

**DEVELOPMENT OF A SOLID TIRE BLACK TREAD
COMPOUND WITH EXTREMELY LOW POLYCYCLIC
AROMATIC HYDROCARBON CONTENT**

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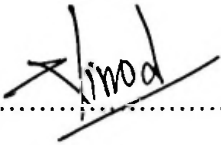
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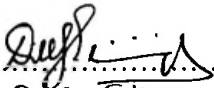


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ABSTRACT

The Polycyclic Aromatic Hydrocarbons (PAHs) can be identified as a large group of organic compounds. These organic compounds have two or more fused aromatic rings that contain only carbon and hydrogen atoms. These PAHs are non-polar compounds, lipophilic and insoluble in water.

Drinking water can be contaminated with PAHs and PAHs can be available mainly in coal and tar deposits. PAHs are hazardous and the extent to which it is hazardous depends on concentration of PAHs, time duration of exposure to PAHs and the type of PAHs. All PAHs are not hazardous to human health. Human exposure has various methods such as smoking rates, fuel types in cooking, pollution control on power plants, industrial processes and moving vehicles. Two methods are readily available in vehicle, which is emission of incomplete combustion of fuel and worn off parts in tires.

Tread compound in tires is a source of PAHs due to the presence of some raw materials used in compounding such as processing oil and carbon black. Tire tread part contains up to 28% of extender oil to provide the required elasticity and stickiness. High aromatic (HA) oil content in car tires is in the range of 6% to 8% of the total tire mass and between 11% to 16% of the tread. These HA oils have a PAH content between 300-700 mg kg⁻¹ and tire has an estimated PAH content in the range of 13.5 mg-112 mg kg⁻¹. Default (tread) compound of industry was selected for this project and a rubber compound was developed with an extremely low PAH level by using alternative raw materials such as PAH free carbon black, glove reclaim (white), vegetable oil derivatives and coconut shell powder. The number of PAHs in the compound reduced to 13.48 mg kg⁻¹ from 51.6 mg kg⁻¹.

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LIST OF ABBREVIATIONS

DNA - Deoxyribonucleic acid

ML - Moment Lowest

MH - Moment Highest

PAHs - Polycyclic Aromatic Hydrocarbons

LFGB – Test for food feed code

EC – European Commission

HA – High Aromatics

ZnO – Zinc Oxide

TRC – Tire Rubber Crumb

SBR – Styrene-Butadiene Rubber

ISO – International Organization of Standardization

REACH – Registration, Evaluation, Authorization & Restriction of Chemicals

PPHR – Parts Per Hundred Rubber

DPG - N,N'-Diphenyl Guanidine

TMTM - Tetramethylthiuram Monosulfide

TBBS – N-Tert-Butyl-2-Benzothiazyl Sulfenamide

CBD - Carbon Black Dispersion

t_{c90} - 90% Cure Time

t_{s2} - Scorch Time

6PPD - N-(1, 3-Dimethylbutyl)-N' - Phenyl-P-Phenylenediamine.

1 INTRODUCTION

Polycyclic aromatic hydrocarbons called as PAHs in shortly are organic molecules that consist of two or more adjacent aromatic rings. Although they only contain the elements carbon and hydrogen with uncharged non-polar molecules, these atoms can exist in many different structural arrangements, so many PAHs exist. These PAHs are can be available naturally in coal, crude oil, and petrol, and can be formed during the incomplete burning of fossil fuels. Generally, the less efficient the burning, the more PAHs are formed and for example, a) incomplete burning of fuel in engines and industrial wastage in incinerators b) biomass burns in forest fires.

In nomenclature and structure of PAHs, as define, they consist of polycyclic aromatic hydrocarbons with multiple cycles. The simplest PAH, according to Environment protection agency in the United States and centers for disease control and prevention in the US called as naphthalene with has two fused aromatic structures. A high number of PAHs with five or six-membered rings can be available.

Previous studies have shown that there are possible short-term and long-term health effects from PAH exposure, and this has resulted in national and international legislation. PAHs may pose a risk to human health by ingestion, skin absorption, and inhalation. Further human and animals on exposure to PAHs may cause eye irritation and vomiting. When the concentration of PAHs increases or serious, they can increase the risk of skin, bladder, liver and stomach cancers and It is this increased long-term risk of causing cancers that is the most significant reason for the new European-wide legislation. Since 27th December 2015, 10 PAHs have been limited to a maximum concentration of 1mg/kg (1 part per million – 1 ppm) and including 8 other PAHs, total PAHs content should not exceed X mg/kg, where X value depends upon skin contact time, in rubber or plastic components that come into contact with the skin or oral cavity. EU 1272/2013 includes the definition direct, as well as prolonged or short-term repetitive contact with the human skin or the oral cavity, under normal or reasonably foreseeable conditions of use. Some wearing item also may be contains PAHs and footwear is specifically listed as an article included in the restriction.

In Europe, there are limits on the amounts of PAHs present in consumer products. Clause 30 of the LFGB (the food and feed code) restricts the amount of 18 PAHs that can be present in food contact items, such as packaging or plastic utensils. Clause 30 of the LFGB is also applicable to

toys for children under 36 months of age that are intended to contact with the skin. There are current European restrictions in REACH 1906/2007/EC Annex XVII entry number 28, which bans the sale of PAHs to the general public in substances or mixtures, and entry number 50, but this cause applies to tires only. Hence, this study was focused to develop a tread compound with a controlled PAHs content. In the table given below, the requirement is highlighted for tires, which is in the category of other products.

It is not permitted to intentionally add PAHs to plastics or rubbers, but could be present as impurities. As previously mentioned, PAHs can be eliminated to open air through the burning of fossil fuels. A commonly used pigment and filler in black rubbers and plastics is carbon black due cost effective and reinforcement properties, which can be manufactured by the partial combustion of oil or natural gas. Some PAHs can be formed during this chemical reaction which as combustion product. Black rubbers and plastics are, therefore, more likely to contain PAHs than other colors. Extender oils (added to modify and cheapen processing or plasticizer oils) may also be manufactured from coal, crude oil or petrol and these substitutes contain PAH impurities. On the other hand, solid tire tread compounds contain a higher amount of reclaimed rubber and tire crumb, which will reduce compound cost and these recycled materials contain a higher number of PAHs, which is uncontrollable. Tread part of the tire is mainly eliminating the PAHs to the environment in several aspects. Tire tread contains 28% of extender oil, used for improving workability and properties and extender oil contains a high number of PAHs. The extender oil contains a high number of PAHs and then can achieve the target using of alternative raw materials, these materials should be substituted using proper materials with the aid of compounding knowledge to optimize the properties and price. According to the experiment results, tire crumb, carbon black and reclaim rubber are the most affective materials for the PAHs in tread compound in tire. In this project, trials are carried out using 8 trials with using alternative materials and different formulations.

In the industry cost is a considerable factor as same as properties and environmental issues. Hence at each sample set cost calculation is done and the most suitable formulae are found with optimization of the above factors.

1.1 Objectives of the Research Study

1.1.1 Main objective

The main objective of this research was to develop extremely low PAH black tread compound with the aid of auxiliary materials (complying with the Regulation EU 1272/2013).

Parameter	Category 1	Category 2		Category 3	
	Materials intended to put in to mouth ,or materials of toys with foreseeable long term skin contact(Longer than 30 Seconds) ppm	Materials not covered by Category 1,With foreseeable skin contact for longer than 30 seconds (long term skin contact) or repeated short term skin contact ppm		Materials not covered by category 1 & 2 with foreseeable skin contact up to 30 seconds(short term skin contact) ppm	
		Toys covered by Directive 2009/48/EC	Other products	Toys covered by Directive 2009/48/EC	Other products
Benzo(a)Pyrene	<0.2	<0.2	<0.5	<0.5	<1
Benzo(e)Pyrene	<0.2	<0.2	<0.5	<0.5	<1
Benzo(a)anthracene	<0.2	<0.2	<0.5	<0.5	<1
Benzo(a)fluoranthene	<0.2	<0.2	<0.5	<0.5	<1
Benzo(j)fluoranthene	<0.2	<0.2	<0.5	<0.5	<1
Benzo(k)fluoranthene	<0.2	<0.2	<0.5	<0.5	<1
Chrysene	<0.2	<0.2	<0.5	<0.5	<1
Dibenzo(a,h)anthracene	<0.2	<0.2	<0.5	<0.5	<1
Benzo(g,h,i)perylene	<0.2	<0.2	<0.5	<0.5	<1
Indeno(1,2,3-c,d)pyrene	<0.2	<0.2	<0.5	<0.5	<1
Acenaphthylene	<1 sum	<5 sum	<10 sum	<20 sum	<50 sum
Acenaphthene					
Fluorene					
Phenanthrene					
Pyrene					
Anthracene					
Fluoranthene					
Naphthalene	<1	<2		<10	
Sum of 18 PAHs	<1	<5	<10	<20	<50

Figure 1.1 PAH parameters and categories

1.1.2 Specific objectives

- To select most suitable substitutes to minimize the PAHs in the tread compound up to extremely low levels.
- To ensure that the physico-mechanical properties (especially abrasion resistance, tensile strength, modulus and elongation at break) of the newly developed compound are in accordance with the required specifications.
- To ensure that the cost of the developed compound should not be unreasonable, for it to be feasible in the implementation stage.

2 LITERATURE REVIEW

2.1 Polycyclic Aromatic Hydrocarbons

Polycyclic Aromatic Hydrocarbons called PAHs in short are a large group of organic compounds and they have two or more fused aromatic rings and contain only carbon and hydrogen. These PAHs can be divided into two categories such as low molecular weight compounds consisting of lower than four rings and high molecular weight compounds of four or higher than four rings. PAHs can be found in coal and tar deposits. Further, they can be produced from thermal decomposition of some organic materials such as incomplete burn of the fuel in engines and incinerators and when biomass burns in forest fires. [1]

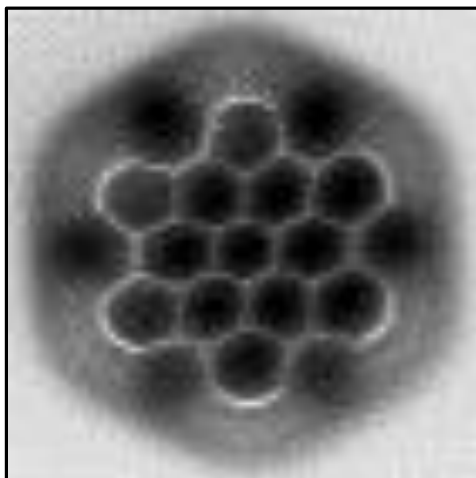


Figure 2.1 Atomic force microscopy image of a PAH

In chemistry, there are a high number of PAHs and this PAH has multiple cycles. Simplest PAH is naphthalene according to the policy of Environment Protection Agency (EPA). However, sometimes consider as PAHs to start with tricyclic species such as phenanthrene and anthracene [2].

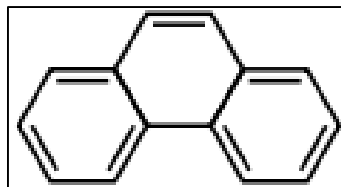
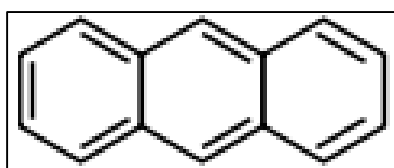


Figure 2.2 Molecular structures of anthracene and phenanthrene

Five or six-membered PAHs are commonly available and six-membered PAHs are called as alternant PAHs, which include benzenoid PAHs. However, there are many numbers of PAHs and main PAHs are indicated in the following figure.

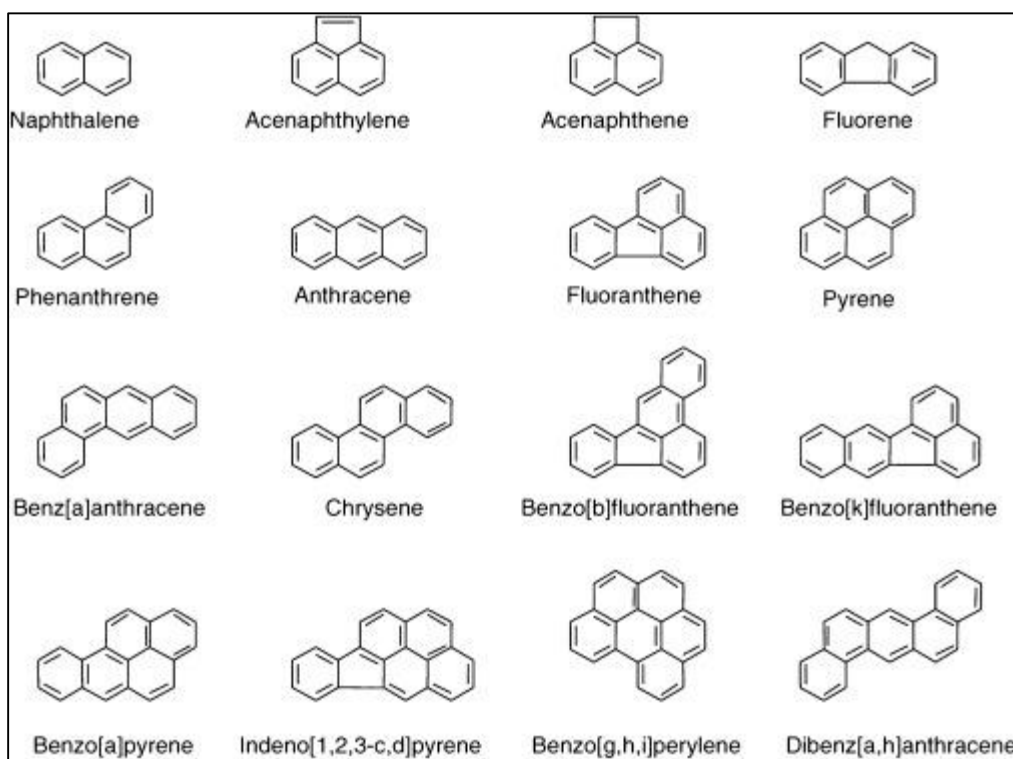


Figure 2.3 Molecular structure of main PAHs

Physical properties and chemical properties of these PAHs are determined from conjugated electron cloud of π and it also depends on numbers of the aromatic ring (mainly depend on sextets). Phenanthrene has two sextets, first and third rings while the other resonance structure

has just one central sextet and these outer rings have greater aromatic character while the central ring is less aromatic with high reactive properties.[1]

In terms of physical properties, these PAHs are usually low in water solubility and solubility can be decreased with increasing molecular weight of PAHs, but PAHs are highly lipophilic. These PAHs are reactive in the atmosphere and they can react with ozone, nitrogen oxide and sulfur dioxide yielding dienes, nitro- and dinitro-poly aromatic hydrocarbons and sulfonic acids. Further, PAHs can be degradation from a microorganism in the soil [1]. Like other gas, the vapor pressure of PAHs decreases with increasing molecular weight. PAHs have some general properties such as light sensitivity, heat resistance, conductivity, imitability, corrosion resistance, and physiological action. [3]. However, PAHs are normally uncharged materials because these do not exhibit any polarity [1].

