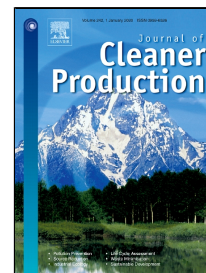


# Journal Pre-proof

The Past, Present and Future of Carbon Black as A Rubber Reinforcing Filler – A Review

Yiran Fan, Geoff D. Fowler, Ming Zhao



PII: S0959-6526(19)33985-X  
DOI: <https://doi.org/10.1016/j.jclepro.2019.119115>  
Reference: JCLP 119115  
To appear in: *Journal of Cleaner Production*  
Received Date: 18 June 2019  
Accepted Date: 30 October 2019

Please cite this article as: Yiran Fan, Geoff D. Fowler, Ming Zhao, The Past, Present and Future of Carbon Black as A Rubber Reinforcing Filler – A Review, *Journal of Cleaner Production* (2019), <https://doi.org/10.1016/j.jclepro.2019.119115>

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2019 Published by Elsevier.

Word count : 9468

# **The Past, Present and Future of Carbon Black as A Rubber Reinforcing Filler – A Review**

**Yiran Fan<sup>a,b</sup>, Geoff D. Fowler<sup>b</sup>, Ming Zhao<sup>a\*</sup>**

<sup>a</sup> School of Environment, Tsinghua University, Beijing, China, 100084  
yf612@mail.tsinghua.edu.cn,

<sup>b</sup> Department of Civil and Environmental Engineering, Imperial College London, SW7 2AZ

\*Corresponding author, ming.zhao@mail.tsinghua.edu.cn, 86-010-62784701

## **Abstract**

Carbon black is a reinforcing filler widely applied in the rubber elastomers manufacture. This review is focused on the development of the life cycle of carbon black. First, in order to assess the efficiency of final rubber performance, the critical physical and chemical properties of carbon black were evaluated. A short and clear illustration of mixing procedure has been discussed. Besides, a summary on eight mechanism theories of the rubber-char filler interaction have been listed, which is the first review summarize and compare the so far reinforcement mechanism theories of carbon black. New directions of the reinforcing mechanism research were raised. The production process of carbon black is not only energy-consuming, contributes to global CO<sub>2</sub> emissions significantly, but also utilizes non-renewable feedstock, making it unsustainable. The future of carbon black – the modification and the production of its substitutes from biomass and relevant materials were proposed.

**Key word: Carbon black, rubber filler, reinforcement, sustainable filler**

## 1. Introduction

Over the past century, the importance of natural rubber to human beings has been increasing continuously. According to the report from ANRPC (Association of Natural Rubber Producing Countries) in July 2019, the global consumption of rubber (both natural and synthetic) were 29.2 million tonnes in 2018 including 13.72 million tonnes of natural rubber. According to ANRPC report on July, 2018, the world natural rubber production is 7.37 million tons with 3.7% growth in the first seven months of 2018. The consumption of the natural rubber rose by 5.2%, and reached to 8.16 million in the first seven months. Rubber play an essential role in many industries (e.g. transportation, agriculture and home decorations). Natural rubber exhibits the advantages of high strength, great toughness and manufacturing versatility. Since some specific group of microorganisms in soil can decompose natural rubber spontaneously, the rubber products need to be used in their vulcanised forms to be resistant to natural degradation mechanisms (Ikram, 2002; Ali Shah et al., 2013). Therefore, engineers at rubber related industries are always working on improving rubber products.

At present, it is uncommon to use the rubber polymer in its natural unfilled state. Most of the engineering rubber has various range of particulate additives during manufacture, such as fillers and sulphur etc. The fillers are added for several purposes, such as reinforcing the elastomers, reducing the material cost and supporting the processing. As a result, the final rubber products can achieve longer lifetime, higher strength and more satisfied modulus of elasticity.

Carbon black is by far the most commonly applied reinforcing filler in rubber manufacture since the First World War. More than 92% of the worldwide production of carbon black is used

in the rubber manufacture, especially in tyre production, such as inner liners, sidewalls carcasses, air springs, belts, conveyor wheels and some vibration isolation devices etc. (ICBA, 2016; 2018). Currently, approximately 8.1 million metric tons of carbon black is produced worldwide, ranking top 50 industrial chemicals manufactured globally (ICBA, 2018). However, the manufacture of carbon black usually has a considerable carbon footprint. Consequently, as already stated by many authors, “green” fillers research has become more and more eye-catching, especially ones from potential recyclable waste materials and industrial/agriculture by-products, for example, peanut shell, rice husk and fly ash etc. (Sae-oui et al., 2009; Tharmaratnam, 2015; Snowdon et al., 2014; Riyajan, 2015; Jain & Tripathi, 2014). They will be explained in detail in Section 6. Therefore, by using these “green” filler, the burden of fossil fuel demand within carbon black manufacture can be significantly released and contouring less environmental impacts to the whole eco-system, so that achieving sustainable material basis.

In this article, the studies on alternative rubber reinforcing fillers and their reinforced rubber products are reviewed, the improvement of the elastomers are studied. Different alternative feedstock of rubber filler substitutes are discussed and the filler-rubber interaction system is suggested. Finally, the further research direction for understanding how the microscopic character is related to the system will be raised.

## 2. Method

The literature selection method has been presented in this section. The selection process consists of two steps: (1) Identifying the literature by searching for key words, such as carbon black, rubber reinforcing filler, reinforcement mechanism, etc.. (2) Extracting papers according to the review content plan. The data based used in the review are mainly includes Imperial

College London library resources, Web of Science, Scopus and Google Scholar. The time line of the literature are quite long, since the traditional theory can be date back to 1930s.

In order to select the relevant papers among the tremendous amount of identified literature, the order of the selection process are set as: (1) top journals, (2) journals with high impact factor, (3) published conference paper and presentation, (4) MSc and PhD dissertation from top ranking universities.

### **3. Carbon black**

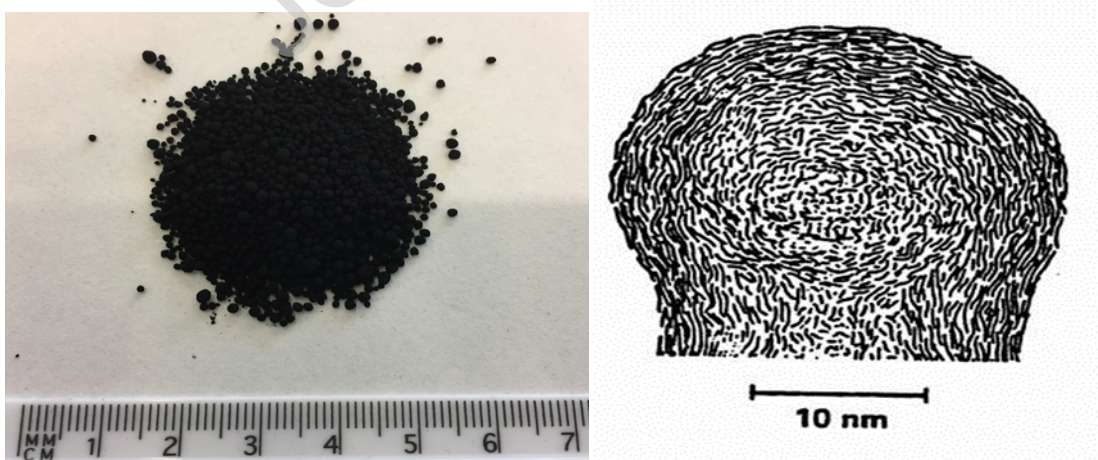
With the presence of carbon black, the physical properties, such as tear strength and tensile strength, of the given rubber compounds can be enhanced. Carbon black increases the hardness and viscosity of rubber-based compounds and is regarded as the most efficient additives among all filler materials (Chandrasekaran, 2010; Kato et al., 2018).

Thermal black, furnace black and channel black are the three main types of carbon black, which were named after their production processes. Furnace black is currently the most widely applied black occupying almost 95% of the total market, 70% of which is used in tyre manufacture and other related automotive products. Thermal black and channel black can only be added to limited types of rubber compound (e.g., fluorocarbon rubbers) with only a few grades, such as N880 and N990. There are two specialist carbon blacks: Lampblacks and acetylene black. Lampblack was invented by the Chinese for ink and lacquer formulations; whereas acetylene black is conductive and used for conducting rubber products (Kühner & Voll, 1993; ICBA, 2016). The carbon footprint for making carbon black is tremendous due to the partial combustion of heavy hydrocarbons. It is reported that in order to produce 1 tonne of

carbon black, 2.4 tonnes of carbon dioxide are calculated to be emitted comparing with 0.8 tonnes of carbon dioxide per tonne of cement during manufacture (IEA, 2007; Athanassiades, 2013).

