

Role of recovered carbon black ash content composition on in-rubber performance

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Abstract. In this study, the role of the ash content in recovered carbon blacks (rCB) on the in-rubber performance was investigated. Material characterization was performed to evaluate the amount of ash, the elemental composition, the BET surface area of the rCB including ash and the organic impurities in the latter. Elemental mapping was performed using Energy Dispersive Transmission Electron Microscopy to locate the ash components in the rCB. Furthermore, the in-rubber performance of rCB was tested.

This study revealed the presence of active sulfur in rCBs originating from the ash content. Additionally, strong evidences were obtained from elemental analysis, cure characteristics and Payne effect measurements regarding the dependency of the amount of the active sulfur on the silica content present in the ash. Finally, elemental mapping showed a high concentration of sulfur deposited on the silica surface present in the rCB.

Introduction

Each year 1.5 billion tires containing a considerable amount of naturally resourced materials are discarded worldwide. Half of them are discarded to landfills and garbage without any treatment [1]. In view of diminishing natural resources, recovery of raw materials from scrap tires seems to be essential. Additionally, scrap tire stock piles represent environmental issues such as breeding ground for harmful insects and fire hazards, concerning both, human health and environment [2]. The recovery of valuable products from this waste stream broadens the possibilities for the reuse of recovered tire materials in high value products such as tires.

Tire recycling can be divided into three categories: (i) reuse/retreading, (ii) energy recovery, and (iii) material recovery[3]. In view of recovering raw materials from scrap tires, there has been a great interest in pyrolysis in last two decades. Pyrolysis is an endothermic nature thermal process typically performed at 300°C-700°C under non-oxidative conditions. Pyrolysis of waste tires yields a solid fraction of 30% - 40% and a volatile fraction of 60% – 70% [4-6]. The volatile fraction is further processed into the condensable fraction of 40% to 50% as tire derived oil (TDO), and the non-condensable fraction of 10 – 15% as tire derived gas(TDG) [7]. TDO is abundant in BTX (Benzene, Toluene, Xylene) and can be used as a substitute for fuel purposes [8]. TDG is an energy-rich gas with a calorific value range of 20 – 65MJ and can be reused to heat the pyrolysis process, thereby making the pyrolysis process sustainable [9].

The solid fraction of pyrolysis is often called char, pyrolytic carbon black or recovered carbon black (rCB). The major part of recovered carbon black consists of the carbon black, that was originally added during tire manufacturing. Carbonaceous deposits are also formed and adsorbed on rCB surface due to the release of organic vapors during pyrolysis [10, 11]. The amount of carbonaceous residue depends on the process conditions. Furthermore, another component of rCB is ash composed of inorganic additives such as silica, zinc oxide, sulfur and other metal compounds added during tire manufacturing. Since varied amounts of inorganic

additives are added in different type of tires, the ash content in rCB varies with respect to the type of the used tire feedstock [12].

Studies were conducted to evaluate the potential use of recovered carbon black as a substitute of conventional carbon black in tires. Colloidal properties of different rCBs were characterized and found to be in a range similar to the values of both, semi reinforcing and high reinforcing carbon blacks [13, 14]. Norris et al. [15] conducted a study on the in-rubber performance of rCBs exhibiting colloidal properties similar to reinforcing carbon blacks (N300 series). However, despite of good colloidal properties, the in-rubber reinforcing potential of rCBs were similar to low- or semi-reinforcing carbon black. The disparity in property – performance relationship was concluded as a result of carbonaceous residue presence reducing the surface activity of rCB, hence, leading to poor polymer-filler interactions. Roy and coworkers [8] characterized the surface activity of rCB exhibiting a surface area comparable to the high reinforcing grades of carbon black. They found that the surface activity of rCB was in the range of semi-reinforcing carbon black.

Several studies were conducted to demineralize the rCB. Removal of ash from rCB was reported performing different acid – base treatments [16-19]. Recently, Martinez et al. [20] studied the effect of ash leaching on in-rubber performance of rCBs. They concluded that reducing the ash content leads to a reduction in Mooney viscosity and slight improvements in tensile strength, elongation and tear strength.

