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L. Moulin, S da Silva, Arezki Bounaceur, M Herblot, Yannick Soudais. Assessment of Recovered Carbon Black Obtained by Waste Tires Steam Water Thermolysis: An Industrial Application. Waste and Biomass Valorization, 2017, 8 (8), p.2757-2770. 10.1007/s12649-016-9822-8 . hal-01915193

**HAL Id: hal-01915193**

**<https://imt-mines-albi.hal.science/hal-01915193>**

Submitted on 7 Nov 2018

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# Assessment of Recovered Carbon Black Obtained by Waste Tires Steam Water Thermolysis: An Industrial Application

L. Moulin<sup>1,2</sup> · S. Da Silva<sup>1</sup> · A. Bounaceur<sup>1,2</sup> · M. Herblot<sup>3</sup> · Y. Soudais<sup>2</sup>

**Abstract** Nearly 300 Millions of waste tires have to be managed in Europe. The main industrial ways to treat this kind of waste are incineration for energetic valorization and tires milling in chips or granulates for material valorization in construction industry. Steam water thermolysis (SWT) of tires, a hybrid of pyrolysis and solvolysis, is a good alternative to valorize waste tires. Recovered carbon black (rCB), which can be reintroduced in rubber industry as reinforcing filler (circular economy concept), is a more economical added value material than shredded tires. Physical and chemical characterizations on SWT-rCB were performed following ASTM analytical standards. A comparison between furnace carbon black (N330) and rCB from pyrolysis (commercial products) was carried out. Oil Absorption Number (ASTM D2414) and nitrogen adsorption (ASTM D6556) measurements demonstrate that rCBs structure and specific surface area are comparable to a furnace carbon black N330. According to data issued from ASTM standards, the behavior of rCBs reinforcement in rubbers is then expected to be equivalent to a N330 carbon black. Rubber compounds were produced with a homemade formula and mechanical characterizations were carried out in order to assess reinforcement properties of SWT-rCB. Comparisons in terms of mechanical properties have been established between rubbers reinforced with 100% of SWT-rCB, rubbers reinforced with furnace carbon blacks (N330, N550 and N772), and mixtures of SWT-rCB and furnace carbon

blacks. The results clearly show that rCBs reinforcement properties are lower than those of N330 carbon black. However, for a same rubber formula, SWT-rCB filled rubbers properties are close or slightly better than N550 and N772 filled rubbers.

**Keywords** Waste tires · Recovered carbon black · Steam water thermolysis · Physico-chemical properties · Mechanical properties

## Introduction

Each year in Europe, over 300 millions of tires are removed from passenger cars, utility vehicles or trucks and become waste that need to be managed [1]. Since the EU Waste Landfill Directive regulation (1999/31/EC), these waste tires can no longer be sent to landfill disposal due to obvious environmental issues, thus they have to be valorized in different ways. The available options for the treatment of waste tires and the foreseen beneficial re-uses of such waste as recovered materials or alternative fuels have been reviewed by Sienkiewicz et al. [2] Fig. 1 shows the distribution of the waste tires valorization routes in Europe for 2014. Approximately 35% of the waste tires were used as solid fuel for energetic valorization mainly in cement kilns and incinerators, while 38% were used for material recovery ranging from shredded chips or granulates employed in civil engineering applications to feedstock for rubber reclaim [3]. However, because regulation and economical context are being increasingly restrictive for waste tires treatment industries, especially regarding the incineration treatment route for which another European Directive (2000/76/EC) has been initiated, studies have been conducted to develop environmentally friendly, technical and

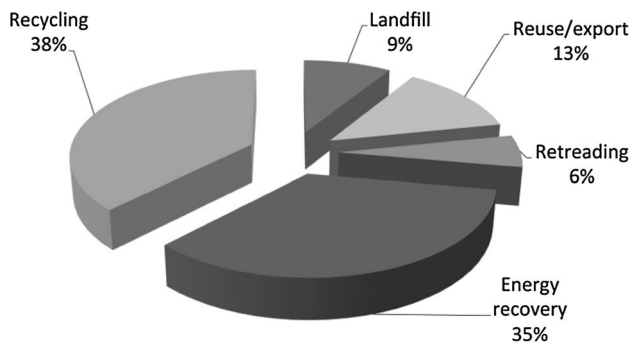
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**Fig. 1** EU waste tires valorization routes of 2014 [1]

economical efficient processes able to recover high added value materials [4].

For many years now, pyrolysis technologies have been targeted as some of the most promising alternatives for the treatment of tires. Pyrolysis consists in a thermochemical decomposition of organic materials and proceeds under non-oxidative conditions at elevated temperatures, typically ranging from 400 to 800 °C. In addition to being an efficient process in terms of energy recovery, the pyrolysis treatment of waste tires is considered to be a clean thermochemical process with nearly no emissions or residual waste [5]. When performed under suitable conditions, the process basically produces char or recovered carbon black (rCB), oil and gases, along with the recovery of steel originally found in the tire, all of which have the potential to be re-used. To treat this kind of waste, several types of reactors and operating conditions have been tested and described by different research groups in the past, from which extensive reviews on the topic by Williams [3] and Martinez et al. [6] have been realized. It is now acknowledged that pyrolysis conditions and parameters should be carefully controlled depending on the desired end-products yield and quality output. The pyrolytic oil generated from the pyrolysis treatment of tires is often recovered as fuel for its calorific value [7] but can also be used as a source of refined chemicals such as limonene [8]. The gas generated is usually used to supply the heating system of the process and in most cases, is even self-sufficient regarding energy needs [6]. The char fraction obtained from the pyrolysis of waste tires has been widely studied in the literature, yet the low value of this product substantially related to its quality has remained the fundamental issue with regards to high operating costs on an industrial scale plant.

Steam water thermolysis (SWT), a hybrid of pyrolysis and solvolysis is an efficient alternative among the thermochemical methods treating waste tires for materials recovery. The process uses superheated steam as an additional factor of heating the waste tires within the reactor.

More than just enhancing the energy input, this superheated steam increases the explosion proofness of the gas in the reactor, reduces the sulfur content in the fuel condensate [9] and is expected to act as a catalyst. In addition to the advantages just mentioned, a recent study [10] has shown that SWT is more efficient than conventional pyrolysis at the same treatment conditions for the recovery of carbon fibers from carbon fiber reinforced polymer waste.

Even though the char product can be used as activated carbon [11–14], as filler in reinforced bitumen or in the ink industry [15], the objective is to valorize the rCBs from SWT of waste tires with a good economical added value, and one of the best ways to do so is to reintroduce them in rubber products as reinforcing fillers.

ASTM key parameters for the use of rCBs as reinforcing fillers in the rubber industry are structure and surface area. Previous studies including rCBs physicochemical characterizations [15–19], have attested a surface area ranging from 60 to 95 m<sup>2</sup>/g and a structure around 80 mL/100 g, depending on pyrolysis processes and conditions. According to ASTM (American Society for Testing and Materials) standard classification, such results suggest a reinforcing potential close to N300 rubber-grade carbon blacks. Several studies using rCBs as partial or total virgin carbon black substitutes have been carried out to evaluate and investigate their reinforcing potential in rubber compounds such as NR/SBR blends [20, 21], SBR [19, 22, 23] or EPDM [24]. The results obtained for the mechanical behavior of these vulcanized rubbers have been inferior to what was expected by physical and chemical characterizations following ASTM analytical standards. In most cases, the high inorganic fraction of the rCB, generally fluctuating from 10 to 30 wt% due to different waste tires feedstock used, has been pointed out as the main responsible, as well as a decrease in particle surface activity, for the decrease on in-rubber performance.