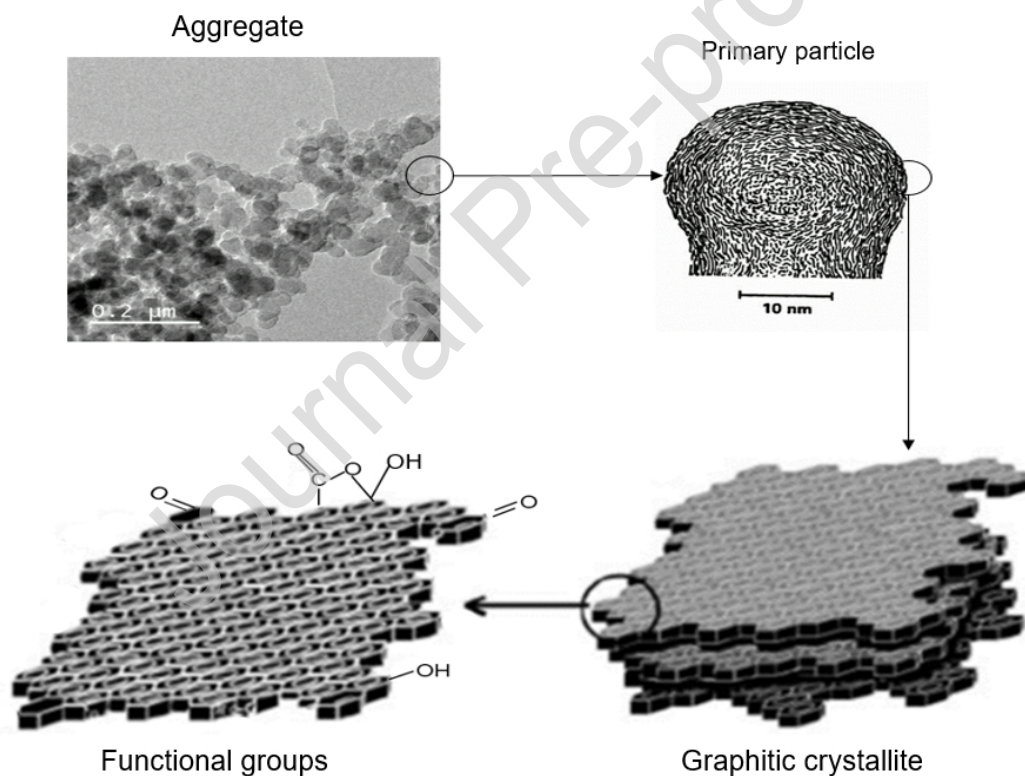
Carbon black consists more than 90% of pure form of elemental carbon, which is made up of tiny and mostly spherical carbon atoms fusing together in clusters referred to as aggregates. Several aggregates then group together as agglomerates which break up during rubber mixing period. In normal condition, the aggregates are regarded as the smallest working dispersible unit in the rubber matrix. As a result, aggregates are often considered as the actual reinforcing objects. The carbon black structure is defined as the types of aggregates (Donnet et al., 2005).

Normally, the diameter of carbon black particle vary from 10 nm to 500 nm. It is reported that larger particle size of carbon black leads to a more graphitic structure (OEC, 2015; Donnet et al., 2018). As observed by TEM, the structure of carbon black can be simplified as a partly graphitic onion-like structure (shown in Figure 1).



**Figure 1 Carbon black and its onion-like structure (after Fan, 2017)**

Moreover, the outer layers show more graphitic structure than those in the centre. At high magnification, the carbon atoms in the aggregates can be seen in overlapping graphitic layers that locally present a quasi-crystalline turbostratic structure with an approximately 0.35 nm interlayer spacing. According to Wang et al., 2000, the graphitic edge of each carbon layer can be regarded as the reactive point of the carbon black since the chemically reactive functional groups can be inferred attached to the edge. It is believed that the higher the structure, the more spherical particles are present in an aggregate, as shown in Figure 2. The greater the number of particles in an aggregate, the larger will be the volume within it that is not accessible to rubber molecules (Quan et al., 2018).



**Figure 2 Carbon black aggregates and particle structure (after Fan, 2017; Wang et al., 2000)**

A variety of characteristics of carbon black contribute to the degree of the reinforcing performance. The microstructure, particle size and the morphology of aggregates are regarded

as the key properties, which have influence on the interaction between carbon black and elastomers. Meanwhile, it is also critical to understand the properties of the carbon black surface, such as the chemical composition, structure and porosity. The lower limit of the surface area for the significant reinforcement performance is  $6 \text{ m}^2/\text{cm}^3$  (a  $1 \text{ }\mu\text{m}$  diameter spherical particle). The largest surface area can reach  $400 \text{ m}^2/\text{cm}^3$  resulting in a high processability of the unvulcanised mix and dispersibility. (Maya, 2007, Fan, 2017).

#### (1) Particle and Aggregate Size

Recently, particle size and distribution are still considered as the most fundamental physical properties for the reinforcement capacity of carbon black. This is the reason why particulate fillers obtained directly from grinding of minerals or by simple precipitation are often classified as non-reinforcing fillers due to their large particle size. Normally, the non-reinforcing fillers applied only bring a slight improvement in modulus and a sharp drop in break properties (Mark et al., 2005).

In the rubber – carbon black system, the aggregates of carbon black particles are regarded as a working unit. Even though the reinforcement capacity of carbon black is not determined by the aggregates but each individual particle in it. As the particle size decreases, the dispersion ability of carbon black in rubber compounds can be improved, so that the interface extension is enhanced and consequently leading to a better reinforcing performance (Donnet et al., 1993; 2005).

The fundamental particle size and its distribution of carbon black can be estimated by several instrumental methods, such as X-ray diffraction (XRD), atomic force microscopy, Scanning



tunnelling microscopy (STM) and transmission electron microscopy (TEM). Recently, Scanning Electron Microscope (SEM) has become the most popular method used for estimating carbon black primary particle size distribution. As to the size of individual carbon black particles, the use of TEM image is necessary for visualising particle aggregates (Donnet et al., 2018). The N<sub>2</sub> adsorption based on the BET (Brunauer, Emmett, and Teller) method can be also used to evaluate the surface area of carbon black since its particle can be regarded as truly spheroidal (Gregg & Sing, 1982).

The particle size of several widely used carbon blacks can be seen from Table 1. Based on ASTM D 1765-17 standard, the letter N of ASTM number refers to the ‘normal curing’ furnace and thermal blacks. The first number of the three-digit suffix defines the different level of carbon blacks, which is basically effected by the particles size and the degree of surface oxidation (related to the cure time during the vulcanation). The remained two number are given randomly (Wampler et al., 2004).

**Table 1 Mean particle size of typical carbon blacks**

ASTM number	Mean particle diameter (nm)	Name
N110	18	Super Abrasion Furnace
N121	19	
N220	21	Intermediate SAF
N234	20	
N330	30	High Abrasion Furnace
N339	26	
N472	21	Special Conductive Furnace
N550	56	Fast Extruding Furnace
N660	67	General Purpose Furnace
N774	79	Semi-Reinforcing Furnace-High Structure
N990	285	Medium Thermal

## (2) Surface area

Surface area is an essential morphological characteristic for the reinforcing capacity of carbon black since it indicates the extension of the interface such as the availability of the surface for the crosslink between rubber chain and carbon black. The result of surface area may help to not only tell how much of the area that can be by rubber into the carbon black, but also provide the data of porosity issue of carbon black particulates. Since the size of rubber chains is normally close to macro-pore size. In other words, if the pore size on the carbon black surface is far below the macro-pore level, the large rubber molecules cannot access the pores. As a result, unlike activated carbon, micro-pore may not improve the crystallization ability under large strain (Wang et al., 2018).

There are three main tools being widely used for the examination of a carbon black's surface area.

### I. Nitrogen Adsorption (BET Method)

BET method was established by Brunauer, Emmett, and Teller in 1938 (Gregg & Sing, 1982; Brunauer et al., 1938), which is the most widely used measurement for the surface examination of carbon black. According to the ASTM standard, both total and internal surface area and pore size distribution can be identified through measuring nitrogen adsorption and desorption at 77K and partial pressure. Additionally, the external surface area (meso & micro pores) which essentially support the crosslink between carbon black and rubber polymer can be calculated through statistical thickness method (Lippens & Boer, 1965; Zhou et al., 2018). The surface area of the filler is determined by the BET Equation:

$$S_{BET} = V_m \times N \times a_m \times 10^{-18}$$

Where  $V_m$  = volume of adsorbed monolayer;  $N$  = Avogadro constant ( $\approx 6.022 \times 10^{23}/\text{mol}$ ) and  $a_m = 0.162 \text{ nm}^2$  (molecular surface area for  $N_2$  at 77 K).

As mentioned before, since the shape of carbon black particles can be assumed to be spheroidal, the average particle diameter can be evaluated from the surface area result.

## II. Iodine Adsorption

It has been confirmed that the result of iodine adsorption method are generally correlated well with BET method. During this process, a unit weight of carbon black firstly mix with a portion of standard iodine solution. Then the standard sodium thiosulfate solution is used to titrate the excess iodine. The final adsorption number is related to the surface area of carbon black. The iodine adsorption numbers of the commercial reinforcing carbon blacks are typically in the 70-160 mg/g range whilst semi-reinforcing blacks are in the 30-45 mg/g range. It is noted that the surface area of the filler can be influenced by pores, volatiles and sometimes the aging (Mark et al., 2013).

## III. Cetyltrimethylammonium Bromide (CTAB) Adsorption

The CTAB adsorption method is thought to be more accurate than the two methods described above since it is not only less influenced by the chemical nature of carbon blacks, but also less sensitive to the particle pores. The testing procedure is quite similar to the other two methods. The foundation of this adsorption is the stoichiometric reaction between polyanion and polycation. A streaming current detector is used for an applicable measure of the charge neutralization. The surface area result can be determined according to the difference between the initial concentration and the residual concentration after the equilibrium reached.

