Chapter

Evaluation of Recycled Carbon Black (r-CB) Based on Styrene Butadiene Rubber, Natural Rubber and Nitrile Rubber Compounds

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Abstract

The enormous accumulation of used tyres has long been a threat to the environment. Pyrolysis is a process of chemically decomposing organic materials at elevated temperatures above 430°C in the absence of oxygen. Pyrolysis can be used to reprocess the tyres into fuel gas, oils, solid residue (char) and low-grade carbon black, which cannot be used in tyre manufacture. Rubber compounds containing r-CB were prepared based on Styrene Butadiene Rubber, Natural Rubber and Nitrile Rubber. Specific formulations were selected for each of the rubber. Natural Rubber was mixed with r-CB to produce pre-cured tread compound for retreading, Nitrile Rubber was mixed with r-CB to produce hose and seals compounds, and finally, r-CB was compounded in accordance to the Standard Test Methods for Styrene-Butadiene Rubber Recipe and Evaluation Procedures. The quality and performance of r-CB in these rubber compounds were compared with the commercial virgin carbon black. The results show that r-CB matches the quality of virgin carbon black such as High Abrasion Furnace (N330) and Fast Extrusion Furnace (FEF, N550) in terms of hardness, tensile strength, abrasion resistance and other relevant physical properties. The prospects of r-CB are very bright and promising. The challenges ahead are to maintain high quality of r-CB, to be competitive in cost in relation to virgin carbon black.

Keywords: r-CB, reinforcing black, tensile strength, hardness, pyrolysis

1. Introduction

It has been reported that nearly 300 millions of waste tyres have to be managed in Europe, and over 1 billion end-of-life tyres generated annually, worldwide [1]. As a general rule, truck tyres should last between 25,000 and 50,000 miles. With proper and regular maintenance and attention, the life of a tyre can reach 70,000 miles before the truck tyres have to be replaced. The enormous accumulation of used tyres has long been a threat to the environment. Disposing of used tyres into empty land, rivers, lakes and jungles generates an ideal environment for the breeding of mosquitoes, snakes and rats. Besides that, it can lead to a potential uncontrolled fire hazards.

Tyre fires can occur easily, burning for months and creating substantial pollution in the air and ground. Deliberate burning in the open air is also forbidden because it breaks air pollution regulations and is no longer allowed. To solve this environmental problem, used tyres have to be reused in a manner that will be environmentally friendly as well as economically viable. The common methods to dispose used tyres are landfill, dumping and stockpiling. Tyres are not desired at landfills, due to their large volumes and 75% void space. Landfill is expensive as a consequence of high price to purchase a piece of land. There are law restrictions in some countries which forbid dumping of used tyres in landfill to avoid potential fire hazards, breeding of mosquitoes, rats and poisonous snakes. One of the promising means of disposing used tyres is by the technique known as pyrolysis. During pyrolysis, used tyres are subjected to heat at elevated temperatures above 430°C in the absence of oxygen. Pyrolysis converts the tyres into fuel gas, oils, solid residue (char) and low-grade carbon black, which cannot be used in tyre manufacture. One of the main issues of recycled carbon black (after this is called r-CB) produced by pyrolysis is concerned with its quality. Although highly reinforcing carbon black grades such as Intermediate Super Abrasion Furnace (ISAF N200 series) and High Abrasion Furnace (HAF N300 series) are used in the tyre compounds, but after pyrolysing, the r-CB produced does not retain the quality of the original virgin carbon black. It was reported that r-CBs reinforcement properties are lower than those of N330 carbon black for a same rubber formula [1].

It is well established that the particle size and chemical surface activity of the carbon black are the determining factor affecting the degree of reinforcement. The aggregates of virgin carbon black are in the range of from 0.09 μm to 0.50 μm. In contrast, r-CB produces aggregates of sizes from ~18 μm – 1 mm [1]. The r-CB composite aggregates composed of the carbon blacks from the tyre, the inorganic ash content, fresh carbon and volatiles [1]. By milling process, the r-CB narrows the particle size distribution to typically ~1–10 μm [1]. The low extent of reinforcement of r-CB is attributed to its big particle size and its low chemical surface activity. In order to improve the quality and consistency of r-CB produced, it is of paramount important to scrutinise and monitor the pyrolysis operation at all stages of the process. Quality control process begins from sorting and segregating of used tyres. To minimise the inconsistency of the quality of r-CB, the first thing to do is not to mix passenger car tyres with truck tyres because the compound formulations of these two tyres are very different. It is also beneficial to segregate tyres according to their respective brands to minimise variations in particular the ash content. The next step is to control the tyre feedstock input, which defines the chemical composition of the r-CB produced. Last but not least, the residence time during pyrolysis and other related controlling parameters. This chapter describes and discusses the work to evaluate the quality of r-CB produced by the local manufacturer Eco Power Sdn Bhd. The main objective is to compare r-CB with the performance of virgin carbon black of the N330, Fine Extrusion Furnace (FEF carbon black N550), General Purpose Furnace (GFP N660) and Semireinforcing Furnace (SRF N760) based on five different compound formulations. The first compound is based on the Standard Test Methods for Styrene-Butadiene Rubber (SBR) Recipe and Evaluation Procedures [2], second is based on black-filled Natural Rubber (NR) standard formulation, third is based on pre-cured tread compound to meet the Malaysian Standard (MS) for retreading tyres MS 1208–2020 (3rd Revision) [3], fourth is based on hose liner compound to meet the British Standard Specification for Rubber Hose and Hose Assemblies for Liquefied Petroleum Gas Lines [4] and lastly, rubber seal (O-ring) compound to meet the American Society for Testing and Materials (ASTM) Standard

Classification System for Rubber Products in Automotive Applications [5]. From this evaluation we can then make some assessments on the prospects, challenges and the future of r-CB to meet its demands in the manufacture of rubber products. Currently, the negative perception of r-CB still exists among the Rubber Compounders in the rubber products' manufacturer. The information laid down in this chapter provides experimental evidence on the quality and performance of r-CB currently produced by the local supplier. With the escalating cost of virgin carbon black, it is timely to consider r-CB as an alternative filler in the manufacture of rubber products since the cost of r-CB is about 40–50% lower than the virgin carbon black. It is very timely that the two big players in the tyre manufacturing, namely Bridgestone and Michelin, are keen to use r-CB in the manufacturing of new tyres because of the environmental benefits of this sustainable material [6]. They have claimed that using r-CB in the new tyre production reduces carbon dioxide (CO_2) emission by up to 85% compared with virgin carbon black [6]. They further envisaged that by substituting just 10% of virgin carbon black by r-CB in making new tyres would reduce CO_2 emissions globally by up 2 million metric tons annually. It is well established that the huge accumulation of waste or used tyres and their disposals are of great concern to us because they pose huge threats to the environments.

2. Evaluation of the physical properties of r-CB based on ASTM D-3191-10 (Reapproved 2014)

Unless otherwise stated, all the work reported and discussed throughout in this chapter used r-CB from Eco Power Sdn Bhd Malaysia. **Table 1** shows the Certificate of Analysis of r-CB produced by LabAlliance Sdn Bhd.

The BET surface area is a measure of the total surface area using the theory of Brunauer, Emmett and Teller (BET) nitrogen gas adsorption [11]. This total surface area includes micropores (where the pore diameter less than 2 nm) existed on the surface of carbon black. In contrast, STSA (Statistical Thickness Surface Area) is a measure of external surface area without considering the area of micropore; thus, STSA is always lower than BET Surface Area. STSA is also claimed as specific surface area that is accessible to rubber, since the internal micropore area is not accessible to rubber molecule. The results show that the average of BET surface area of r-CB is 44m^2/g while the STSA is 43m^2/g. Compared with virgin carbon black, both results

Property	Minimum	Maximum	Test Result
Heating loss (moisture) (%) [7]	0.0	2.0	0.62
Ash content (%) [8]	5.0	20.0	15.8
Carbon Black Content (%) [9]	78.0	100.0	83.58
Comparison of surface area			
Type of carbon black	N330	N550	r-CB
BET SA (m^2/g) [10]	78	40	44.0
STSA (m^2/g) [10]	75	39	43.0

Table 1.
Certificate of Analysis (CoA) number: CA21-0137.

are higher than the surface area of N550, but still lower than N330. Based on these results, the r-CB is closer to N550, which is a semi-reinforcing grade of carbon black.