2.2 Effects of PAHs on Health

There are many effects on human health from PAHs and this effect depends on the extent of the time duration of exposure, the concentration of PAHs, the toxicity of PAHs and the exposure method. There are some routes of exposure such as inhalation, ingestion, skin contact, etc. It may be a cause of impaired lung function in asthmatics and thrombotic effects in people affected by coronary heart disease. There is currently no shortage of potential human health impacts on circulating concentrations of PAHs. In contrast, PAHs with high pollutant concentrations in occupational exposure cause eye irritation, nausea, vomiting, and diarrhea. PAH blends cause skin irritation and inflammation. Anthracene, benzo (a) pyrene and naphthalene directly irritate the skin, and anthracene and benzo (a) pyrene are reported to be sensitive skin, animals, and humans [3]. The following chart shows the short term and long-term effects on the human body.

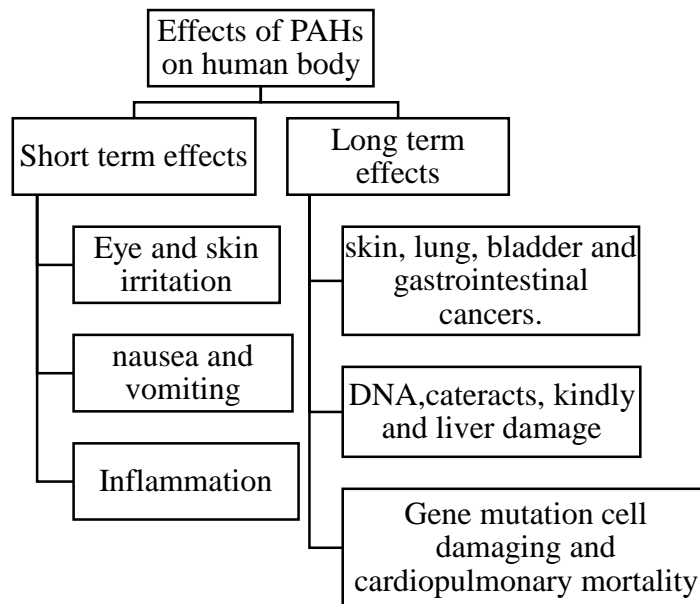


Figure 2.4 Effects of PAHs on human body

2.3 Tires and PAHs

The tire industry can be divided into two categories; solid tires and pneumatic tires according to application and construction of tires. Both tires have different constructions and each part has different properties. The tread of tire is a more important part of tire and it has wearing properties.

Traffic-related non-exhaust (NE) emission comprising tire, road and brake wear is one of the important non-point sources. The wearing of tire (mainly tread part) is a significant source of elemental carbon and organic carbon. This wearing of tire constitutes potentially toxic components such as polyaromatic hydrocarbons (PAHs), aromatic oil that is part of compound formulation for tires and rubber stock is made workable by the aid of extender oil. Tire tread part contains up to 28% of extender oil to provide the required elasticity and stickiness. One of the main components of extender oil is high aromatic oil (HA) in PAHs. HA oil content in car tires is in the range of 6% to 8% of the total tire mass and between 11 to 16% of the tread part. These HA oils have a PAH content in between of 300-700 mg kg⁻¹ and tire particles have an estimated PAH content in the range of 13.5 mg-112 mg kg⁻¹. Tire wear is the main problem due to these PAHs in the tread and it also affects several aspects of environmental pollution, such as air pollution, urban runoff, and climate change. Tire wear will ultimately outweigh the exhaust as the exhaust is cleaner with the use of catalytic converters and improved fuels and engines. Some laboratory studies have proved that water extracts of tires are toxic also to aquatic organisms [4].

It is necessary to determine the PAHs in tires, especially in tread compound and reduce PAHs in the tread compound or development of PAHs comply tread compound. ISO 21461 was introduced to determine the PAHs and for this method, nuclear magnetic resonance is used. This method developed in Europe and European Tire & Rubber Manufacturers Association supports the European Union PAH standards.

Process oil is a main PAH source in the compounding process and Southwest Research Institute developed its own method of determination of PAHs in process oils. Fine-tuning of the oil cleanup technique of using liquid-liquid partition was done according to the description given in the Grimmer method by gravity liquid chromatography using columns packed with activated silica gel and adopting the isotope dilution technique.

2.4 Types of PAHs available in the Environment

A high amount of PAHs exists in the environment, which affects human beings and they can be listed as follows. [3]

- Naphthalene
- Fluorene
- Acenaphthene
- Acenaphthylene
- Phenanthrene
- Anthracene
- Fluoroanthene
- Pyrene
- Benzo[a]anthracene
- Chrysene
- Benzo[b]fluoroanthene
- Benzo[a]pyrene
- Benzo[e]pyrene
- Perylene
- Benzo(g,h,i)perylene
- Indeno[1,2,3-cd] pyrene
- Anthanthrene
- Coronene

Naphthalene is the simplest PAH and it is a white crystalline solid with two fusion benzene rings in molecular structure. It is detectable at concentrations as low as 0.08 ppm by mass.[5] Naphthalene can destroy red blood cells when exposed to large amounts. Naphthalene mostly used in industrial applications as a non-detergent wetting agent due to effectively disperse colloidal in aqueous solution.[6] Fluorene is a white crystalline chemical with a similar odor to naphthalene. Fluorene is harmful to the kidney and liver. Mainly used for making plastics, pesticides, and dyes.[7]

Acenaphthene looks like a white or pale-yellow crystalline powder with an application of dyes and optical brighteners. Coal tar contains about 0.3% of acenaphthene. Acenaphthene can be irritated to skin and eyes and when breathing of acenaphthene, it can irritate the nose and throat causing coughing and wheezing.[8] Acenaphthylene is a yellow solid chemical with saturation after hydrogenation. Acenaphthylene is a low hazard chemical.[8] Phenanthrene is a hydrocarbon with three fused benzene rings with colorless crystal-like solid looks as a pale yellow. Mainly used in the industry to produce plastics, pesticides, dyes and explosives.

Anthracene is also a hydrocarbon with three fused benzene rings with colorless hydrocarbon used to produce dyes. The human body can be affected by hydrocarbon according to the explosive route. When in skin contact can cause irritation, itching and burning, which is greater aggressive. When breathing may be caused to lungs causing, coughing and wheezing and eyes can be burn when they touch the eyes.[9] Benzo[a]pyrene is a polyaromatic hydrocarbon produced by incomplete combustion of organic

material between 300°C to 600°C. Benzo[a]pyrene is a more hazardous hydrocarbon that can affect the human body in various routes for different systems such as the immune system, reproductive system and nervous system. Further Benzo[a]pyrene is a type of carcinogen and DNA system can be destroyed due to interaction with it.[10] Fluoroanthene is a polycyclic aromatic hydrocarbon produced from incomplete combustion of fuel and a colorless chemical, soluble in non-polar solvents. This causes little hazard on the human body, while somewhat hazardous on animal health.

3 MATERIALS AND METHODOLOGY

Initially, all the susceptible materials containing PAHs were tested for 18 PAHs from an authorized body. Selection and testing of the materials were done within the tread compound. The materials which are not eligible were substituted by proper alternatives. According to the literature, there are four substances that should be replaced by other auxiliary materials which are carbon black, process oil, reclaimed rubber and tire crumb.

In the initial stage of the project the above materials were substituted by proper alternatives and the physical properties of the compounds produced were evaluated according to the ASTM standards and compared with those of the standard sample. Simultaneously, samples were submitted to an authorized testing body to evaluate the PAH content. After confirmation of the PAH content, a batch of the approved compound was produced to check the processability during compound mixing and in tire production. After validating the compounding process, tire testing was done using a tire testing machine and, in the field, to see the actual difference in performance in relation to the standard compound.

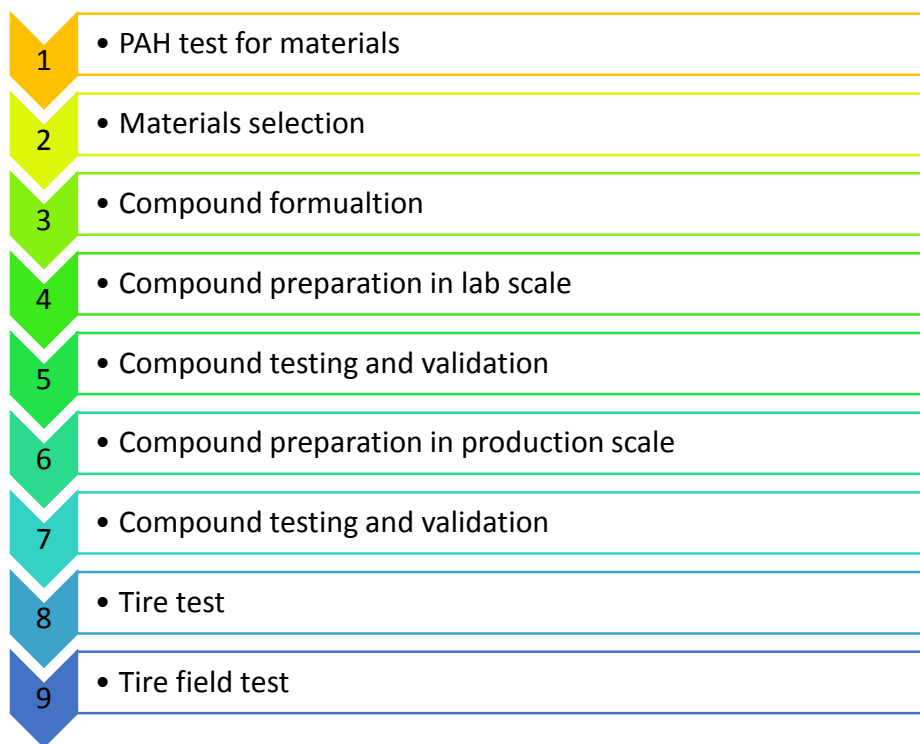


Figure 3.1 Methodology

According to the steps given under methodology, compounds were prepared according to 7 formulations and it is given in below table.

3.1 Compound Formulations

Property requirement for the tread compound is given in Table 3.1

Table 3.1 Specifications of the compound

Specific Gravity	Hardness (Shore A)	Rebound Resilience (%)	Abrasion Volume Loss (mm ³)	Tensile Strength (kg/cm ²)	Modulus at 300 % (kg/cm ²)	Elongation at break (%)
1.145-1.160	64-69	35-43	<=110	>=140	>=90	>=400

Table 3.2 Formulations of rubber compounds

No	Raw Materials / Chemicals	S1	S2	S3	S4	S5	S6	S7
01	Natural Rubber-RSS	50.0	50.0	60.0	50.0	50.0	50.0	50.0
02	Synthetic Rubber	40.0	40.0	40.0	40.0	40.0	40.0	40.0
03	Reclaimed Rubber-Black	30.0	30.0	-	-	-	-	-
04	Reclaimed Rubber-White	-	-	-	20.0	20.0	20.0	20.0
05	Carbon Black	45.0	40.0	45.0	42.0	42.0	42.0	-
06	Carbon Black-PAH Free	-	-	-	-	-	-	48.0
07	Precipitated Silica	10.0	10.0	10.0	10.0	10.0	10.0	10.0
08	Rubber Process Oil	6.0	-	-	-	-	-	-
09	Vegetable Oil Derivatives	-	-	7.0	7.0	7.0	7.0	7.0
10	Tire Crumb, 30 Mesh	10.0	10.0	10.0	10.0	-	-	-
11	Coconut Shell Powder	-	-	-	-	-	10.0	10.0
12	Silane Coupling Agent	1.0	1.0	1.0	1.0	1.0	2.0	2.0
13	Resin	2.5	2.5	2.5	2.5	2.5	2.5	2.5
14	Antioxidant	4.0	4.0	4.0	4.0	4.0	4.0	4.0
15	ZnO-99.5%	4.5	4.5	4.5	4.5	4.5	4.5	4.5
16	Stearic Acid	2.2	2.2	2.2	2.2	2.2	2.2	2.2
17	Accelerator	1.3	1.3	1.3	1.3	1.3	1.3	1.3
18	Prevulcanization Inhibitor	0.5	0.5	-	0.5	0.5	0.5	0.5
19	Sulphur	1.5	1.5	1.5	1.5	1.5	1.5	1.5

Formulation 1 was considered as the control. Except Formulation 3, all other 6 formulations contain 50 pphr NR and 40 pphr synthetic rubber. Rubber process oil was not included in Formulation 2 to ascertain the effect of rubber process oil on PAH conformity. Reclaimed rubber-black was removed from Formulation 3 and vegetable oil derivative added to determine the effect of reclaimed rubber. Reclaimed rubber –white was added to Formulation 4 replacing 30 pphr Reclaimed rubber-black. Tire crumb 30 mesh (TRC 30) removed from Formulation 5 to detect its effect on PAH. Formulations 6 and 7 contain the same amount of white reclaim, vegetable oil derivative and coconut shell powder replacing TRC 30 from Formulation 5. PAH free carbon black was added to Formulation 7. According to the chart

given above, Formulation 7 contain white reclaimed rubber, vegetable oil derivative, PAH free carbon black and coconut shell powder replacing black reclaimed rubber, process oil, TRC 30 and carbon black.

3.2 Material Specifications and the Purity

When the experiment was designed more attention was given to choose a specific material source throughout the experiment, even though the same material can be obtained from many other sources and are available in the inventory for usage. This action ensures the minimum influence of material quality variations on results.

3.2.1 Main polymers

NR, RSS 3 was selected as base polymer since it provides intended properties like excellent tensile strength, green tack, tear resistance and excellent heat build-up resistance during flexing, which makes it a material of choice when shock and dynamic load requirements are important for tread compounds. This inherited property is due to strain induced crystallization behavior of natural rubber. Natural rubber was sourced from one specific supplier in Sri Lanka. Principal intension of this action was to control the viscosity of the base polymer. Styrene-butadiene rubber (SBR) can be identified as one of the cheaper synthetic rubbers used in general-purpose. SBR sometimes used as a substitute for natural rubber (NR). It can be produced by free-radical solution polymerization or by emulsion polymerization either warm at 30 to 60°C (hot rubber) or cold at temperatures near 0°C (cold rubber). The addition of SBR reduces the price and gives good wear and bonding properties. The addition of SBR also gives the strength, abrasion resistance, and blend properties of polybutadiene. With comparing to the natural rubber SBR show high fatigue resistance and low temperature properties. SBR 1502 purchased from Reliance Industries Limited was used for this study.