Since ash consists of several inorganic compounds, it is not clear what the role of different ash components on the rCB in-rubber performance is. In this study, the effect of ash content on in-rubber performance was evaluated. For different ash contents, recovered carbon blacks were obtained from different feedstock. The presence of active sulfur in ash was revealed. Furthermore, within the ash, the role of silica on the presence of active sulfur in rCB was elaborated.

Experimental

Materials

Recovered carbon blacks characterized in this study were obtained by pyrolysis of passenger car tires, truck tires and a mixture of both. The ash content of recovered carbon blacks from different feedstock is given in Table 2. For comparative evaluation, the semi reinforcing N660 grade of carbon black was used. Carbon black with the trade name of CORAX N660 was manufactured and supplied by Orion Engineered Carbon GmbH Frankfurt, Germany.

The polymer used for in-rubber evaluation was a solution-styrene butadiene rubber (S-SBR) copolymer with 37.5 parts per hundred rubber (phr) oil (Buna VSL 2538-2, ARLANXEO USA LLC).

Material characterization

Thermo-gravimetric analysis (TGA) was performed using a TA Instrument Discovery TGA 550. The measurements were performed under a gas flow rate of 40ml/min in the temperature range of 25°C to 1000°C, and the heating rate was set to 20°C/min. From 25 °C till 650 °C, a nitrogen environment was used to measure removal of volatile components. From 650 °C onwards, air

was introduced for carbon burn-off. After the measurement, the remaining weight was measured as ash content or non-volatile matter as shown in Table 2.

Elemental analysis was performed using the JSM 6400 from Jeol. The equipment is a scanning electron microscope connected with an energy dispersive x-ray analyzer (SEM-EDX). Samples were prepared by gluing carbon black onto metal bars. After drying, the samples were placed in the oven at 100°C for 24 hours for degassing.

Elemental mapping was done using energy filtered transmission electron microscopy (EFTEM). Philips CM300ST-FEG Transmission Electron Microscope 300 kV was used with GATAN energy filter. Samples were prepared by dispersing carbon black in ethanol using ultrasonic bath.

The Brunauer Emmet Teller (BET) surface area was measured using the nitrogen (N₂) adsorption isotherm method in a Gemini VII 2390 Micrometrics apparatus. Samples were initially degassed at 300°C for 24 hours. The BET surface area and STSA (statistical thickness surface area) were then determined at -196°C. Data was analyzed using software TriStar 3000V6.04.

The degree of toluene discoloration by carbon black extractables was measured according to the ASTM standard D1618-99. Transmittance measurements were performed using Cary 300 UV – Vis spectrophotometer from Agilent.

Mixing, curing and in-rubber testing

Mixing of carbon black and recovered carbon black compounds was done according to the mixing recipe given in Table 1. Mixing was carried out in a Brabender Plasticorder 350S internal batch mixer. A two stage mixing procedure was followed. In the first stage, all the ingredients were mixed except curatives. The internal batch mixer for the first stage mixing was operated at a rotor speed of 100rpm, a fill factor of 75% and a temperature of 90°C. The dump temperature of the batch compounds after first stage mixing was 160°C. Curatives were added in the second stage of mixing. The internal batch mixer for the second stage mixing was operated at a rotor speed of 80rpm, a fill factor of 75% and a temperature of 50°C, the dump temperature was 110°C. The mixed compounds were then sheeted using a two roll mill. Each compound containing a certain type of carbon black was prepared three times to control the reproducibility of the results. The compounds are referred to according to the carbon black used.

Table 1 Mixing recipe for rubber compounding.

Mixing step	Materials	Reference recipe for N660 (phr)	rCB recipe (phr)
1	S-SBR oil extended	137.5	137.5
1	Carbon black	60	60*
1	6PPD / TMQ / Wax anti-ozone/ Zinc oxide / Stearic acid	1.5 / 1 / 2.5 / 3 / 2	1.5 / 1 / 2.5 / 3 / 2
2	Sulfur / TBBS	1.65 / 0.7	1.65 / 0.7

*adjusted in grams according to the ash content.

For a similar amount of carbon black in all compounds, recovered carbon black compounds were adjusted by weight according to their ash content (see Table 2).

Table 2 Adjustment of carbon black amount according to the ash content present in rCB.