In this paper we studied the SWT of waste tires to recover rCBs. Physical and chemical characterizations have been carried out to predict the reinforcing properties of the carbon fillers. These analyses have been followed by the evaluation of the rCBs filler effect upon the mechanical properties of vulcanized rubbers.

## Materials and Methods

### Waste Tires Samples

The tires disposal company SOREGOM has provided the samples of shredded waste tires used in this study. These samples are typically shaped as rectangles of 2 × 3 cm<sup>2</sup> and come from whole light vehicles tires.

## Recovered Carbon Black (rCB)

rCBs were produced by SWT of waste tires samples at two different pilot scales; from the laboratory bench scale reactor (samples rCB\_1, rCB\_2, until rCB\_6) up to the pre-industrial continuous pilot reactor with a capacity of 200 kg/h (rCB\_ind). Details on the conditions for the laboratory pilot experiments are given in “Pilot and Protocol” section of this study. The pre-industrial process was conducted according to *a method for treating carbonaceous materials by vapour thermolysis* (Patent no. WO2014135754 [25]). An additional rCB sample comes from the treatment in the laboratory reactor of a model-formulated rubber filled with virgin N330 carbon black (rCB\_N330).

## Model Laboratory Filled Rubbers

### Raw Materials Selection

The descriptions of the selected formulations for dumping applications are provided in Table 1. Two rCBs (rCB\_ind and rCB\_N330) were used in comparison with three virgin carbon blacks (CB): N772, N550 and N330 respectively for low, medium and high level of reinforcement.

### Compounding Equipment and Processing Conditions

Considering compounding process, all formulations were blended in a 1.5L Banbury mixer. The accelerators and sulfur were incorporated on a roll mill 300×700 mm equipped

**Table 2** Mixing process conditions

Initial temperature: 60 °C Rotors speed: 60 rpm Fill factor: 0.64	
Timing (Min. sec.)	Incorporation process of ingredient
0.00	NR
1.00	Protecting agents, ZnO + stearic acid
1.30	½ CB or rCB
2.30	½ CB or rCB
3.30	Sweep
4.30	Rotors speed up to 80 rpm
5.00	Dump

with a cooling device. Table 2 presents the mixing conditions common to every compound.

### Curing Conditions and Samples

Cure time was determined by rheometric measurements for each formula: i.e.  $t_{98}$  at 160 °C. All compounds were compression moulded on 300×300×2 mm in size sheet, compression set plots and sheet for fatigue test.

## Pilot and Protocol

Experiments were conducted in a bench-scale reactor composed of a vertical cylinder tube furnace surrounded by heating coils, with a 1 L alumina crucible as shown in Fig. 2. The reactor is pre-heated at a target temperature

**Table 1** Description of the rubber-based formulations

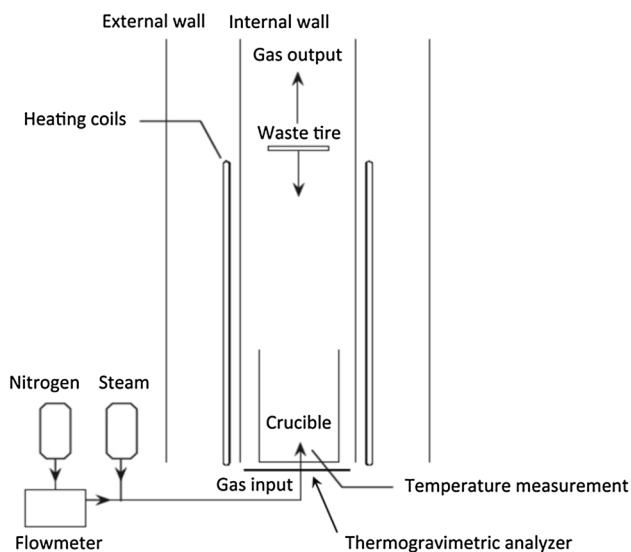
Ingredient	Rubber compounds					
	N772	N550	N330	100%	50/50	20/80
	phr	phr	phr	phr	phr	phr
NR <sup>a</sup>	100	100	100	100	100	100
N772	50					
N550		50				
N330			50		25	40
rCB_ind or rCB_N330				50	25	10
Stearic Acid	2	2	2	2	2	2
ZnO	3	3	3	3	3	3
6PPD <sup>b</sup>	1.5	1.5	1.5	1.5	1.5	1.5
Antilux 500 <sup>c</sup>	2	2	2	2	2	2
Sulfur	1.1	1.1	1.1	1.1	1.1	1.1
CBS <sup>d</sup>	1.1	1.1	1.1	1.1	1.1	1.1
Total	161	161	161	161	161	161

<sup>a</sup>Natural rubber 10 CV 60

<sup>b</sup>Antiozonant *N*-phenyl-*N'*-1,3-dimethylbutyl-*p*-phenylenediamine

<sup>c</sup>Antiozonant and weather protector wax

<sup>d</sup>Accelerator *N*-cyclohexyl-2-benzothiazole sulfenamide



**Fig. 2** Simplified diagram of the steam water thermolysis recycling process [26]

**Table 3** Operating conditions applied to the steam water thermolysis unit for waste tires from light vehicles and the model laboratory N330 filled rubber

Samples	Temperature (°C)	Residence time (min)	Nitrogen flow rate (L/min)	Steam flow rate (g/h)
rCB_1	450	30	5	30
rCB_2	500	30	5	30
rCB_3	450	60	5	30
rCB_4	500	60	5	30
rCB_5	450	30	0	30
rCB_6	450	60	0	30
rCB_330	450	30	0	30

measured by a thermocouple located at the bottom of the crucible, prior to the loading operation. It allows us to simulate at best the semi-continuous industrial process. Once the desired temperature is reached, the waste tires samples are introduced using a knife gate valve located in the upper part of the furnace and fall directly into the crucible. The reactor is connected to the steam generator providing the superheated steam and a nitrogen input. The superheated steam at 180 °C mixed with nitrogen is introduced through six opening holes at the bottom of the crucible. When the isothermal residence time set is reached, heating and steam introduction are stopped and the system is cooled down under nitrogen to room temperature at a constant rate of 5 °C/min. The solid part was collected from the reactor and rCBs were recovered after separation from the remaining steel. A thermogravimetric analyzer located under the crucible is used to track the weight loss during the reaction.

Table 3 describes rCB samples designation and conditions presented in this study.

### Pre-treatment: Grinding of rCBs

Prior to the characterization, the rCBs produced after each run of SWT are separated from the metallic thread and then grinded in a laboratory knife mill for 30 s.

### Waste Tire Sample Characterization Methods

#### Determination of Weight Loss by Thermogravimetric Analysis

Experiments have been carried out using a TG-DTA 92 SETARAM equipment. 10–40 mg of tire sample are placed in the first alumina crucible, the second one being the blank. These experiments are conducted under a nitrogen atmosphere associated with a WETSYS SETARAM controlled humidity generator starting with a 10 min isotherm at 30 °C, and followed by a heating rate of 5 °C/min from 30 to 800 °C. A second isotherm of 60 min is then applied before cooling. When temperature reaches 30 °C, a last 10 min isotherm closes the heating cycle.