Nowadays, a similar but more advanced procedure has been suggested by Lamond and Gillingham and published in ASTM D3765 - 04. Commercial reinforcing carbon blacks have CTAB values in the 80-140 m<sup>2</sup>/g range, whilst semi-reinforcing grades are in the range 30-45 m<sup>2</sup>/g (Bele et al., 1998).

### (3) Structure

Understanding the structure of carbon black is crucial, since it can help to identify the real volume of the filler works in the rubber-filler system and the level of strain amplification of the deformable phase. Primary and secondary structure are two expressions widely used to describe the inner-structure of carbon black. The degree to how the carbon particles join together as aggregate is illustrated by primary structure. Besides, the secondary structure is defined as the agglomeration of aggregates due to Van der Waals force. It has been reported that the secondary structure is weaker than the primary structure. Most of the agglomeration (secondary structure) would be diminished and much of it is lost during the pelletisation process providing minor effects. On the contrast, primary structure is considered to contribute relatively most of the structure-related within the crosslink system. Higher structure of the carbon black will lead to more irregular shape of aggregates with better dispersion capacity imparted (Blow, 1975).

According to ASTM D 2412-16e1, the structure of the per unit weight of carbon black can be determined by evaluating the total volume of space between the carbon aggregates using dibutyl phthalate (DBP). The absorptometer is the main instrument applied in this standard. During adding DBP, the carbon black powder changes to a semi-liquid mass with an increasing torque. After all the spaces are filled, the whole mass would stiffen up, while the machine is set to turn off at this point and the DBP adsorption is recorded as cm<sup>3</sup> /100 g of black. Normally,

low structure blacks have the values in the range 60-80 ml/100 g, with high structure types in excess of 120 ml/100 g (ASTM, 2016; Loaman, 1998).

#### (4) Surface chemistry of carbon black

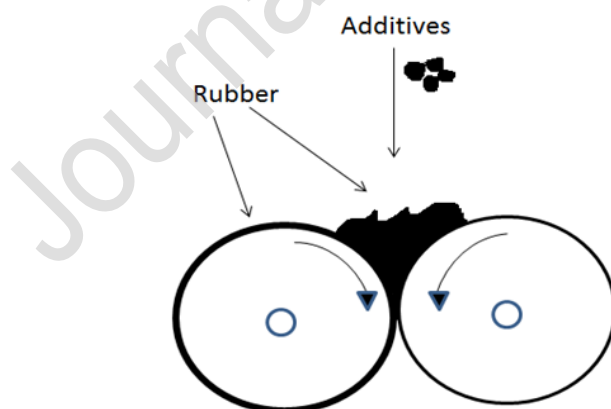
In terms of the reinforcing mechanism of carbon black, high surface area may contribute a good reinforcing ability. Moreover, the structure and the surface chemistry of the blacks may also be important. Carbon black is consisted of over 90% elemental carbon. If the carbon atom is an integral part of the stable layer plane, then it is relative unreactive. However, when there is H atom or a resonance-stabilised free radical crosslink on the edge position of the carbon atoms, they may become very reactive. The H atom is provided by the original hydrocarbon feedstock of carbon black and attached to its surface. Besides H, several evidences have confirmed the existence of four general oxygen-containing chemical groups on carbon black surface: lactones, phenolic, carboxylic and ketonic (Wampler et al., 2004; Lin, 2002; Boehm, 1994). Such chemical groups are considered to be essential during the curing time in many vulcanizing system. A few amount of sulphur may also be contained in the carbon black, due to the characteristic of its feedstock. Additionally, a large percent of sulphur is regarded to be inert for the crosslink of rubber, since it is chemically combined.

The “Boehm titration” method is usually considered to be a very popular wet chemical method for the study of oxygen surface groups on carbon materials (Goertzen et al., 2010). Different acidities of chemical groups on the carbon surface are the criteria of this titration method, since bases with different strengths can help to identify the oxygen groups. Particularly, NaOH as the strongest base reacts with almost all Brønsted acids (including phenols, lactonic groups and carboxylic acids). Besides, sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) would neutralize carboxylic and lactonic groups (e.g. lactone and lactol rings). Finally, sodium bicarbonate ( $\text{NaHCO}_3$ ) can only

neutralize carboxylic acids. By the help of this difference, the oxygen groups on the carbon black can be classified and quantified (Tsecansky & Graber, 2014).

#### 4. Rubber and carbon black mixing process

The calender and two-roll mill are the most fundamental facility used in every rubber-additives mixing process (Wang et al., 2018). The additives and rubber can achieve a good mixture situation within this equipment. Both of the two kinds of machine share similar mechanism (Figure 3). The two horizontally opposed rollers rotate at slight different speed in opposite directions. Since the right roller rotates slower than the left one, the rubber will be sheared and bulk up in the nip. That is why the rubber will attach on the left roller subsequently. The rubber is masticated by the shearing force between the two rollers, and any additives required for the rubber products can be added in between the rollers. The additives then would finely distribute throughout the mixture.



**Figure 3 Diagram of mastication and the addition of additives**

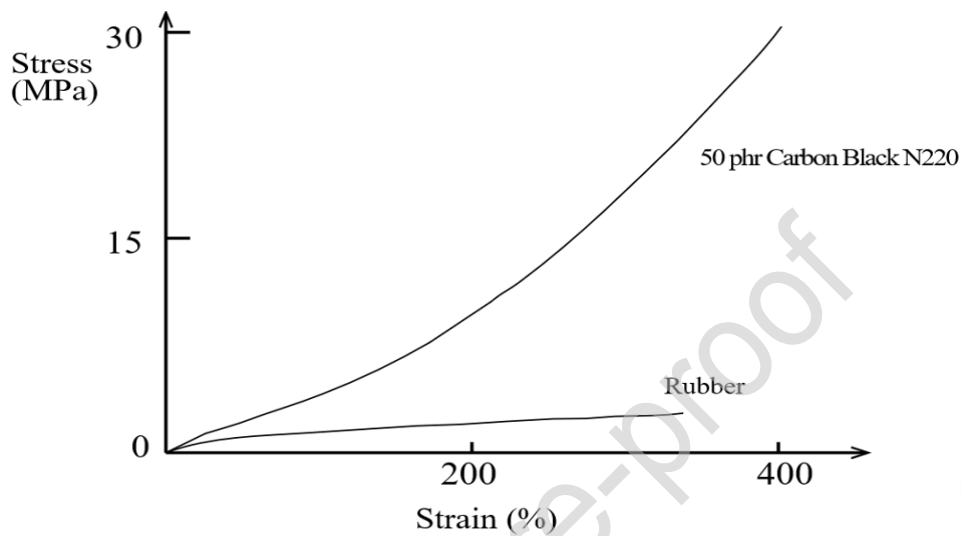
In 1916 Fernley Banbury developed the open-to-air mill to more compact equipment named ‘Banbury’ mixer, which is still popular mixer for rubber matrix all over the world today. The

upgrade facility offers a cleaner working environment with less time and power consumed. Despite some refinements such as temperature controller for rollers, the safety modification and modern-looking cover, the basic principal of both the calender and two-roll mill remain the same as 150 years ago (Sridharan et al., 2018).

## **5. Outstanding issue – Reinforcement mechanism study**

The studies of the reinforcement mechanism of carbon black can be dated back to 1960s. However, the knowledge of its mechanism still remains fragmentary today. In most cases, the vulcanization process can only yield springy materials with elastic properties but less strength. By the present of the reinforcing fillers, the strength feature can be introduced to the polymer system. In terms of ‘reinforcement’, it conveys a range of different meaning when applied to different matrices and application, such as thermosets, thermoplastics, or elastomers. Normally, the partially replacement of the deformable matrix (e.g. thermosets, thermoplastics, etc.) by particulate fillers would decrease the matrix deformability. While the situation is very different when reinforcing fillers are added into the elastomers, as the fillers increase modulus and deformation of the elastomers at break simultaneously. There are several changes occur after fillers added to the vulcanization system: (i) an increase in modulus, or stress at a particular strain; (ii) an increase in elongation at break for vulcanizates having a given degree of cross-linking; and (iii) consequently, an increase in tensile strength. The increase in stiffness and the improvement of the tear resistance, tensile strength and abrasion resistance are regarded as the key standards for reinforcing ability evaluation (Fan, 2017). Even though this attractive paradox has not been fully understood by scientists, they share a common view about the contribution to the stress-strain behaviour of filled vulcanizates from fillers. The reinforcing ability of a filler is shown in Figure 4, where two SBR vulcanizates are compared, the only

difference between them is the presence or absence of 50 phr carbon black N220 in the rubber recipe. The formulation of the SBR (Styrene-Butadiene Rubber) can be seen in Table 2. According to the stress-strain curve, there is a sharp rise almost ten-fold than the unfilled rubber with the addition of carbon black N220 (Huang et al., 2018; Mark et al., 2005).



