We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900
Open access books available

185,000
International authors and editors

200M
Downloads

Our authors are among the

154
Countries delivered to

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Chapter 5

The Potential of Pyrolytic Biomass as a Sustainable Biofiller for Styrene-Butadiene Rubber

Yiran Fan and Geoff D. Fowler

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/intechopen.79994

Abstract

This chapter explains the significant potential of the pyrolytic biomass char for use as a sustainable carbon black replacement filler for rubber materials. The manufacture of rubber filler is not only energy-consuming, contributing significantly to global CO_2 emissions, but uses nonrenewable feedstock in production making it unsustainable. Ongoing work focused upon the development of carbonaceous rubber fillers based on coconut shell, a sustainable and renewable source, is presented in this chapter. A comparison between coconut char and commercial carbon black N772 demonstrates the profound potential of the pyrolytic coconut char to be used as filler. The char filler obtained was mixed with SBR and the resulting rubber product was evaluated for their technological performance, exhibiting high surface area and good tensile strength.

Keywords: rubber, reinforcing filler, carbon black, pyrolysis, biomass

1. Introduction

At present, it is seldom to see a rubber product using the polymer in an unfilled condition. Various materials are added during the rubber manufacture process. Carbon black is widely used as a rubber reinforcing filler from the third century B.C. in China. It is added to help to enhance the physical properties of the given rubber, such as hardness, tensile strength, and tear strength, etc. In 2015, the global production of carbon was about 13.9 million metric tons. It is indicated that by 2022, the production will reach 19.2 million metric tons [1]. There is no doubt that the cost of making carbon black will increase rapidly. As a result, the potential effect of the prediction may lead to an increasing demand of the fossil fuel hydrocarbon feedstock. On the other hand, the manufacture of carbon black is not only energy-intensive but also

IntechOpen

© 2018 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/3.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. CC BY

unsustainable in the long term as a feedstock due to the finite supply and the contribution to global warming.

Given the increasing pressure against using nonrenewable resources, it is essential to develop alternative materials to act as novel rubber fillers. Recently, several researches have been conducted focusing "green" fillers, which are based on the waste materials having potential "renewability" [2]. By using bio-based fillers, the dependence on fossil fuel would be improved and a sustainable material basis for rubber filler production could be established. In this chapter, the development of new type of fillers for rubber materials based on char produced during pyrolysis of biomass (coconut shell) is illustrated.

2. Rubber reinforcing filler: carbon black

Over the past century, the importance of rubber to human society has been paid more and more attentions. Several types of particulate fillers have been applied in rubber industry for different purposes, which are based on reinforcement, low material cost, and processing ease. The presence of fillers is key to achieve durable products, increase strength, and prolong life. The modulus of elasticity which is a measure of stiffness of the given materials can also be improved by fillers. Currently, carbon black is the most widely used particulate fillers, which has the ability to bond with the elastomer component enhancing the strength of vulcanized rubbers more than 10-fold as well as imparting durability to the materials [3]. Due to the incomplete combustion of fossil-origin hydrocarbon fuels during the carbon black manufacture, the process has a considerable carbon footprint. About 2.4 tons of CO_2 are estimated to be emitted per ton of carbon black, which compares to 0.8 tons of CO_2 per ton of cement for cement manufacture [4, 5].

Carbon black is usually present as types of aggregates. According to the TEM graph, its structure can be defined as partly graphitic. More graphitic structure can be observed from the outer layers than from center. Although carbon black particle aggregates are reported to work as a unit in the rubber matrix, its reinforcement ability is not determined by the aggregate units but by each individual particle within the unit. With the particle size decrease, the dispersion ability of carbon black, as well as the interface extension, can be improved, resulting in good reinforcement ability [6, 7].

Particle size, the morphology of aggregates, and the microstructure offered by carbon black can be considered as the key properties contributing to the reinforcement of elastomers. Furthermore, the surface of carbon black and its structural organization, surface area, and its chemical composition are also important. The development of a large polymer-filler interface is highly expected. The upper limit of useful specific surface area for significant reinforcement can reach 300–400 m^2/cm^3, and is determined by considerations of dispersibility, processability of the unvulcanized mix, and serious loss of rubbery characteristics of the composite [8, 9].

The surface area of carbon black is an important morphological characteristic for reinforcing. It indicates how much available surface can be accessed by rubber molecules for the interaction

http://dx.doi.org/10.5772/intechopen.79994

between the rubber and the filler surface. It is necessary to note that meso- and macropores seem to play the decisive role on the surface unlike micropores for the application of activated carbon. Since the rubber polymer chains are much larger than the micropores, the polymer cannot access these pores.

The research of the reinforcement mechanism offered by carbon black has been widely undertaken since 1960s [10]. It is widely known that the vulcanization process can only achieve resilient properties with little strength. Then, the strength properties need to be introduced by the addition of "reinforcement" fillers. After carbon blacks are added to the rubber compound, several changes occur: (1) an increase in modulus, or stress at a particular strain, (2) an increase in elongation at break for vulcanizates having a given degree of cross-linking, and (3) consequently, an increase in tensile strength [10, 11]. The improvement of stiffness and the physical properties such as tear resistance, tensile strength, and abrasion resistance are regarded as the crucial contribution of carbon black. The reinforcing ability of a filler can be demonstrated in **Figure 1**; the only difference between two SBR vulcanizates is the presence or absence of 50phr carbon black N220 in the recipe. With the addition of carbon black N220, the stress-strain curve shows a sharp rise, almost 10-fold compared with the unfilled rubber.