#### Virgin Carbon Black and rCB from Steam Water Thermolysis Characterization

##### Determination of the Specific Surface Area (ASTM D6556-10)

The specific surface area was evaluated from the nitrogen adsorption isotherms at 77 K in the range of  $p/p_0=0.05-0.30$  using the Brunauer, Emmett and Teller (BET) theory of multilayer gas adsorption behavior [27] and following the standard ASTM D6556-10 test method. The BET specific surface area was measured using a Micromeritics Gemini 2360 analyzer (Micromeritics). Prior to nitrogen adsorption, rCBs were degassed at 125 °C for 24 h at a residual pressure of  $10^{-4}$  Torr with a Micromeritics VACPrep 061 degasser. The results presented were obtained using the B.E.T equation.

##### Determination of the Moisture Content, Ash Content and Heat of Combustion

TG-DSC analyses were conducted on a TG-DSC 111 SETARAM. These analyses were used to determine the moisture content, some other volatile matter, the ash content and the heat of combustion for the rCBs from SWT. 10–20 mg of rCB sample placed in a platinum crucible was first heated from 30 to 125 °C at 10 °C/min, subjected to a

1 h isotherm at this temperature under air and then cooled to 30 °C at 20 °C/min to determine the moisture and volatile matter content. 30 mg of sample placed in a platinum crucible was also heated from 30 to 550 °C at 10 °C/min, the 550 °C isotherm was hold for 6 h before cooling to 30 °C at 20 °C/min, this operation allows us to identify the ash content and the heat of combustion.

#### *Determination of Metals and Minerals Content*

The inorganic content of the rCBs was studied by inductively coupled plasma atomic emission spectroscopy (ICP-AES) with an Ultima 2, Jobin-Yvon-Horiba spectrometer after a 3h mineralization treatment at 80 °C using nitric acid (69%) and hydrochloric acid (37%).

#### *Determination of C.H.N.S.O.*

Elemental analysis was performed using a Flash 2000 C.H.N.S./O. analyzer from Thermo Fisher Scientific.

#### *Determination of the Oil Absorption Number (ASTM D2414-09a)*

The determination of the Oil Absorption Number (OAN) for the rCBs has been achieved following the ASTM D2414-09a on a Brabender Absorptometer “C” using dibutyl phthalate (DBP) oil. The absorption of DBP in mL/100 g was calculated using the equation:

$$OAN = \frac{A}{B} \times 100 \quad (1)$$

where *A* is the volume of oil used in mL and *B* the mass of the tested sample in g.

#### *Determination of the rCB Morphology*

The morphology of our particles is observed using Environmental Scanning Electronic Microscopy (ESEM Philips XL30 FEG). Coupled to an Energy Dispersive X-ray detector (EDX), the microscope has allowed us to determine qualitatively the main chemical species found in our samples and therefore confirm ICP-AES results.

### **Mechanical Characterizations of rCBs Filled Rubbers**

#### *Apparatus*

Rheological properties of raw compounds were measured with a 1500 S Mooney (Monsanto<sup>®</sup>) and a 2000E MDR (Moving Die Rheometer, Monsanto<sup>®</sup>) according to test standard NF-ISO 289-1 and ISO 6502 respectively.

Mechanical behaviour of cured compounds was determined with a T2000 tensile tester (Monsanto<sup>®</sup>) for tensile and tear properties according to NF ISO 34 and 37. Hardness (Shore A) and density were measured respectively with a durometer (Bareiss<sup>®</sup>) according to NF ISO 7619-1, and a lab balance (Mettler Toledo<sup>®</sup>) according to NF ISO 2781. Specific trials for the Fatigue-to-Failure Test (FTFT, Monsanto<sup>®</sup>), compression set (during 70 h at 70 °C) and abrasion resistance (Zwick<sup>®</sup>) were conducted according to respectively NF ISO 6943, NF ISO 815-1 and NF ISO 4649.

Viscoelastic behaviour was obtained applying a strain sweep with a Rubber Process Analyzer (RPA2000—Alpha Technologies<sup>®</sup>). Thermal aging was performed according to NF ISO 188 conditions.

## **Results and Discussion**

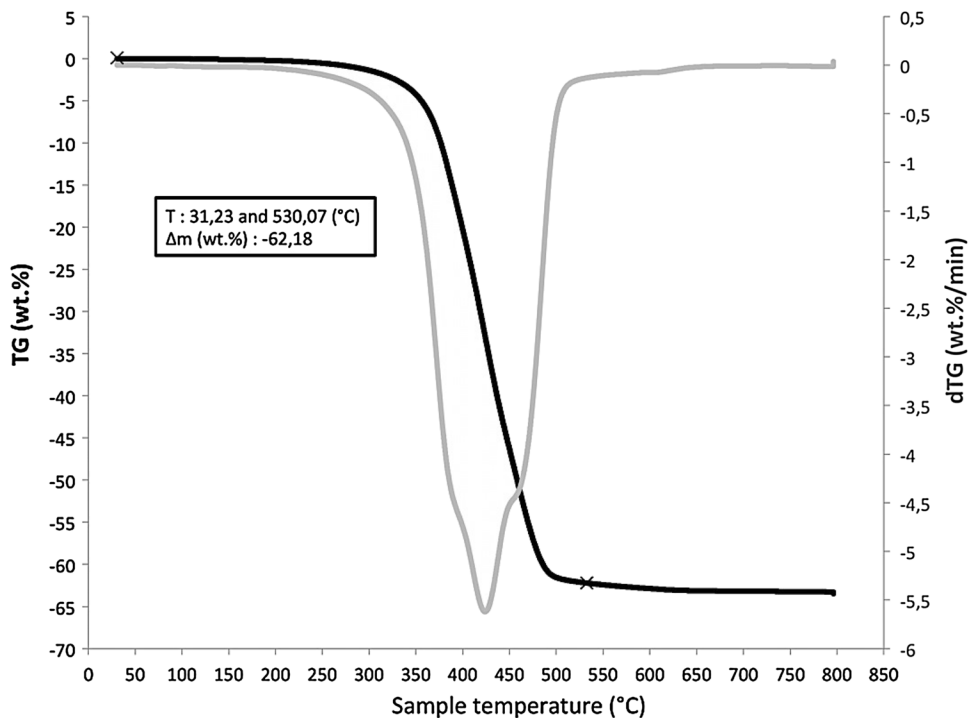
### **Thermogravimetric Analyses at Lab Scale**

A preliminary thermogravimetric analysis (TGA-DTA) was performed on the shredded waste tires sample provided by SOREGOM and is presented in Fig. 3. The analysis was conducted under a nitrogen atmosphere with a controlled relative humidity of 50% at 40 °C to reflect at best the SWT operating conditions. Temperature was ranging from 30 to 800 °C at a 5 °C/min heating rate according to the protocol described previously.

TG and dTG obtained from the waste tire sample suggest that degradation starts at 150 °C. We are first able to determine a slight decrease in the weight loss until around 300 °C, which is attributed to the volatilization of chemicals additives such as plasticisers and processing oils originally present in a tire. Then, starting from 300 up to 575 °C, the main weight loss associated to the rubber degradation is observed. This is confirmed by the dTG curve showing an important peak in this temperature range. Indeed, the dTG curve indicates the major weight loss event to occur between 350 and 500 °C. It corresponds to the temperature range of decomposition for the major rubber components in tires such as styrene-butadiene rubber (SBR), natural rubber (NR), and polybutadiene rubber (BR). These results are in fair agreement with previous studies conducted on tires pyrolysis [28].