**Figure 4 Comparing between filled and unfilled rubber matrix (after Edwards, 1990)**

**Table 2 SBR (Styrene-Butadiene Rubber) Formulation**

SBR (Styrene-Butadiene Rubber) Formulation	
SBR 1502	100phr
Zinc Oxide	3phr
Stearic Acid	1.5phr
Santoflex 13	0.5phr
Santoflex 77	0.5phr
Sundex 8125	3phr
accelerator DPG	0.3phr
Santousure NS	1.2phr
Sulphur	2phr
(Carbon Black N220)	50phr
Press cure: 40 min at 153°C	

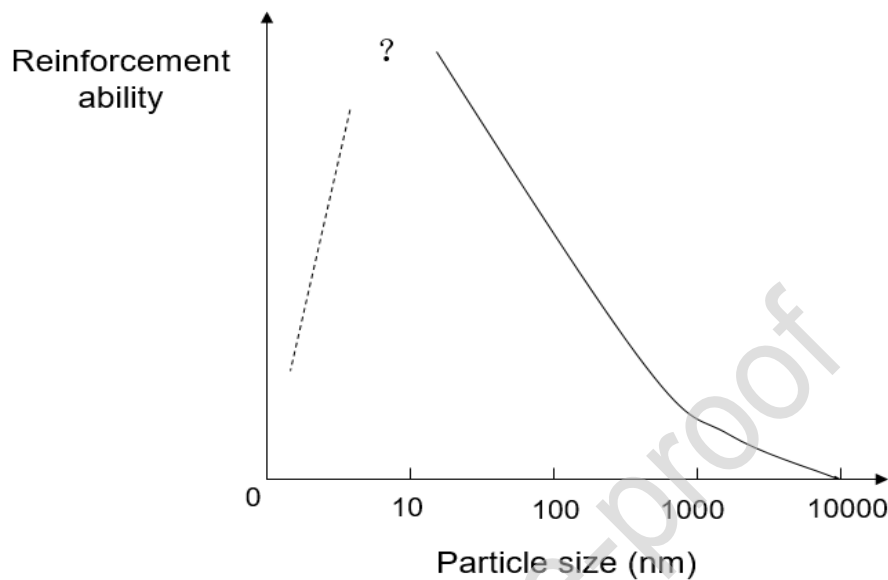


The reinforcement property of fillers has been a hot topic of a very large body of literatures for several decades. So far eight theories have been applied to illustrate reinforcement mechanism. According to much research on carbon black reinforcement mechanism, there are three postulations which have gained most of the agreement: (1) particle size, (2) slippage at interface and (3) chemical reaction.

#### (1) Particle size

It has been reported that almost all the material that have been proved to have reinforcement effects have a common properties of extremely small particle size, even though they may represent different characteristics of their surface. Therefore, several researchers summarized that the particle size has a significant influence to the reinforcement mechanism. They even pointed out a hypothesis that reinforcement in rubber compound can be achieved by any finely divided solid material dispersing within polymeric matrix. Schmidt (1951) who investigated the strong reinforcing effects in SBR filled with colloidal stannic oxide, silica, Prussian Blue, polystyrene and casein, concluded that *“small particle size of the pigment is of prime importance in elastomer reinforcement, whereas the chemical nature of the pigment appears to be of secondary importance”* (Edwards, 1990; Fan, 2017). Additionally, carbon blacks obviously follow this rule. It is widely known that as the grade of black is above N330 (whose particle diameter is above 300 nm), the blacks are named as “semi-reinforcing”. Then with the particle diameter decreases, the reinforcing ability of carbon blacks is improving. After the diameters drop below 35 nm, the blacks can be grouped as “super-abrasion” grades. Gent and Tompkins (1969) have found that the smaller size a gas bubble has, the larger pressure will be needed to maintain the bubble shape. They also suggested that this conclusion may relates to the relation between the rubber matrix and carbon black behaviour. In the carbon black aspect, the gas bubble in the hypothesis is replaced by solid carbon black particles. However, how will the reinforcement property change when the diameter region below 10 nm remains unexplored.

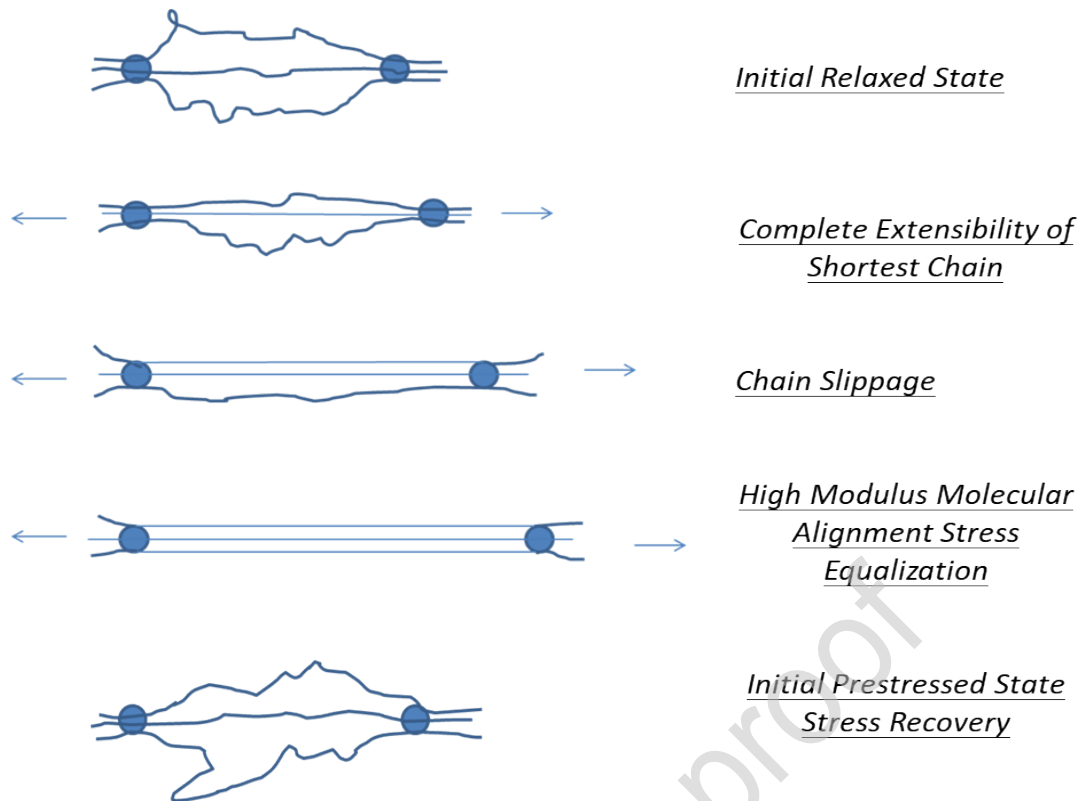
It is predicted that the carbon black may be more like to a molecular solution below one particular point. Thus, the best particle size is suggested to be worked out. Figure 5 illustrates this question schematically.



**Figure 5 The effect of carbon black particle size on reinforcing ability (after Edwards, 1990)**

## (2) Slippage at interface

In the early 1980s, the interface slippage postulation was raised by Danneberg (1966). By the slippage on the rubber chain and carbon black interface, the stress can be redistributed. Furthermore, the molecular rupture can be prevented. It has been also stated by Danneberg that, the friction heat generated during the slippage is essential for releasing the strain energy, which helps to prevent matrix breaking up (Jha, 2008). Figure 6 shows the proposed phenomenon in the reinforcing system under strain

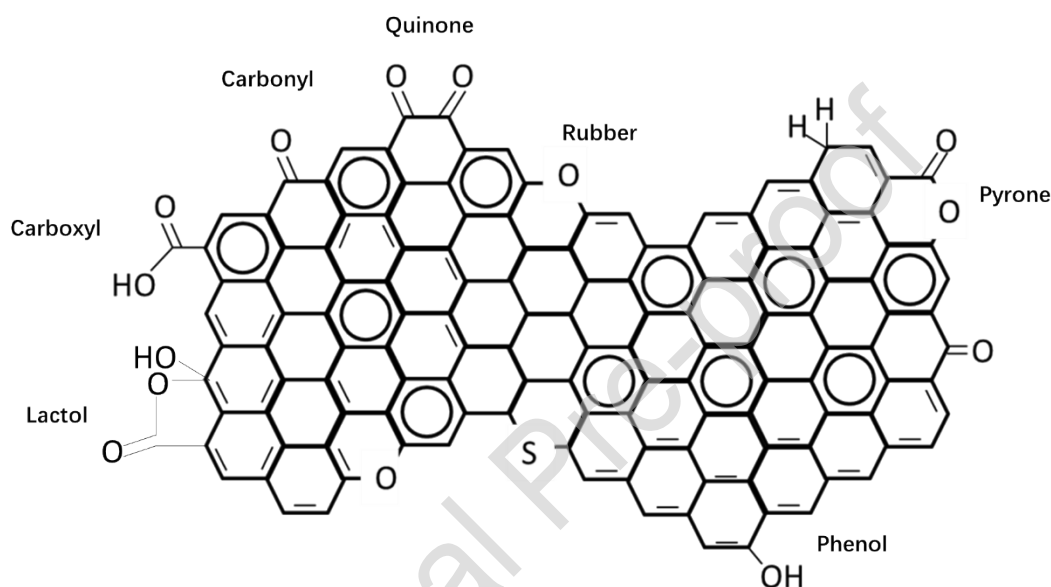


**Figure 6 Slippage phenomenon in the microstructure of the reinforcing system under strain (after Dannenberg, 1966)**

### (3) Chemical reaction on surface

A lot of functional groups can be found on the carbon black surface. They are believed to support several inter- and intra-molecular interaction, mainly including acid-base reaction and hydrogen bonding. Dating back to 1960s, H.P. Boehm (1994) has already characterized the oxygenated functional groups on the carbon surface. From that time, some researchers started to believe that the crosslink at the interface of carbon black and rubber molecule was the result of chemical reactions between the acidic groups on the carbon black surface and the basic moieties within the rubber matrix. In order to prove this mechanism, scientists once removed the reaction sites from carbon black and observe the change of the rubber product. As postulated before, the modulus and abrasion resistance have witnessed a large deduction. Strong chemical bonding is reported to contribute to two different aspects: first, it can help to

make the filler agglomerates break up in the mixing step, and prevent the particle re-agglomeration. Besides, it has some advantage for the physical properties, like modulus and resilience, etc. during the vulcanization process. According to the above, the rubber researchers have kept working on the development of the crosslinking process during vulcanization step. Some typical functional groups found on the carbon black surface have been identified in Figure 7 (Bueche, 1960; 1961; 1965; Nagornaya et al., 2016 ).