Carbon black	Feedstock	Ash content (%)	Amount (grams)
N660	-	-	93.7
PCT	Passenger car tire	27	119
TT	Truck tire	15	107
Mix 1	Mixture of TT and PCT	21	113
Mix 2	Mixture of TT and PCT	21	113

Samples were vulcanized in a Wickert press WLP 1600 with a pressure of 100 bar at 160°C to sheets with a thickness of 2mm. They were vulcanized according to their respective t_{90} calculated from the cure curves using the tangent method. A Rubber Process Analyzer RPA Elite from TA instruments was utilized for cure curve measurements, and the procedure followed was according to ISO 3417. For hardness measurements, round discs with a thickness of 5mm and a diameter of 60mm were vulcanized. Cure curves were also measured for batch compounds (without curatives) for active sulfur determination.

The marching modulus intensity (MMI) of all cure curves was calculated by following equation[21],

$$MMI\left(\frac{dNm}{min}\right) = \frac{T_{60} - T_{40}}{60min - 40min}$$

Where T60 and T40 are the torque at 60minutes and 40minutes respectively.

Tensile properties were measured using a Zwick Roell universal tensile tester. The measurements were performed on 2mm thick tensile dumbbells. The uncured Payne effect was measured using a RPA Elite at 100°C. Strain varied in the range of 0.5% to 80%.

Results and Discussion

Material characterization

The TGA analysis was performed from 25°C to 650°C in nitrogen environment and 650°C to 1000°C in air. Initially, up to 100°C, moisture removal of 1% to 2% was evident in all cases. At temperatures higher than 450°C, 2% to 4% volatile hydrocarbons were removed in all recovered carbon blacks (rCB). Since N660 does not contain any volatiles, no weight loss was observed for the reference sample. At temperatures higher than 650°C and after change from N₂ to air, rapid weight loss was observed in all rCBs and carbon black N660 due to the carbon burn-off. The recovered carbon blacks reach a plateau after certain percentage of carbon burn-off, representing the amount of non-volatiles (ash) present in rCBs. rCBs from different feedstock contain different amount of non-volatiles: rCB from truck tires contained the lowest amount of 13.5% while, rCB from passenger car tires had the highest amount of 28%, and the mixture of both contained around 21%. The ash content present in rCBs is mainly due to the use of inorganic fillers and minerals in tire manufacturing. Since in truck tire manufacturing, only small amounts of inorganic fillers are used, a lower amount of non-volatiles was present. During passenger car tire manufacturing, a higher amount of inorganic fillers is incorporated leading to higher ashcontent.

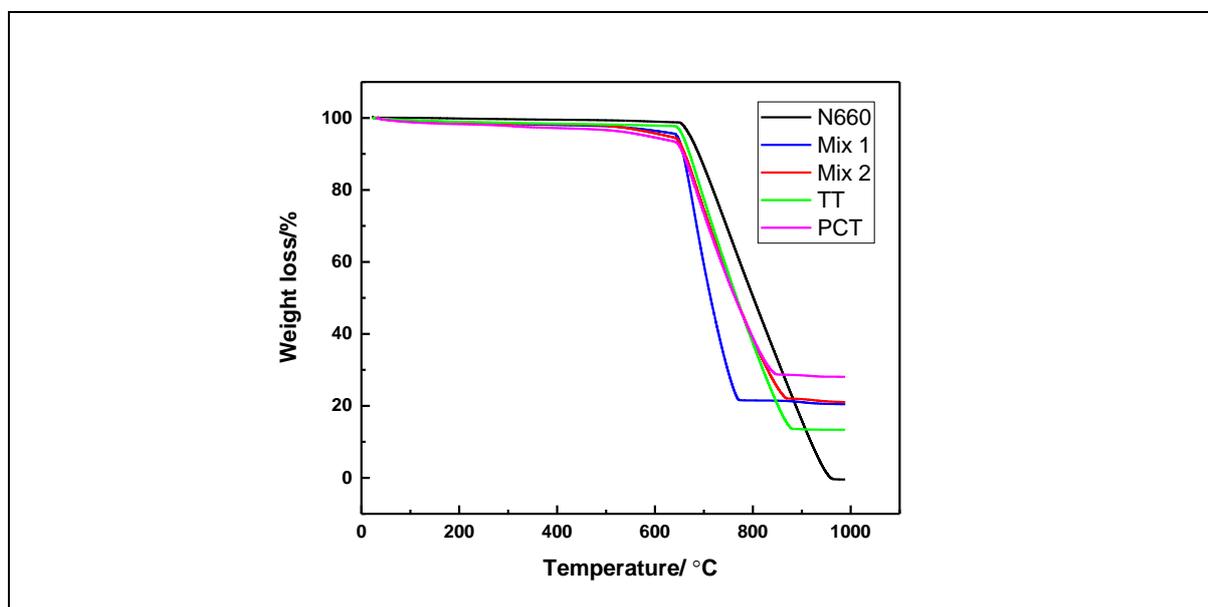


Figure 1. Weight loss % of recovered carbon blacks and carbon black N660 as a function of temperature.