The decomposition seems complete after 550 °C, which implies no further weight loss. We can report that the total weight loss of our sample is close to 62 wt% when using nitrogen atmosphere with a controlled relative humidity. This result is equivalent to the weight loss of the sample in conventional pyrolysis conditions at the same 5 °C/min heating rate.

**Fig. 3** TGA-DTA analysis on the waste tire sample at lab-scale at 5 °C/min heating rate



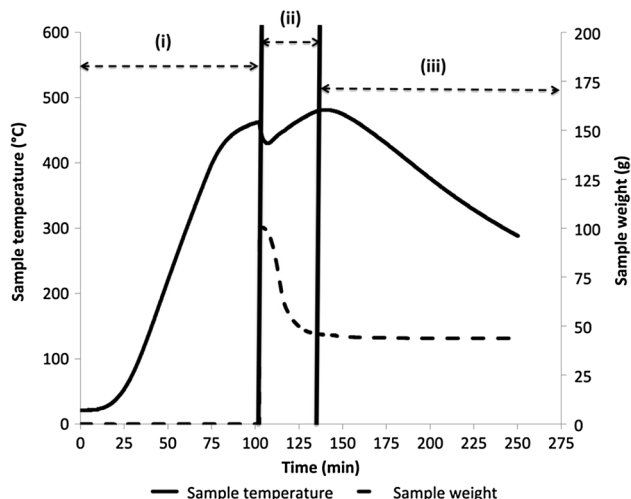
The remaining 38 wt% represents the solid components within the tire: carbon black/silica fillers, curing agents, textiles and residual metallic thread parts.

### Thermogravimetric Analyses at Pilot Scale

The successive steps of a typical SWT trial in the pilot-scale reactor are presented in Fig. 4. The diagram can be divided in 3 main stages: (i) reactor heating until the targeted temperature, (ii) introduction of tire sample corresponding to the start of both isothermal residence time and degradation process and (iii) reactor cooling. According to the thermogram displayed in Fig. 4, we can assume that the weight loss starts to stabilize 29 min after introduction of the waste tire sample into the reactor.

Table 4 shows the results of thermogravimetric measurements for the different conditions applied to our steam water thermolysis process. The weight losses for all conditions are comprised between 68.32 and 69.84 wt%. These results are in good agreement with preliminary experiments conducted on laboratory scale equipment and show that for the designated temperature of 450 and 500 °C, no significant differences on the final degradation are observed regardless of the nitrogen and/or steam water flow rates and the residence time.

The rCB yield from our thermolysis is set around 30 wt%. Previous studies had revealed that a SWT conducted between 400 °C might not have degraded totally the waste tire sample. Resulting rCBs have then been characterized physically and chemically.



**Fig. 4** Thermogram model for rCB\_1 at pilot scale

**Table 4** Weight losses on the waste tire samples at different operating conditions

Sample	Initial weight (g)	Final weight (g)	Metal weight (g)	% Weight loss (metal free)
rCB_1	100	46.14	14.46	68.32
rCB_2	100	41.48	10.51	69.03
rCB_3	100	46.68	15.60	68.92
rCB_4	100	47.87	17.21	69.34
rCB_5	100	45.03	14.87	69.84
rCB_6	100	42.46	42.46	69.48

**Table 5** Properties of rCBs from steam water thermolysis (rCB\_1 to rCB\_6 with rCB\_ind from waste tires, and rCB\_N330 from laboratory N330 filled rubber) in comparison with virgin N330 rubber grade carbon black

		N330	rCB_1	rCB_2	rCB_3	rCB_4	rCB_5	rCB_6	rCB-ind	rCB_N330
Operating conditions	T (°C)	–	450	500	450	500	450	450	–	450
	Res. time (min)	–	30	30	60	60	30	60	–	30
	N <sub>2</sub> flow (L/min)	–	5	5	5	5	0	0	–	0
	Steam flow (g/h)	–	30	30	30	30	30	30	–	30
Property	ASTM standard									
ASTM target values										
NSA BET <sup>a</sup> ± SD (m <sup>2</sup> /g)	D6556-10	77.21 ± 1.36	74.60 ± 1.13	80.10 ± 2.53	94.77 ± 0.69	93.06 ± 0.44	77.78 ± 0.16	87.41 ± 1.69	52.55 ± 0.39	76.76 ± 9.47
OAN (mL/100 g)	D2414-09	103.2	100.7	100.4	102.8	98.3	88.8	89.9	102.2	93.2
Proximate analysis (wt%)										
Moisture and volatiles	D1509-95	0.22	0.83	0.50	1.00	0.90	0.60	0.60	0.96	0.77
Ash	1506-99	0.70	16.13	14.02	16.57	15.38	15.95	19.50	13.73	6.63
Heat of combustion (kJ/g)	–	29.50	23.10	23.90	23.50	19.50	24.10	24.10	–	26.40
Ultimate analysis <sup>b</sup> (wt%)										
Carbon	–	99.00	82.91	82.69	81.58	83.60	82.85	81.27	82.65	94.21
Hydrogen	–	0.27	0.55	0.59	0.72	0.52	0.73	1.03	0.75	0.54
Nitrogen	–	0.12	0.34	0.49	0.43	0.50	0.96	1.08	0.28	0.35
Sulphur	–	0.08	1.76	1.97	1.86	1.47	1.73	1.91	2.07	1.64
Oxygen	–	0.90	1.98	2.57	2.01	2.27	2.25	2.55	–	–
Metals and minerals <sup>b</sup> (wt%)										
Zn	–	–	6.20	5.80	6.29	7.06	5.60	5.47	4.33	2.88
Si	–	0.06	0.15	0.81	0.14	0.11	0.60	0.80	2.08	0.08
Ca	–	0.05	1.56	0.84	1.08	0.22	1.00	0.70	0.58	0.06
Fe	–	–	0.33	0.22	0.22	0.32	0.13	0.10	0.28	0.01
Al	–	–	0.15	0.22	0.10	0.14	0.18	0.16	0.26	0.01
Na	–	0.05	0.06	0.23	0.15	0.14	0.20	0.16	0.12	0.05

<sup>a</sup>NSA BET are mean values from 3 measurements

<sup>b</sup>Ultimate analysis and Metals and minerals values are mean values from at least 3 measurements, with associated standard deviations comprised within 1–25 wt%, related to both detection sensitivity of the unit and heterogeneity of the analyzed samples

## rCB Characterization

### Physical and Chemical Characterization

Specific analytical test methods are performed on virgin carbon blacks to determine their chemical composition but mainly to identify if they are polluted by exogenous species such as moisture, hydrocarbons (ASTM D1509-95) and inorganics from water used along the manufacturing process (ASTM D1506-99). A comparison was made between the virgin carbon black (N330), rCBs from waste tires (rCB\_1–rCB\_6) at laboratory pilot scale, at the industrial pilot (rCB\_ind) and from the laboratory N330 filled rubber (rCB\_N330) treated by SWT. ASTM D1509-95 and D1506-99 test methods were supplemented by ultimate

analyses, with a special interest in metals and minerals from ashes.