**Figure 7 Functional groups on carbon black surface (after Bueche, 1960)**

In addition, not only chemical functional groups can help the crosslink, a large amount of reactive carbon double bond have been observed on the black surface by STM (Scanning Tunnelling Microscope) at the same time. As studied by Medalia and Kraus (1994), the chemical bond between rubber matrix and carbon black can be generated by the reaction of such double bonds and sulfur, olefins and radicals. However, the number of these bonds still can not be illustrated quantitatively until now. Based on huge number of literatures, there must be a correlation between hydrogen content of carbon black, which is determined by isotopic exchange, and their reinforcement capacity (Mark et al., 2005).

Even though, several lines of evidence suggested that strong polymer-filler bonding are not always necessary or desirable in some cases. The polymer/filler slippage can occur on most of the interfacial area with only minor bonding under stress. Meanwhile, the timing of bonding also has effect on the final rubber compound. If the bonding is introduced to the mixture before vulcanization, the network between carbon black and rubber may be over-developed and lead the whole system difficult to process. If excessive bonding happens during vulcanization, it may cause the extreme condition that the polymer connect to the filler would become totally immobile. And furthermore, result in a tremendous decrease in extensibility (Mark et al., 2013). The remaining five relatively less supported theories are list in Table 3.

**Table 3 Theories on filled elastomer**

Theories on filled elastomer	Summary	Reference
<b>Stored energy function</b>	The relationship between stress and strain is studied through thermodynamic concepts.	Treloar, 1943
		Mooney, 1940
	The extension of the molecular chains will lead to order or disorder system.	Rivlin, 1956
		Gent, 1969
<b>Hydrodynamic Theory</b>	Rigid fillers increase the stiffness and lead to large local strains.	Guth & Gold, 1938
		Guth, 1945
		Payne, 1962
<b>Strain Amplification</b>	Hydrodynamic model at high strains.	Mullins & Tobin, 1965
		Blanchard & Parkinson, 1948
		Bueche, 1960
<b>Model of weak and strong linkage</b>	Linkages are generated between filler and rubber.	Blanchard & Parkinson, 1948; 1952
	Weak linkages can be broken contributing to softening.	
<b>The Bueche model</b>	Molecular network chains are within a filled rubber.	Bueche, 1961; 1965
		Nagornaya et al., 2016

However, none of these postulations gains common recognition and acceptance among researchers. The polymer-filler bonding issue remains one of the most controversial topic of the reinforcing system. It can be concluded that the present reinforcement mechanisms of the carbon black raised by different studies tend to be based on a single point of view. For example, the particle size and interface slippage theory consider more on physical forces, whereas the functional groups postulation is based on the chemical reaction aspects. The rubber-filler reinforcing system need to be considered as an integral whole. Physical, chemical, dynamical and even thermal parameters have to be studied in the same time. Furthermore, it is also difficult to exam the vulcanized products so as to identify the rubber-filler interface under their service condition. Upon the practical point of view, the fluorescence microscopy and atomic force microscopy can be applied to observed the transformation of the filled rubber aggregates under working condition with different surrounding atmosphere. 3D-TEM may also help to quantitatively identify the relationship with the mechanical properties of the carbon black-filled rubber elastomers (Kato et al., 2018).

## 6. New Horizon

Despite more than a century that carbon black industry has existed, there are still a number of chances to improve carbon black for certain application. Carbon black with better behaviours and from different alternative ‘green’ feedstock has recently been paid increasing attentions.

### (1) Surface modification

Since the surface is one of the most important features of carbon black and for the interaction between blacks and rubber compound, suitable modification of the surface chemistry has been investigated for decades. Given the presence of the surface reactive functional groups, total

surface area and surface activity of carbon black are often recognized as the modification targets. Nowadays, carbon black manufactures and researcher are making progress on improving the morphology of the carbon structure, enhance the crystalline site and the stress oriented active plane so as to obtain better vulcanizate properties.

Aromatic polyhydroxy compounds has selected as the modifier for carbon black in natural rubber by Chakraborty's group (Ganguly et al., 2003; 2005). The rubber filled with the treated carbon black results in higher modulus, heat build-up, hysteresis loss and several dynamic properties. The improvement can be attributed to a high charge density in surface, supplied by the proportion and nature of surface functional groups present on the surface of modified blacks. As a result, some form of higher crosslink density can establish. In addition, the fact that the higher stress induced crystallization due to interactive sites may also contribute to the system. The formations of crosslink density and the compactness of crystal structure are reported to increase the heat build-up properties. Usually a more ordered crystalized structure results in stronger bond formation. The  $-OH$  group in aromatic linkages can help increase its degree of nucleophilicity, which in turn improve linkages between polymer and filler surface. According to the results of secondary ion mass spectroscopy (SIMS) on dry carbon black, the complex hydrocarbon structures are suitable for chemical reactivity on the surface. These complex structures present at the edges of the graphite-like layers providing an environment suitable for chemical reactivity. Furthermore, a considerable amount of hydrogen can be observed on the surface as complex hydrocarbon structure, which supports the importance of hydrogen to the surface activity of carbon blacks. The concentration of hydrogen ion introduced by the surface modifiers is much higher than original carbon black.

The development of polar basic (KOH) and nonpolar ( $C_6H_6$ ) chemical surface modification procedures and consequently mechanical properties of the filled rubber polymer have been investigated by Park's group (Park & Kim, 2000; Park et al., 2002). According to their result, the two modification methods do result in a considerable improvement of the nonpolar characteristics of carbon black surface. It is believed by Park et al. (2002) that both the stable microstructures and the functional groups of the nanostructured surface of carbon black are enhanced by the chemical modification. The filled rubber products show better cure behaviours, tensile stress, and dynamic mechanical properties than virgin carbon black filled rubber. It is noted that the degree of adhesion between the carbon black and rubber is essential for the increase of hardness, modulus, and tensile strength carbon black-filled rubber composites. It can be interpreted as the active functional groups, surface energy, and energetically different crystallite faces of the filler surface can be regarded as the foundation of the reinforcing system.

For the primary modified carbon black, the enhancement of the dispersion ability of carbon black aggregates during the vulcanization process is possibly attributed to high surface roughness (specific surface area) and the chemical erosion on the surface. At the same time, the increasing amount of basic functional groups can be observed from the carbon black surface edges. As to the nonpolar modified carbon black, the improvement for the final rubber products can be regarded as the result of the increasing of surface aromatic nonpolar functional groups and the improvement of both the viscosity and the crosslinking density (Park et al., 2002).

Carbon black having surface modified by vegetable oil filled rubber usually have high tensile elongation and strength properties, but low abrasion and hardness compared with commercial carbon blacks filled ones. It is reported that si-69 modified carbon black can introduce higher



hysteresis and improved abrasion resistance at a large range of temperatures in the reinforcing system. Same enhancement can also be achieved by modifying carbon black with aliphatic dihydric and trihydric alcohol. Surface modification with a phenolic plant product provides carbon black a higher flex crack growth resistance. Some researches proved that diazonium salt modification is a very popular and efficient way in rubber and plastic application (Ganguly et al., 2003; 2005).

## (2) Carbon black substitute and alternative feedstock

Given the higher demand of rubber quality and the increasing price of the raw rubber and other component ingredients, the rubber industry has made a lot of efforts to limit the cost as well as increase competitiveness.

There are several concerns about the conventional petroleum based carbon black feedstock. On one hand, the price of hydrocarbon oil see a gradually increase very year. As Cooper Tires Company suggests, carbon black oil is now the largest expense in the production of carbon black nowadays. The feedstock cost accounts for 30-35% of the total carbon black sale price. Take tyre production as an example, the population of world vehicle was 1.0 billion in 2010; and it is believed that the number will reach 2.5 billion by 2050 (Andrews, 2014). The consumption of carbon black will be immeasurable since at least 30% of the tyre is contributed by carbon black.

