7	0.3	1.3	5.3	2.4	92.3	75.4
8	92.0	0.7	0.3	1.2	5.6	2.1	92.1	79.1
Reagent/CBp ratio (mL/g)								
5	91.6	0.6	0.3	1.0	5.9	2.6	91.5	78.4
10	92.9	0.6	0.3	1.1	4.9	2.5	92.6	76.3
15	92.0	0.5	0.3	1.1	5.5	2.3	92.2	78.1

(d.b): dry basis; C: carbon; H: hydrogen; N: nitrogen; S: sulfur; A: ash; VM: volatile matter; FC: fixed carbon; S_{BET} : BET surface area

Table 7. Sequential acid/base treatment effect on the demineralization process

Treatment	R (mL/g)	T (°C)	t (min)	Ultimate analysis wt.% (d.b)				Proximate analysis wt.% (d.b)		
				C	H	N	S	A	VM	FC
HCl 4M	10	60	60	92.9	0.6	0.3	1.1	4.9	2.5	92.6
NaOH 5M	10	60	60	95.1	0.7	0.3	0.8	3.1	2.7	94.2

(d.b): dry basis; C: carbon; H: hydrogen; N: nitrogen; S: sulfur; A: ash; VM: volatile matter; FC: fixed carbon; S_{BET} : BET surface area

Table 8. Properties of dCBp and commercial CBs								
Sample	Ultimate analysis wt.% (a.r)				S_{BET} (m ² /g)	ρ_{real} (g/cm ³)	Interparticle porosity (%)	Intraparticle porosity (%)
	C	H	N	S				
dCBp	92.9	0.6	0.3	1.1	76.3	1.92	21.4	62.5
N234	95.2	0.3	0.3	1.1	120.4	1.97	13.4	65.3
N375	97.3	0.3	0.3	0.6	89.6	1.96	13.8	61.5
N550	98.7	0.3	0.3	0.6	44.8	1.92	16.8	63.7
N772	98.5	0.3	0.3	0.9	26.8	1.90	10.7	49.9

(a.r): as received; C: carbon; H: hydrogen; N: nitrogen; S: sulfur; S_{BET} : BET surface area; ρ_{real} : real density

Table 9. EDX characterization of both N550 CB and dCBp									
Sample	Element (wt.%)								
	C	O	S	Si	Al	Mg	K	Na	Cl
N550	93.8	5.5	0.6	0	0	0	0	0	0
dCBp	17.5	41.4	0.5	25.5	10.5	2.2	1.3	0.5	0.5

Table 10. Rheological parameters obtained in rubber processing

Parameter	Vulcanized		
	CBp	dCBp	N550
Mooney viscosity at 100°C	98.0	91.8	80.6
M _L (dN.m)	3.21	3.04	2.61
M _H (dN.m)	20.22	28.81	19.64
M _S (dN.m)	17.01	17.71	17.03
ΔM= M _H -M _L (dN m)	17.01	25.77	17.03
ts ₁ (min)	3.35	1.87	4.25
ts ₂ (min)	5.17	3.89	6.96
tc ₁₀ (min)	4.81	3.52	6.45
tc ₅₀ (min)	10.07	8.64	11.63
tc ₉₀ (min)	22.08	17.81	21.53
tc ₉₇ (min)	30.84	24.56	28.97

Table 11. Mechanical properties obtained in rubber compounding

Parameter	Vulcanized		
	CBp	dCBp	N550
Modulus at 300 % (MPa)	13	13	15.5
Tensile strength (MPa)	14.1	17.5	16.8
Elongation at break (%)	319	350	320
Tear strength (kN/m)	61	68	78
Hardness (Shore A)	68	69	69
Abrasion loss (mm ³)	58	68	55
Density (g/cm ³)	1.15	1.15	1.15