The results of the elemental analysis are presented in Table 3. Lowest impurities were present in carbon black N660. A small amount of oxygen in carbon black N660 was detected, which is generally attributed as carbon black surface functionality. Among recovered carbon blacks, the highest amount of carbon was detected in truck tire rCB (TT) while the lowest amount was found in PCT (TT>Mix>PCT). The reduction in carbon from TT to PCT can also be seen in terms of an increasing mineral ash content (TT<Mix<PCT). Zinc was found in the range of 2.5% to 4%, and sulfur in the range of approximately 2% in all rCBs. The major ash component difference on the basis of feedstock was silicon and oxygen content (TT<Mix<PCT). The increase in silicon and oxygen is due to the use of silica in tire manufacturing. Generally, higher amount of silica is used in passenger car tire compared to truck tire manufacturing, where carbon black is still used in higher proportions.

Table 3 Elemental analysis of carbon black N660 and recovered carbon blacks.

	N660 (%)	TT (%)	Mix 1 and 2 (%)	PCT (%)
C	98.5	84	76	68
Si	-	2	5.5	8
S	0.3	2	2.3	2
Zn	-	4	4	2.3
O	1	6	11	18

The BET surface area and external surface area (STSA) were determined for rCBs and carbon black N660 using N₂ adsorption. The BET surface area of carbon black N660 was the lowest, while rCB surface areas were in the range of 74m²/g to 87m²/g. Similarly, STSA was also higher

for rCBs compared to carbon black N660. Since process conditions for rCBs were unknown and the specific surface area is dependent on them, no relation was found among rCBs with respect to their feedstock compositions.

Table 4 BET surface area and external surface area of N660 and rCBs.

	BET surface(m²/g)	STSA(m²/g)
N660	48	32
TT	83	61
Mix 1	78	54
Mix 2	74	53
PCT	87	64

Transmittance of the toluene extract was measured for all samples to characterize the organic impurity content. In Table 5, N660, TT and PCT had a similar transmittance. Mix 2 had the highest transmittance indicating the lowest amount of organic impurities. In contrast, Mix 1 had the lowest amount of transmittance, indicating the highest organic impurity concentration. The amount of organic impurities depends on process conditions, after-treatments as well as feedstock composition, but it is difficult to define the different contributions of these factors.

Table 5 Transmittance of toluene extracts.

	Transmittance/ %
N660	90
TT	90
Mix 1	80
Mix 2	95
PCT	90

In-rubber performance

In Figure 2(a), N660 based compound showed lowest initial torque while having highest scorch time. Additionally, it had lowest marching modulus. However, all recovered carbon blacks compared to N660 had higher initial torque and shorter scorch times. Also, rCB compounds had higher marching modulus. Among rCBs, influence of different feedstock was found with rCB-PCT exhibited highest initial torque, however, rCB-TT had the lowest. Since the major difference among these rCB feedstock compositions is the ash content, therefore, systematic increase in initial torque (TT<Mix<PCT) was attributed as the ash content variation effect.