On the other hand, due to the nondegradability of the petroleum based carbon black feedstock, it may cause severe environmental problems. The environmental conservation is a permanent issues, a lot of research are being undertaken with the aim to reduce the dependence of carbon black feedstock on fossil fuel and transform to sustainable material basis. Recently, there is a

newfound interest in filler in industry from biodegradable feedstock, which has potential “recyclability”, so that the conventional crude oil can be replaced. When considering the new feedstock selection, the recyclability and utilization has become a major driving factor, as well as low cost and abundant availability. Therefore, biobased biodegradable composites have become the next generation feedstock in carbon black industry. The new generation of carbon black feedstock consists of natural sources (e.g., natural fibers), industrial by-products (e.g., saw dust, rice husk), and even industrial waste material (e.g., rice husk ash). Since the application of these materials can help to change the rejects into no damage or even valuable material, this concept of study has become more and more attractive from either ecological or economic point of view (Intharapat et al., 2013; Gopalan & Dufresne, 2003).

#### I. Rice husk ash

Rice husk ash (RHA), considered as an industrial waste material, is the residue from rice husk burned for electrical power. RHA is a material with tough, woody and abrasive characteristics along with a high silica content, so that make its disposal neither easy nor safe. Given that the main components of rice husk as is amorphous silica and residual carbon black, rice husk ash has already attracted increasing attention (Chaudhary et al., 2004). Arayaprane et al. (2005) studied the quality of the rice husk filled rubber composites, and compared it with other two commercial reinforcing fillers, Hi-Sil 233s silica and carbon black N330. Their observation indicates that the incorporation of RHA filler loading from 0 to 40 phr can help provide high hardness but low tear and tensile strength, the viscosity and cure time of the RHA filler rubber also drop. Only a better resilience property is observed in the product than silica or carbon black filled ones. No significant change appears in Young’s modulus and abrasion loss etc. According to the scanning electron micrographs, the dispersion of RHA filler in the crosslink system is not continuous ending up with a relatively weak structure than carbon black and silica. Sea-oui and co-workers (2002) got similar conclusion as well. The inferior mechanical

characteristics given by RHA have been confirmed, such as abrasion resistance, hardness, modulus, tensile and tear strength, regardless of the carbon content. Costa et al. (2000; 2002) tested properties of rubber filled with 20 phr milled rice husk, which only shows slightly inferior to the commercial carbon black and silica filled polymer in physical properties aspects, except for abrasion resistance. The incorporation of RHA into polypropylene was tested by Faud's group (1995), and an increased flexural modulus of the composites was obtained. Meanwhile, elongation at break, tensile strength and Izod impact strength (impact resistance of materials) saw a decrease (Crompton, 2012). According to results above, it can be indicated that rice husk ash can be applied as a low-cost filler in rubber industry when mechanical properties improvements are not essential.

Besides, if manufacturing cost is not very restricted, some surface modification of RHA can be considered. There are a few investigation suggest that the rubber compounds filled with 20phr NaOH or HCl chemical treated RHA shows slightly superior behaviour (such as tensile strength) than commercial carbon black filled rubber (Arayaprane, 2005). The compatibility between RHA silanol groups and reactive polar groups within rubber matrix has also been studied by many research groups (Chaudhary, 2004). Meanwhile, researchers have also investigated the function of a compatibilizer [poly (propylene –ethylene acrylic acid)] and a silane coupling agent [3-aminopropyl-trithoxy silane (3-APF)] in the milled RHA-filled polypropylene/natural rubber system. Ismail et al. (2001) investigated RHA filled polypropylene/natural rubber blends and observed a slight enhancement in mechanical properties of polypropylene-natural rubber blends with amino-silane agents, which may introduce some improvement in filler-matrix interaction with silanation. It is indicated by Ishak' study (1995) that it is possible to partially replace carbon black by RHA. However, it is necessary to notice that the similarity only obtained at low filler load ( $\approx 20$  wt%). With an excessive filler added, the interaction

between filler and polymer will be inhibited, which will result in a reduced tensile properties and poorer elongation at break (Genieva et al., 2008). Recently, more and more investigations are undertaken to identify the application of peroxide based silane on chain-scission and to study the bonding effect between RHA silanol groups and rubber epoxy groups (Manna et al., 1999).

## II. Peanut shell powder

Peanut shell powder (PSP), as a waste material from peanut, accounts for a very large amount. It is reported that the global production of peanuts (in shell) in 2014 was about 43.9 million tonnes (FAO, 2017). The chemical composition of peanut shell powder is close to hard wood, but with high cellulose content. Its bulk density can reach to  $0.10 \text{ g/cm}^3$  and moisture content is 25%. Sareena et al. (2012) suggested the most efficient load of PSP is 10 phr loading. After chemical modification by alkali treatment, the filler reinforcement ability of modified PSP increased and the result polymer shows better physicommechanical properties. Until now, researches about peanut shell powder are still limit; many further works can be done, such as other modification method, and mixing process improvement etc.

Several other alternative materials as fillers in rubber products have been tabulated in Table 4.

**Table 4 Materials used as rubber fillers**

<b>Material</b>	<b>Short Summary</b>	<b>Reference</b>
<b>Chicken Eggshell</b>	The eggshell calcium carbonate filled epoxidized natural rubber shows higher tensile properties and lower tension set value.	Intharapat et al., 2013
<b>Limestone Dust Waste</b>	The addition of lime dust waste has a little effect on compound processability. It has been grouped as non-reinforcing filler due to the low surface area.	Sae-oui et al., 2009
<b>Fly ash</b>	Fly ash is used as a non-reinforcing filler for ESBR compounds providing normal abrasion resistance.	Dasgupta et al., 2012
<b>Soy spent flakes</b>	The soy spent flakes can partially replace carbon black as the reinforcement co-filler in rubber. The elasticity of the co-filler network is close to that of carbon black.	Jong. L., 2007
<b>Lignin</b>	Reinforcing properties of lignin in nitrile rubber can obtain good thermal stability with suitable chemical treatment.	Setua et al., 2010
<b>Pyrolytic tyre</b>	Chars obtained from pyrolytic tyre can be successfully reused as semi-reinforcing fillers in rubber. The physical and mechanical properties provided by pyrolytic tyre are comparable to carbon black N772.	Athanassiades, E., 2013
<b>Waste newsprint fibres</b>	The sodium silicate and magnesium chloride treated newsprint fiber waste at 40phr can improve the electrical and mechanical properties of the rubber.	Nashar et al., 2004
<b>Marble sludge with carbon black</b>	Marble sludge can be used as a co-filler with carbon black in natural rubber. High tensile strength, modulus, tear strength and hardness can be achieved.	Ahmed et al., 2013

## 7. Conclusions and Outlook

At present, carbon black is widely applied reinforcing filler in rubbery elastomers manufacture.

A fundamental understanding of the rubber-char filler interaction and the performance of the

sustainable fillers was developed. Eight widely accepted postulations on the reinforcing mechanisms of carbon black have firstly been summarized. Fluorescence microscopy and AFM can be considered to test the filled system for new reinforcing mechanism research. Due to the unsustainable manufacture of carbon black and the increasing pressure against the continued use of non-renewable sources of feedstock, the modification of carbon black and the development of alternative materials to act as rubber fillers have gained more and more attention as the future research horizon for both environmental and economic reasons. According to the knowledge obtained from this review, several further investigations can be identified. Factors such as carbon black surface modification using acidic or basic solutions introducing more functional groups and improving the surface activity, further enhancing the filler-polymer crosslink system should be undertaken. Besides, since fillers from alternative feedstock are not carbon black, the reformulation of rubber matrix needs to be considered. In order to commercialize the alternative sustainable rubber filler, economic analysis needs to be addressed.