Large amount of literatures report about the reinforcement properties of carbon black for decades. So far, there are more than eight postulations have been wieldy applied to explain the reinforcement mechanisms, which are given in **Table 1**.

Due to the increasing price of natural rubber and other compounding ingredients, there are several concerns about the ongoing use of nonrenewable resources based carbon black feedstock.

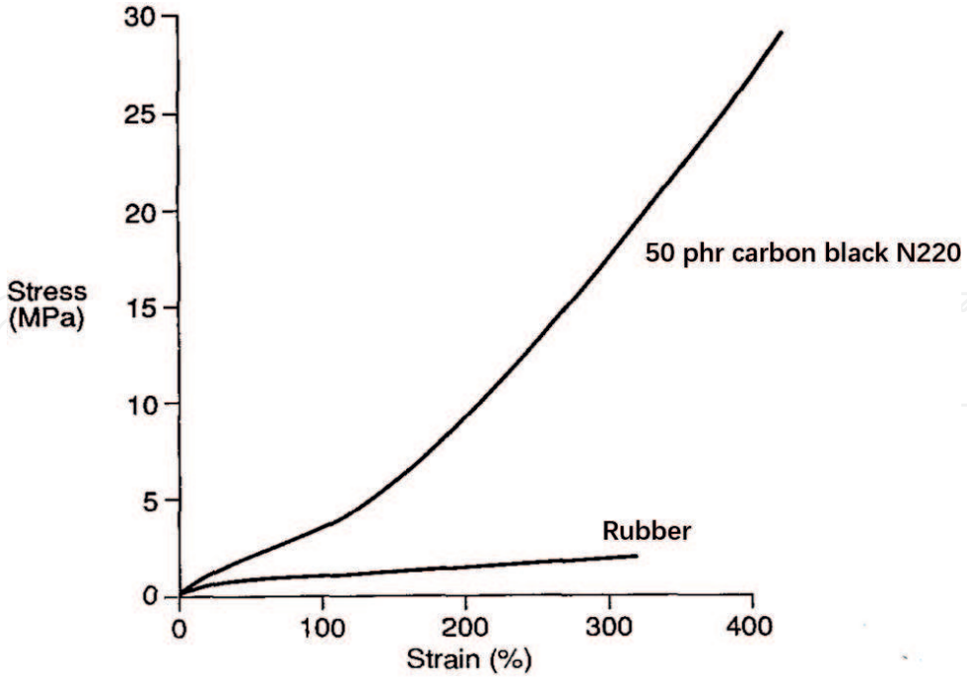


Figure 1. Comparison between filled and unfilled rubber matrix [11, 12]. (Rubber: SBR 1502, 100; zinc oxide, 3; stearic acid, 1.5; Santoflex 13, 0.5; Santoflex 77, 0.5; Sundex 8125, 3; DPG, 0.3; Santousure NS, 1.2; Sulfur, 2. Press cure: 40 min at 153°C. Same formulation with addition of 50 phr N220 carbon black).

Theories on filled elastomer	Summary	References
Small particle size	The reinforcement mechanism is attributed to an interfacial effect consequent upon small particle size. Any finely divided solid material that can be dispersed in the polymeric matrix will reinforce rubber compounds.	[12–14]
Slippage at interface	Stress can be redistributed by the slippage of molecular chains, and then helps prevent the molecular rupture. The frictional heat occurring during the relative motion between rubber molecular chains and filler can help release the strain energy so that hysteresis can be seen in the matrix instead of breakup.	[15, 16]
Chemical reaction	Functional groups on the surface of carbon black are most likely subjected to a variety of inter- and intramolecular interactions. Acid/base reaction and hydrogen bonding are probably the main reactions that may occur between the rubber matrix and the carbon black.	[17–19]
Stored energy function	Use thermodynamic concepts to study the relationship between stress and strain. The order and disorder of system correlate to the extension of the molecular chains.	[20–23]
Hydrodynamic theory	Rigid fillers typically increase the stiffness of the elastomer. The presence of the rigid fillers lead to local strains, which is greater than globally applied strains.	[24–26]
Strain amplification	Modifications to hydrodynamic model at high strains.	[19, 27, 28]
Model of weak and strong linkage	The filled rubber can be regarded to be made of strong and weak linkages. Different weak linkages can be broken by different stresses contributing to softening.	[28, 29]
The Bueche model	The fillers are connected with the molecular network chains within a filled rubber.	[30, 31]

Table 1. Eight postulations of carbon black reinforcement mechanisms [11].