2.1 Rubber compound formulations

Table 2 shows the rubber compound formulations based on the Standard Test Methods for Styrene-Butadiene Rubber (SBR) Recipe and Evaluation Procedures [2]. Emulsion polymerised Styrene Butadiene Rubber (SBR 1502) was used. The gum compound was included so that one can assess and evaluate the magnitude of reinforcement attributed to r-CB and virgin carbon black. The "gum" or sometime known as "unfilled" refers to a rubber compound that does not contain any filler apart from the basic ingredients necessary for vulcanisation such as zinc oxide, stearic acid, sulphur and accelerator. All the units of the rubber compound formulations are expressed in parts per hundred of rubber (phr).

All rubber compounds shown in **Table 2** were prepared on a laboratory two-roll mill. Mixing was done in accord with the mixing procedures laid down in Standard Test Methods for Styrene-Butadiene Rubber (SBR) Recipe and Evaluation Procedures [2]. All test pieces were compression moulded at 145°C for 50 minutes.

2.2 Results and discussions

2.2.1 Hardness

Figure 1 shows the histogram of hardness for vulcanised rubber compounds tested according to the Standard Test Method For Rubbery Property-Durometer Hardness [12]. SBR is an amorphous rubber; therefore, it is an ideal rubber to evaluate the degree of reinforcement of filler. All the compounding ingredients and the quantity used were the same apart from different grades of virgin carbon black. Thus, the physical properties of the vulcanizate are attributed to the influence of the carbon black solely. Gum (unfilled) rubber acts as a reference of the strength associated with the cross-link network and viscoelastic effects. The quantity of carbon black used was fixed to 50 phr. Unfilled (gum) SBR has low hardness 41 Shore A. N330 gives 69 Shore A, an increase of 68.3% in hardness compared with gum vulcanizate. Overall the hardness of SBR compound filled with r-CB is lower than all the virgin carbon black filled SBR. Based on the results shown in

Reference	Gum (phr)	r-CB (phr)	HAF (N330) (phr)	FEF (N550) (phr)	GPF (N660) (phr)	SRF (N700) (phr)
SBR1502	100	100	100	100	100	100
ZnO	3	3	3	3	3	3
Stearic acid	1.0	1.0	1.0	1.0	1.0	1.0
r-CB	—	50	50	50	50	50
TBBS	1.0	1.0	1.0	1.0	1.0	1.0
Sulphur	1.75	1.75	1.75	1.75	1.75	1.75

Table 2.
Rubber compound formulations.

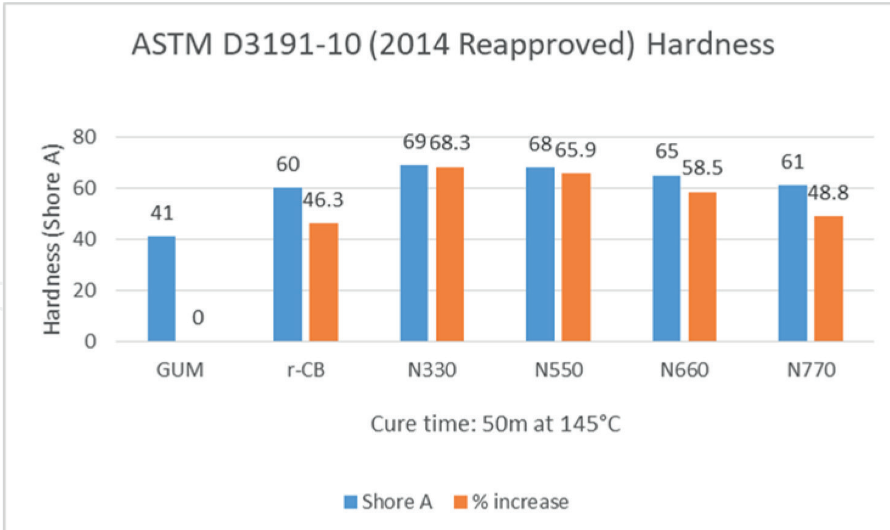

Figure 1.
A histogram showing the hardness of r-CB in comparison with virgin carbon black.

Figure 1, the degree of reinforcement of r-CB is close and comparable to N770. The reason for the low hardness is not entirely clear, but might be attributed to poor rubber-filler interaction because of the high level of ash content covering the r-CB particles. The ash content of r-CB is 15.8% as shown in **Table 1**; in contrast, virgin carbon black has very low ash content less than 1% [13]. However, r-CB still meets the hardness of 58 Shore A for pyrolysed carbon black for rubber as reported by William *et al* [14].

2.2.2 Tensile properties

The tensile test was done in accordance to the International Organisation for Standardisation (ISO) for Rubber, vulcanised or thermoplastic [15]. **Figure 2** shows the results of tensile stress at 100% strain (M100) and tensile stress at 300% strain (M300). The M100 and M300 of r-CB are still lower than those of all grades of virgin carbon black. The lower hardness, M100 and M300 of r-CB than those of virgin carbon black reflect the poor rubber-filler interaction. The contaminants (ash, oil, etc.) on the surface of r-CB might interfere in the surface activity of r-CB and prevent the formation of efficient linkages or interaction between the filler and the molecular rubber chains.

Figure 3 shows the tensile strength of r-CB against the virgin carbon black. The tensile strength of vulcanised SBR filled with r-CB meets the minimum requirement of 18.2 MPa for a black filler for rubber from tyre pyrolysis [14]. The tensile strength r-CB is 11 times higher than that of vulcanised unfilled (gum) SBR indicating a substantial reinforcement produced by r-CB. However, the tensile strength of r-CB is still slightly lower than that of N330 and N550. The tensile strength of SBR filled with N330 is 21% higher than that of r-CB and SBR filled with N550 is 13% higher than r-CB. The tensile strength of SBR filled with N770 is 4% lower than that of r-CB. The level of reinforcement of r-CB based on tensile strength is equivalent to semi-reinforcing carbon black N660. Vulcanised SBR filled with r-CB gives the highest elongation at break than all grades of virgin carbon black as shown in **Figure 4**. The low hardness, low M100 and M300 all contribute to high elongation at break of r-CB. The minimum requirement for elongation at break for pyrolysed carbon black is

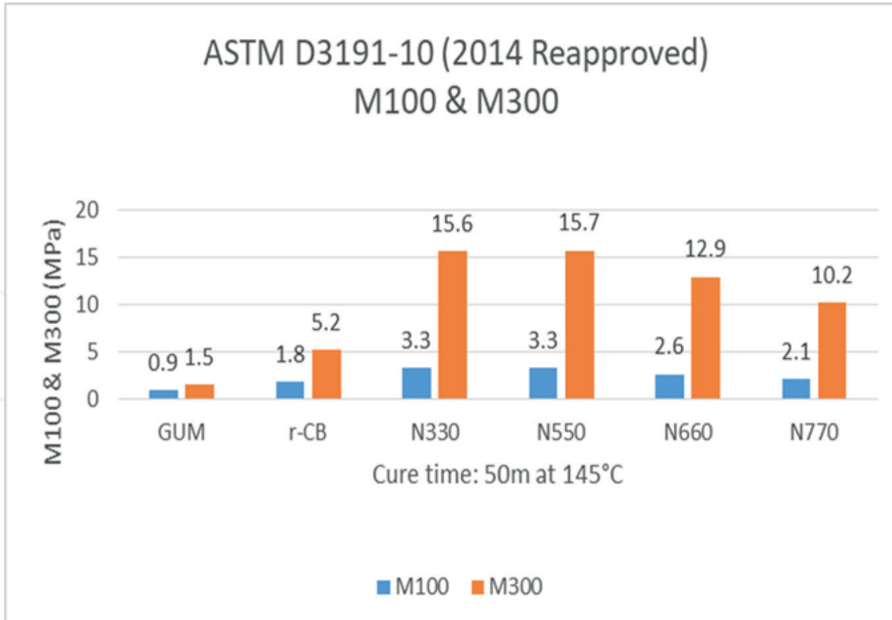

Figure 2.
A histogram showing the results of M100 and M300.