3.2.2 Reclaimed rubber (NR based)

Black reclaimed rubber RRB-9 grade purchased from Weltek International Co. Ltd was used. White reclaimed rubber produced using off-grade latex medical gloves was purchased from same source and utilized for the tests.

3.2.3 Reinforcing fillers

Carbon black is the organic filler widely used worldwide. Filler with high surface area (particle size 26–30 nm) is used to obtain required physical properties of tread compounds. N375 carbon black purchased from Philips Carbon Black Limited was used in tread compound. PAH free Carbon black is a pelletized reinforcing carbon black which is recommended for rubber articles that require a very low PAH and higher reinforcement, strength, abrasion and tear resistance than semi-reinforcing carbon blacks was used for the study. Vulcan 6 –LP from Cabot Corporation was selected. Precipitated silica is a form of synthetic amorphous silicon dioxide. This is derived from quartz sand. The performance can enhance with the physical properties of precipitated. Precipitated silica from Shanxi Tonga Chemical Co. Ltd was used for test compound preparation.

3.2.4 Rubber processing oil (Low PAH oils)

In recent years, the carcinogenicity of polycyclic aromatic hydrocarbons comes to be regarded as important. Oils containing 3% or more of polycyclic aromatic compounds (PCA) are obliged to indicate that they are toxic and there is a trend towards regulation of their use. Accordingly, it becomes an urgent task to reduce the content of PCA in rubber process oil to less than 3%, these oils are called Low PAH oils. Low PCA Green 222 grade purchased from PSP Specialties Co. Ltd. was used. Eco- friendly bio oil, Witprol AES 200G from Witmans Industries Pvt. Ltd was used as vegetable oil derivative.

3.2.5 Non-reinforcing fillers

Crumb rubber is recycled rubber that is produced using automotive and truck scrap tires. During the recycling process, steel and tire cord (fluff) are removed. Processing is continued with a granulator or cracker mill to further reduce the size of the particles. The granulate is sized by passing through a screen, the size based on a dimension. This was added to compounds as a black colour filler to reduce cost, while maintaining the required properties. 30 mesh particle size crumb rubber purchased from Lakjewa Industries Pvt. Ltd. was used for this study. Coconut shell powder with 300 mesh particle size produced at Silver Mill Group Pvt. Ltd. was used.

3.2.6 Coupling agent

Coupling agent Silane-69 (Si-69) is a bifunctional, sulphur containing organosilane and also it is one of the most functional rubber additives. Also, this Si-69 reacts with fillers containing silanol groups during mixing and with the polymer during the vulcanization process under formation of covalent bonds. This provides better tensile strength, higher modulus, reduced compression set, increased abrasion resistance and optimized dynamic properties. Si-69 used in many applications where white fillers containing silanol groups are involved such as silica and optimum technical properties are required.

Si-69 Coupling Agent - $C_{18}H_{42}O_6S_4Si_2$. Silane coupling agent (Crosile-69) purchased from Ecopower (Yongxiu) New Materials Co. was used

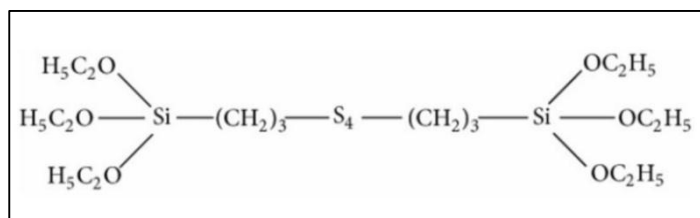


Figure 3.2 Si-69 Coupling Agent

3.2.7 Resin

The C5 petroleum resin is an aliphatic hydrocarbon resin widely used in rubber compounding, the resin has no aromatic content and is fully compatible with NR and SBR. In the process of rubber compounding, C5 petroleum resin functions as an excellent tackifier and extender. It improves green tack, extensibility and heat aging resistance. Guangzhou Eco power New Materials Co. Ltd. provided the C5 petroleum resin was used as tackifier.

3.2.8 Antioxidants

6PPD offer excellent antioxidant, static and dynamic ozone resistance and anti-flex cracking properties. Exhibits optimum migration rate and less volatile than di-alkyl PPDs. Lower losses during storage, processing and cure. Offer long term protection to rubber vulcanizates. 6 PPD is not easily leached out in water and exhibits high solubility in rubber, hence no blooming. 6PPD is stable and has good shelf-life.

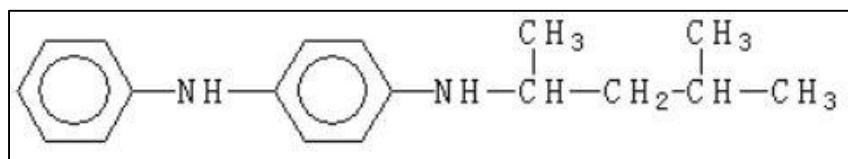


Figure 3.3 Molecular Structure of 6PPD

3.2.9 Activators

Activators are both inorganic and organic chemicals used to activate or extract the full potential from the organic accelerators or activate the process of crosslink formation and produce a uniform state of cure in the compound. Modulus of the rubber vulcanizates is also improved by activators. Zinc oxide is the most widely used inorganic activator (lead and magnesium oxides are also used, but less often), while stearic acid is normally the organic activator of choice. Many rubber compounds today incorporate a combination of zinc oxide and stearic acid in sulfur-cured compounds. High purity (99.5%) zinc oxide from Rubamin Co. Limited, India was used for the study. Rubber grade stearic acid is not a pure compound of stearic acid, it is normally a mixture of stearic acid (60%), palmitic acid (20%) and oleic acid (20%).

Stearic Acid Palmac 1400 purchased from IOI Pan-Century Oleochemicals Sdn. Bhd was used for the study.

3.2.10 Accelerators

There are different varieties of accelerators available for rubber compounding. The sulfenamide class accelerators include CBS, TBBS, MBS, and DCBS etc. and are most popular in the tire industry due to their delayed action as well as faster cure rate offered by them during vulcanization of rubber compounds containing furnace blacks. These accelerators provide wide range of crosslink densities depending on accelerator type and dosage of accelerator used and exhibit flat and reversion resistant cure. Progressive increase in dosage of sulfenamide accelerator shows improvement in scorch delay, cure rate and state of cure. Sulfenamide accelerators can be boosted by using DPG, TMTM type basic accelerators for further increase of cure rate. Sulfenamide accelerators can be effectively retarded using small proportions of PVI (e.g. CTP) without affecting their rate of cure. Vulcanizates of sulfenamide accelerators exhibit higher stress-strain properties along with better resilience and flex-fatigue resistance.

Considering advantages, TBBS accelerator purchased from Zibo Huamei Chemical Co. Ltd. with the specifications given below was used for this study.

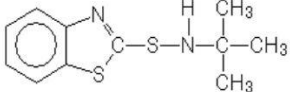
N-tert-butyl-2-benzothiazole sulfenamide (TBBS)		Group: Sulfenamides Speed: Delayed Action. Ultra fast. Use: As a Primary accelerator
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Figure 3.4 TBBS

3.2.11 Prevulcanization Inhibitor (PVI)

A proper balance of rubber processing safety and faster curing rates is essential for increased productivity. Normally higher processing temperatures for compound mixing used along with faster accelerator combinations and also higher vulcanization temperatures are used to reduce the vulcanization time. Sometimes the rubber processing temperatures reach a temperature just 10°C below the actual vulcanization temperature and this induces 'onset' which is known as scorch or premature vulcanization. To avoid scorch with faster curing systems and / or with higher processing temperatures and prolonged storage, 'Retarders' or 'Pre vulcanization Inhibitors (PVI)' are added during compounding.

Pre-vulcanization Inhibitor (PVI), N-cyclohexyl thiophthalimide (CTP) is used due to its excellent characteristics. CTP (PVI) of Shandong Derek New Materials Co. Ltd was used.

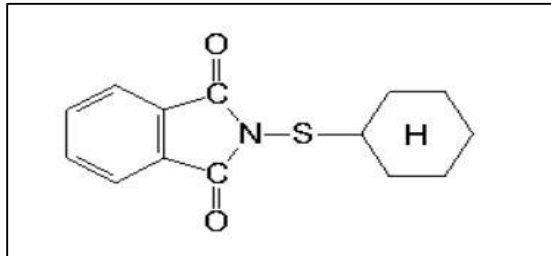


Figure 3.5 Chemical structure of CTP

3.2.12 Vulcanizing agent (Sulphur)

Commonly use Sulphur as vulcanizing agent, because its easy availability and affordable price. Tire industry consumes almost 80% of elastomers and all tires worldwide are conventionally cured with the sulphur accelerator system. Sulphur powder from Miwon Chemicals Co. Ltd. was used to prepare the rubber compounds.

3.3 Processing of Rubber Compounds and Sample Preparation

Laboratory scale internal mixer and mixing mill was used for the compounding stage.

3.3.1 Mixing in internal mixer

Farrell BR1600 Banbury mixer was used for compound mixing. It is a variable speed mixer, but rotors are maintained at a constant speed of 30 rpm during the experiments, these rotor speeds generate the friction ratio of 1:1.16. The ingredients listed in the compound formula were sequentially added into the mixer and mixing was done as per the times defined in the mixing cycle. In addition to mixing time, temperature rise was also considered in discharging the compound from the mixer.

Table 3.3 First stage of the mixing cycle

Raw Materials and Mixing Sequence	Time (Seconds)	Total Ram Down Time (Seconds)
Added NR+SBR +Reclaimed Rubber + Tire Crumb (30 mesh) +Coconut Shell Powder	80	80
Added Silica +Silane Coupling Agent + Stearic Acid+ ZnO + Antioxidant + Resin	60	140
Added Carbon Black (N375) +Rubber Processing Oil	60	200
Ram Sweep	05???	205
Dumped	65	270

Dump Temperature: 150 °C - 155 °C

Table 3.4 Second stage of the mixing cycle

Raw Materials and Mixing Sequence	Time (Seconds)	Total Ram Down Time (Seconds)
Added Masterbatch Compound	30	30
Added Acclerator + Sulphur+ PVI	60	90
Dumped	0	90

Dump Temperature: 100 °C - 105 °C

3.3.2 Mixing on two-roll mill

Mill mixing was done using a laboratory scale two-roll mill. Mill size was 200 X 400 mm. Mill roll speed can be adjusted independently to variable speeds, this feature provides different friction ratios. 1:1.2 friction ratio was used during the study. The rubber compound lump taken from the internal mixer was passed five times through the tight nip to get a smooth band on mill rolls and proper mixing. Finally, the compound was sheeted out at a fixed nip gap to orient the fiber dispersion preferentially in one direction.

3.3.3 Vulcanization using laboratory hydraulic press

Electrically heated hydraulic press was used to prepare the vulcanizates. Pressure on compounds were maintained at 4.5 bar (ASTM requirement is minimum 3.5 bar). Temperature for curing of rubber compounds was 150 +/- 2 °C.

3.4 Testing

3.4.1 Mooney viscosity

Viscosity of rubber compounds was measured using Ektron Viscometer, EKT -2003M model. The compounds were introduced into the heated die cavity using knurled disc rotor and subjected to a rotational shear. This reading was considered as viscosity of rubber compounds. The viscosity reported in ML (1+4)100°C (ASTM D-1646) was taken as the measurement.

Both 1st stage compounds (rubber mix without curatives, accelerators and prevocalization inhibitor) and 2nd stage compounds (1st stage compound, subjected to further mixing with curatives, accelerators and pre-vulcanization inhibitor) were tested as given below.

3.4.2 Cure characteristics

The Moving Die Rheometer, MDR-M2000 measures the change in stiffness of a rubber compound according to the ASTM D5289. The compound is heated by two plates and an oscillating force is given to the rubber by these plates. The degree of vulcanization determines the cure characteristics of the rubber compound as it is heated and compressed. Maximum torque (MH), minimum torque (ML), scorch safety time (t_{s2}) and 90% cure time (t_{c90}) were measured.

3.4.3 Specific gravity

Densimeter instrument based on Archimedes' Principle was used to measure the specific gravity directly according to the ASTM D 297. Alfa Mirage MD 300S Electronic Densimeter was used for this test. Theoretical specific gravity according to the formula and the actual specific gravity of the compound will indicate the accuracy of mixing and quality of the compound.

3.4.4 Hardness

Shore A scale is used for measure hardness of soft elastomers (rubbers) and other soft polymers. Resistance to indentation of rubber vulcanizates was measured using the Durometer rubber hardness tester. ASTM D 2240 test procedure was followed to measure hardness of test samples. It is expressed as a number referring to the scale of the instrument by which it is measured. This hardness is an important property for rubber industry along with tensile properties to which it is somewhat related.

3.4.5 Tensile properties

Tensile testing machine was used to determine the relationship between the applied force and the deformation produced. Dumb-bell shaped test-pieces were used for test. Moulded sheets both along and across the fiber direction were used to cut test pieces. Test pieces of standard dimensions were prepared by die punching (ASTM D-412 Method A).

The test pieces were conditioned at the test temperature of 27 +/- 2 °C for 24 hours before testing. The thickness was measured by a micrometer gauge. Three test pieces were used to get test results of each vulcanizate.

The dumb-bell test pieces were placed at the center position of the grip and the following force at break and elongation at break were taken whilst the test pieces were stretched. These measurements were subjected to the calculations given below and results were expressed accordingly.

Tensile Strength = F/A

F- Breaking Force, A –Initial cross-sectional area

Elongation at Break (%) = $(L-L_0)/L_0 \times 100$

L_0 - Initial length, L – Length at break

Modulus at 300% Elongation = f / A

f- force required at 300% elongation , A- Initial cross-sectional area

3.4.6 Abrasion resistance

Rubber products especially tires are usually subjected to rubbing action during its application. Abrasion resistance is measured in order to compare its behavior under service conditions. In other words, if the laboratory test show that trial compound gives less abrasion than the standard rubber, it is usually expected a better service life for products.

Abrasion volume loss was determined according to the standard ASTM 5963(Method A) . Gotech GT - 7012 D Din abrasion resistance tester was used for this study.

3.4.7 Carbon black dispersion

Gotech GT-505-CBD model was used to observe the state of dispersion of carbon black in a rubber compound. The carbon black dispersion tester can determine the dispersibility of the carbon black in rubber swiftly and exactly with the help of exact optical lens, CCD camera of fine quality, special-purpose video capture card of high resolution and powerful software according to ASTM D 2663 standard.

3.4.8 Rebound resilience

Resilience tester was used to measure the rebound resilience of rubber vulcanizates. Measured the resilience of the test specimens after impact with an indenter. Gotech GT-7042-RE model was used to carry out this test according to ASTM D7121.

3.4.9 Aging properties

Rubber and rubber products must resist deterioration of physico-mechanical properties with time caused by oxidative and thermal aging. This test method provides a way to assess these performance characteristics of rubber, under certain accelerated conditions as specified.