Material	Short summary	References
Chicken eggshell	The eggshell calcium carbonate filled epoxidized natural rubber showed superior vulcanization characteristics (higher maximum torque and cure rate index, lower cure time, and scorch time), higher tensile properties, and lower tension set value.	[32]
Fly ash	Fly ash (up to 60 phr) can be used as a nonreinforcing filler for ESBR compounds, where abrasion resistance is not significantly required. The 300% modulus values remained unchanged with increasing loading.	[34]
Soy spent flakes	The soy spent flakes can partially replace carbon black as the reinforcement cofiller in rubber composites. The elasticity of the cofiller network structure is close to that of carbon black-filled composites.	[35]
Lignin	Reinforcing properties of lignin as filler in nitrile rubber can be improved on suitable chemical treatment for good thermal stability.	[36]
Pyrolytic tire	Chars obtained from pyrolytic tire can be successfully reused as semireinforcing fillers in rubber formulations. The physical and mechanical properties of the rubber filled with pyrolytic tire were found to be comparable to rubber containing N772 and with N772 and silica.	[4]
Waste newsprint fibers	The sodium silicate and magnesium chloride treated newsprint fiber waste at 40phr can improve the electrical and mechanical properties of the rubber composite.	[37]
Marble sludge with carbon black	Marble sludge can be used as a cofiller with carbon black in natural rubber. High tensile strength, modulus, tear strength, and hardness can be achieved.	[38]

Table 2. Novel rubber filler from green feedstock [11].

http://dx.doi.org/10.5772/intechopen.79994

On one hand, the price of carbon black feedstock witnesses a gradual increase every year. On the other hand, severe environmental problems have been caused by the nondegradability feedstock of carbon black. Consequently, many researches have been conducted in the rubber industry to develop fillers derived from biodegradable waste feedstock, by which transforming its sourcing to a sustainable material basis. Their recyclability and utilization has become a major driving factor in their acceptance and employability, as well as low cost and abundant availability. This new class of carbon black-like feedstock includes natural sources (e.g., natural fibers), industrial by-products (e.g., saw dust, rice husk, coconut shell), and even industrial waste material (e.g., rice husk ash). This field is very attractive from both the ecological and economic point of view, since it could enable rejected material to become valuable material, which could be reused in industry [32, 33]. Some of the popular green feedstocks of novel rubber filler have been summarized in **Table 2**.

3. Process description

3.1. Feedstock and reference material

3.1.1. Feedstock: coconut shell

As a single and simple genus species, coconut is grown around the world sharing similar properties. In order to make the experiments standardized, after being crushed into to small pieces (less than 10 mm) by a laboratory-scale hammer miller (Glen Creston, UK), the small pieces of coconut shell were then dried at 105°C to constant weight, to reduce the moisture content (**Figure 2**).

3.1.2. Reference material: carbon black N772

Carbon black N772 belongs to low to semidispersion, middle-active grades of carbon black, which has the largest particle size and lowest structural and surface area among the whole



Figure 2. Dried coconut shell [11].

range of carbon black. N772 provides high elasticity, low heat-up, good aging-resistance, and superior dynamic performance to the technical rubber products or tire frames.

3.2. Pyrolysis process

Pyrolysis is a thermal treatment with limited oxygen by which organic materials are chemically decomposed by heat. It is a promising method by using waste materials such as biomass as feedstock to convert waste into energy and other valuable products. During the pyrolysis, large molecules break down into small molecules, resulting in carbonaceous materials, combustible gases, and condensable liquid hydrocarbons for renewable energy resources [39–42]. According to Sienkiewicz et al. [43], it is obvious that there is a significant potential of pyrolysis treatment based on ongoing works along with increasing cost of energy and petroleum and resources such as carbon black.

The pyrolysis of coconut shell was performed in a Carbolite 11/150 laboratory scale rotary furnace (Carbolite, Hope Valley, UK) situated in a walk-in fume cupboard. As shown in **Figure 3**, a rotatory horizontal tubular quartz vessel with the capacity of almost 5 liters is suspended by air-tight rotary fixtures inside an electrically heated box-furnace. According to several studies, the rotation rate is set as 10 ramp/min. The temperature is controlled at 600°C by the thermal system with a thermocouple in the box furnace. Nitrogen gas is introduced into the reaction vessel from the gas inlet ports at 550 ml/min flow rate [44]. The nitrogen flow maintaining in the vessel throughout the pyrolysis is to protect the char from oxidation and help to carry and remove the pyrolytic volatiles (oil and gas) toward the oil trap. At the same time, the noncondensable volatiles (gases) were vented from a small opening on the top of the oil trap to the fume cupboard.

3.3. Postpyrolysis grinding by wet TEMA milling

All the char samples after the pyrolysis were ground by wet TEMA milling using a vibratory disc mill (Tema Machinery Company Ltd., UK). Wet milling is used for the more intensive and efficient properties than dry grinding since it can break the char samples into finer

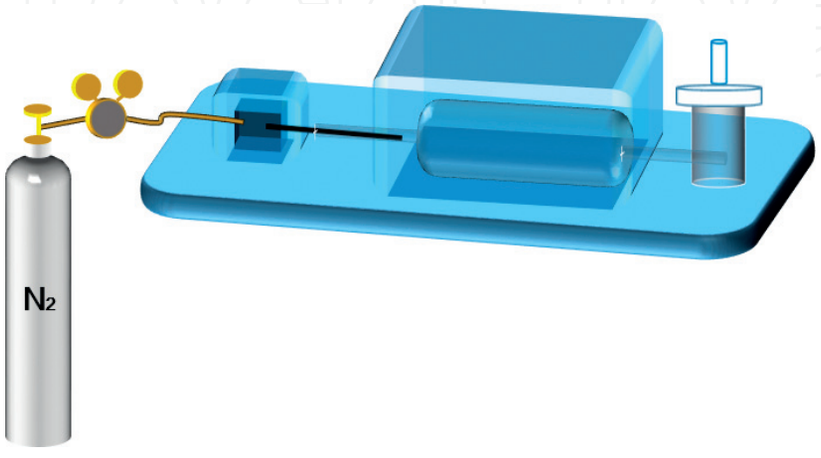


Figure 3. Illustration of rotary furnace.

http://dx.doi.org/10.5772/intechopen.79994

particles in the micron and submicron (or nanometer) particle size. Moreover, it has been found that wet milling can cost-effectively create uniformly fine particles with limited or no contamination [45]. The optimum condition for wet TEMA milling was confirmed as 1:1 liquid and solid ratio, 1.5 min grinding time. After the milling process, the wet samples were dried at 105°C for 24 h until constant weight.