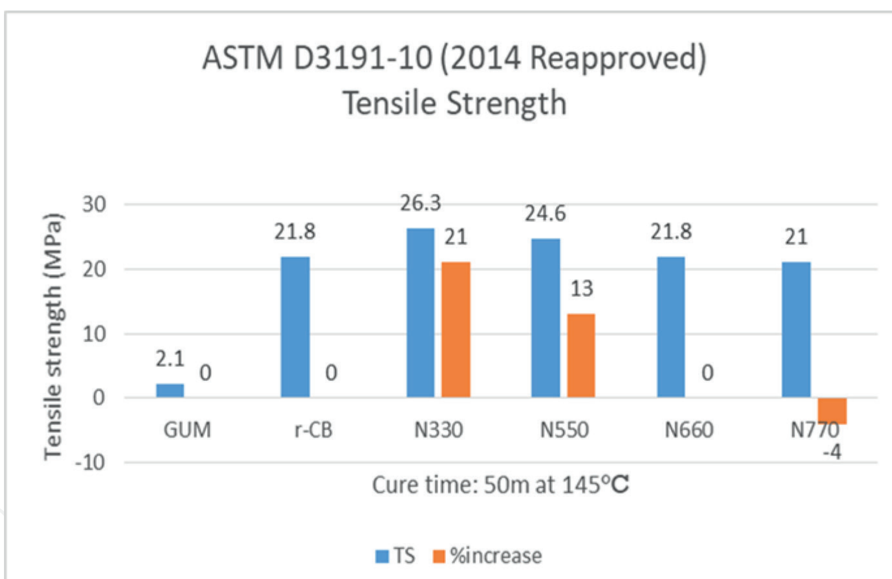

Figure 3.
A histogram showing the tensile strength of r-CB against virgin carbon black.

620% [14]. Again the r-CB used here meets the ASTM D3191 requirement for pyrolysed carbon black. The r-CB provides high resistance to deformation at high strain.

2.2.3 Tear strength

The tear strength was done by using trouser test pieces in accord with the ISO 34-1: 201 [16]. The results are shown in **Figure 5**. Although the tensile strength of r-CB is lower than N330 and N550, r-CB filled SBR produces the highest tear strength compared with all grades of virgin carbon black. Tear strength of r-CB is 520% higher than unfilled that of (gum) vulcanised SBR and 35.5% higher than that of black-filled

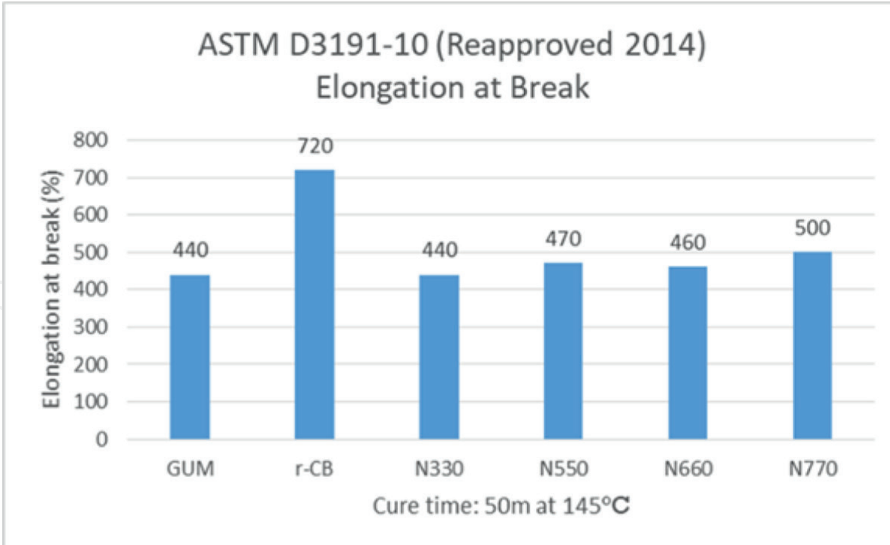

Figure 4.
A histogram showing the elongation at break of r-CB against virgin carbon black.

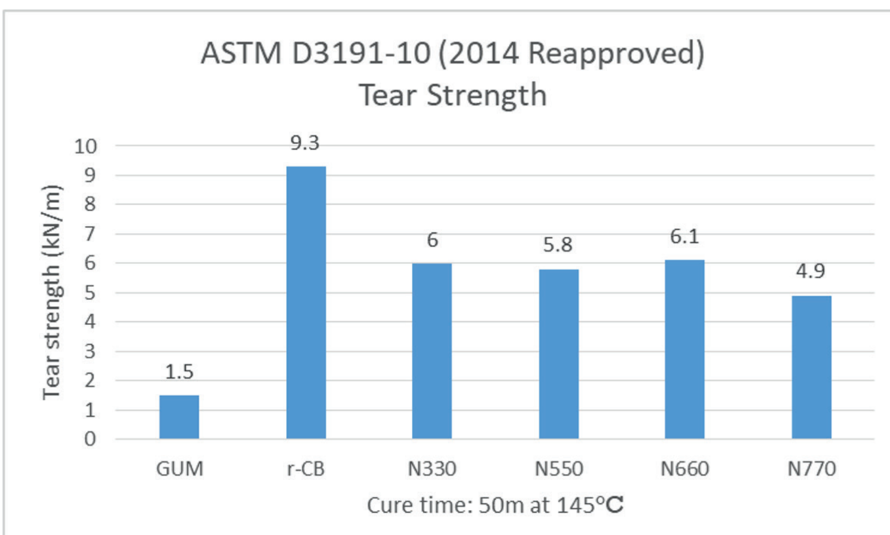

Figure 5.
A histogram showing the tear strength (trouser test-piece) of r-CB against virgin carbon black.

(N330) SBR. The tear strength does not correlate with the tensile strength because the failure mechanisms between the two are different. Tear failure involves crack growth process and greatly influenced by the energy dissipation process (hysteresis); in contrast, tensile failure is a single fatigue process.

The possible explanation why r-CB shows high tensile strength and high tear strength in spite of the low hardness, M100 and M300 is as follow: **Figure 6** shows a schematic diagram of r-CB. A virgin carbon black has very low ash content (less than 1%), and its surface activity is greatly influenced by the oxygenated functional groups such as carboxyls, phenols and ketones that are responsible for chemical interactions between the carbon black particles and the rubber molecular chains. In contrast, r-CB has high ash content (15.8% as shown in **Table 1**). The presence of ash and impurities on the surface of r-CB would interfere in the extent of wettability and the strength of the rubber-filler interaction. The ash content has been considered as a major barrier for r-CB to form a strong interaction with the rubber because the ash covers r-CB