According to the standard, ASTM D 573, test pieces were kept in an aging oven and heated at a constant temperature of 100 °C for 24 hours and physico-mechanical properties; hardness, abrasion volume loss and tensile properties were evaluated.

4 RESULTS AND DISCUSSION

According to the experiment, the test results can be categorized into main four sectors. These sectors are results of lab scale trial, production trial, tire test and test results. The variation of PAH value according to the formula and product selection are discussed in this Chapter.

4.1 PAH Conformity Analysis

Table 4.1 PAH conformity results

No	Parameter	Other Products (Category 3 Specification)	S1	S2	S3	S4	S5	S6	S7
1	Benzo(a)Pyrene(mg/Kg)	< 1	N/D	N/D	0.63	1.01	0.32	N/D	0.22
2	Benzo(e)Pyrene(mg/Kg)	< 1	0.34	N/D	1.34	0.30	0.31	0.41	0.88
3	Benzo(a)Anthracene(mg/Kg)	< 1	N/D	N/D	N/D	N/D	N/D	N/D	N/D
4	Benzo(a)fluoroanthene(mg/Kg)	< 1	N/D	N/D	N/D	N/D	N/D	N/D	N/D
5	Benzo(j)fluoroanthene(mg/Kg)	< 1	N/D	N/D	N/D	N/D	N/D	N/D	N/D
6	Benzo(k)fluoroanthene(mg/Kg)	< 1	N/D	N/D	N/D	N/D	N/D	N/D	N/D
7	Chrysene(mg/Kg)	< 1	N/D	N/D	N/D	N/D	N/D	N/D	N/D
8	Dibenzo(a,h)anthracene(mg/Kg)	< 1	N/D	N/D	N/D	N/D	N/D	N/D	N/D
9	Benzo(g,h,i)perylene(mg/Kg)	< 1	2.72	N/D	0.59	1.16	3.83	1.62	0.71
10	Indeno(1,2,3-c,d) Pyrene(mg/Kg)	< 1	N/D	N/D	N/D	N/D	0.32	N/D	N/D
11	Acenaphthylene(mg/Kg)	< 50 Sum	5.09	0.72	1.22	2.88	1.01	2.58	3.21
12	Acenaphthene(mg/Kg)		0.59	0.37	0.57	0.54	N/D	N/D	0.51
13	Fluorene(mg/Kg)		0.68	0.28	N/D	N/D	0.77	0.70	N/D
14	Phenanthrene(mg/Kg)		10.0	2.32	1.78	1.18	0.47	1.70	1.44
15	Pyrene(mg/Kg)		38.5	5.64	11.0	6.99	9.95	5.70	7.67
16	Anthracene(mg/Kg)		0.59	N/D	N/D	N/D	N/D	N/D	N/D
17	Fluroanthene(mg/Kg)		10.4	1.79	1.50	1.75	2.87	1.19	1.69
18	Napthalene(mg/Kg)		< 10	2.74	13.3	0.77	2.64	N/D	N/D
	Sum of 18 PAHS(mg/Kg)	< 50	71.6	24.4	19.4	18.4	19.8	13.4	19.5

According to the test results of PAH conformity analysis, S1 has higher amount of Benzo (g, h, i) perylene which should be maintained below 1. S2 was prepared without adding rubber process oil. Though Napthalene content should be below 10 mg/kg, S2 has 13.35 mg/kg. Hence S2 does not comply with PAH requirements.60:40,NR: Synthetic rubber ratio was used to prepare S3. Instead of rubber

process oil, renewable oil derived from vegetables was used. For this purpose, Witprol AES- 200G soya bean oil was added. When sample was subjected to PAH conformity test, Benzo (e) Pyrene was detected with much higher value that made the sample a non-PAH comply tread compound. White reclaimed rubber, 20 pphr was added replacing black reclaimed rubber, 30 pphr with the Witprol AES- 200G natural oil instead of petroleum based oil to prepare S4. According to test results, Benzo (a) Pyrene and Benzo (g, h, i) Perylene were detected with a value of greater than 1 and S4 was also a non-PAH comply compound. S5 was prepared without using tire crumb (30 mesh), but with similar materials as in S4. In this sample, Benzo (g, h, i) Perylene with high amount was detected. Coconut shell powder was added replacing tire crumb to prepare S6 and S7. Vulcan 6- LP carbon black from Cabot Chemical Co., Ltd. was added instead of N375 carbon black for S7 without changing other materials. According to the test results, S6 has a much higher value for Benzo (g, h, i) Perylene. No any substance was detected from S7, which has PAH complied carbon black. Except S1, all the samples from 2-7 maintain the sum of 18 PAHs according to given specifications. According to the test results of PAH conformity, eventually S7 which was prepared by adding white reclaimed rubber, witprol AES- 200G natural oil, coconut shell powder and PAH comply carbon black is a PAH comply tread compound. These results imply that carbon black has a significant impact on PAHs.

4.2 Analysis of Physical Properties

4.2.1 Specific gravity of compounds

Specific gravity (SPG) of all the masterbatch compounds was measured using a specific gravity meter.

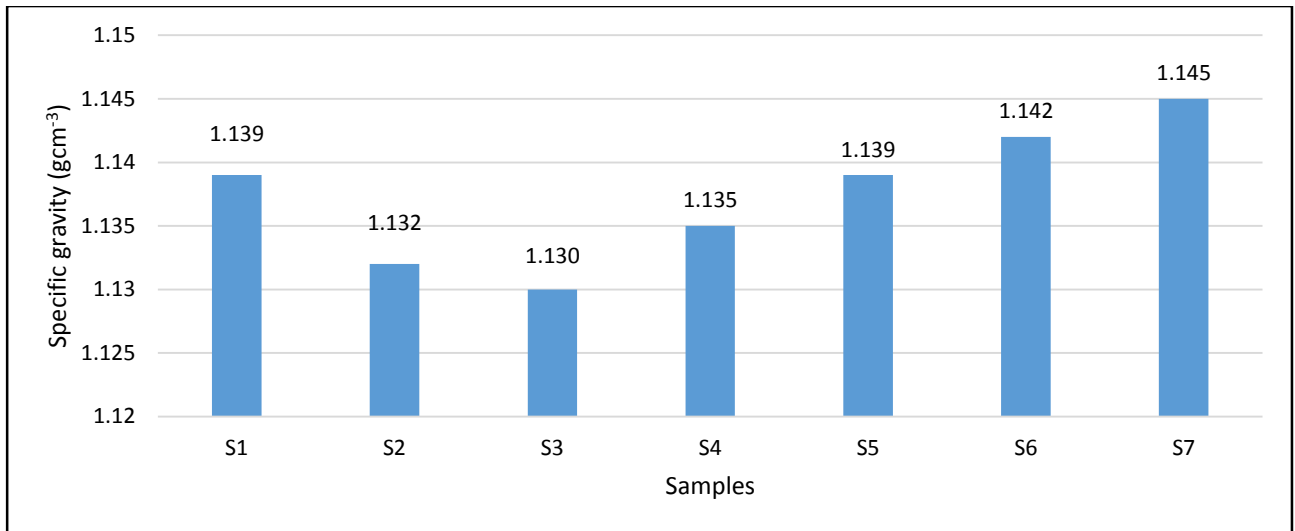


Figure 4.1 Specific gravity variation of compounds

Specific gravity of S1 is 1.139. S2 has low value with respect to S1 due to carbon black reduction and removal of rubber process oil. Natural rubber to Synthetic Rubber ratio was changed for S3 and vegetable oil derivative was added. This change reduced the SPG value to 1.132. S5 has a much higher SPG value because of removal of tire crumb (TRC 30) from formulae when it is compared with S3 and 4. Adding coconut shell powder, replacing TRC 30 has high impact on SPG value due to high SPG value of coconut shell powder. S7 has higher value with respect to S6 due to increment of carbon black to maintain tensile properties within the given specifications.

4.2.2 Cure characteristics of masterbatch compounds

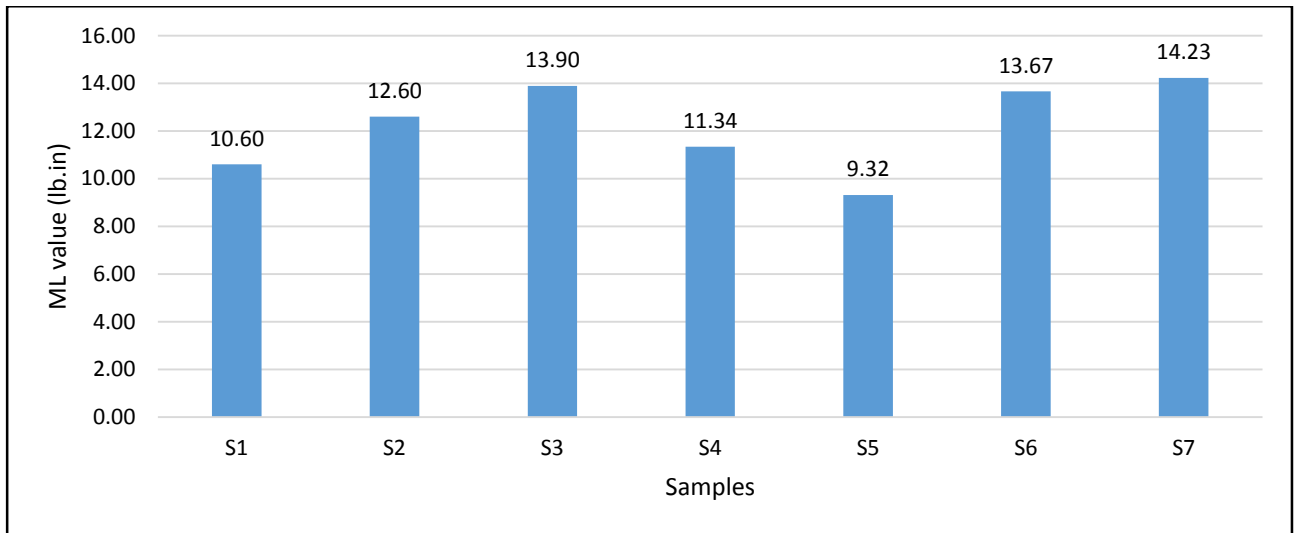


Figure 4.2 ML variation of compounds

As the compound gets heated under pressure, the viscosity decreases and the torque fall. The lowest value of torque recorded is called ML and it indicates the viscosity of the compound. According to the test results, S2 which does not contain any rubber process oil has much higher value when it is compared with S1 because physical lubricating action of rubber process oil to reduce viscosity is not with S2. Increase of Natural rubber content of formulae S3 has a higher impact on ML value due to high viscosity value of Natural rubber. Natural rubber has higher viscosity when it is compared with other general-purpose synthetic rubbers due to high molecular weight and broad molecular weight distribution. Replacement of black reclaimed rubber with white reclaimed rubber and reduced NR content reduced the viscosity of the compound. Therefore, S4 exhibits a low ML value than S3. Removal of TRC 30 has imparted a low ML value for S5. Adding coconut shell powder has a high impact on the ML property. Hence, S6 and 7 have a much higher value for ML. Increment of carbon black and adding PAH comply carbon black increased the ML value of S7 compared to S6.

4.2.3 Cure characteristics of final compounds

The rheological properties of final compounds were measured at 150 °C for 30 minutes using MDR Gotech M2000 model. The test results obtained are given below in the Table 4.1. Rheological properties were measured also at 150 °C to detect differences deeply and comparison was interpreted.

Table 4.2 Cure characteristics of final compounds at 150 °C

Parameter	ML (lb.in)	MH (lb.in)	t _{s2} (min.)	t _{c90} (min.)
S1	7.87	22.68	6.18	8.58
S2	8.47	24.68	6.35	9.01
S3	9.87	25.68	8.18	12.58
S4	8.33	23.74	5.18	7.56
S5	6.78	21.33	5.31	7.73
S6	9.61	24.51	5.45	8.01
S7	9.79	23.72	5.66	8.23

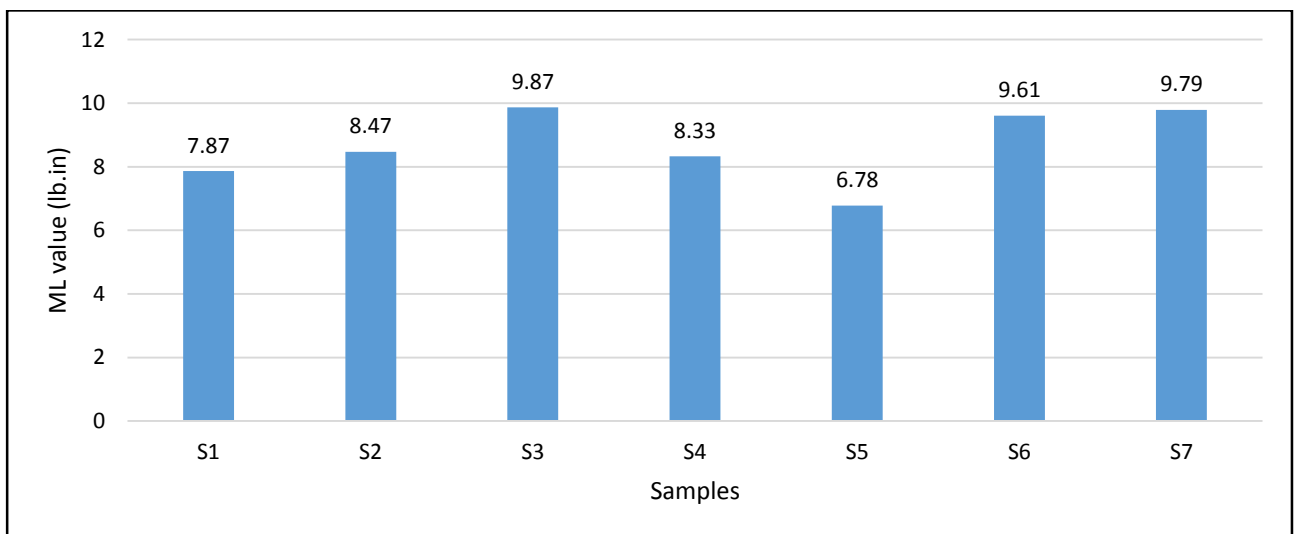


Figure 4.3 ML variation of final compounds at 150 °C

ML, minimum torque is a measure of processability and viscosity of rubber compounds. Processability and viscosity of the final compounds vary according to a manner like those of the masterbatch compounds. MH, maximum torque is an indication of stiffness of rubber compounds. As curing starts, the torque increases proportionately, and it reaches a maximum value. MH is the highest torque recorded in a plateau curve. S5 exhibits the lowest viscosity and stiffness, whilst S3 exhibits the highest.