3.4. Char filler characterization

3.4.1. Textural characterization

Surface area of the samples were characterized by liquid nitrogen (at 77 K) adsorption and desorption method using the OMNISORP 100. The BET surface area can be calculated with the isotherms by using the Brunauer-Emmett-Teller equation [46]. The t-plot method was used to find the micropore volume and the combined macropore and mesopore surface area [47]. The significant surface areas were concluded from the difference between the BET surface area and the macropore and mesopore surface area and used to establish the relationship between pore size distribution and rubber uptake capacity of the fillers.

3.4.2. Toluene extraction

Toluene extraction of the char filler was test according to the ASTM D 1618-99 (Standard Test Method for Carbon Black Extractables—Transmittance of Toluene Extract) [48]. This method covers the measurement of the degree of toluene discoloration by carbon black extractables and is useful in controlling the reaction process for the production of carbon black.

3.4.3. pH value

Test Method A—Boiling Slurry of ASTM D1512-05 Standard Test Method for Carbon Black—pH value [49] was applied to obtain the pH value of the char filler. The pH value is very essential since it can affect the vulcanization of some rubber compounds.

3.4.4. Boehm titration

The oxygen surface groups on char filler were investigated by the Boehm titration [17]. This method is based on the principle that oxygen groups on surfaces have different acidities and can be neutralized by bases of different strengths. Sodium hydroxide (NaOH) is the strongest base generally used, and is assumed to neutralize all Brønsted acids, while sodium carbonate (Na_2CO_3) neutralizes carboxylic and lactonic groups and sodium bicarbonate ($NaHCO_3$) neutralizes carboxylic acids. The difference between the uptake of the bases can be used to quantify the oxygen surface groups on a char sample [50].

3.4.5. In-rubber testing

Styrene-butadiene rubber (SBR) is widely applied in tire treads. When protected by additives, excellent traction properties, good abrasion resistance, and good aging stability can be achieved [51]. It is reported that the most common use of SBR is in pneumatic tires with around 50% of car tires being made from a range of types of SBR. A widely used generic SBR

Ingredient	Parts per hundred of rubber
SBR 1502	100
Char filler	60
TDAE oil	10
Zinc oxide	5
Stearic acid	2
6PPD	1.5
TBBS	1.5
Sulfur	1.5

Table 3. SBR formulation [9, 11].

formulation is shown in **Table 3**, which was applied in the compounding process to investigate the performance of the char filler in rubber. Compounds were produced using a 60 cc Brabender mixer set at 40°C and 60 rpm.

The moving die rheometer (MDR) test was conducted based on ASTM D5289, at 160°C for 30 min. The results of the MDR were used to evaluate the cure characteristics of each compound and to allow preparation of cured sheet using a cure time of T90 + 5 min. Shore A hardness was tested according ASTM D2240. Tensile properties were determined following ASTM D412. A scanning electron microscopy (SEM) (Auriga Cross Beam, Zeiss) was applied to analyze the surface morphology of the char filler-filled rubber sample and to understand the mechanism of the char filler with the rubber matrix.

4. Results and discussion

4.1. Char characterization

The char yield, oil yield, and gas yield from the pyrolysis process are 31.6, 16.0 and 52.4%, respectively. The char yield is satisfying and encouraging in terms of the potential commercial opportunity for coconut shell to be used as a feedstock to produce a substitute carbon black. The oil yield and gas yield are both beneficial so that further implications of these two by-products have great potential.

Table 4 summarizes the transmittance of toluene extract (T%), pH value, BET surface area, T-plot surface area, and acidic groups and basic groups on the surface of both commercial carbon black N772 and the pyrolytic coconut char filler.

Toluene transmittance correlates to the amount of tarry or leachable contents in the carbon black as the leachable and unburned tarry or oil-residues on the surface of carbon black or the char can be dissolved into it. This is very important for potential applications, since the presence of a high leachable (oily) content may cause contamination during processing into rubber or other applications and present problems in the appearance and performance of the final rubber products. According to **Table 4**, the toluene transmittance of char fill is 99.95; it

	T%	pH value	BET surface area (m^2/g)	T-plot surface area (m^2/g)	Acidic groups (mmol/g)	Basic groups (mmol/g)
Char filler	99.95	9.70	373.3	315.89	0.062	0.316
CB N772	65.9	8.5	28.5	26.6	0	0.079

Table 4. Characterization of char filler and carbon black N772.

shows that the filler is quite clean and pure with little surface contamination. However, the carbon black N772 only has 65.9% of the T%, which indicates that a significant amount of leachable components exists indicating a limiting effect on the purposes.