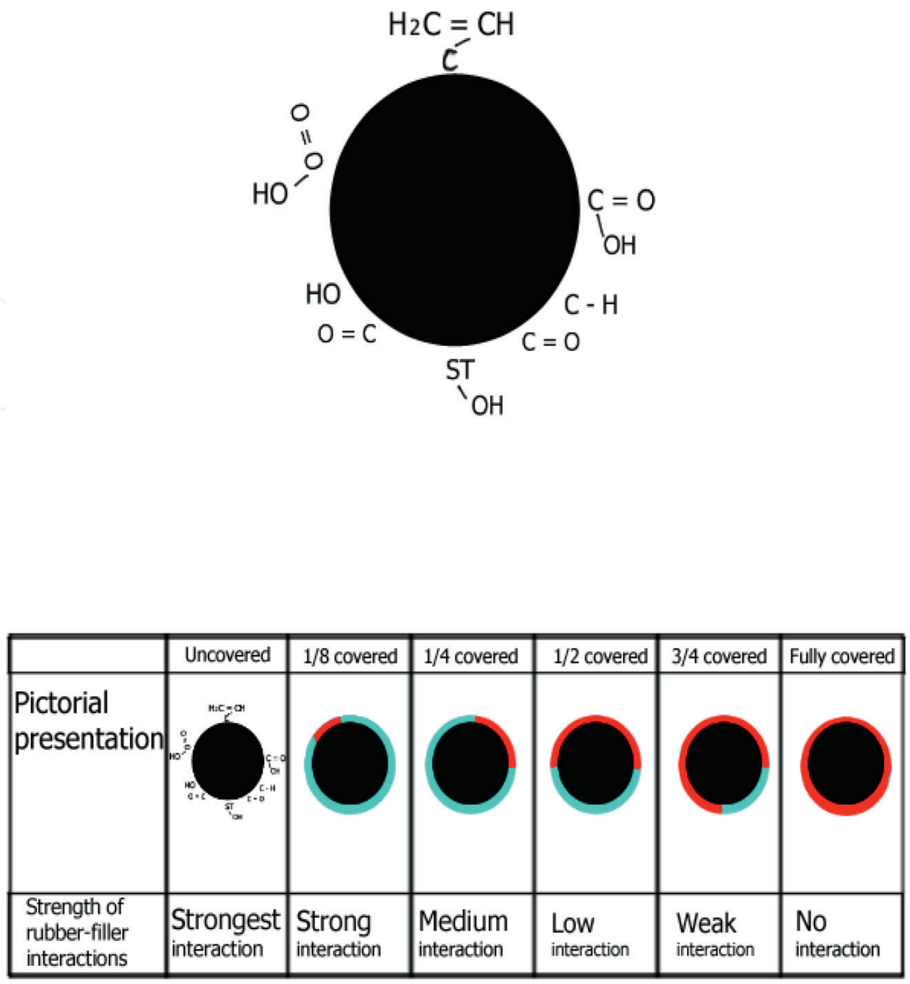

Figure 6.
Schematic diagram of r-CB showing the extent of impurities covering the r-CB particles. The red colour represents the impurities covering the r-CB particle. The red colour indicates the ash and impurities covering the carbon black particle, the light blue indicates the available space for rubber-filler interactions.

particles and hinders the interaction between r-CB and the rubber. The extent of the interaction is influenced by the availability of the area not covered by ash. Taking into two extreme cases, if the particle of r-CB is fully covered by ash, then there will be no interaction between the filler and the rubber. If the whole surface of r-CB is not covered by ash, then we have full interaction between filler and rubber. In reality, the amount of ash covering the surface of r-CB varies randomly. In the case of r-CB, the rubber-filler interaction might not be uniform, but a mixture weak and strong interactions.

There will be varying distribution of the strength of the interaction between filler and rubber depending on how much area is covered by ash and how much area is available for rubber filler interaction. In the regions where the ashes covering the r-CB particles are high, the rubber-filler interaction is low. It requires low stress to deform at a given strain level. For these reasons, the hardness, M100 and M300 are low in r-CB compared with virgin carbon black.

Tensile strength, elongation at break and tear strength involve high strain level reaching the breaking or fracture point. When the stress is applied, the weak interaction is broken first and then transfers the stress to next strong interaction. In so doing, the stress is relieved before reaching the breaking point, and the network is able to support further higher load. The process involves stress-relieving mechanism. The cycles repeat themselves until complete rupture occurs. The load transferring process also gives rise to energy dissipation or hysteresis. This is one of the reasons why r-CB provides higher tear strength compared with virgin carbon black.

2.2.4 Comparison of tensile strength and elongation at break at the same hardness level (60 Shore A)

Figure 7 shows the comparison of r-CB against Sterling V (Carbon black produced by Cabot), N550, N660 and N772 based on Cabot's Product Data Sheet [17, 18]. Cabot's compounding formulations were based on the Standard Test Methods for Styrene-Butadiene Rubber (SBR) Recipe and Evaluation Procedures [2], but the carbon black loading was adjusted to produce 60 Shore A hardness. The tensile strength

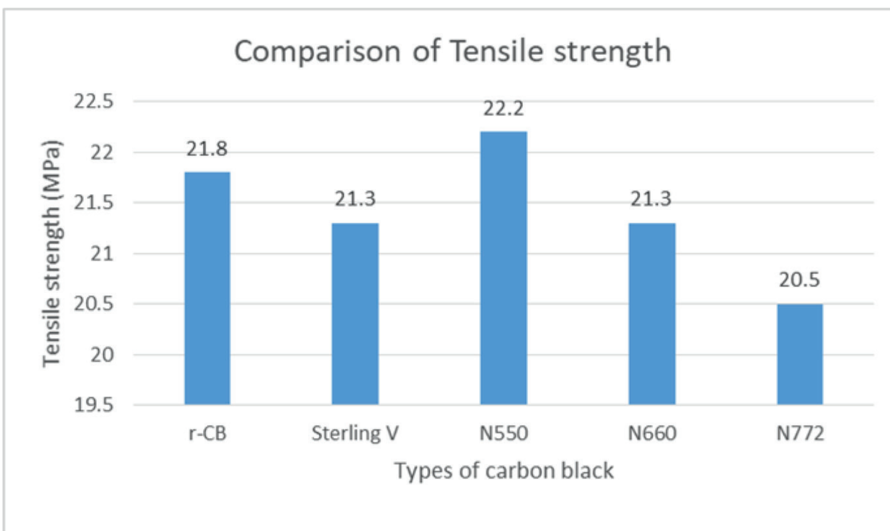

Figure 7.
A histogram showing the comparison of tensile strength of r-CB with Cabot's carbon black reported in the Technical Data. Comparison at the same hardness 60 Shore A.

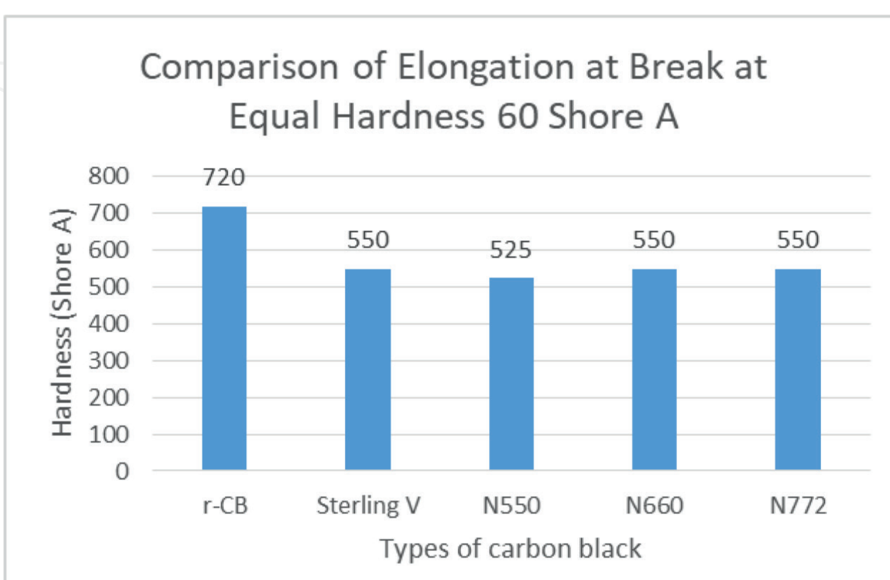

Figure 8.
A histogram showing the comparison of elongation at break at equal hardness 60 shore.

of r-CB black filled SBR is almost similar to N550 but slightly higher than Sterling V and N660 and that of N772.

Figure 8 shows the comparison of elongation at break at equal 60 Shore A hardness. It is clear that r-CB gives higher elongation at break by 31% compared with all the Cabot's virgin carbon black.