## Acknowledgements

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

**Funding:** This work is supported by the Chinese Postdoctoral Science Foundation.

## Reference

- ANRPC (Association of Natural Rubber Producing Countries), 2018. ANRPC Releases Natural Rubber Trends & Statistics. <http://www.anrpc.org/html/market-news-details.aspx?ID=26&PID=28&NID=2080> (accessed 7 October 2018).
- ANRPC, 2019. Natural rubber products: Untapped area. <http://www.anrpc.org/html/market-news-details.aspx?ID=26&PID=28&NID=2443> (accessed 1 August 2019).
- Ahmed, K., Nizami, S. S. & Raza, N. Z., 2012. Characteristics of natural rubber hybrid composites based on marble sludge/carbon black and marble sludge/rice husk derived silica. *J. Ind. Eng. Chem.* 19(4), 1169-1176. <https://doi.org/10.1016/j.jiec.2012.12.014>.
- Ali Shah, A., Hasan, F., Shah, Z., Kanwal, N., Zeb, S., 2013. Biodegradation of natural and synthetic rubbers: A review. *Int. Biodeter. Biodegr.* 83, 145-157. <https://doi.org/10.1016/j.ibiod.2013.05.004>.
- Andrews, S., 2014. Cooper Tire Perspective. *Carbon Black World*. October, 2014.
- Arayaprane, W., Na-Ranong, N., & Rempel, G., 2005. Application of Rice Husk Ash as Fillers in the Natural Rubber Industry. *J. Appl. Polym. Sci.* 98(1), 34-41.
- ASTM Standard D6556-16, 2016. Standard Test Method for Carbon Black—Total and External Surface Area by Nitrogen Adsorption. West Conshohocken, ASTM International.
- ASTM Standard D3765-04, 2007. Standard Test Method for Carbon Black—CTAB (Cetyltrimethylammonium Bromide) Surface Area. West Conshohocken, ASTM International.
- ASTM Standard D2414-16e1, 2016. Standard Test Method for Carbon Black – Oil Absorption Number (OAN). West Conshohocken, ASTM International.
- Athanassiades, E., 2013. Waste tyre pyrolysis: Sustainable recovery and reuse of a valuable resource. PhD thesis. Imperial College London. U.K.
- Blanchard, A. F. & Parkinson, D., 1948. Structures in rubber reinforced by carbon black. Second Rubber Technology Conference, London, Great Britain.
- Blanchard, A. & Parkinson, D., 1952. Breakage of Carbon-Rubber Networks by Applied Stress. *Ind. Eng. Chem.* 44(4), 799-812. <https://doi.org/10.1021/acs.jpca.5b04889>.
- Blow, C. M., 1975. *Rubber Technology and Manufacture*. U.K., Butterworth-Heinemann.
- Brunauer, S., P. H. Emmett, and E. Teller., 1938. Adsorption of gases in multimolecular layers. *J. Am. Chem. Soc.* 60(2):309–19. <https://doi.org/10.1021/ja01269a023>.
- Boehm, H. P., 1994. Some aspects of the surface chemistry of carbon blacks and other carbons. *Carbon.* 32(5), 759 – 769. [https://doi.org/10.1016/0008-6223\(94\)90031-0](https://doi.org/10.1016/0008-6223(94)90031-0).
- Bueche, F., 1960. Molecular basis for the mullins effect. *J. Appl. Polym. Sci.* 4(10), 107-114. <https://doi.org/10.1002/app.1960.070041017>.
- Bueche, F., 1961. Mullins effect and rubber–filler interaction. *J. Appl. Polym. Sci.* 5(15), 271-281. <https://doi.org/10.1002/app.1961.070051504>.
- Bueche, F., 1965. In: Kraus G. (Ed.) *Reinforcement of elastomer*. New York, Wiley.

- Chandrasekaran., 2010. Rubber and their relevant properties for the chemical and mineral processing industries. A Compr. Guide. For. Process. Equip. Designers.
- Chaudhary, D., Jollands, M., Cser, F., 2004. Recycling rice hull ash: A filler material for polymeric composites? *Adv. Polym. Technol.* 23(2), 147-155. <https://doi.org/10.1002/adv.20000>.
- Cheng Huang, Guangsu Huang, Shiqi Li, Mingchao Luo, Han Liu, Xuan Fu, Wei Qu, Zhengtian Xie, Jinrong Wu., 2018. *Res. Architecture. Compos. Natural. Netw. Nat. Rubber. Polym.* 154(10), 90-100.
- Costa, H. M. D., Visconte, L. L. Y., Nunes, R. C. R. & Furtado, C. R. G., 2000. The effect of coupling agent and chemical treatment on rice husk ash- filled natural rubber composites. *J. Appl. Polym. Sci.* 76(7), 1019-1027.
- Costa, H. M. D., Visconte, L. L. Y., Nunes, R. C. R. & Furtado, C. R. G., 2002. Mechanical and dynamic mechanical properties of rice husk ash-filled natural rubber compounds. *J. Appl. Polym. Sci.* 83(11), 2331-2346.
- Crompton, T. R., 2012. *Physical Testing of Plastics*. Shropshire, Smithers Rapra Technology Ltd, pp. 1-102.
- Dannenberg, E. M., 1966. Molecular slippage mechanism of reinforcement. *Transactions of the Institution of the Rubber Industry.* 42, 26.
- Dasgupta, M., Kar, S., Gupta, S. D., Mukhopadhyay, R. & Bandyopadhyay, A., 2013. Effect of fly ash as filler in rubber – A comprehensive study of the vulcanisate properties of styrene butadiene rubber compounds. *Prog. Rubber. Plast. Re.* 29(3), 151-168.
- Donnet, J., Bansal, R. C. & Wang, Meng-Jiao, 1993. *Carbon black : Science and technology* (2nd Ed., revised and expanded Ed.). New York: Dekker.
- Donnet, J., Bansal, R. C. & Wang, Meng-Jiao, 2018. *Carbon black : Science and technology* e-book. <https://www.taylorfrancis.com/books/e/9781351462624> (Accessed 3rd November 2018).
- Edwards, D., 1990. Polymer-filler interactions in rubber reinforcement. *Journal of Materials Science.* 25(10), 4175-4185. <https://doi.org/10.1007/BF00581070>.
- Fan, Y., Fowler, G. D., & Norris, C., 2017. Potential of a Pyrolytic Coconut Shell as a Sustainable Biofiller for Styrene-Butadiene Rubber. *Ind. Eng. Chem. Res.* 56(16), 4779-4791. <https://doi.org/10.1021/acs.iecr.7b00405>.
- Food and Agriculture Organization of the United Nations, 2017. Crops and livestock products – Groundnuts shelled in 2013. <http://www.fao.org/faostat/en/#data/TP> (accessed on 13 March 2019).
- Fuad, M. Y. A., Ismail, Z., Mansor, M. S., Ishak, Z. A. M. & Omar, A. K. M., 1995. Mechanical Properties of Rice Husk Ash/Polypropylene Composites. *Polym. J.* 27(10), 1002-1015.
- Ganguly, S., Bhattacharya, P., Banerjee, A. N. & Chakraborty, S., 2003. 1,3,5-trihydroxy benzene as a surface modifier of carbon black and its effect on the filler–rubber interaction. *J. Appl. Polym. Sci.* 87(14), 2272-2278.
- Ganguly, S., Chakraborty, S., Banerjee, A. N. & Bhattacharya, P., 2002. Effect of meta -dihydroxy benzene as a surface modifier on filler–filler and filler–polymer interaction of carbon black polymer composite. *J. Appl. Polym. Sci.* 85(9), 2025-2033.
- Genieva, S., Turmanova, D., Dimitrova, C. & Vlaev, A., 2008. Characterization of rice husks and the products of its thermal degradation in air or nitrogen atmosphere. *J. Therm. Anal. Calorim.* 93(2), 387-396.



- Gent, A. N. & Tompkins, D. A., 1969. Nucleation and Growth of Gas Bubbles in Elastomers. *J. Appl. Phys.* 40(6), 2520-2525. <https://doi.org/10.1063/1.1658026>.
- Goertzen, S. L., Thériault, K. D., Oickle, A. M., Tarasuk, A. C. & Andreas, H. A., 2010. Standardization of the Boehm titration. Part I. CO<sub>2</sub> expulsion and endpoint determination. *Carbon*. 48(4), 1252-1261. <https://doi.org/10.1016/j.carbon.2009.11.050>.
- Gopalan Nair, K. & Dufresne, A., 2003. Crab shell chitin whisker reinforced natural rubber nanocomposites. 2. Mechanical behaviour. *Biomacromolecules*. 4(3), 666-674. <https://doi.org/10.1021/bm0201284>.
- Gregg, S. J. & Sing, K. S. W., 1982. Adsorption, Surface Area and Porosity, London, Academic Press. <https://doi.org/10.1149/1.2426447>.
- Guth, E. & Gold, O., 1938. On the hydrodynamical theory of the viscosity of suspensions. *Phys. Rev.* 53, 322.
- Guth, E., 1945. Theory of Filler Reinforcement. *J. Appl. Phys.* 16(1), 20-25. <https://doi.org/10.1063/1.1707495>.
- Harini Sridharan, Abhilash Guha, Sanjay Bhattacharyya, Anil K. Bhowmick, & R. Mukhopadhyay, 2018. Effect of Silica Loading and Coupling Agent on Wear and Fatigue Properties of a Tread Compound. *Rubber Chemistry and Technology* In-Press.
- Ikram, A., 2002. Natural rubber biodegradation in soil in relation to the waste disposal of used latex products. <http://www.rubbernews.com/article/20020101/DATA/301019985/natural-rubber-biodegradation-in-soil-in-relation-to-the-waste> (accessed 13 March 2019).
- International Carbon Black Association (ICBA), 2016. Carbon Black User's Guide. <http://www.carbon-black.org/images/docs/2016-ICBA-Carbon-Black-User-Guide.pdf> (accessed 13 March 2019).
- International Carbon Black Association (ICBA), 2018. Carbon Black User's Guide. <http://www.carbon-black.org/index.php/carbon-black-uses> (accessed 13 March 2019).
- International Energy Agency (IEA), 2007. Tracking Industrial Energy Efficiency and CO<sub>2</sub> Emissions. [https://www.iea.org/publications/freepublications/publication/tracking\\_emissions.pdf](https://www.iea.org/publications/freepublications/publication/tracking_emissions.pdf) (accessed 13 March 2019).
- Intharapat, P., Kongnoo, A. & Kateungngan, K., 2013. The Potential of Chicken Eggshell Waste as a Bio-filler Filled Epoxidized Natural Rubber (ENR) Composite and its Properties. *J. Polym. Environ.* 21(1), 245-258. <https://doi.org/10.1007/s10924-012-0475-9>.
- Ishak, Z. A. M. & Bakar, A. A., 1995. An investigation on the potential of rice husk ash as fillers for epoxidized natural rubber (ENR). *Eur. Polym. J.* 31(3), 259-269.
- Ismail, H., Nizam, J. M. & Abdul Khalil, H. P. S., 2001. The effect of a compatibilizer on the mechanical properties and mass swell of white rice husk ash filled natural rubber/linear low density polyethylene blends. *Polym. Test.* 20(2), 125-133.
- Jain, A. & Tripathi, S. K., 2014. Fabrication and characterization of energy storing supercapacitor devices using coconut shell based activated charcoal electrode. *Mater. Sci. Eng. B.* 183, 54-60.
- Jha, V., 2008. Carbon Black Filler Reinforcement of elastomers. PhD Thesis. University of London. U.K.
- Jian Wang, Kaiye Zhang, Zhengang Cheng, Marino Lavorgna and Hesheng Xia, 2018. Graphene/carbon black/natural rubber composites prepared by a wet compounding and latex mixing process. *Plast. Rubber. Compos.* 47, 9, 398-412.