It is widely known that pores on the surface of solids are classified into three size ranges: micropores (<2 nm width), mesopores (<2–<50 nm with), and macropores (>50 nm width). Normally, if the pores (micropores and small mesopores) are significantly smaller than the very large rubber polymer chains, then the polymer molecules cannot access to these pores. Therefore, unlike micropores present in activated carbon, meso- and macropores may play the decisive role on the filler surface. From **Table 4**, the area of all pores on N772 is 28.5 m^2/g and the area of meso- and macropores is 26.6 m^2/g. The results indicate that meso- and macropores occupied most of the surface area of carbon black, which reaffirms previous statements about the importance of these pores in carbon black's application in the rubber industry. The BET surface area of the char filler is 373.31 m^2/g, whereas the t-plot surface area is 315.86 m^2/g, which follows the same trend with N772. Moreover, the surface areas are much greater than N772. These data further support the assertion that char samples can be used as an alternative rubber filler.

The pH value of the char surface has been recognized as a foundation of the reinforcing ability of the fillers. It is reported that basic materials may accelerate vulcanization reactions, while acidic ones may delay the vulcanization time of a rubber compound [17, 48]. According to the above, a solution pH value close to 9 makes N772 suitable filler for a wide range of application with reasonable vulcanization time and ideal amount of free radicals. The pH value of the char sample was close to 9, which also supports the proposition that coconut shell could be a promising feedstock for rubber fillers. The surface chemical groups on the surface of char filler are much more plentiful than the carbon black N772, which makes char surface more active resulting in a better interaction and reinforcement from coconut shell char.

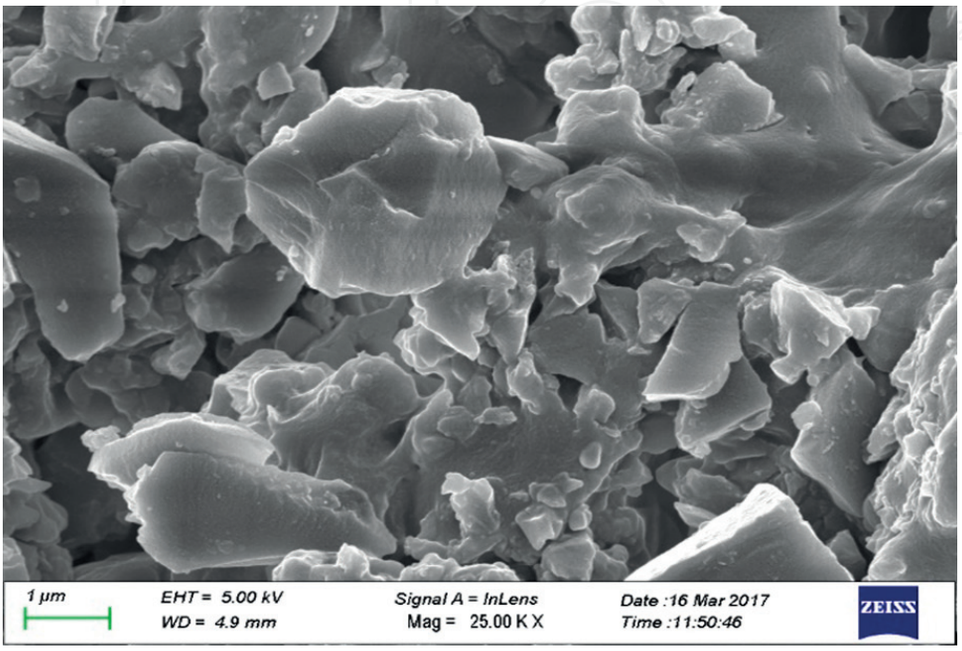
4.2. In-rubber characterization

The cure and physical properties of the rubber compounds filler with the two fillers assessed by the moving die rheometer (MDR) test are summarized in **Table 5**. At the beginning, a mixture is heated in the cavity of the rheometer under pressure. Then, the viscosity decreases

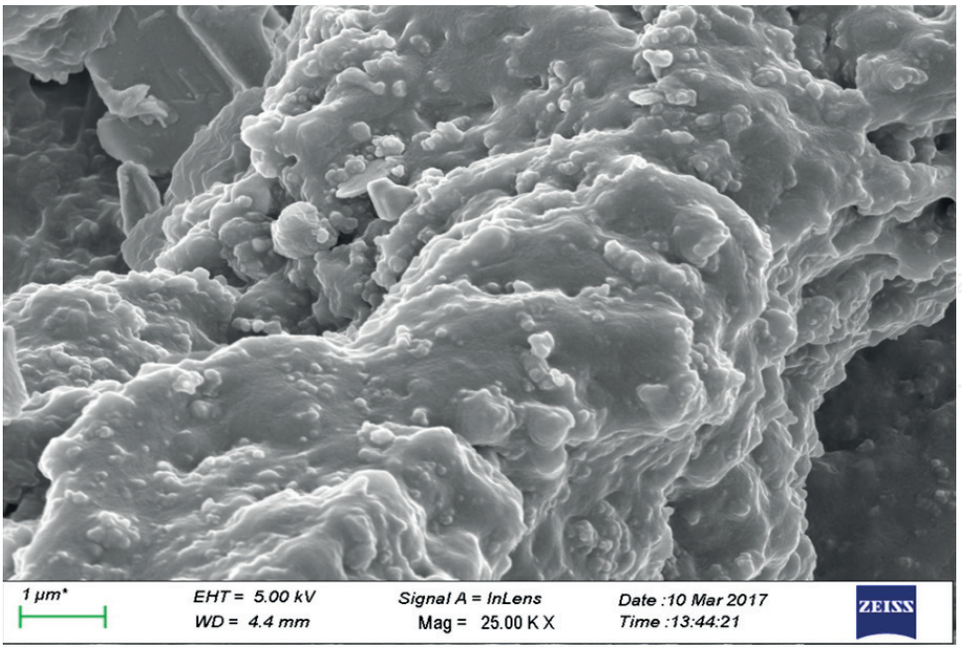
	Min (dNm)	Max (dNm)	Ts2 (mm:ss)	T90 (mm:ss)	Shore A (°)	M100% (Mpa)	M300% (Mpa)	Tensile strength (Mpa)	Elongation at break (%)
Char filler	1.16	14.42	7.04	13.48	59	1.99	2.82	5.68	653
CB N772	1.23	13.66	4.33	9.19	57	1.63	9.3	20.4	586