Following the results showed in Table 5, it is observed that rCBs produced from tires have a carbon content up to 83, 94.21 wt% for the rCB obtained from the laboratory formulated rubber, and 99 wt% for the virgin N330 carbon black. TG-DSC analyses were performed on the rCBs following the procedure described in the experimental methods and adapted from ASTM D1509-95 standard. Heating loss of the rCBs consists primarily of moisture and other volatile materials and has been identified after a 1 h isotherm at 125 °C. Both the inorganic components present after combustion, better known as ash content, and the heat of combustion of the rCBs produced have been also determined. Results showed that moisture and highly volatiles



content stay under 1 wt% for all samples. rCBs heats of combustion are slightly reduced, ranging from 19.5 to 26.4 kJ/g in comparison with the 29.5 kJ/g of virgin N330. These data do not reveal significant differences between the virgin and the rCB regardless of its process conditions. The main discrepancy from the proximate analysis is the ash content, which is above 14 wt% for all the rCBs from waste tires. This is much more important than the 0.7 wt% measured for the virgin N330 carbon black. This high amount of ash observed for the rCBs from tires is obviously related to the additives included during the formulation of the tire. Results from ICP-AES analyses reveal that metals and minerals content is indeed rather important. Overall, impurities found in ashes come mostly from other reinforcing fillers added to increase the mechanical properties of tires and from vulcanization agents incorporated to control the rubber curing process. The rCBs samples presented in this study mainly contain zinc, which roughly accounts for 30–40 wt% of the total inorganic components content. This result has been rather expected as zinc oxide (ZnO) is commonly used as an activator agent in the vulcanization process in order to control the kinetics of the cross-linking reaction. Other trace metals elements such as Si, Ca, Fe, Al and Na have also been detected in samples. This can be explained by the fact that minerals fillers such as SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> are frequently added in the formulation of tires. A sulfur content ranging from 1 to 2 wt% is also detected for the rCBs. This high sulfur content in comparison with the virgin N330 comes from the curing system used for the tire formulation, where sulfur is the main cross-linking vulcanization agent.

Physical properties of carbon blacks were obtained using D2414-09 (Oil Absorption Number) and D6556-10 (Total and External Surface Area by Nitrogen Adsorption) ASTM standards. The purpose of D2414-09 standard is to ascertain the structure of carbon black by determining the amount of oil (frequently DBP) that a given mass of carbon black can absorb to fill all the voids between the aggregates before reaching a predetermined torque endpoint. High OAN measurement indicates a high-structure carbon black with aggregates characterized by an important number of primary particles. Inversely a low OAN suggests a low-structure carbon black with aggregates consisting of only a few particles. The objective of D6556-10 is to determine the total surface area (inversely related to particle size) by the Brunauer, Emmett, and Teller (B.E.T. NSA) theory of multilayer gas adsorption behavior using multipoint determinations. Both standards allow the carbon black manufacturers and rubber industries to classify virgin carbon blacks for rubber products (ASTM D1765-10) and to assess the reinforcing behavior of the fillers.

According to these ASTM target values, specific surface area measurements versus Oil Absorption Numbers are

reported in Figs. 5, 6 and 7. Figure 5 shows the effect of the steam water thermolysis parameters on physical properties of rCB. The influence of residence time on specific surface area for 2 samples at 450 and 500 °C, increasing from 74 to 77 m<sup>2</sup>/g for 30 min to 93–94 m<sup>2</sup>/g for 60 min, is clearly observed. The superheated steam water is suspected to have an impact on the rCBs porosity considering the residence time parameter.

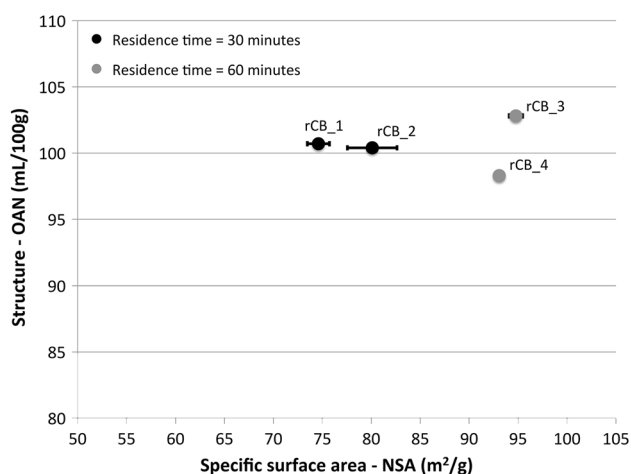
Figure 6 reports the influence of the nitrogen flow on carbon black structure and bears out the influence of residence time on specific surface area. Results display an increase of the OAN from around 88–89 mL/100 g without nitrogen flow up to 100–102.8 mL/100 g with nitrogen flow for the respective same processing conditions (T °C=450 °C, steam water flow=30 g/h) while an improvement of the specific surface area is still observed from 30 to 60 min residence time. The addition of a nitrogen flow to the superheated steam must enhance the heat exchanges by convection phenomena.

Figure 7 gives a typical diagram of the major carbon blacks used for the formulation of tires in comparison with the products obtained during this study. According to their specific surface area and OAN reported in this study, rCBs obtained from SWT hold both structure and particle size quite close to a carbon black from the N300 grade.

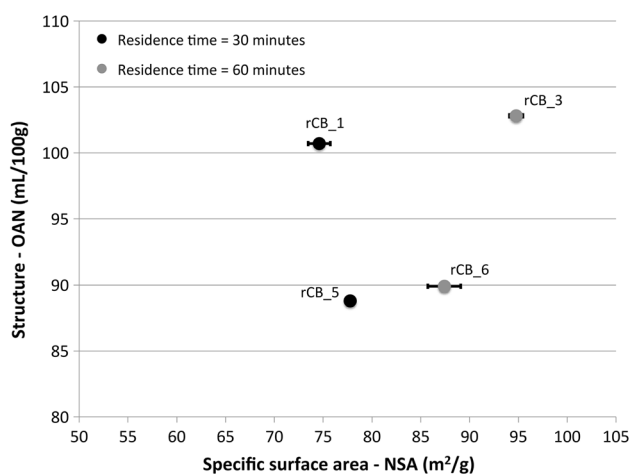
#### *Morphology of the rCBs*

An Environmental Scanning Electron Microscopy was used to examine the morphology of the rCBs. Figure 8 displays the micrographs of particles from a sample obtained by the SWT process for specific operating conditions in comparison with a virgin N330 carbon black. Figure 8a, c show respectively agglomerates of a few micrometers revealing the pseudo-spherical and elongated shape of the rCB whereas the N330 exhibits a well-defined spherical shape. At higher magnifications, the rCB agglomerate presented in Fig. 8b is still composed of aggregates in the form of chain-like clusters after the thermochemical treatment, which corresponds to what is also observed for the N330 displayed in Fig. 8d. As expected, the main noticeable difference concerns the appearance of minerals and metals components at the surface of some rCBs agglomerates. The main chemical species in the sample have been examined during the microscopic study using an EDX detector. The results presented in Fig. 9 indicate that the main minerals and metals present in the sample are in good agreement with the previous ICP-AES analysis: Zn, Al, Si, or Ca. According to this brief morphological study, the observations reveal the rCB and the virgin carbon black morphologies to be quite similar.