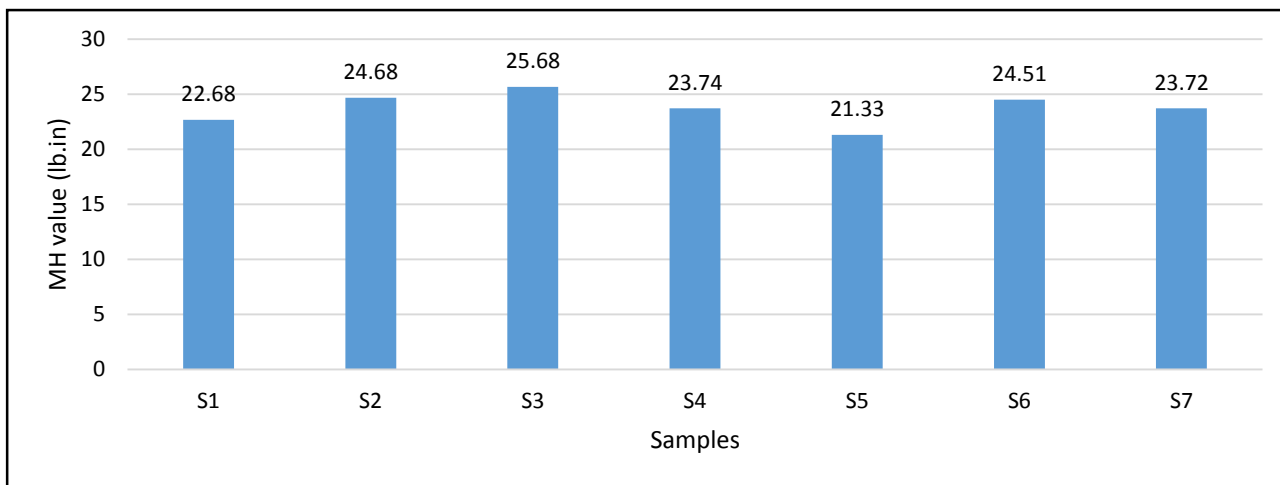


Figure 4.4 MH variation of final compounds at 150 °C

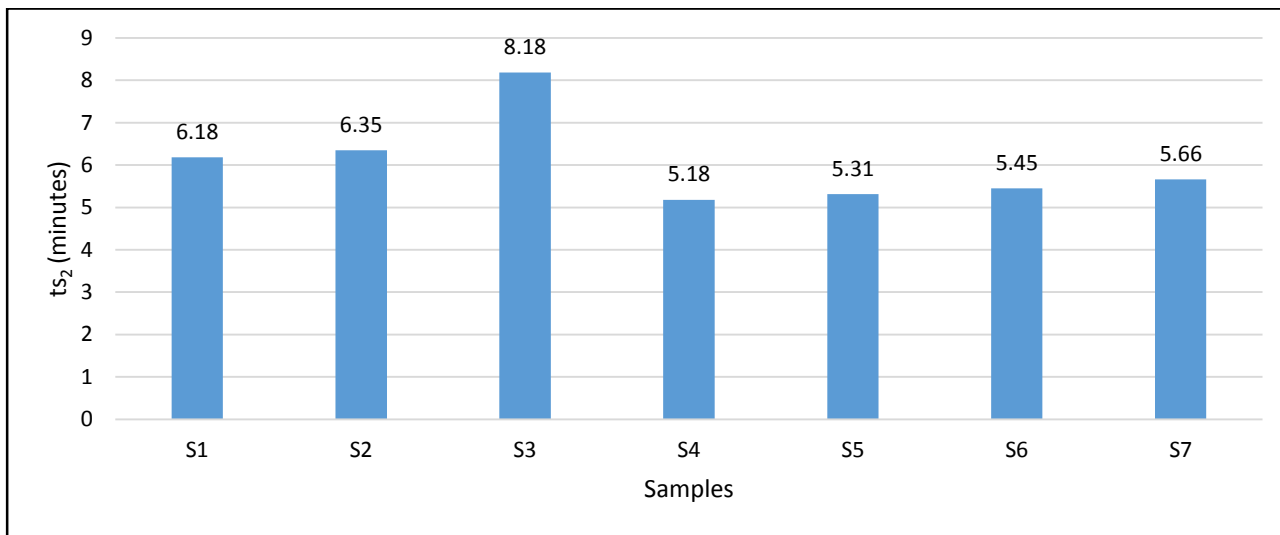


Figure 4.5 ts₂ variation of final compounds at 150 °C

ts₂ is recorded as the rise in torque by 2 units above ML. Scorch mean premature vulcanization in which the rubber becomes partly vulcanized before the product have its final form. This scorching reduces plastic properties of the compounds so that it can no longer be processed easily. Scorching can be happened by overheating of the temperature during processing and the amount of time that the

compound is exposed to elevated temperatures. This period before vulcanization starts is generally referred to as “scorch time”. Since scorching ruins the rubber, it is important that vulcanization does not start until this process is completed. t_{c90} is the time at which 90% of cure has taken place.

Due to the presence of 30 pphr reclaimed rubber in S1 and S2, scorch safety of the final compounds is almost similar, but lower in respect to S3 and somewhat higher in respect to S4, S5, S6 and S7. Scorch safety of S3 is greater than any other sample due to the presence of 60 pphr natural rubber. When the elastomer content increases, time required to form crosslinks among main chains increases. Therefore, S3 has the highest t_{c90} value in respect to other samples. Formulae of S1 and S2 contain 30 pphr reclaimed rubber. t_{c90} of S1 and S2 is higher than that of S4, S5, S6 and S7, which contain 20 pphr reclaimed rubber. Reclaimed rubber contains active crosslinking sites and hence curing is faster in reclaimed rubber containing compounds. Also, t_{c90} depends on the virgin rubber content of a compound. Therefore, the compound with a higher virgin rubber content and lesser amount of active crosslinking sites, i.e. S3 exhibits a higher t_{c90} value.

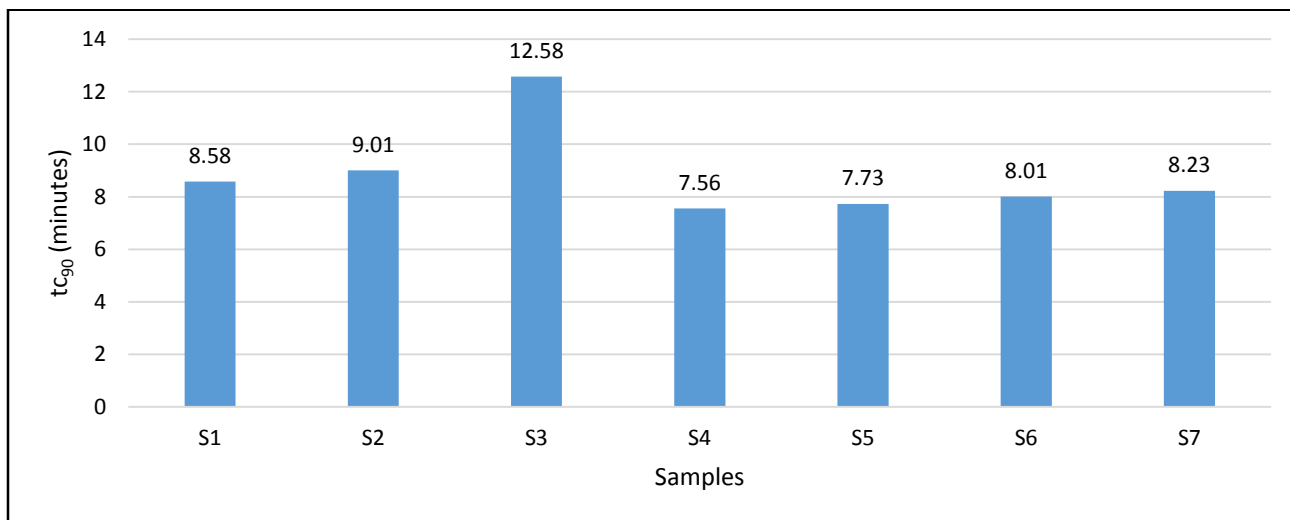


Figure 4.6 t_{c90} variation of final compounds at 150 °C

4.2.4 Tensile Properties

Ultimate tensile strength, ultimate elongation and tensile stress at 100 %, 200 % and 300 % elongations were measured. Ultimate tensile strength is the maximum stress when the specimen breaks during elongation. Ultimate elongation is the applied strain when the break occurs.

Table 4.3 Tensile properties of the samples

Sample ID	Tensile strength (kg/cm ²)	Modulus at 100% (kg/cm ²)	Modulus at 200% (kg/cm ²)	Modulus at 300% (kg/cm ²)	Elongation at break (%)
S1	153.34	19.85	54.89	98.49	440.00
S2	155.74	22.19	60.47	111.32	450.00
S3	173.34	17.99	49.78	95.52	500.00
S4	154.56	25.42	66.56	115.21	440.00
S5	157.34	21.34	59.71	118.27	450.00
S6	149.34	22.14	56.17	92.29	410.00
S7	151.23	21.19	55.20	93.26	430.00

According to the test results, S3 has the highest tensile strength due to the presence of 60 pphr natural rubber, which imparts excellent tensile properties. Black reclaimed rubber added S1 and S2 and white reclaimed rubber added S4 and S5 have ultimate tensile strength, which are approximately equal. Although S4 and S5 have 20 pphr white reclaimed rubber, it imparts better tensile properties than 30 pphr black reclaimed rubber containing S1 and S2 as white reclaimed rubber is produced with latex based product waste. Replacement of TRC30 with coconut shell powder has lowered tensile strength.

Modulus is a measure of stiffness, which is defined as resistance to deformation. It describes the ability to bear loads at dynamic applications. Due to the presence of white reclaimed rubber, S4 and S5 have high modulus compared to S1 and S2. S6 and S7 have a lower modulus at 300 % elongation than S4 because it contains coconut shell powder. S3 has the lowest modulus and results in the highest elongation for the same.

Elongation is the percentage increase of the original length of a rubber sample as a result of tensile force being applied to the sample. Elongation is inversely proportional to hardness, tensile strength, and

modulus. That is, the greater a material's hardness, tensile strength, and modulus, the less it will elongate under stress. It takes more force to stretch a hard material having high tensile strength and high modulus, than to stretch a soft material with low tensile strength and low modulus. Ultimate elongation is the elongation at the moment the specimen breaks. Generally, it is noted along with tensile strength and modulus during tensile testing. S3 has the highest elongation due to more NR than other samples. However, other samples have approximately similar elongation values. During dynamic applications, elongation is an important parameter to predict the behaviour of rubber compounds. Tire tread compound should have proper balance in tensile strength and elongation to avoid chipping and chunking during running applications.

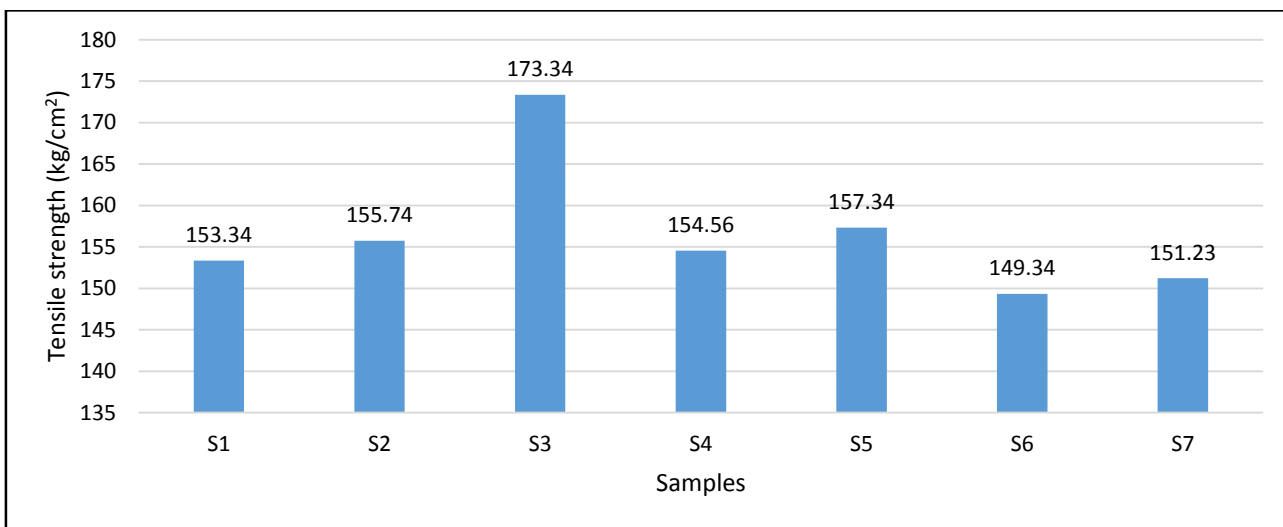


Figure 4.8 Tensile strength (before aging)

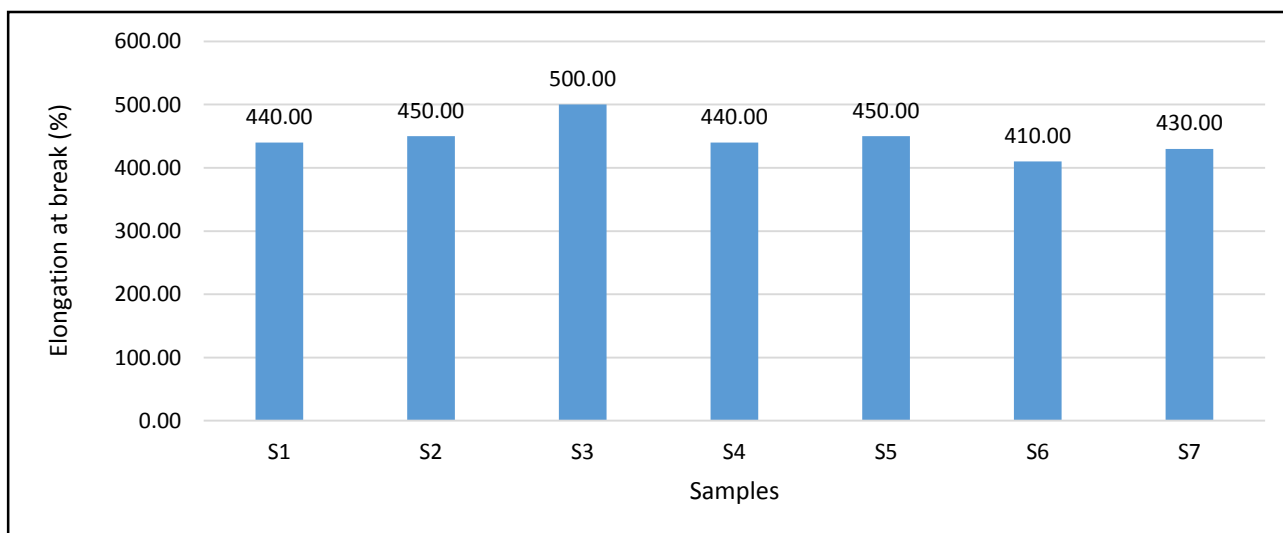


Figure 4.7 Elongation at break (before aging)