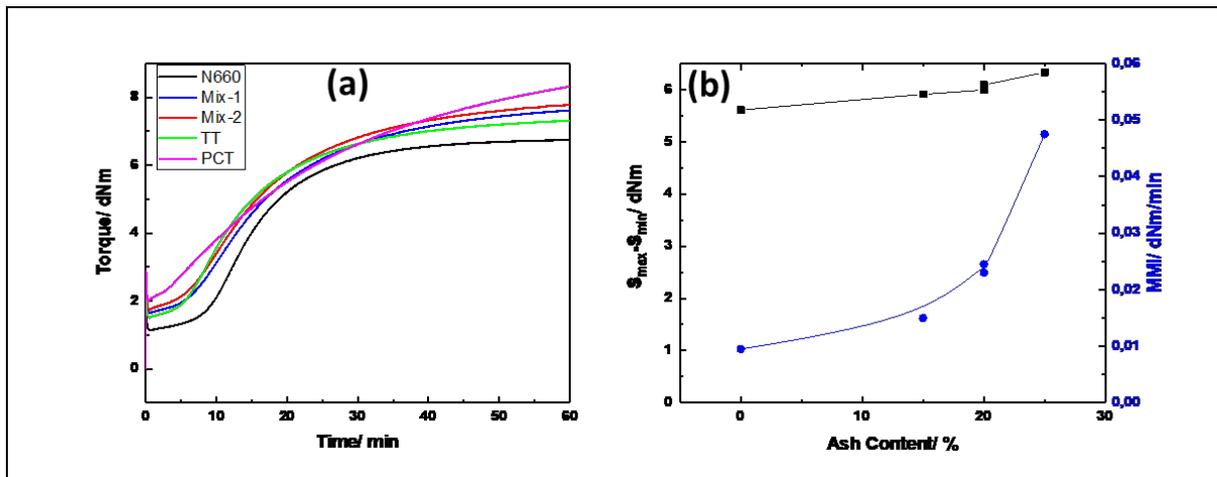


Figure 2(a) Cure characteristics of compounds containing carbon black N660 and rCBs from different feedstocks; (b) total torque and marching modulus as a function of ash content.

In Figure 2(b), total torque and marching modulus intensity were plotted as a function of ash content. A clear increasing trend in both, delta torque and marching modulus intensity, with respect to increasing ash content was observed. Since the amount of carbon black is the same in all cases, a systematic increase in delta torque and marching modulus intensity is due to the effect of ash components onto rubber matrix vulcanization. Considering this and the initial torque increase seen in Figure 2(a), it indicates the presence of active sulfur originating from ash content. Since the dump temperature after first step mixing of batch compounds (without curatives) was 160°C, the active sulfur might cause pre-sorch leading to a higher viscosity, noticeable as higher initial torque. Similarly, the presence of active sulfur from the ash content results in an increase of the total sulfur amount present in the rubber matrix. This would eventually cause higher crosslinking and would lead to higher modulus.

Considering the above mentioned indications, the presence of active sulfur was characterized by measuring the cure characteristics of batch compounds without curatives. The delta torque of all samples are shown in Figure 3.

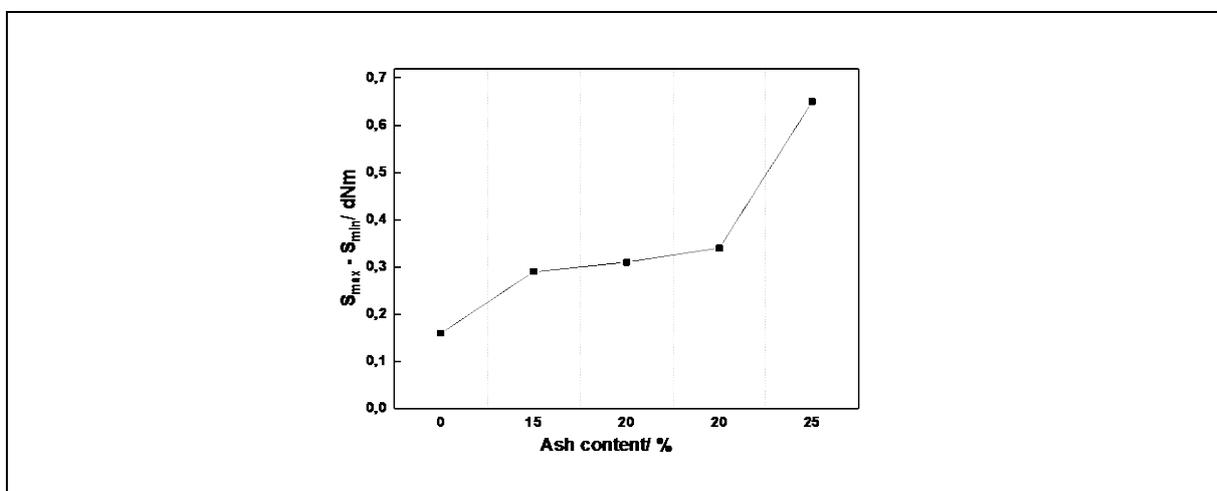


Figure 3. Total torque of carbon black and rCBs batch compounds without curatives.