It was demonstrated that rCB\_1 to rCB\_6 have physical properties close to a virgin N330 carbon black.



**Fig. 5** Effect of steam water thermolysis residence time on ASTM target values (OAN and NSA) for rCB\_1 and rCB\_3 (at 450 °C) compared to rCB\_2 and rCB\_4 (at 500 °C)



**Fig. 6** Effect of steam water thermolysis nitrogen flow on ASTM target values (OAN and NSA) for rCB\_1 and rCB\_3 (with N<sub>2</sub> flow) compared to rCB\_5 and rCB\_6 (without N<sub>2</sub> flow) at a 450 °C temperature

However the rCBs obtained are actually assumed to be a combination of all the carbon black grades used in a tire, added to an important amount of inorganic components and to possible residues in the form of carbonaceous deposits [27]. Consequently, even if the chemical and physical properties of rCB are in good agreement with the virgin N330 carbon black, all of these standardized tests were developed for virgin carbon blacks and too little feedback has been reported in scientific literature about the relationship between ASTM standards and rCBs. It is therefore difficult to conclude unequivocally that these standards should not be used to predict the in-rubber performance of the rCB filler or to study the mechanism of reinforcement [29].

The specific surface area value of 52.55 m<sup>2</sup>/g for the rCB\_ind obtained at the pre-industrial scale is generally lower than the values for all rCBs obtained in the laboratory reactor. This discrepancy could be explained by a non-optimization of the process operating conditions on the pre-industrial pilot, especially regarding the residence time parameter (30 min).

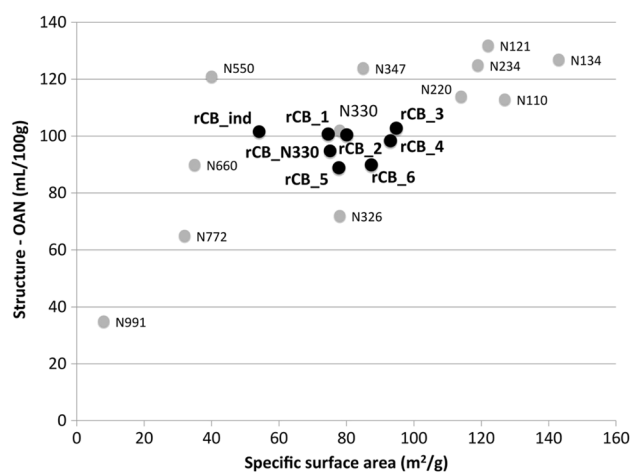
Results presented so far in this paper should only give a first insight on the real physicochemical properties of the product. Rheometric and mechanical tests have been carried out in order to evaluate and assess more clearly the reinforcing properties of the rCBs from SWT. These tests have been performed on the two following samples: rCB\_ind and rCB\_N330.

## Rheometric and Mechanical Properties

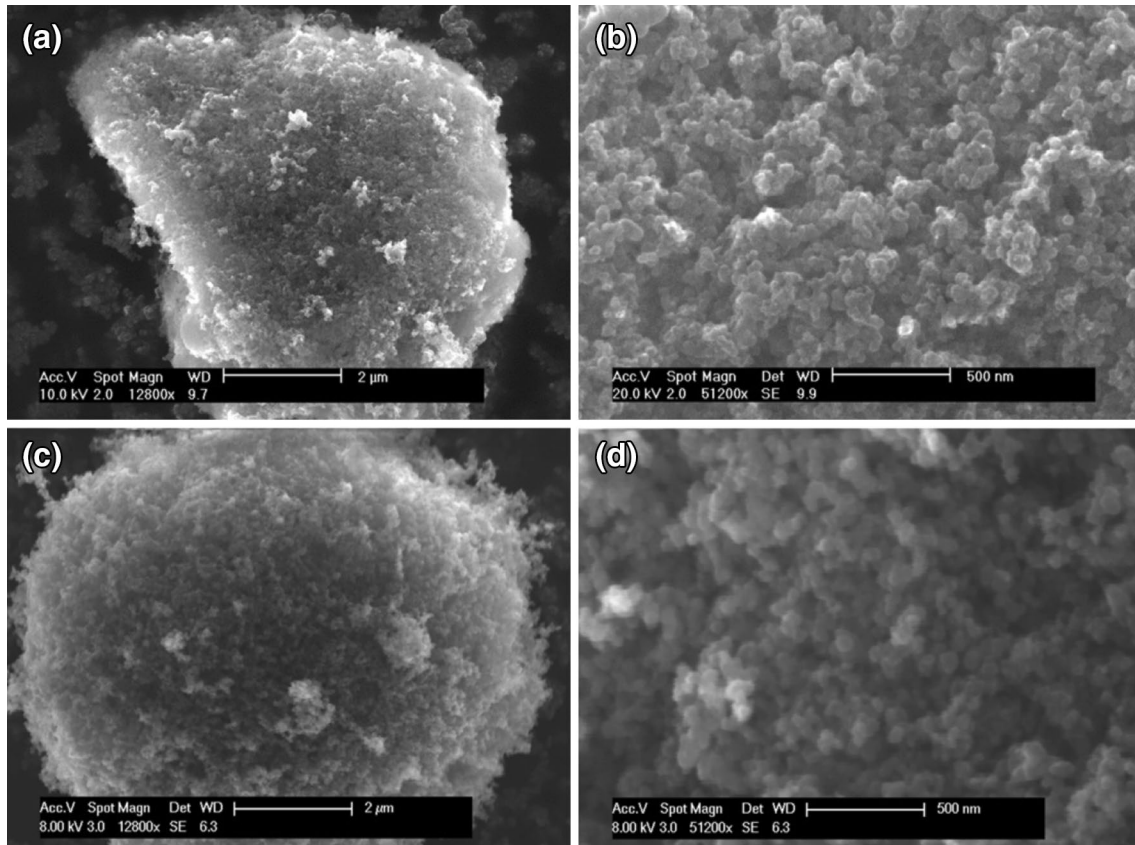
### Compounds with 100% of rCB

Properties of two compounds composed of 100% of each rCB (rCB\_ind and rCB\_N330) were compared to the three references N772, N550 and N330.

Rheometric controls at 160 °C were done to compare the cure properties of the different compounds depending on the recovered fillers at 100%. An increase of both scorch and curing times is observed in Table 6 for the rCB\_N330 whereas the same characteristic times are observed for the rCB\_ind compared to the N330 carbon black reference. This phenomenon could be explained by a possible difference on surface activity (and so reactivity) of these two rCB samples during the SWT process. Concerning the final cured properties, the two rCBs show a level of cross-linking density of vulcanization between N772 and N550 references as seen in Fig. 10. Mooney