Table 5. Rheology and physical data of coconut shell char and N772.

and the torque exerted on the rotor drops. The lowest torque value is called moment lowest (ML), which can be used to study the stiffness of the uncured rubber compound at a given temperature, noted as "Min" in **Table 5**. After the curing process begins, the torque rises. When the torque increases 2 dNm unit above ML value, the time is recorded as Ts2. It tells about the moment the curing process actually starts. With the curing progressing, the torque



(a)



(b)

Figure 4. SEM plots of compounded rubber sheets at 25 K magnification, illustrating rubber-filler bonding system [11]. (a) SEM plot of Run 20 filled rubber sheet. (b) SEM plot of N660 filled rubber sheet.

http://dx.doi.org/10.5772/intechopen.79994

continues increasing. After some time, the torque reaches the maximum value and a plateau appears. The highest torque is regarded as moment highest (MH), also noted as "Max" in **Table 5**. The time from the beginning of the test to the point where 90% of the MH value attained is called T90. The hardness of the filled rubber compound is tested by the Shore A with degree unit according to the ASTM D2240 standard. The M100 and M300% are the stresses required to produce an elongation of 100 and 300% of the test sample. The maximum tensile stress recorded in extending the test piece to a breaking point is shown as tensile strength; and the elongation at break is the tensile strain in the test length at breaking point [11, 52].

According to **Table 5**, the time to onset of cure (Ts2) and cure times (T90) of the coconut char filled SBR were comparable but slightly longer than conventional carbon black N772. Different surface chemistry may be the reason, since it may have some interactions with the cure package. The hardness value was slightly high than N772, also indicating that coconut shell has the potential to be used as the parent material of rubber filler. The M100% values are found to be higher than the commercial carbon black. The low tensile strength and high elongation to break values imply that there are low filler-polymer interactions and structure levels, allowing for chain slippage over the filler surface, which can be enhanced through modification of the rubber mix formulation [9]. Based on this data, the sample can be considered as a semi- to low-reinforcing filler with broadly similar cure characteristics to conventional carbon black.

The SEM plots of coconut char compounded rubber sheet and N660 (which behaves better in the rubber matrix than N772) filled rubber sheet at 25 K magnification are shown in **Figure 4**. According to the images that base layer is the rubber matrix, the small particles on the surface are fillers (char filler and N660). It can be seen from the images, the fillers are unevenly attached to the surface of the rubber, indicating that the mechanism of the interaction between char filler and rubber is similar to conventional carbon black. Particle shapes, sizes, and its distribution are the main differences between coconut char and commercial carbon black. Smaller aggregate size and more uniform size distribution of carbon black plus spheroid particles may be helpful during the vulcanization process leading to good reinforcement.

5. Conclusion

Coconut shell, as a high-volume problematic waste material, has the potential to be successfully converted into a high-quality carbon black-like char filler, and high heat value, renewable energy materials (mainly oil and some gases) at relatively small scale. Thus, global fossil fuel-derived emissions can be reduced by the help of the ability of biochar to sequester the carbon contained in the coconut shell by conversion into a stable and nonavailable form. This type of process has been regarded as popular sector with growth potential in the global carbon market with a controllable, clean, and simple manufacturing process.

High external surface area values (315.89 m^2/g), along with high levels of purity (99.95%) and suitable surface pH (9.70), can be achieved by the coconut shell char filler. The char filler produced

was comparable on a physicochemical basis with the commercial semireinforcing carbon black N772. Since most of the performance testing of the rubber products was highly comparable, the semireinforcing carbon black can be partially replaced by the coconut char filler. If the level of filler-polymer interaction can be enhanced, while the current level of filler-filler interactions maintained, the char filler would have very interesting properties with regard to low energy losses, such as tire rolling resistance. Further surface modification for the char filler has been identified as a part of post-production process for further optimization, such as filler-rubber interaction. At the same time, since coconut shell char is a new type of rubber filler, the vulcanization and mixing process needs to be to be investigated for further improvement for short cure time and good tensile strength.

Acknowledgements

I would like to thank Imperial College London for the support of this research. I would like to express my gratitude to Dr. Geoff Fowler, Dr. Chris Norris, and the Avon Rubber (Artis UK) for their technical advice and help for rubber analysis. Finally, I would like to thank the Chinese Postdoctoral Science Foundation for the support.