In Figure 3, a systematic increase of delta torque with respect to increasing ash content is observed. Since no curatives were added, this provided clear evidence of active sulfur presence in rCB ash which caused the increase in delta torque. Nevertheless, the elemental analysis showed that the amount of sulfur present in all rCBs was similar i.e. around 2%. The only ash component which mainly differed according to the feedstock was the amount of silica. Therefore, it can be depicted that the presence of active sulfur is related to the amount of silica present in the ash. This finding can be linked to the tire manufacturing process, in which sulfur-containing silane coupling agents are added according to the amount of silica. This silane could be the source of active sulfur present in the ash content of the recovered carbon black. Additionally, passenger car tires have the highest amount of silica, therefore contains the highest amount of active sulfur.

Payne effect measurements were performed on uncured final compounds to understand the filler-filler interactions and the polymer-filler interactions. In Figure 4(a), a sigmoidal decrease in storage modulus (G') at 10% strain was observed in all cases and attributed to breakdown of the filler-filler network. The N660-containing compound had the lowest magnitude of G' at small strains, indicating lower filler-filler interactions and better dispersions compared to rCB compounds. In case of rCB compounds, a clear trend of increasing G' with increasing ash content is seen. However, considering G' at higher strain amplitudes, the N660 compound also had the lowest G' magnitude compared to rCBs. G' at higher strains for rCB increased with increasing ash content; this generally reflects the polymer-filler interactions. Although, cure characteristics indicated previously that rCBs with increasing ash content exhibit a higher amount of active sulfur. Therefore, the systematic increase of G' at higher strains with respect to ash content was attributed as the pre-scorch effect of active sulfur present in recovered carbon blacks.

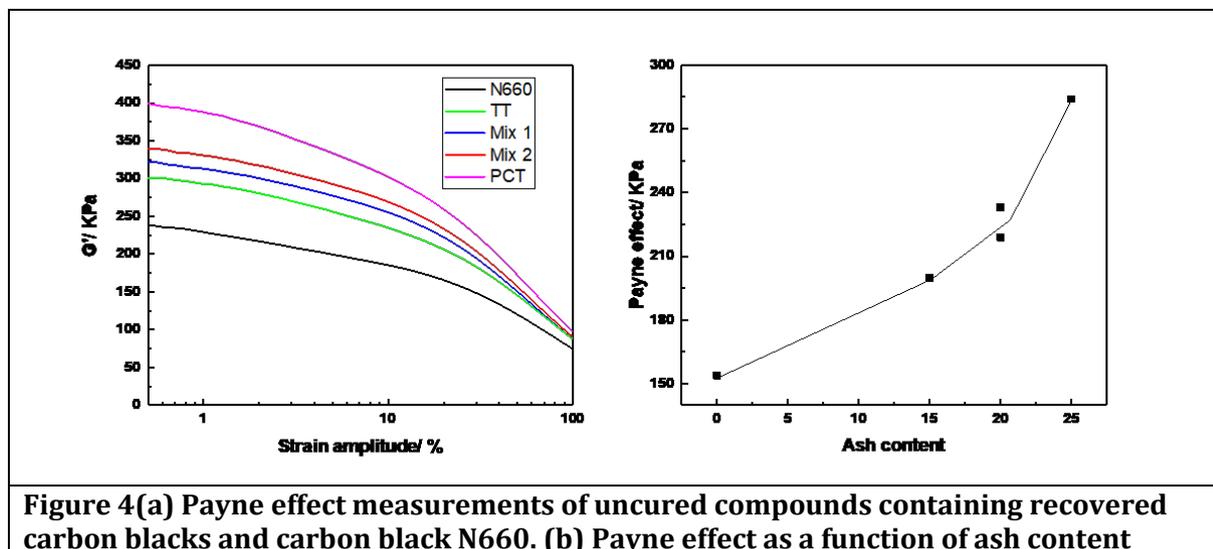


Figure 4(a) Payne effect measurements of uncured compounds containing recovered carbon blacks and carbon black N660. (b) Payne effect as a function of ash content

In Figure 4(b), the Payne effect (ΔG) of all samples were plotted as a function of ash content for micro dispersion analysis of fillers in the polymer matrix. The N660 compound had the lowest Payne effect indicating good dispersion, while rCB compounds had an increasing trend of Payne effect with increasing ash content.