3. Evaluation of r-CB based on black-filled natural rubber (NR) standard formulation

Table 3 shows the basic black-filled Natural Rubber (NR) compound formulation. The Control compound was reproduced from the author's own work [19]. The aim here is to make relative comparison on the tensile properties of r-CB with that of virgin carbon black HAF (N330). The amount of r-CB used was 60 phr and would be compared against control compound filled with 50phr of HAF (N330) without processing additives. Compound AZBF1 contained processing additives such as Rubber Process Oil (RPO) and fatty acid zinc soap (FAZS) to facilitate filler dispersion and wettability. Rubber Process Oil was incorporated to facilitate flow and ease of mixing. The accelerator used was based on sulphonamides the fast curing, delayed action accelerators. The sulphur level was increased from 1.2 phr in the control compound to 1.3 phr for compounds AZBF1 and AZBF2. In compound AZBF2, the amount of r-CB was reduced to 50% to 30 phr with the addition of 3.5 phr of graphene Nanoplatelets. The aim here is to see whether graphene Nanoplatelets could enhance the tensile

Ref. no →	*Control (phr)	AZBF 1 (phr)	AZBF 2 (phr)
Natural Rubber (SMR 10)	100	100	100
HAF (N330)	50	—	—
r-CB	—	60	30
Graphene oxide	—	—	3.5
Fatty Acid Zinc Soap	—	1	—
Amide Fatty Acid Soap	—	1	—
Rubber Process Oil (RPO)	—	5	—
Zinc Oxide	5	5	5
Stearic Acid	2	2	2
N,N′-diaryl-p-phenylenediamines	—	1	1
Polymerised 2,2,4-trimethyl-1,2-dihydroquinoline	2	—	—
Morpholinylbenzonthiazole–2-sulphenamide	1.2	—	—
N-cyclohexylbenzothiazole-2-sulphenamide	—	1.2	1.2
Sulphur	1.2	1.3	1.3

**Reproduced from Reference [19]: A. B. Samsuri, Tear Strength of Filled Rubbers, PhD Thesis, Council for National Academic Awards, England, May 1989.*

Table 3.
Evaluation of tensile properties of r-CB based on standard NR black-filled compound.

Ref. no →	Control (phr)	AZBF 1 (phr)	AZBF 2 (phr)
Cure time @150°C (minutes)	25	8	8
Tensile Properties (ISO 37: 2017)			
M100 (MPa)	0.8	1.2	1.4
M300 (MPa)	1.64	4.7	4.1
Tensile strength (MPa)	26.9	24.7	27.2
Elongation at break (MPa)	749	750	780

Table 4.
Tensile properties of vulcanised r-CB filled NR.

properties of r-CB since it is well established that Nanofiller enhances the strength properties of polymer substantially. The Nanofiller (xGnP® Graphene Nanoplatelets Grade M) used was purchased from XG Sciences [20]. Grade M particles have an average thickness of approximately 6–8 nanometres and a typical surface area of 120–150 m^2/g. The average particle diameters of 15 microns. Preparation of the rubber compounds was done on a two-roll mill using the standard or normal mixing practice and procedures.

3.1 Results and discussions

The tensile properties are shown in **Table 4**. The NR filled with 50 phr of N330 gave tensile strength of 26.9 MPa about 8.9% higher than 60phr r-CB filled NR. In terms of elongation at break r-CB filled NR gives higher EB than 50 phr N330 NR filled although the former is filled with 60 phr r-CB, and the latter is filled with 50 phr N330. The reason might be associated with the presence of process in the 60 phr r-CB compound. When the r-CB loading was reduced to 30 and 3.5 phr of Nanoplatelet was added into AZBF2 compound, the tensile strength increases to 27.2 MPa. The tensile strength of r-CB filled with small quantity of graphene platelet is equivalent to the reinforcement produced by N330 HAF black although the quantity of r-CB is only at 30 phr. The degree of reinforcement is affected by the particle size, the filler structure, physical nature of the surface and the degree of filler dispersion [21]. The particle size of graphite is 0.34 nm; in contrast, the primary particle of carbon black is between 20 and 50 nm [22]. Particle size of graphite is 100 times smaller than that of N330 particle size. The small-size particle of graphite provides higher surface area than that of the particle size of N330 black. The high surface area enhances the ability of the filler to wet the rubber and enhances the interaction at the rubber-filler interface, thus giving very high reinforcement. The quantity of graphene required is only small because of the high surface area of the particle size.

4. Evaluation of r-CB in pre-cured tread compound

Table 5 shows the r-CB Natural Rubber (NR) masterbatch for the evaluation of pre-cured tread compound. Processing additives were used to facilitate mixing and ease fo filler dispersion. The total carbon black in each masterbatch (MB) was 60 phr. In the case of MB1, r-CB was mixed with virgin carbon black N220 (ISAF) in the ratio 50:50 (r-CB:N220). The aim was to see whether the addition of ISAF would enhance

Reference	MB1	MB2	MB3
Materials	phr	phr	phr
SMR10	100	100	100
r-CB	30	60	60
ISAF N220	30	—	—
Fatty Acid Zinc Soap	1	1	1
Amide Fatty Acid Soap	1	1	1
Rubber Process Oil (RPO)	5	5	—
Epoxidised Palm Oil (EPO)	—	—	5
Total	167	167	167

The abbreviations MB1, MB2 and MB3 refer to rubber compound masterbatch with different compounding ingredients.

Table 5.
r-CB NR masterbatch.

the tensile strength and hardness for the r-CB. In the case of MB2 and MB3, r-CB was used alone at 60phr loading. MB2 used RPO as the lubricant, and MB3 used EPO as the lubricant. EPO is more environmentally friendly than EPO since the former used waste palm oil instead of crude oil as the starting material. The full formulations for the pre-cured tread compound are shown in **Table 6**. Rubber compounds AZTC1–AZTC3 were based on 140 phr of rubber (NR 100 + BR 40phr). In 167 phr of MB, the NR content is 100 phr and the carbon black content is 60 phr. When 40 phr of BR is added, the carbon black content is diluted to (60/140 = 42.8phr. It was necessary to top up 24phr of carbon black so that the total carbon black is 60 parts. (60 + 24)/140 = 60 phr. For this reason, additional 24 phr of N220 was added in rubber compounds AZTC1 and AZTC3. In the case of AZTC2 rubber compound, 24phr of r-CB was added to produce total loading of 60phr.

For compounds AZTC4 and AZTC5, the MB1 and MB2 used were 102phr. In this case, the NR content was 60 phr and the carbon black content was 36 phr. It was necessary to top up 24 phr of either N220 or r-CB to make it to 60 phr when 40 phr of BR was added. The control compound was reproduced from the truck tyre retread formulation based on the Natural Rubber Formulary and Property Index [23] for the purpose of comparison. The control compound incorporated 70 phr of ISAF (N220) virgin carbon black.

The masterbatches shown in **Table 5** were prepared by using an internal mixer with batch weight of 2.5 kg. The fill factor used was 0.75. The internal has a fixed rotor speed of about 80 rpm. The NR was loaded first and premasticated for 1 minute before adding processing additives and half of the filler. Mixing was allowed to mix for another 1 minute before adding the remaining filler and oil. Mixing was allowed to continue until the temperature shown at the panel reached 120°C and the rubber masterbatch was discharged. The actual temperature of the masterbatch was measured by means of a thermocouple and recorded. The recorded temperature was in the range of 130–135°C. Rubber compounds shown in **Table 6** were prepared on a two-roll mill. All compounds shown in **Table 6** were cured at 150°C to t90, except the control compound where it was cured at 140°C for 20 minutes. The physical properties of pre-cured tread rubber compound produced by the local retreader are also included for comparison. The rubber compound of the retreader was made of blends

Sample reference	Control	AZTC 1	AZTC 2	AZTC3	AZTC4	AZTC5
OENR 75/25A	107	—	—	—	—	—
MB1 (r-CB 30: ISAF 30)	—	167	—	—	102	—
MB2 (r-CB 60)	—	—	167	—	—	102
MB3 (r-CB 60)	—	—	—	167	—	—
Polybutadiene rubber (BR)	20	40	40	40	40	40
r-CB	—	—	24	—	—	24
ISAF (N220)	70	24	—	24	24	—
Rubber Process Oil-2	—	—	—	—	5	5
Ppt. silica (VN3)	—	15	15	15	12	12
Coupling agent	—	1	1	1	1	1
Zinc oxide	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2
N,N′-diaryl-p-phenylenediamines	2	1.5	1.5	1.5	1.5	1.5
Wax blend	1	—	—	—	—	—
Polymerised 2,2,4-trimethyl-1,2-dihydroquinoline	—	1.5	1.5	1.5	1.5	1.5
Sulphur	1.5	1.8	1.8	1.8	1.6	1.8
N-t-butylbenzothiazole-2-sulphenamide	1.5	1.4	1.4	1.4	1.4	1.4
Diphenylguanidine	—	0.4	0.4	0.4	0.4	0.4

The abbreviations AZRTC 1–AZTC 5 refer to sample reference for five different tread compound formulations.