Author details

Yiran Fan* and Geoff D. Fowler

*Address all correspondence to: yf612@mail.tsinghua.edu.cn

Department of Civil and Environmental Engineering, Imperial College London, UK

References

[1] Industry Experts. Carbon Black—A Global Market Overview. 2016. Available from: http://www.authorstream.com/Presentation/industryexperts-2711012-cp024-carbon-black-global-market-overview/ [Accessed: Jul 6, 2018]

[2] Chaudhary D, Jollands M, Cser F. Recycling rice hull ash: A filler material for polymeric composites? Advances in Polymer Technology. 2004;**23**(2):147-155. DOI: 10.1002/adv.20000

[3] Li Z, Zhang J, Chen S. Effects of carbon blacks with various structures on vulcanization and reinforcement of filled ethylene-propylene-diene rubber. Express Polymer Letters. 2008;**2**(10):695-704. DOI: 10.3144/expresspolymlett.2008.83

[4] Athanassiades E. Waste tyre pyrolysis: Sustainable recovery and reuse of a valuable resource [PhD thesis]. UK: Imperial College London; 2013

[5] International Energy Agency (IEA). Tracking Industrial Energy Efficiency and CO_2 Emissions. 2007. Available from: https://www.iea.org/publications/freepublications/publication/tracking_emissions.pdf [Accessed: Aug 3, 2017]

[6] Orion Engineered Carbons (OEC). What is Carbon Black. 2015. Available from: https://www.thecarycompany.com/media/pdf/specs/orion-what-is-carbon-black.pdf [Accessed: Jul 7, 2017]

[7] Donnet J, Bansal RC, Wang M-J. Carbon Black: Science and Technology. 2nd ed. (revised and expanded ed.) ed. New York: Dekker; 1993

[8] Maya KS. Studies on in situ precipitated silica filled rubber composites with special reference to NR, NBR and SBR [PhD thesis]. India: Cochin University of Science and Technology; 2007

[9] Fan Y, Fowler GD, Norris C. Potential of a pyrolytic coconut shell as a sustainable biofiller for styrene-butadiene rubber. Industrial and Engineering Chemistry Research. 2017; **56**(16):4779-4791. DOI: 10.1021/acs.iecr.7b00405

[10] Mark EJ, Erman B, Eirich FR. Science and Technology of Rubber. 3rd ed. San Diego; London: Elsevier Academic Press; 2005. p. 368. DOI: 10.1016/B978-0-12-464786-2.X5000-7

[11] Fan Y. The development of novel sustainable carbonaceous materials as substitutes for carbon black in rubber-based products [PhD thesis]. UK: Imperial College London; 2017

[12] Edwards D. Polymer-filler interactions in rubber reinforcement. Journal of Materials Science. 1990;**25**(10):4175-4185. DOI: 10.1007/BF00581070

[13] Gent AN, Tompkins DA. Nucleation and growth of gas bubbles in elastomers. Journal of Applied Physics. 1969;**40**(6):2520-2525. DOI: 10.1063/1.1658026

[14] Schmidt E. Effect of colloidal noncarbon pigments on elastomer properties. Industrial & Engineering Chemistry Research. 1951;**43**(3):679-683. DOI: 10.1021/ac5010794

[15] Jha V. Carbon black filler reinforcement of elastomers [PhD thesis]. UK: University of London; 2008

[16] Dannenberg EM. Molecular slippage mechanism of reinforcement. Transactions of the Institution of the Rubber Industry. 1966;**42**:26

[17] Boehm HP. Some aspects of the surface chemistry of carbon blacks and other carbons. Carbon. 1994;**32**(5):759-769. DOI: 10.1016/0008-6223(94)90031-0

[18] Mark EJ, Erman B, Roland CM. The Science and Technology of Rubber. 4th ed. Waltham: Academic Press; 2013

[19] Bueche F. Molecular basis for the mullins effect. Journal of Applied Polymer Science. 1960; **4**(10):107-114. DOI: 10.1002/app.1960.070041017

[20] Treloar LRG. The statistical length of paraffin molecules. Proceedings of the Physical Society. 1943;**55**(5):345-361

[21] Rivlin RS. In: Eirich FR, editor. Rheology. New York: Academic Press; 1956

[22] Mooney M. A theory of large elastic deformation. Journal of Applied Physics. 1940;**11**(9): 582-592. DOI: 10.1063/1.1712836

[23] Gent A, Hwang N. Internal failures in model elastomeric composites. Journal of Materials Science. 1990;**25**(12):4981-4986. DOI: 10.1007/BF00580117

[24] Guth E, Gold O. On the hydrodynamical theory of the viscosity of suspensions. Physical Review. 1938;**53**:322

[25] Guth E. Theory of Filler Reinforcement. Journal of Applied Physics. 1945;**16**(1):20-25. DOI: 10.1063/1.1707495

[26] Payne A. The dynamic properties of carbon black-loaded natural rubber vulcanizates. Part I. Journal of Applied Polymer Science. 1962;**6**(19):57-63. DOI: 10.1002/app.1962.070061906

[27] Mullins L, Tobin N. Stress softening in rubber vulcanizates. Part I. Use of a strain amplification factor to describe the elastic behavior of filler-reinforced vulcanized rubber. Journal of Applied Polymer Science. 1965;**9**(9):2993-3009. DOI: 10.1002/app.1965.070090906

[28] Blanchard A, Parkinson D. Breakage of carbon-rubber networks by applied stress. Industrial & Engineering Chemistry Research. 1952;**44**(4):799-812. DOI: 10.1021/acs.jpca.5b04889