Stress-strain properties of cured compounds with different recovered carbon blacks and carbon black N660 were measured and plotted in Figure 5. Despite of exhibiting higher surface areas, the stress strain behaviors of rubber containing rCB were similar or lower than of the ones with N660. Higher surface areas of carbon black are generally related to higher reinforcement. However, in case of recovered carbon black, even though the surface area differed in the range from 74m²/g to 87m²/g, the stress strain curves were more or less similar. Since stress-strain properties of rCBs are similar or lower to N660 while, previously in payne effect measurements, higher polymer-filler interactions of rCBs are seen. This contrast can be attributed as the consequence of pre-scorch of rCBs due to the presence of active sulfur leading to higher G' ($\gamma=80\%$) in payne effect measurements.

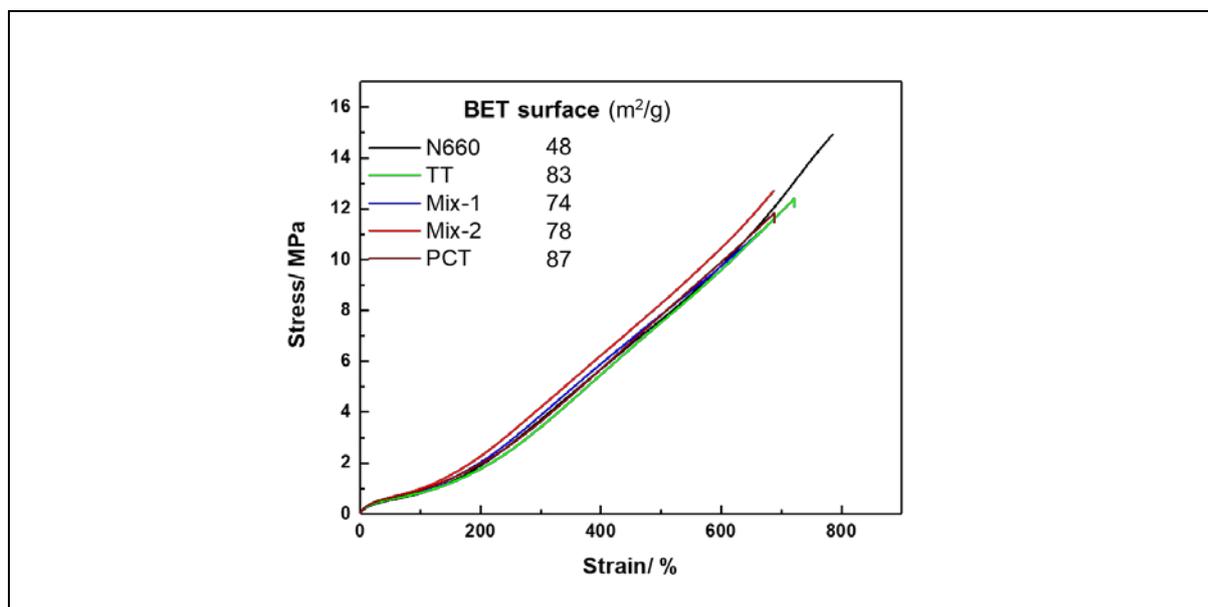


Figure 5. Stress-strain curves for compounds containing carbon black N660 and recovered carbon blacks with different specific surface areas.

In Table 6, the physical properties are summarized. Modulus at 100% strain and 300% strain of TT with lowest ash content had the lowest values, while samples with higher ash contents had higher ones. Elongation at break was highest for rubber with N660, while for recovered carbon black samples the elongation decreased systematically with increasing ash content. Similarly, tensile strength was also slightly decreased with increasing ash content. This trend of ash content on modulus and elongation is in line with the previously mentioned finding of the effect of active sulfur: A higher amount of active sulfur leads to a higher degree of crosslinking, resulting in both, increase of modulus and reduction of elongation. N660 and TT had similar shore A hardness, while other samples had a slightly higher hardness.