Table 6.
Pre-cured tread compound for tyre retreading formulations.

of NR, SBR and BR. The carbon black used was N234 (High structure ISAF) with 63 phr loading. Details of the formulations cannot be disclosed here [24].

4.1 Results and discussions

4.1.1 Hardness

The hardness results are shown in **Figure 9**. All compounds meet the Shore hardness specified by the Malaysian Standard Precured Tread for Retreading Tyres – Specification (3rd Revision): MS1208:2020 except AZTC4. Compound AZTC4 has higher N220 (42phr) than r-CB (18 phr) that exceeds the maximum hardness limit specified by the Malaysian Standard Precured Tread for Retreading Tyres – Specification..

4.1.2 M100 and M300

All compounds meet the M300 specified by the Malaysian Standard Precured Tread for Retreading Tyres – Specification the Malaysian Standard Precured Tread for Retreading Tyres – Specification as shown in **Figure 10**. The M300 exceeds the minimum value of 7.0 MPa. AZTC1 and AZTC4 produce high M300 because of the high

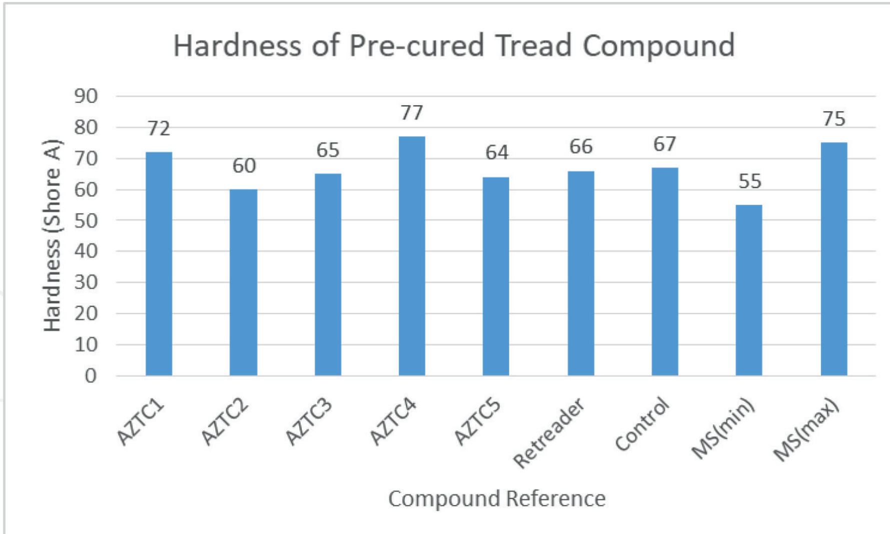

Figure 9.
Hardness of pre-cured tread compounds.

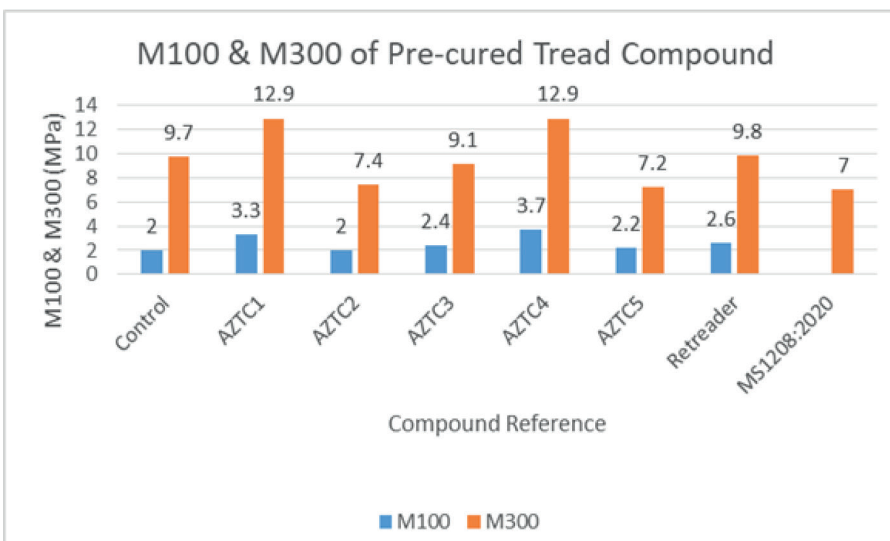

Figure 10.
M100 and M300 results of pre-cured tread compounds.

content of N220. However, the Malaysian Standard Precured Tread for Retreading Tyres does not specify M100.

4.1.3 Tensile strength

The tensile strength results are shown in **Figure 11**. All the compounds meet the minimum tensile strength (14.0 MPa) specified by the Malaysian Standard Precured Tread for Retreading Tyres. In fact, compounds AZTC1–AZTC4 produce higher tensile strength (12.2%–19.1%) than the retreader [24] that used 63phr of N234 and that of control compound that used 70 phr of ISAF (N220). The results show clear experimental evidence that r-CB can be used 100% on its own (AZTC2 and AZTC5) or blended with N220 (AZTC3) in pre-cured tread tyre compound and still meet all the requirements in the Malaysian Standard Precured Tread for Retreading Tyres.

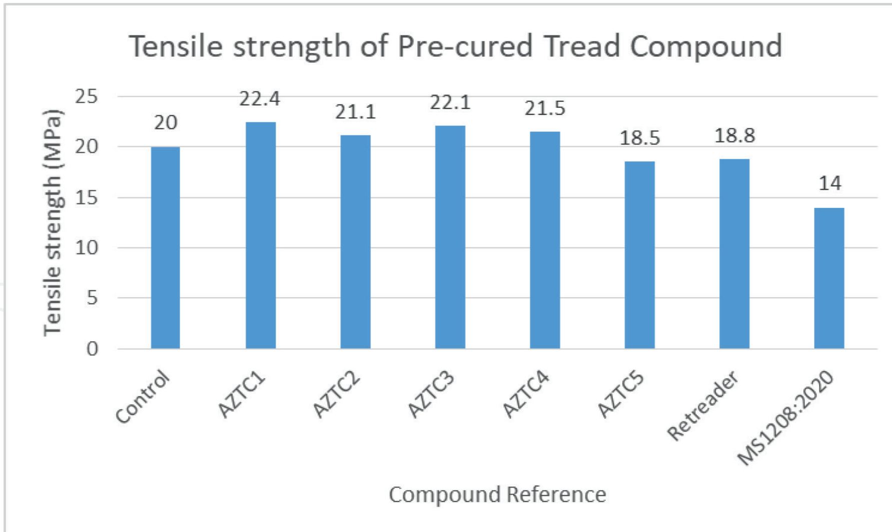

Figure 11.
Tensile strength of pre-cured tread compounds.

4.1.4 Elongation at break

The elongation at break results are shown in **Figure 12**. All the compounds meet the minimum elongation at break, EB (400%) specified by the Malaysian Standard Precured Tread for Retreading Tyres. Compounds having high content of N220 and low content of r-CB produce lower EB than compounds having more r-CB since the former gives higher hardness and M300 than the latter.

4.1.5 Ageing test results

The Malaysian Standard Precured Tread for Retreading Tyres specified ageing conditions at 70°C for 168 hours. The ageing test results for hardness, tensile strength and elongation at break are shown in **Table 7**. All the compounds meet the

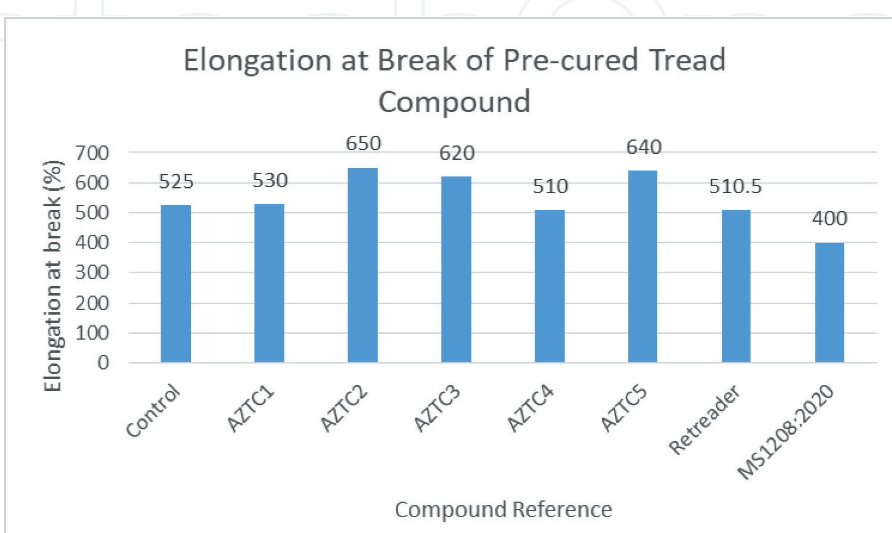

Figure 12.
Elongation at break of pre-cured tread compounds.