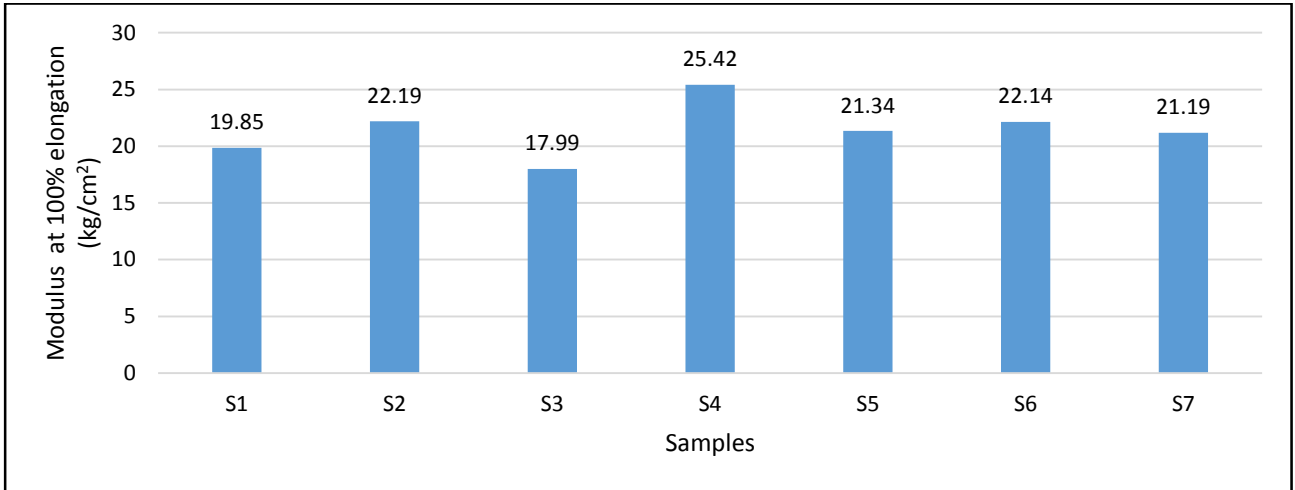


Figure 4.9 Modulus at 100% elongation (before aging)

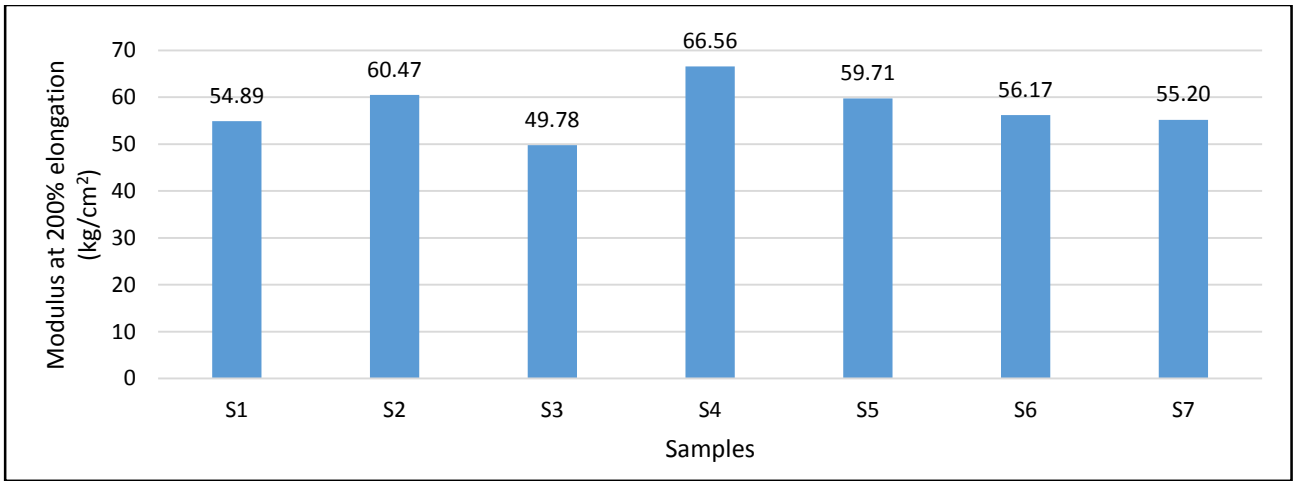


Figure 4.10 Modulus at 200% elongation (before aging)

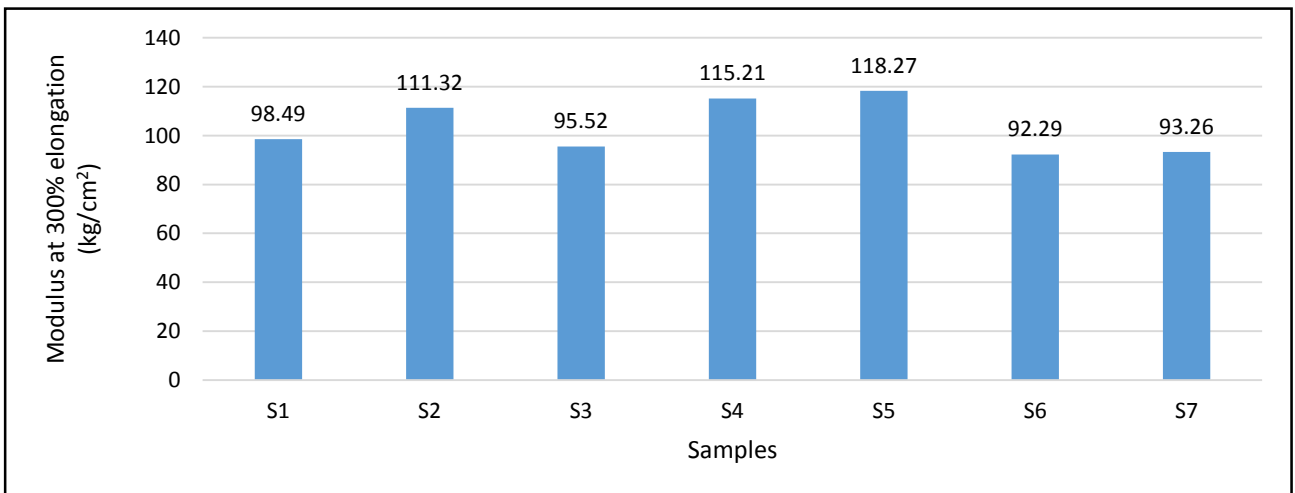


Figure 4.11 Modulus at 300% elongation (before aging)

4.2.5 Specific gravity of final compound

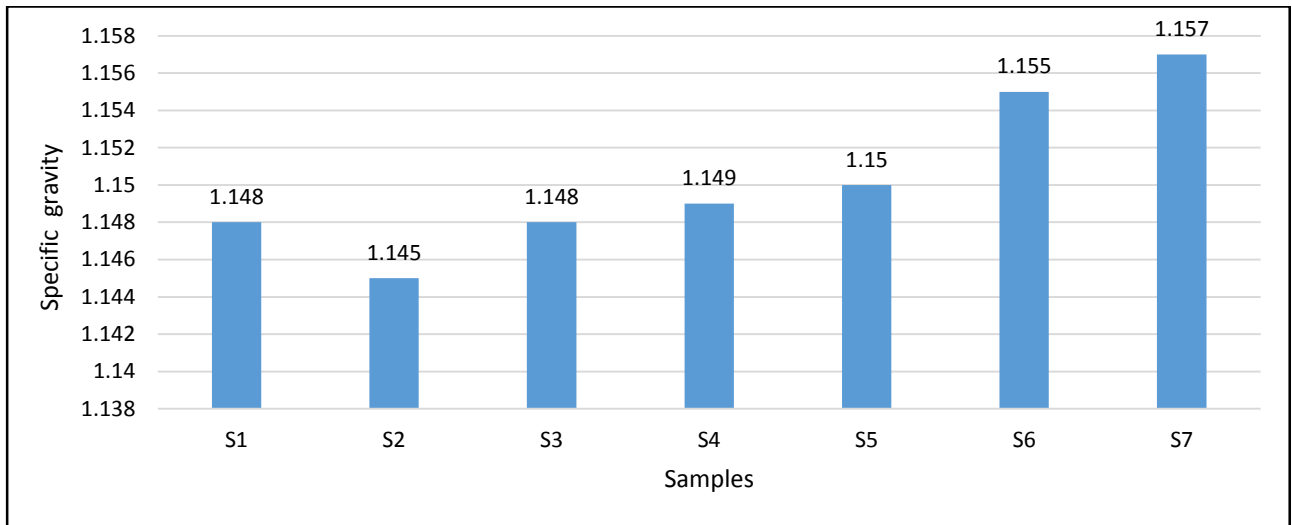


Figure 4.12 Specific gravity of final compound

Specific gravity (SPG) variation with the formula is given by the above graph. S2 has a lower carbon black content than S1. Therefore, S2 has a lower specific gravity than S1. S1 and S3 have the same amount of carbon black. S3 contains a higher quantity of NR and vegetable oil derivative. However, specific gravity values of S1 and S3 are equal. White reclaimed rubber added S4 also has an approximately equal specific gravity value as S1 and S3. Removal of tire crumb from the formulae has increased the specific gravity of S5 by 0.001 in respect to S4. Adding coconut shell powder has significantly increased the specific gravity of S6 and S7. S7 has the highest SPG value because high amount of PAH free carbon black was added, and coconut shell powder is also present in the formula.

4.2.6 Hardness properties of final compound

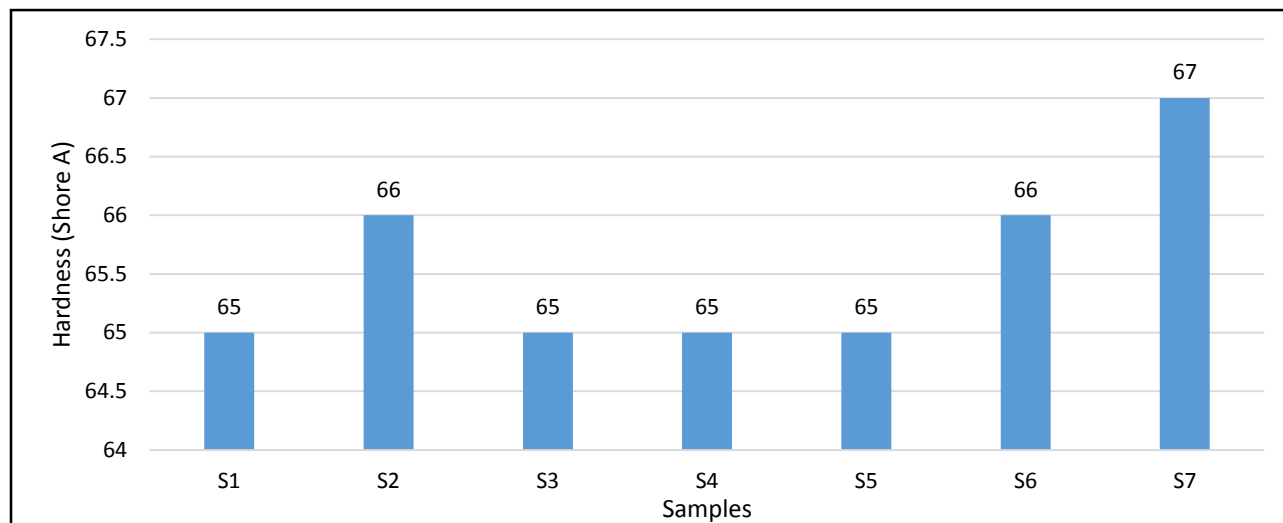


Figure 4.13 Hardness of final compound (before aging)

According to the hardness values obtained, hardness of S1 is 65 Shore A units. Without changing the rubber content and curative content, carbon black content of S2 was decreased by 5pphr in respect to S1. However, rubber process oil was not added to the formulae. Hardness drop due to the presence of rubber process oil has not taken place and the hardness is 66 for S2. Although 7 pphr vegetable oil derivative and 45 pphr carbon black were added to formulae S3, hardness value has not changed, and it is equal to the value of S1. S4 and S5 have equal rubber and curative contents. However, S4 has a higher filler loading and additional 10 pphr tire crumb than S5. There is no any chemical bonding between vulcanized tire crumb and rubber. Therefore, hardness values are equal. 2pphr silane coupling agent was added to formulations 6 and 7 to improve properties by forming crosslinks between lignin units of coconut shell powder and the rubber. Formula of S7 contains more carbon black than that of S6. Hence S7 has a slightly higher hardness value than S6. In overall, results show that there is no marked difference between the hardness of the seven samples studied.

4.2.7 Rebound resilience of final compound

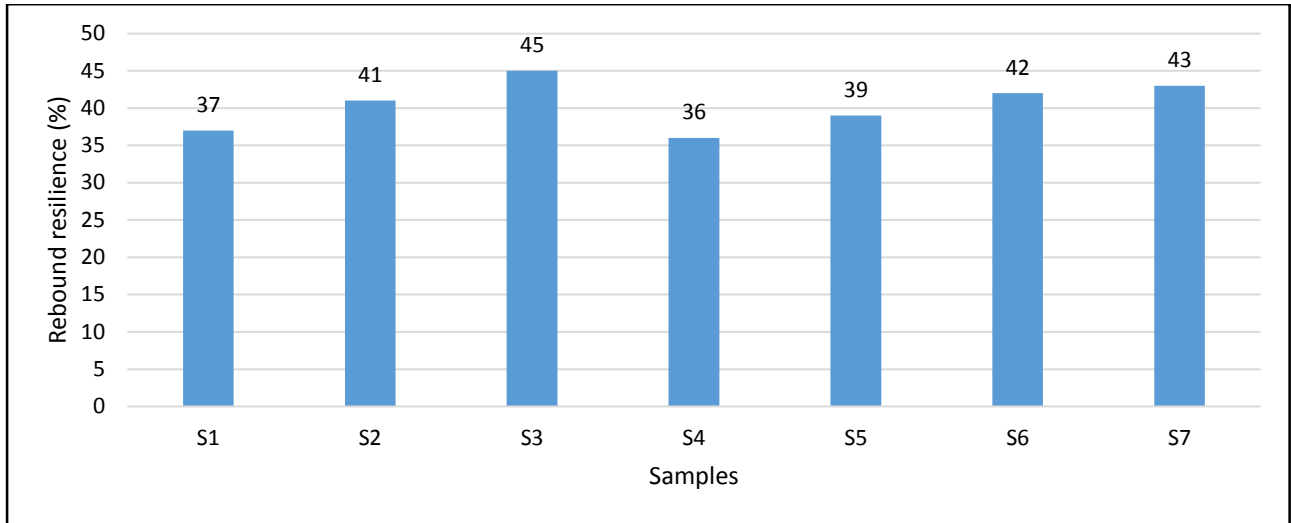


Figure 4.14 Rebound resilience of final compound (before aging)

Resilience is the percent of energy required for a deformed piece of rubber to rebound back to its original shape after a deformation. According to the test results, S3 has the highest rebound resilience compared to the other samples because it has more natural rubber. Rebound resilience of S7 is 43 and that of S6 is 42. Significant improvement in rebound resilience of S6 and S7 can be monitored. Adding high particle size filler and coconut shell powder impart this improvement to the compound. High rebound resilience means, it has more of the elastic component than the viscous component, which helps to generate heat by hysteresis. This helps to reduce heat build-up during dynamic applications. A blend of NR and SBR was used to improve resistance to heat build-up in dynamic applications.