Jiazhen Zhou, Anran Luo & Youcai Zhao, 2018. Preparation and characterisation of activated carbon from waste tea by physical activation using steam. *J. Air. Waste. Manage.* <https://doi.org/10.1080/10962247.2018.1460282>.

Jong, L., 2007. Effect of soy spent flakes and carbon black co-filler in rubber composites. *Compos. Part A.* 38(2), 252-264. <https://doi.org/10.1016/j.compositesa.2006.05.003>.

Kato, A., Ikeda, Y. & Kohjiya, S. 2018. Reinforcement Mechanism of Carbon Black (CB) in Natural Rubber Vulcanizates: Relationship Between CB Aggregate and Network Structure and Viscoelastic Properties. *Polymer-Plastics Technol. Eng.* 57, 14, 1418-1429. <https://doi.org/10.1080/03602559.2017.1381257>.

Kühner, G. & Voll, M., 1993. Manufacture of carbon black. In: Donnet J., Bansal R. C. & Wang M. (Eds.) *Carbon Black, Science and technology, Revised and Expanded*, pp. 1-66.

Lin, J., 2002. Identification of the surface characteristics of carbon blacks by pyrolysis GC–MASS. *Carbon.* 40(2), 183-187.

Lippens, B. C. & J. H. D. Boer. 1965. Studies on pore systems in catalysts: V. The t method. *J. Catal.* 9 (1):8–14. [https://doi.org/10.1016/0021-9517\(65\)90307-6](https://doi.org/10.1016/0021-9517(65)90307-6).

Loadman, M. J. R., 1998. *Analysis of Rubber and Rubber-like Polymers*. Netherlands, Springer Netherlands, p. 278.

M. Bele, A. Kodre, I. Arčon, J. Grdadolnik, S. Pejovnik, & J. O. Besenhard, 1998. Adsorption of cetyltrimethylammonium bromide on carbon black from aqueous solution. 36 (7-8), 1207-1212.

M. R. Snowdon, A. K. Mohanty and M. Misra, 2014. A Study of Carbonized Lignin as an Alternative to Carbon Black. *ACS Sustain. Chem. Eng.* 2, 1257-1263.

Manna, A. K., De, P. P., Tripathy, D. K., De, S. K. & Peiffer, D. G., 1999. Bonding between precipitated silica and epoxidized natural rubber in the presence of silane coupling agent. *J. Appl. Polym. Sci.* 74(2), 389-398.

Mark, E. J., Erman, B. & Eirich, F. R., 2005. *Science and technology of rubber* (3<sup>rd</sup> Ed.). San Diego; London: Elsevier Academic Press, p. 368. <https://doi.org/10.1016/B978-0-12-464786-2.X5000-7>.

Mark, E. J., Erman, B. & Roland, C. M., 2013. *The Science and Technology of Rubber* (4<sup>th</sup> Ed.). Waltham, Academic Press.

Maya, K. S., 2007. Studies on in situ precipitated silica filled rubber composites with special reference to NR, NBR and SBR. PhD Thesis. Cochin University of Science and Technology. India.

Medalia, A. I. & Kraus, G., 1994. Reinforcement of elastomers by particulate fillers. In: Mark J. E., Erman B. & Eirich F. R. (Ed.) *Science and Technology of Rubber* (2<sup>nd</sup> Ed.). Academic Press, pp. 387-418.

Mooney, M., 1940. A Theory of Large Elastic Deformation. *J. Appl. Phys.* 11(9), 582-592. <https://doi.org/10.1063/1.1712836>.

Mullins, L. & Tobin, N., 1965. Stress softening in rubber vulcanizates. Part I. Use of a strain amplification factor to describe the elastic behavior of filler-reinforced vulcanized rubber. *J. Appl. Polym. Sci.* 9(9), 2993-3009. <https://doi.org/10.1002/app.1965.070090906>.

Nagornaya, M. N., Razdyakonova, G. I., & Khodakova, S. Y., 2016. The effect of functional groups of carbon black on rubber properties ☆. *Procedia Eng.*, 152, 563-569.

Nashar, D., Abd-El-Messieh, S., & Basta, A., 2004. Newsprint paper waste as a fiber reinforcement in rubber composites. *J. Appl. Polym. Sci.* 91(1), 469-478. <https://doi.org/10.1002/app.13726>.

Orion Engineered Carbons (OEC), 2015. What is Carbon Black. <https://www.thecarycompany.com/media/pdf/specs/orion-what-is-carbon-black.pdf> (accessed 13 March 2019).

Park, S. J. & Kim, J. S., 2000. Role of Chemically Modified Carbon Black Surfaces in Enhancing Interfacial Adhesion between Carbon Black and Rubber in a Composite System. *J. Colloid. Interf. Sci.* 232(2), 311-316.

Park, S. J., Kim, H. C. & Kim, H. Y., 2002. Roles of Work of Adhesion between Carbon Blacks and Thermoplastic Polymers on Electrical Properties of Composites. *J. Colloid Interf. Sci.* 255(1), 145-149.

Payne, A., 1962. The dynamic properties of carbon black-loaded natural rubber vulcanizates. Part I. *Journal of Applied Polymer Science.* 6(19), 57-63. <https://doi.org/10.1002/app.1962.070061906>.

Pena, J., Allen, N., Edge, M., Liauw, C., Santamaria, F., Noiset, O. & Valange, B., 2001. Factors affecting the adsorption of stabilisers on to carbon black (flow micro-calorimetry and FTIR studies). Part I Primary phenolic antioxidants. *J. Mater. Sci.* 36(12), 2885-2898.

Quan, Y., Liu, Q., Zhang, S. & Zhang, S. 2018. Comparison of the morphology, chemical composition and microstructure of cryptocrystalline graphite and carbon black. *Appl. Surface Sci.* 445, 335-341.

Rivlin, R. S., 1956. In: Eirich, F.R. (Ed.) *Rheology*. New York, Academic Press.

S. Riyajan., 2015. Robust and biodegradable polymer of cassava starch and modified natural rubber. *Carbohydr. Polym.* 134, 267-277.

Sae-oui, P., Rakdee, C. & Thanmathorn, P., 2002. Use of rice husk ash as filler in natural rubber vulcanizates: In comparison with other commercial fillers. *J. Appl. Polym. Sci.* 83(11), 2485-2493.

Sae-oui, P., Sirisinha, C. & Thaptong, P., 2009. Utilization of limestone dust waste as filler in natural rubber. *J. Mater. Cycles Waste Manage.* 11(2), 166-171.

Sareena, C., Ramesan, M. & Purushothaman, E., 2012. Utilization of coconut shell powder as a novel filler in natural rubber. *J. Reinf. Plast. Compos.* 31(8), 533-547.

Schmidt, E., 1951. Effect of colloidal noncarbon pigments on elastomer properties. *Ind. Eng. Chem.* 43(3), 679-683. <https://doi.org/10.1021/ac5010794>.

Setua, D., Shukla, M., Nigam, V., Singh, H., & Mathur, G., 2010. Lignin reinforced rubber composites. *Polym. Compos.* 21(6), 988-995. <https://doi.org/10.1002/pc.10252>.

T. Tharmaratnam., 2015. Investigation on the Uses of Coconut Shell Powder Replacing Carbon Black as Filler in Natural Rubber. In *Proceeding of the 5<sup>th</sup> Research Yymposium of Uva Wellassa University*, January 29-30, pp. 44-46, Sri Lanka.

Treloar, L. R. G., 1943. The statistical length of paraffin molecules. *Proceedings of the Physical Society.* 55(5), 345-361.

Tsechansky, L. & Graber, E. R., 2014. Methodological limitations to determining acidic groups at biochar surfaces via the Boehm titration. *Carbon.* 66, 730-733.

Wampler W. A., Carlson T. F. & Jones W. R., 2004. Carbon Black. In: Rodgers B. (ed) *Rubber Compounding, Chemistry and Applications*, Marcel Dekker, pp. 239-284.

Wang, M. J., Gray, C. A., Reznick, S. A., Mahmud, K. & Kutsovsky Y., 2000. Carbon Black. In: Kirk-Othmer Encyclopedia of Chemical Technology. (5th Ed.). John Wiley & Sons Inc., Hoboken, pp. 761-803.

Journal Pre-proof

**Declaration of interests**

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

--

## Highlights

- The development of the life cycle of carbon black has been fully investigated.
- The first summarized the so far reinforcement mechanism theories of carbon black.
- The new research directions of carbon black have been raised.
- The modification of the carbon black has been reviewed.
- The production of carbon black substitutes from renewable materials were proposed.