**Fig. 7** rCBs from steam water thermolysis relative to ASTM rubber grades

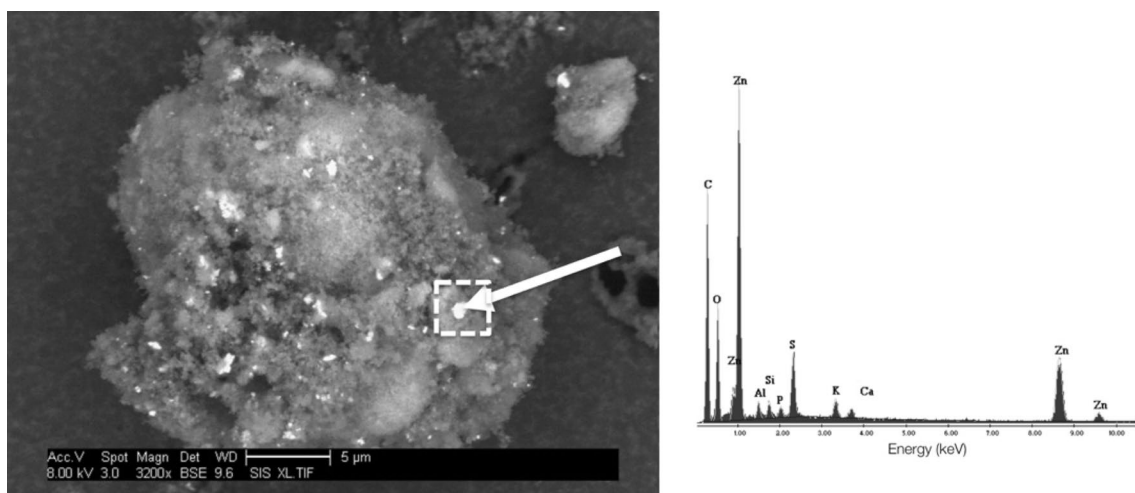


**Fig. 8** ESEM micrographs of **a–b** rCB\_1 sample and **c–d** N330 rubber grade carbon black

consistence at 100 °C is 24 and 38MU for rCB\_ind and rCB\_N330 respectively. Viscosity of the two compounds is then clearly different with a value closer to N330 reference (41 MU) when rCB N330 is used.

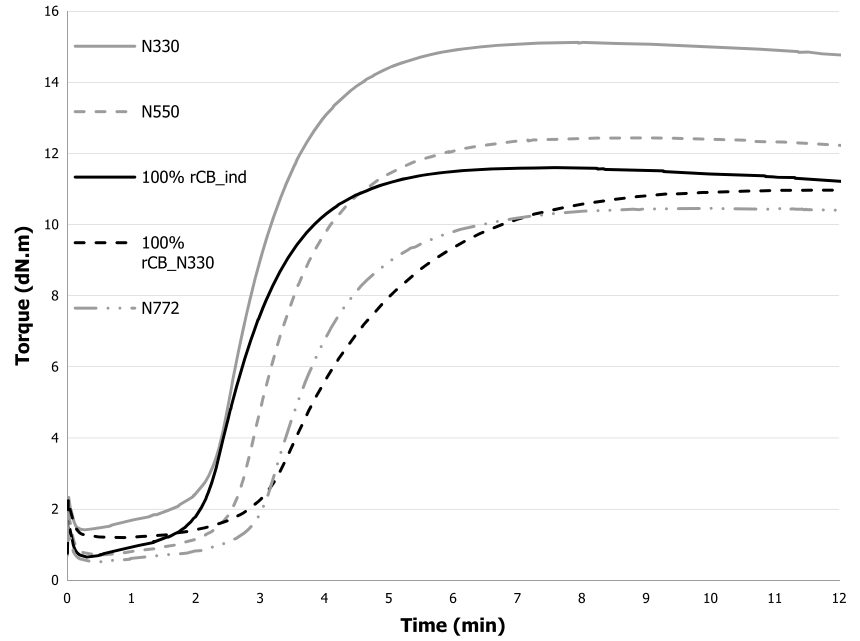
Mechanical properties of these two compounds were compared to three virgin carbon blacks (N772, N550 and N330) at initial and after heating conditions.

Considering unaged compounds, the investigated mechanical properties in Table 7 showed close values



**Fig. 9** ESEM micrograph of rCB\_1 sample and its EDX spectrum from one point on the sample

**Fig. 10** Rheometric properties at 160 °C of 100% rCBs compounds



**Table 6** Rheometric properties at 160 °C of 100% rCBs compounds

	N772	N550	N330	100% rCB_ind	100% rCB_N330
ML(1+4) @ 100 °C (MU)	21	31	41	24	38
Torque min (dN m)	0.5	0.8	1.7	0.7	1.2
Torque max (dN m)	10.3	12.6	15.4	11.6	11.0
T <sub>max</sub> – T <sub>min</sub> (dN m)	9.8	11.8	13.7	10.9	9.8
ts <sub>2</sub> (min:s)	2:45	2:38	2:14	02:14	03:21
t <sub>98</sub> (min:s)	7:13	6:27	5:49	05:31	08:50

**Table 7** Mechanical properties of cured 100% rCBs compounds

	N772	N550	N330	100% rCB_ind	100% rCB_N330
Shore A hardness (point)	50	55	61	53	54
Density	1.11	1.12	1.11	1.11	1.12
Tensile strength (MPa)	24.0	22.6	26.4	22.3	23.5
Elongation at break (%)	617	562	578	600	629
M100% (MPa)	1.4	2.0	2.2	1.5	1.5
M300% (MPa)	7.0	9.5	11.2	7.2	6.8
M100/M300	4.9	4.7	5.2	4.8	4.5
Delft tear (N)	120	97	145	148	105
Compression set (%)	39	35	40	44	43
Abrasion (mm <sup>3</sup> )	163	146	114	138	173
FTFT (×10 <sup>3</sup> )	69	58	89	48	62

**Table 8** Mechanical properties of compounds after thermal aging at 70 °C during 70 h

	N330 reference	rCB_N330
ΔHardness (points)	3	6
ΔTensile strength (MPa)	2.4	3.0
ΔElongation at break (%)	–34	–37
ΔM100 (MPa)	0.7	0.5
ΔM300 (MPa)	3.3	2.8

between both rCB-based compounds, except for delft tear, abrasion and fatigue resistance. No significant influence of ash content was observed. When rCB was introduced at 100% in this formula, mechanical properties were close to N550 reference for hardness, rupture properties (tensile strength and elongation at break), delft tear, abrasion resistance and fatigue test. The level of reinforcement (100 and 300% modulus) is the unique less performing property, compared to N550 reference, for both rCB samples. Both of these rCBs from SWT give the same reinforcement properties as the N772 grade. Table 8 indicates the same

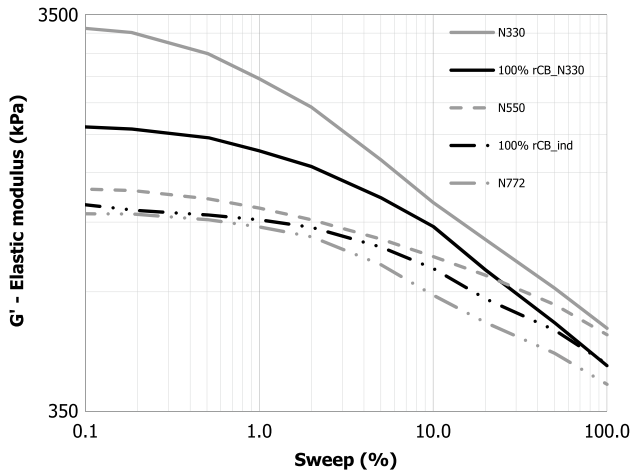
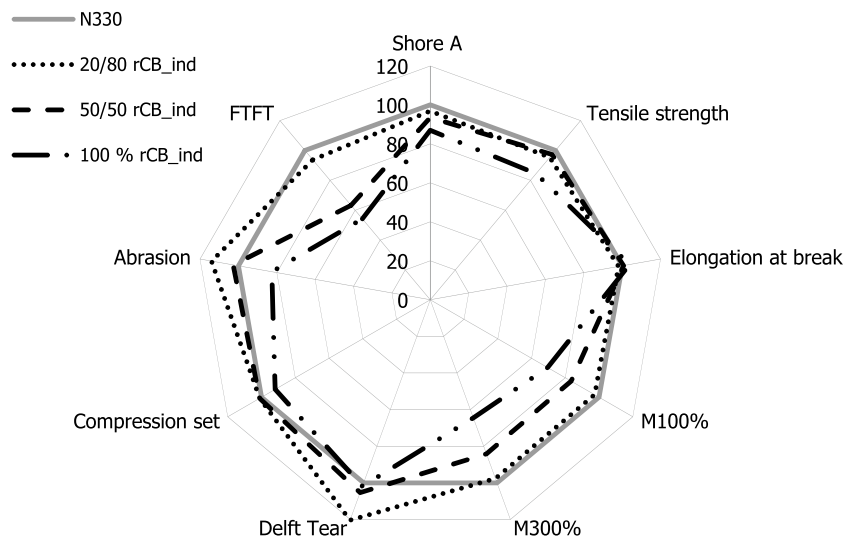