4.2.8 Abrasion volume loss of final compound

Abrasion resistance is the ability of a material to resist mechanical action such as rubbing, scraping, or erosion that tends progressively to remove material from its surface. When a product has abrasion resistance, it will resist erosion caused by scraping, rubbing, and other types of mechanical wear. Abrasion resistance gives an idea about the lifetime of a tire.

S3 has the lowest abrasion volume loss because reclaimed rubber has not been added to the formulae. It contains more natural rubber. S6 and S7, which have coconut shell powder have much higher abrasion volume loss values. However, S7 exhibits a lesser value than S6 due to addition of more carbon black to the formulae. Abrasion volume loss of S7 is within the given specifications.

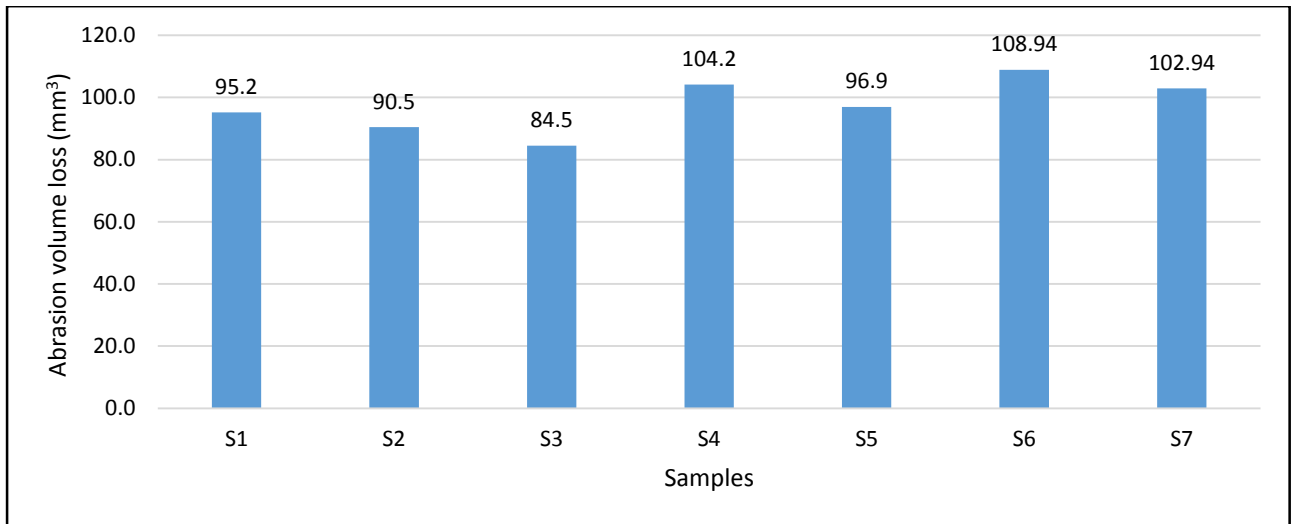


Figure 4.15 Abrasion volume loss of final Compound (before aging)

4.2.9 Physico-mechanical property results after aging

All polymers and products are subjected to degradation on exposure to the degradative environments such as storage aging, oxygen, heat, UV light and weathering, catalytic degradation due to the presence of heavy metal ions (Cu, Mn, Fe, etc.), dynamic flexing, fatigue, ozone (static / dynamic / intermittent exposure). These factors degrade rubber products causing substantial changes in their technical properties and ultimately lead to their failure during service or shorten the expected service life. Ability to withstand the degradative forces was determined by subjecting samples to the aging test, keeping samples at 100 °C for 24 hours and then conducting the above test again.

4.2.9.1 Tensile properties (after aging)

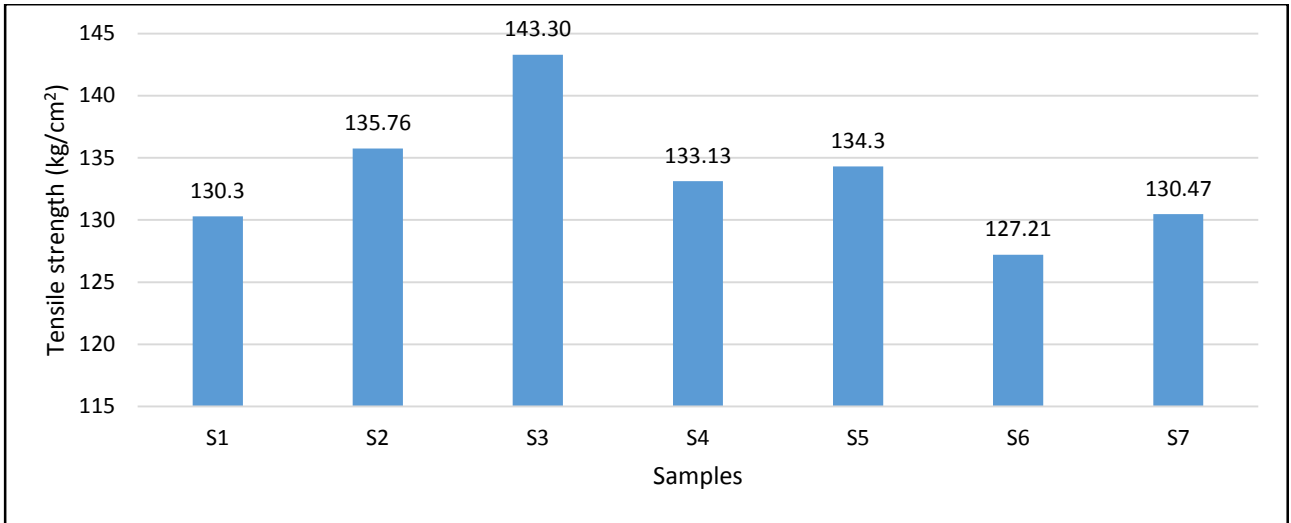


Figure 4.16 Tensile strength of the samples (after aging)

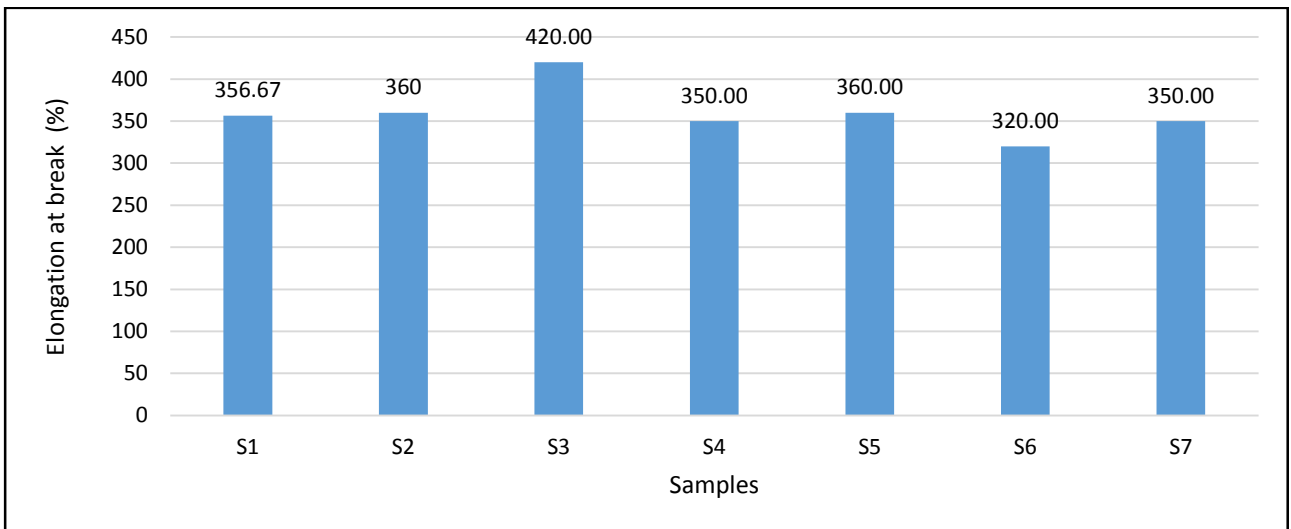


Figure 4.17 Elongation at break of the samples (after aging)

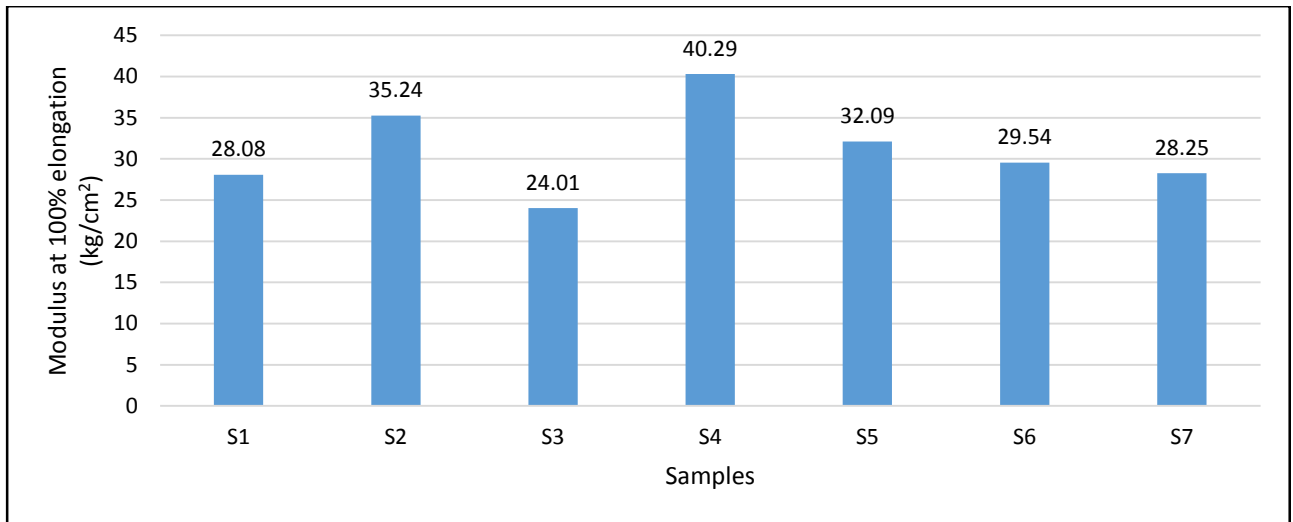


Figure 4.18 Modulus at 100% elongation of the samples (after aging)

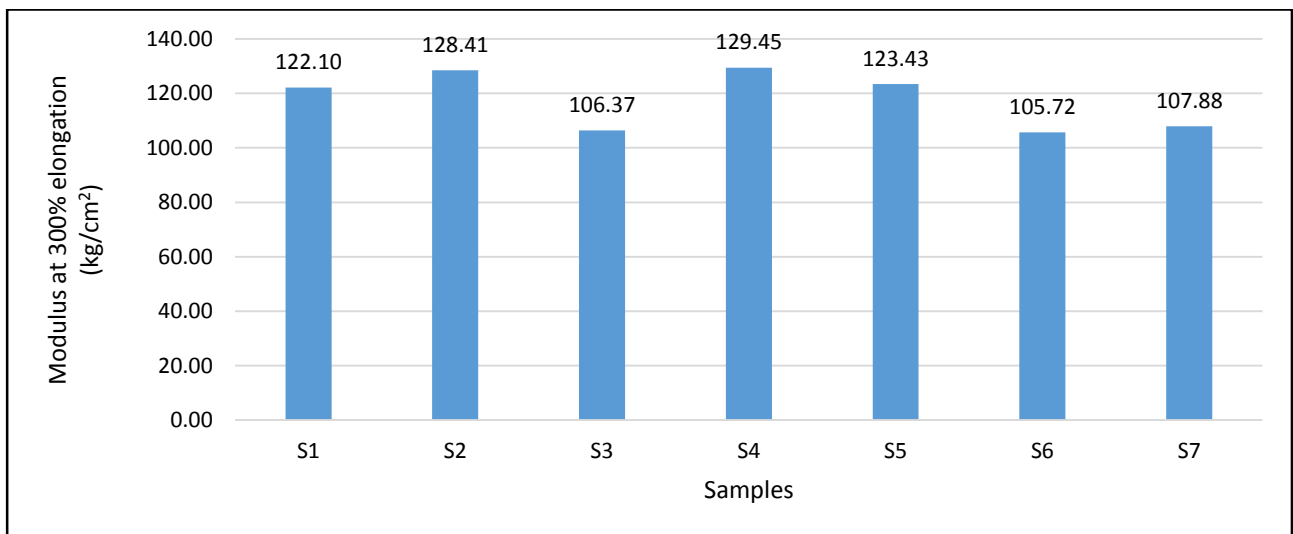


Figure 4.19 Modulus at 300% elongation of the samples (after aging)

During aging, degradative forces act on the vulcanizate and decrease its mechanical properties. Although S3 has the highest tensile strength, after aging it has significantly decreased in comparison to the other samples. Natural rubber tends to degrade more when exposed to degradative environments. Therefore, a significant drop in tensile properties was observed. S7 has a high ability to withstand the degradative forces maintaining the properties without a drastic drop.