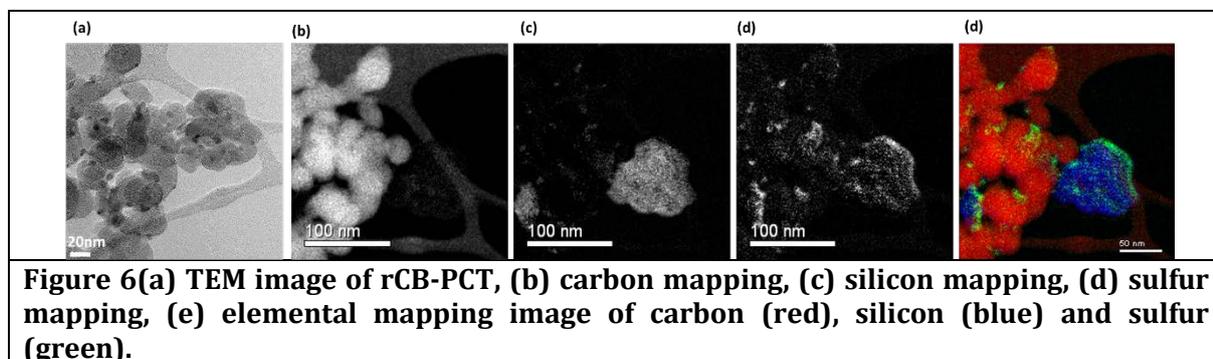
Table 6 Physical properties of recovered carbon blacks and carbon black N660.

	N660	TT	MIX-1	MIX-2	PCT
MODULUS AT 100%	0.8 ± 0.01	0.8 ± 0.01	0.9 ± 0.01	0.9 ± 0.01	0.95 ± 0.01
MODULUS AT 300%	3.7 ± 0.16	3.3 ± 0.08	3.9 ± 0.05	4 ± 0.08	3.8 ± 0.08
TENSILE STRENGTH/ MPA	14 ± 1.5	12 ± 0.4	11 ± 0.6	11.5 ± 0.6	11.5 ± 0.4

ELONGATION/ %	770 ± 60	713 ± 20	670 ± 20	675 ± 20	668 ± 20
HARDNESS/ SHORE A	39 ± 1	39 ± 1	41 ± 1	41 ± 1	41 ± 1

Evidences from elemental analysis, cure characteristics, stress-strain properties and Payne effect measurements indicate the presence of active sulfur in recovered carbon blacks. Additionally, the influence of this additional sulfur was found to be related to the silica content present in the recovered carbon black. In order to locate the presence of the active sulfur, elemental mapping was performed. Since rCB-PCT has the highest amount of silica and has shown a profound effect of active sulfur, elemental mapping was performed for this sample of rCB.

In Figure 6(a), a TEM image of recovered carbon black is shown. Recovered carbon black had a non-uniform particle size, which was due to the use of different carbon black grades during tire manufacturing. For the same reason, the right side of the rCB structure is more open while on the other side it exhibited a more closed structure. In Figure 6(b), only the left part - only in the left part - the closed structure part - of image 6(a) is visible, indicating the presence of carbon on the surface. The right part of picture 6(a) is seen in Figure 6(c) in the elemental mapping of silicon, indicating the presence of silica as impurity. In Figure 6(d), sulfur mapping was performed: Sulfur was found at different parts of the agglomerate, but interestingly a higher amount of sulfur was present near or on the silica surface. Figure 6(e) is a combination of all three elemental mappings, which confirmed the presence of a sulfur layer around the silica aggregate. EFTEM mapping revealed that a part of silica aggregate is still silanized. This is a strong indication of active sulfur present on the silica surface originating from a sulfur containing silane used during tire manufacturing.



Conclusion

Recovered carbon blacks from different feedstock and containing different amounts of ash were analyzed as such and in a compound. Despite of different process conditions, the effect of ash content was clearly evident in the in-rubber performance of rCB. Cure behavior of the compound without curatives and uncured Payne effect revealed the presence of active sulfur originating from the ash content. The cure characteristics of the final compound confirmed the active sulfur presence. Elemental analysis and mapping elucidated the role of silica for the presence of active sulfur. Finally, based on the aforementioned evidences, it was concluded that the origin of the active sulfur in the ash content was due to the presence of sulfur-containing silane used for silica-polymer coupling during tire manufacturing.

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