Fig. 11 RPA strain sweeps of cured 100% rCB compounds

hardness and strain properties variations after a thermal aging of 70 h at 70°C for the rCB\_N330 in comparison to the N330 reference.

Figure 11 displays the viscoelastic properties of both compounds determined by RPA tests. A lowering of the elastic modulus  $G'$  at 0.1% of strain and Payne Effect ( $\Delta G'$ ) was observed when rCB\_ind is used. Moreover, rCB\_ind curve matches with the one for the N772 reference whereas the behaviour of the rCB\_N330 curve seems to be closer to the N330 reference. Mechanical properties from RPA analysis confirm a level of performance of rCB\_ind similar to N772 reference. Inversely, rCB obtained from the N330 rubber model formulation brings better level of properties, intermediate between N330 and N550 carbon black grades. Thus, a difference between both grades of rCBs is observed, which can not only be attributed to ash content itself.

Fig. 12 Mechanical properties of cured rCB\_ind compounds



### Compounds with Blend rCB\_ind and N330 Standard Carbon Black

To improve the level of properties, two others compounds were realised with two different blends:

- 20% of rCB\_ind and 80% of N330,
- 50% of rCB\_ind and 50% of N330.

Observations of mechanical properties in Fig. 12 and curves from RPA tests in Fig. 13 show that when the proportion of rCB\_ind increased, their physical properties became lower than N330 reference. When 20% of the filler amount is constituted of rCB\_ind, properties are similar to N330 reference even for the 100 and 300% modulus. Inversely, 50% of rCB\_ind with 50% of N330 indicate a clear decrease of modulus and fatigue

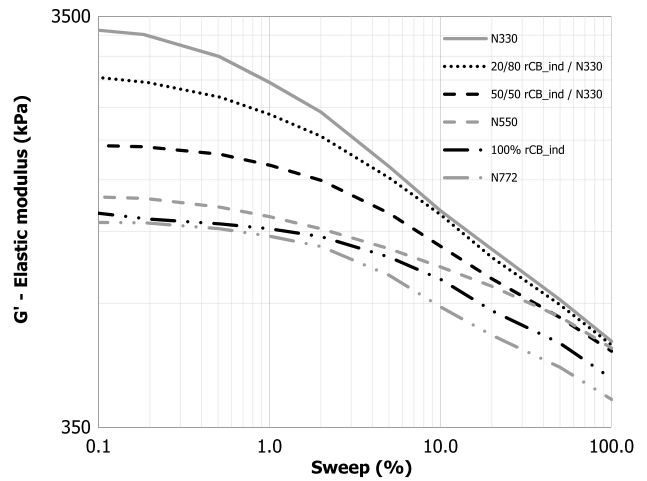


Fig. 13 RPA strain sweeps of cured rCB\_ind compounds

resistance. In this case, global properties were closer to the 100% rCB\_ind compound.

Results presented in this study for the rCBs exhibit a mechanical behaviour inferior to what has been observed for the N330 filled vulcanized rubbers. The noticeable difference in terms of carbon content, ash content and all the other inorganic components found in the recovered product are generally the main reasons advanced to explain the loss of mechanical properties. Roy and coworkers [30] have nevertheless studied extensively rCBs or *pyrolytic carbon black* recovered from waste tires using a vacuum pyrolysis treatment process. By conducting more fundamental surface characterizations, they have shown that carbonaceous deposits coming from the decomposition of elastomers are formed on the original carbon black. These deposits were found responsible for the reduction of available interactions sites at the surface of the recovered filler.

A significant decrease of filler-rubber interactions can be therefore suspected in our study, leading to a low degree of reinforcement and affecting the overall in-rubber performance of rCBs.

## Conclusion

The tire industry uses principally N330 carbon black, which has a specific surface area of 78 m<sup>2</sup>/g and an oil absorption number of 102 mL/g. As shown in this paper, specific surface area and oil absorption number of rCBs obtained from SWT are very close to N330 values.

Rubber manufacturers systematically compare reinforcing properties of rCBs to the N330 grade. However, the general reinforcement potential of the recovered filler is lower than a N330 carbon black especially concerning the 100% modulus, the 300% modulus and the fatigue resistance. Rheometric and mechanical properties have appeared to be closer to N772 grade. Currently, rCB contains an amount of ashes close to 20 wt% (less than 1% for conventional carbon black), mainly composed of inorganic matter coming from compounding components used during tire manufacturing. It is likely that this high ash content decreases the reinforcing properties. This might be the reason why such a material still encounters some difficulties being sold to tire manufacturers and why it is confined to niche markets in the rubber or plastics industries. So far, rCBs are addressed to plastic and rubber industries for non-technical products. However, the dissemination of the rCB product in the rubber industry is still limited because of its intrinsic physical and chemical properties. The ash content and its constituents oblige the users to modify their formulations and then develop an entirely new product containing rCB. Furthermore, the mechanical resistance of rubber filled with rCB is lower than the same rubber filled with

virgin carbon black. Ash content is thus undeniably a barrier for the broad acceptance of rCB in the marketplace.

Nevertheless, preliminary studies presented in this paper have shown that, even when a model laboratory filled rubber is treated, the in-rubber performance stays considerably reduced. According to the 6–7 wt% ash content of the rCB\_N330 coming from the model rubber, we can suspect without difficulty that the loss of reinforcing properties can not only be attributed to a considerable amount of ashes. It seems like a more widespread recognition from the scientific community and related industries has to be acknowledged regarding rCBs surface interactions with rubber. Work in our laboratory is already in progress to give a deeper understanding of rCB filler-rubber interaction. To do so, advanced physical and chemical characterization such as Raman Spectroscopy, Transmission Electron Microscopy, X-ray Photoelectron Spectroscopy and Time of Flight SIMS will be performed on the rCBs surface.

**Acknowledgements** Partial funding was received for this work from the French Association for Research and Technology (ANRT) and is gratefully acknowledged. In-rubber performance studies have been performed under the framework of the BIOPROOF project partially funded by the French government (BPIFRANCE). The authors also wish to acknowledge Celine Boachon and Christine Rolland from the Centre RAPSODEE for technical support.

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