Sample reference	MS1208:2020	AZTC 1	AZTC 2	AZTC3	AZTC4	AZTC5
Hardness before ageing	55–75	72	60	65	77	64
Hardness after ageing	—	73	62	64	75	64
% change in hardness	+6	+1	+2	-1	-2	0
Tensile strength before ageing	14.0 MPa (min)	22.4	21.1	22.1	21.5	18.5
Tensile strength after ageing	—	18.8	18.6	20	20.5	17.1
% Retension in tensile strength	80	84	88	91	95	92
EB before ageing	400% (min)	530	650	620	510	640
EB after ageing	—	440	600	580	510	560
% Retension in EB	70	83	92	94	100	88

Table 7.
Ageing (70°C/168 h) test results for hardness, tensile strength and elongation at break.

MS1208:2020 specification after ageing at 70°C for 168 hours. The use of r-CB in the pre-cured tread compound does not affect the physical properties after ageing.

4.2 Abrasion resistance index (ARI)

The Abrasion Resistance Index (ARI) was done according to ISO 4649: 2017 (Method B) [25]. **Figure 13** shows the Abrasion Resistance Index (ARI). Abrasion resistance is a very important property in tyre because it determines the service life of the tyre in the long run. However, the Malaysian Standard Precured Tread for Retreading Tyres does not include this property in the specification. But we can compare with the ARI of the retreader. It is very surprising and interesting to note that the use of 100% r-CB (AZTC2 & AZTC5) gives comparable or even slightly better abrasion resistance than that of retreader that used 63phr of N234. Rubber compounds AZTC1 and AZTC4 give 30% and 47% higher than the retreader compound.

4.3 Tear strength

Trouser test pieces were used for the tear test [16]. **Figure 14** shows the tear strength results. Tear strength is another important property of a tyre.

It reflects the resistance to cutting by sharp and hard objects such as concrete curbs and sharp stones. All the results show comparable tear strength values.

4.4 Rebound resilience

Rebound resilience was done according to ISO 4662: 2017 [26]. **Figure 15** shows the rebound resilience results. Rebound resilience is another important property of a tyre. Resilience reflects the heat generation and rolling resistance of a tyre because it is influenced by the hysteresis or energy dissipation. High resilience indicates low

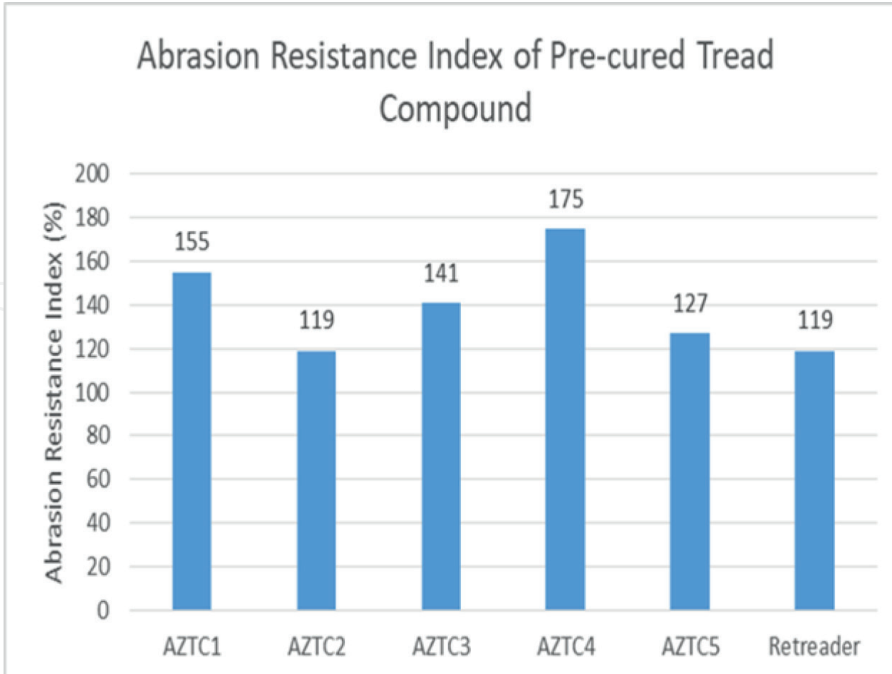

Figure 13.
Abrasion Resistance Index of pre-cured tread compounds.

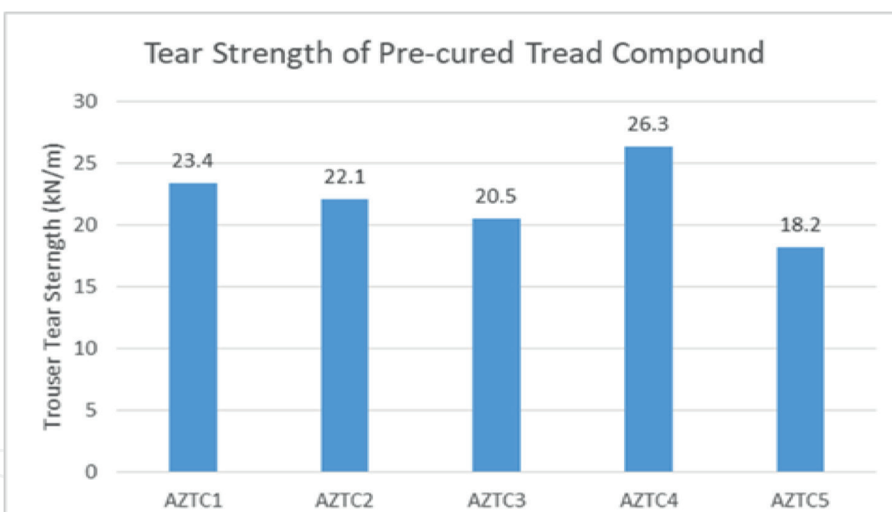

Figure 14.
Tear strength of pre-cured tread compounds.

rolling resistance and low heat build-up. All compounds having high r-CB produce higher resilience than compounds having high N220 and low r-CB. The retreader compound gives the lowest resilience because of the high loading of N234.

4.5 Summary

- The r-CB has high quality equivalent to virgin ISAF (N220).

- The incorporation of N220 into r-CB enhances further the mechanical strength and physical properties.

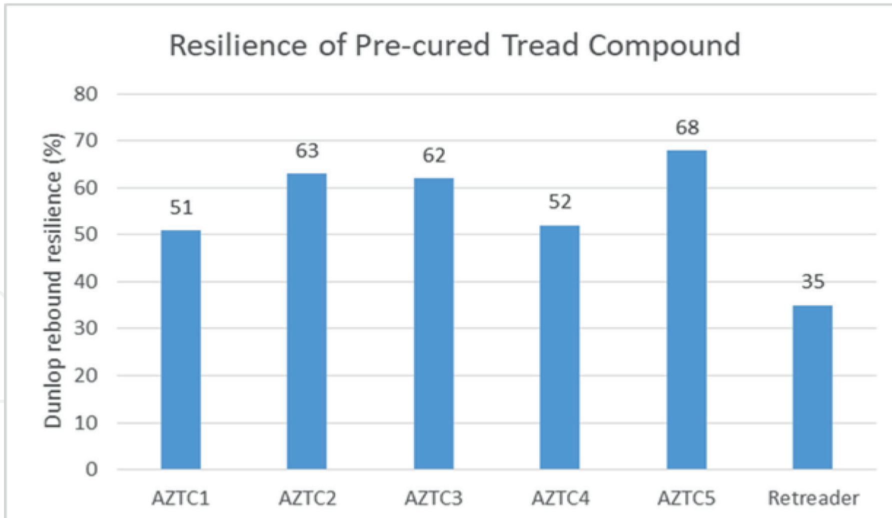

Figure 15.
Rebound resilience of procured tread compounds.