[29] Blanchard AF, Parkinson D. Structures in rubber reinforced by carbon black. In: Second Rubber Technology Conference; Cambridge. New York: Rubber Age; 1948

[30] Bueche F. Mullins effect and rubber-filler interaction. Journal of Applied Polymer Science. 1961;**5**(15):271-281. DOI: 10.1002/app.1961.070051504

[31] Bueche F. In: Kraus G, editor. Reinforcement of Elastomer. New York: Wiley; 1965

[32] Intharapat P, Kongnoo A, Kateungngan K. The potential of chicken eggshell waste as a bio-filler filled epoxidized natural rubber (ENR) composite and its properties. Journal of Polymers and the Environment. 2013;**21**(1):245-258. DOI: 10.1007/s10924-012-0475-9

[33] Gopalan Nair K, Dufresne A. Crab shell chitin whisker reinforced natural rubber nanocomposites. 2. Mechanical behaviour. Biomacromolecules. 2003;**4**(3):666-674. DOI: 10.1021/bm0201284

[34] Dasgupta M, Kar S, Gupta SD, Mukhopadhyay R, Bandyopadhyay A. Effect of fly ash as filler in rubber—A comprehensive study of the vulcanisate properties of styrene butadiene rubber compounds. Progress in Rubber, Plastics and Recycling Technology. 2013; **29**(3):151-168

[35] Jong L. Effect of soy spent flakes and carbon black co-filler in rubber composites. Composites: Part A Applied Science and Manufacturing. 2007;**38**(2):252-264. DOI: 10.1016/j.compositesa.2006.05.003

[36] Setua D, Shukla M, Nigam V, Singh H, Mathur G. Lignin reinforced rubber composites. Polymer Composites. 2010;**21**(6):988-995. DOI: 10.1002/pc.10252

[37] Nashar D, Abd-El-Messieh S, Basta A. Newsprint paper waste as a fiber reinforcement in rubber composites. Journal of Applied Polymer Science. 2004;**91**(1):469-478. DOI: 10.1002/app.13726

[38] Ahmed K, Nizami SS, Raza NZ. Characteristics of natural rubber hybrid composites based on marble sludge/carbon black and marble sludge/rice husk derived silica. Journal of Industrial and Engineering Chemistry. 2012;**19**(4):1169-1176. DOI: 10.1016/j.jiec.2012.12.014

[39] Mohan DU, Pittman CH Jr, Steele P. Pyrolysis of wood/biomass for bio-oil: A critical review. Energy & Fuels. 2006;**20**(3):848-889. DOI: 10.1021/ef0502397

[40] Roy C, Unsworth J. Pilot plant demonstration of used tyres vacuum pyrolysis. In: Ferrero GL, Maniatis K, Buckens A, Bridgewater AV, editors. Pyrolysis and Gasification. London: Elsevier Applied Science; 1989. pp. 180-189

[41] Cunliffe AM, Williams PT. Properties of chars and activated carbons derived from the pyrolysis of used tyres. Environmental Technology. 1998;**19**(12):1177-1190. DOI: 10.1080/09593331908616778

[42] Environment Agency. Life cycle assessment of the management options for waste tyres. In: Environment Agency R&D Report Ref. No. P1 437/TR. Bristol: Environment Agency; 2004

[43] Sienkiewicz M, Kucinska-Lipka J, Janik H, Balas A. Progress in used tyres management in the European Union: A review. Waste Management. 2012;**32**(10):1742-1751. DOI: 10.1016/j.wasman.2012.05.010

[44] Miguel SG. Activated carbon produced by pyrolysis and physical activation of waste tyres [PhD Thesis]. UK: Imperial College London; 1999

[45] Retsch. 2017. Available from: http://www.retsch.com/products/milling/disc-mills/rs-200/function-features [Accessed: Jul 7, 2017]

[46] Gregg SJ, Sing KSW. Adsorption, Surface Area and Porosity. London: Academic Press; 1982. DOI: 10.1149/1.2426447

[47] Do D. Adsorption Analysis: Equilibria and Kinetics (Series on Chemical Engineering; v. 2). London: Imperial College Press; 1998. DOI: 10.1142/9781860943829

[48] ASTM. Standard D1618-99 Standard Test Methods for Carbon Black Extractables-Transmittance of Toluene Extract. West Conshohocken: ASTM International; 2004. DOI: 10.1520/D1618-99R04

[49] ASTM. Standard D1512-05 Standard Test Methods for Carbon Black—pH Value. West Conshohocken: ASTM International; 2012. DOI: 10.1520/D1512-05R12

[50] Goertzen SL, Thériault KD, Oickle AM, Tarasuk AC, Andreas HA. Standardization of the Boehm titration. Part I. CO_2 expulsion and endpoint determination. Carbon. 2010;**48**(4):1252-1261. DOI: 10.1016/j.carbon.2009.11.050

[51] Rodgers B, Waddell W. The science of rubber compounding. In: Mark JE, Erman B, Eirich FR. (eds). Science and Technology of Rubber. 3rd ed. Burlington: Elsevier Academic Press; 2005. pp. 401-454. ISBN: 0-12-464786-3

[52] Saville BP. Physical Testing of Textiles. The Netherlands: Elsevier; 1999. pp. 116-118

IntechOpen

IntechOpen