- r-CB can be used 100% on its own in pre-cured tread compound meeting all the specifications (both before and after ageing at 70°C 168 h) laid down in MS1208:2020.

- In addition, r-CB can provide cooling running tyre, low heat generation and low rolling resistance as reflected by the high rebound resilience. Low rolling resistance tyre saves fuel consumption and emits low smoke which are essential features of a green tyre that provides friendliness to the environment.

5. Applications of r-CB in automotive NBR compounds

Table 8 shows the rubber compound formulations based on Nitrile Rubber (NBR) for Rubber Seal such as O-ring and Inner Liner for Liquefied Petroleum Gas Lines. Rubber compounds AZOR1 and AZOR2 represent Rubber Seal (O-ring) formulations loaded with 100phr r-CB and 80phr r-CB respectively to replace 25phr of N-550 (FEF) and 95phr of N-990 (MT) in the Control 1 compound. Rubber compounds AZIL1 and AZIL2 represent Hose Inner Liner containing 100phr of r-CB and 80phr of r-CB respectively to replace 50phr of N-550 (FEF) and 50phr of N-990 (MT) in the Control 2 compound.

Rubber compounds shown in **Table 8** were prepared in a Farrel Banbury (BR1600) at a starting temperature of 70 °C, fill factor 0.7 and rotor speed of 100 rpm.

Curatives were added into the masterbatch the next day using a pre-heated two-roll at 50 °C. The mixing process took about 6 minutes.

5.1 Rubber seal (O-ring)

All the results are shown in **Table 9**. The ageing test was done at 100°C for 70 hours. The two NBR rubber compounds AZOR1 and AZOR2 meet the tensile strength and elongation at break requirements before ageing in accord with the ASTM Standard Classification System for Rubber Products in Automotive Applications [5]. However, rubber compound AZOR2 does not meet the minimum hardness

Materials/Ingredients	Control 1	AZOR1	AZOR2	Control 2	AZIL1	AZIL2
NBR (33% ACN)	100	100	100	100	100	100
N-550 (FEF black)	25	—	—	50	—	—
N-990 (MT black)	95	—	—	50	—	—
Carbon black (r-CB)	—	100	80	—	100	80
Stearic acid	0.5	0.5	0.5	1	1	1
Polymerised 2,2,4-trimethyl-1,2-dihydroquinoline	2	2	2	2	2	2
ZMBI	2	2	2	2	2	2
Dioctyl Phthalate	10	10	10	20	20	20
Zinc oxide	15	15	15	5	5	5
Processing aid Ultra flow 600 T	—	2	2	2	2	2
Sulfasan R	1.5	1.5	1.5	1	1	1
N-cyclohexylbenzothiazole-2-sulphenamide	3	3	3	3	3	3
Tetramethylthiuram disulphide	4	4	4	3	3	3
MC Sulphur	0.3	0.3	0.3	—	0.2	0.2

AZOR1–AZOR2 and AZIL1–AZIL2 refer to sample references for O-ring (OR) and inner liner (IL).

Table 8.
Nitrile rubber compounds for rubber sheet gasket and hose inner liner.

Sample reference	Control 1	AZOR1	AZOR2	Specifications [5]
Hardness before ageing (Shore A)	75	68	63	65–75
% change in hardness after ageing	6	7	5	0 (min) - +15 (max)
Tensile strength before ageing (MPa)	10	14.9	11.6	10.3 (min)
% Retension in tensile strength after ageing	+2	−16	−25	−15 (max)
EB before ageing	190	440	480	200 (min)
% Retension in EB after ageing	−34	−36	−41	−40 (max)
Compression set at 22 h/100 °C (%)	26	37	34	50 (max)
IRM 903 Oil immersion 70 h/100 °C	2	3	3	9 (max)

Table 9.
Physical properties before and after ageing for rubber seal.

requirement. It appears that 80 phr of r-CB is not adequate to meet the minimum hardness requirement of 65 Shore A. After heat ageing at 100°C for 70 hours, rubber compound AZOR1 meets the hardness and elongation at break requirements, but narrowly exceeds the maximum limit of the tensile strength retention. Both compounds AZOR1 and AZOR2 meet the compression set requirement below the maximum value of 50%. The ASTM Standard Classification System for Rubber Products in Automotive Applications specification for the change in volume after immersion in IRM903 oil for 70 h/100°C is +10% (maximum) [5]. IRM 903 oil (Formerly known as ASTM Oil No 3) is a testing oil to be used in testing rubber components as per ASTM standards. Both compounds AZOR1 and AZOR2 also meet the specification limit for

Sample reference	Control 1	AZIL1	AZIL2	Specifications [4]
Tensile strength before ageing (MPa)	10.8	13.3	10.3	9.81 (min)
Tensile strength after ageing (MPa)	10.9	11.5	8.8	
% Retension in tensile strength after ageing	100	86.5	85.4	75 (min)
EB before ageing (%)	370	670	660	200 (min)
EB after ageing (%)	292	563	548	
% Retension in EB after ageing	78.9	84	83	75 (min)
Swelling in n-pentane 72 h/20 °C	8	11	11	25 (max)

Table 10.
Physical properties of hose inner liner before and after ageing at 100°C for 70 hours.

swelling resistance in oil immersion where the change in volume after immersing in IRM903 oil for 70 h/100°C is only +3%.

5.2 Hose liner compounds

Table 10 shows the results of inner liner hose rubber compounds to meet the British Standard Specification for Rubber Hose and Hose Assemblies for Liquefied Petroleum Gas Lines [4] before and after ageing at 70°C for 96 hours. Both rubber compounds AZHL1 and AZHL2 meet the minimum requirements of tensile strength and elongation at break before and after ageing. In fact, the tensile strength of AZHL1 before ageing is 35.6% higher than the minimum tensile strength specified and its elongation at break is 235% higher than the minimum EB specified. The retention of tensile strength and retention of elongation at break after ageing are more than 80%. All the compounds also meet the change in volume after immersion in n-pentane for 72 hours at 20°C. The results above provide experimental evidence that r-CB reported here is of high quality and suitable for applications in the manufacturing of rubber products such as pre-cured tread liner, rubber seals (O-ring) and hose inner liner.

The prospects of r-CB are very bright to penetrate into the rubber industry market. With the escalating price of virgin carbon black, r-CB is the best alternative substitution of black filler because the cost of r-CB is around 40–50% cheaper than most of the grades of virgin carbon black. The challenges ahead are to maintain high quality of r-CB, to be competitive in cost in relation to virgin carbon black, to reverse the misconception of r-CB as a low-quality material with the view to promote and to gain acceptance of r-CB as a suitable quality material by the Rubber Industry players worldwide. The future of r-CB is very bright with the acceptance of big tyre manufacturers to use r-CB in their tyre rubber compounds.

6. Conclusions

- The recycled carbon black used in this investigation is of high quality approaching the properties of reinforcing carbon black N330 (HAF black).

- r-CB meets the tensile strength minimum requirement of 18.2 MPa for a black filler for rubber from tyre pyrolysis specified by the ASTM D3191.

- At equal hardness (60 Shore A) based on the Standard Test Methods for Styrene-Butadiene Rubber (SBR) Recipe and Evaluation Procedures, the tensile strength of r-CB is equivalent to N550 and higher than that of the commercial virgin carbon black such as Stirling V, N660 and N770.

- The r-CB can be used 100% on its own or in combination with N220 (ISAF) to produce pre-cured tread compound for retreading and meeting all the technical requirements specified in the Precured Tread for Retreading Tyres-Specification, The Malaysian Standard MS1208:2020.

- The r-CB can be used to replace virgin carbon blacks in NBR compounds to produce rubber seal such as O-ring and hose inner liner for rubber hose and hose assemblies for liquefied petroleum gas lines.

- The prospects and future of r-CB are very promising and bright with very competitive price about 40–50% cheaper than most of the commercial virgin carbon black.

- The biggest challenge is to produce high-quality r-CB with high assurance of consistency and uniformity.

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