4.2.9.2 Hardness, rebound resilience and abrasion volume loss (after aging)

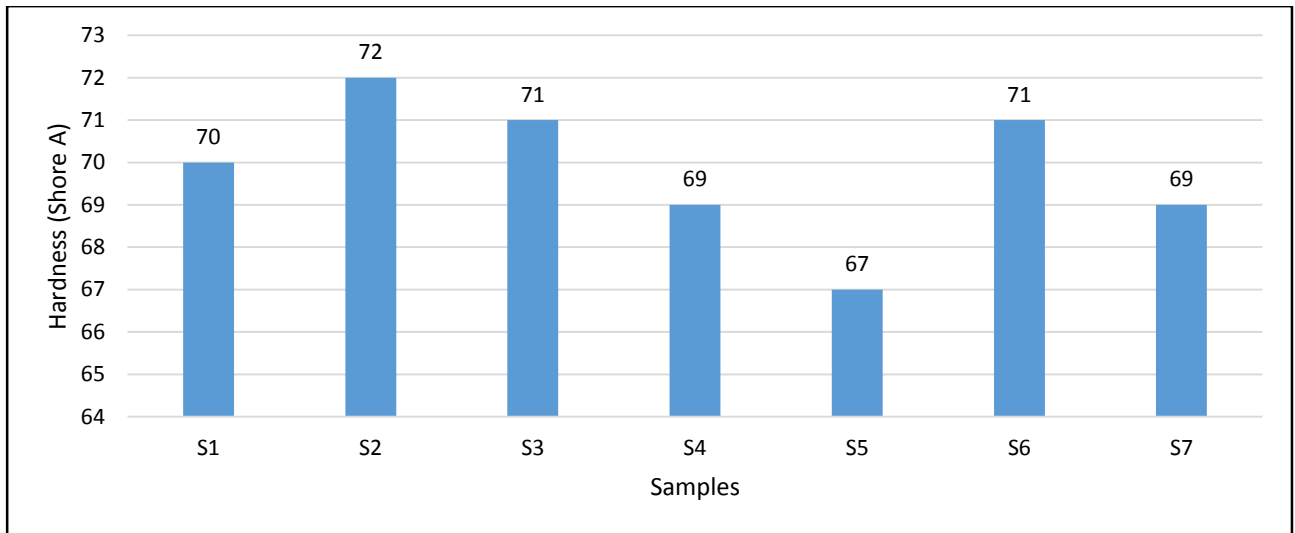


Figure 4.20 Hardness of the samples (after aging)

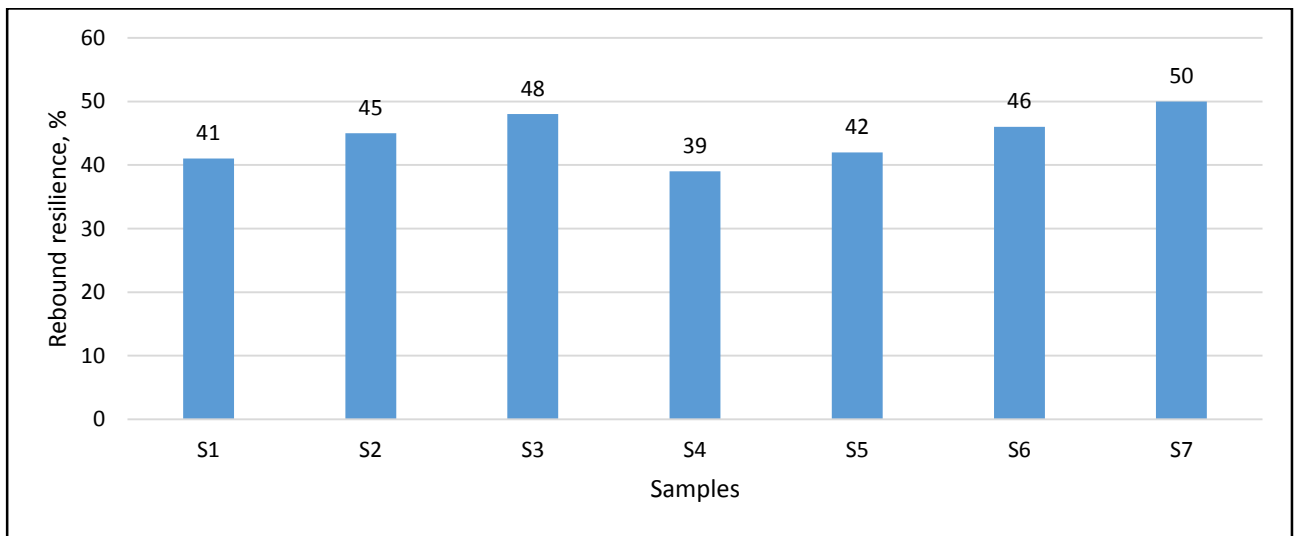


Figure 4.21 Rebound resilience of the samples (after aging)

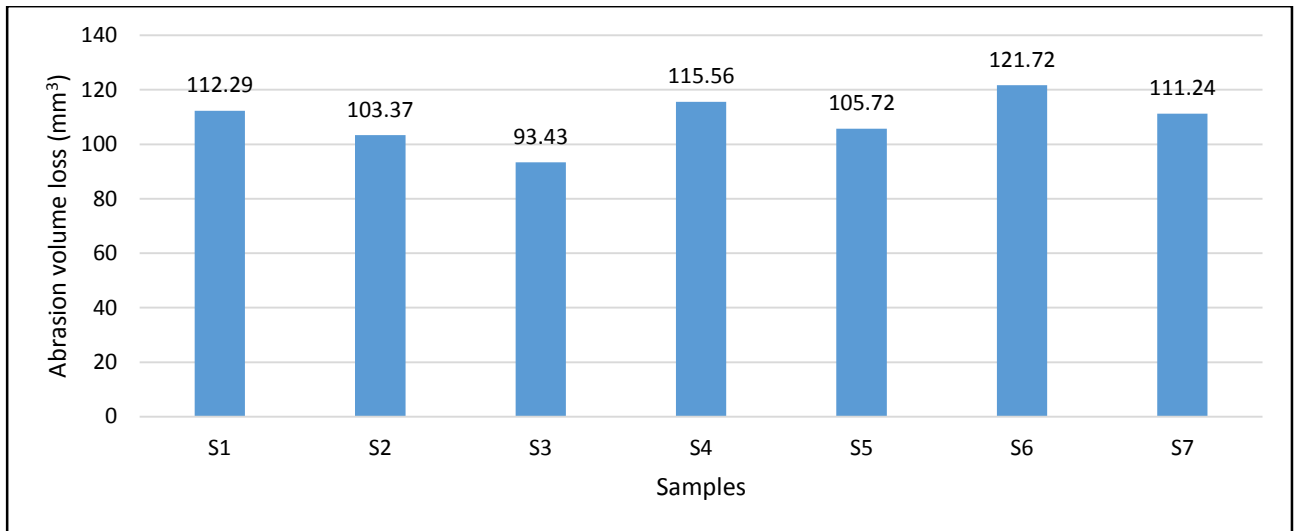


Figure 4.22 Abrasion volume loss (after aging)

Hardness values of each and every sample have increased after the ageing test. However, the increase in hardness of S7 is lower in respect to the other samples. The increase in abrasion volume loss of S7 after ageing is lower when compared to the other samples. This is probably due to addition of white reclaimed rubber, carbon black and coconut shell powder. Adding more silane coupling agents to form extra crosslinks between lignin and rubber helps to retain properties even in degradative environments. S7 has a higher ability to withstand degradative forces and provides a longer life time.

4.3 Production Trials

Considering physico-mechanical properties, cure characteristics and PAH conformity test results, PAH complied S7 tread compound was used to do further trials to ensure the compatibility with real applications, conducting the endurance test by preparing test tires and carrying out field tests.

Masterbatch and final compounds were prepared using GK100 internal mixer at 27 rpm rotor speed and fill factor of 0.78 with the Control S1 according to the mixing cycle and mixing sequence given earlier. Properties before and after ageing were determined as described previously following the same standard methods.

4.3.1 Specific gravity and minimum torque of compounds of production trial

Table 4.4 Specific gravity (SPG) and minimum torque (ML) of compounds

Parameter	Specification	S1	S7
SPG	1.130-1.145	1.136	1.144
ML (lb.in) (MDR)	9.0-14.5	12.71	13.39

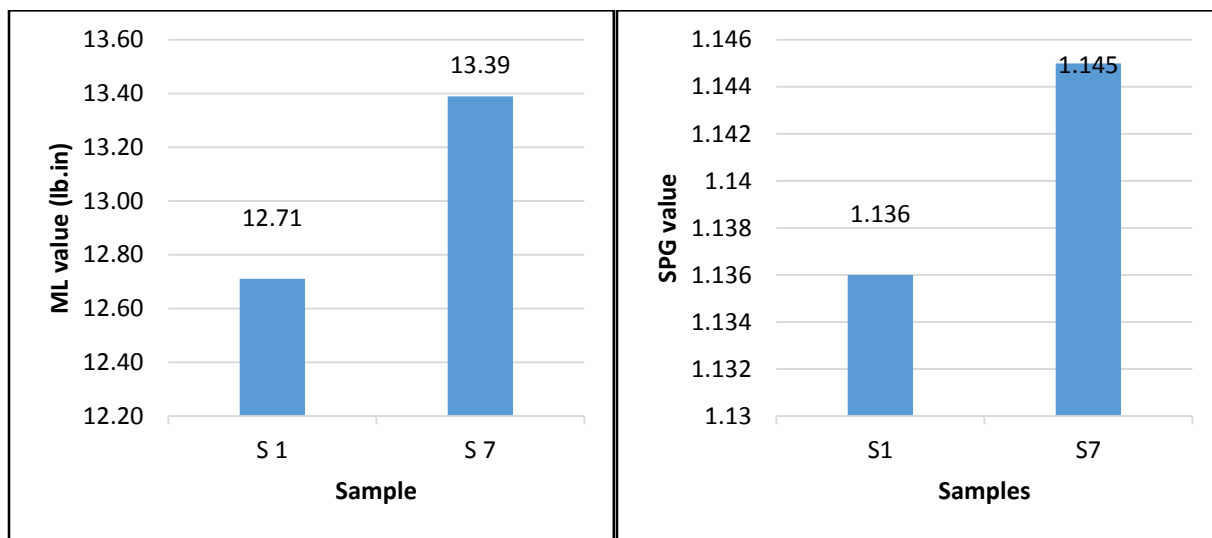


Figure 4.23 Variation of SPG and ML of compounds of production trial

Results show that specific gravity and ML of S7 are within the defined specifications.

Processability of the compound during production was observed to ensure suitability for mass production without any difficulty. No any issue was recorded.

The masterbatch compound was subjected to second stage mixing by adding sulphur, accelerator and PVI according to the previously described mixing cycle and mixing sequence. All the physico-mechanical and rheological properties were evaluated as previously described.

4.3.2 Cure characteristics of final compounds

Table 4.5 Cure characteristics of the final compound of production trial

Parameters	Specification	S1	S7
ML (lb.in)	6.0-10.5	9.27	10.34
MH (lb.in)	22.5-28.5	26.42	25.39
t_{s2} (min.)	0.58-0.73	0.66	0.62
t_{c90} (min.)	0.95-1.15	1.10	1.04

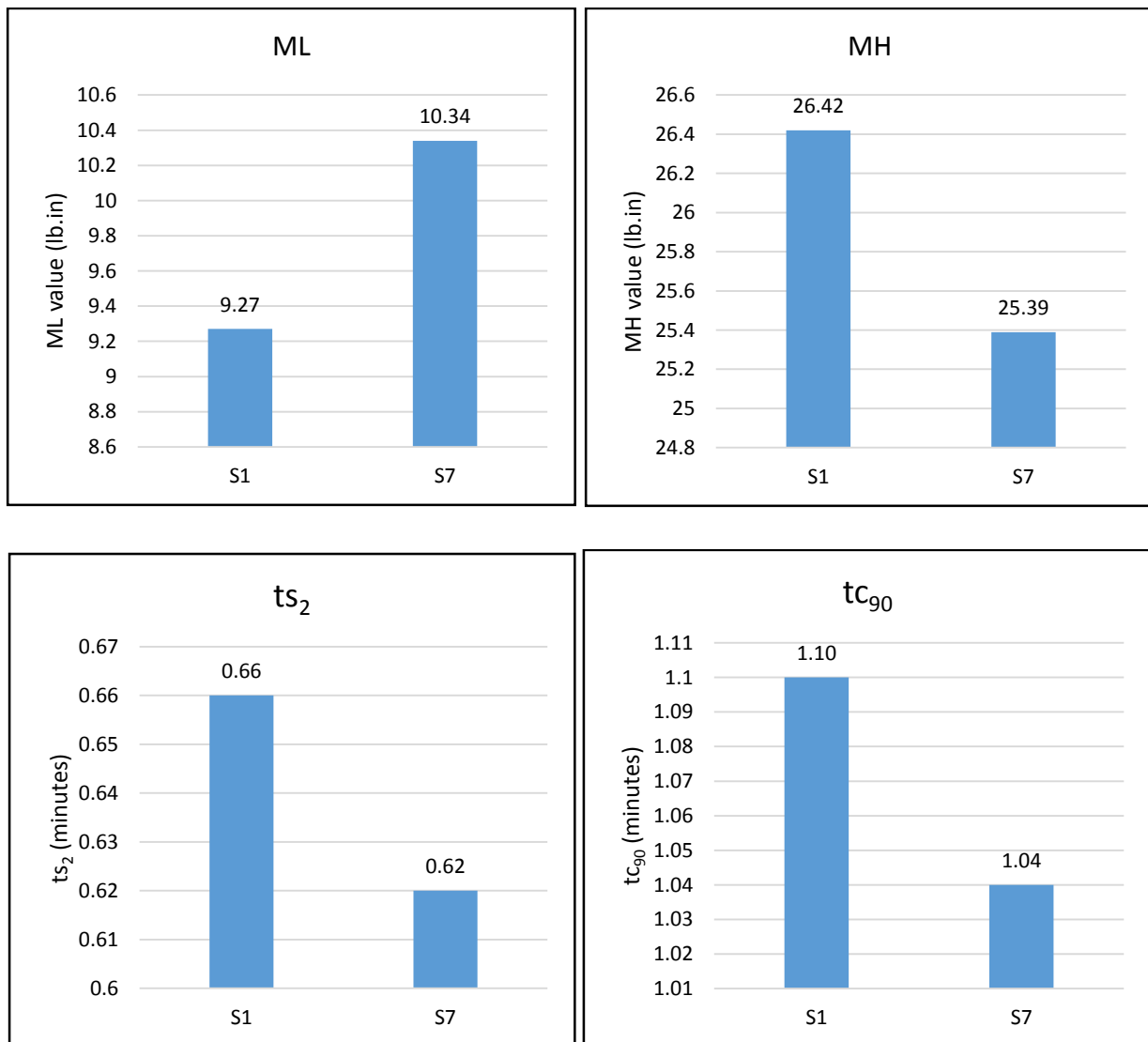


Figure 4.24 Cure characteristics of the final compound of production trial

Cure characteristics of S7 are within the given specifications and are approximately equal to those of S1 (Control), except the ML value.

4.3.3 Physico-mechanical properties of production trial

Table 4.6 Physico-mechanical properties of production trial

Parameters	Specification	S1	S7
SPG	1.145-1.160	1.146	1.158
Hardness (Shore A)	64-69	66	67
Resilience (%)	35-43	38	43
Abrasion volume loss (mm ³)	<=110	92.23	104.91
Tensile strength (kg/cm ²)	>=140	157.34	151.23
Modulus at 100% (kg/cm ²)		21.89	23.17
Modulus at 200% (kg/cm ²)		57.83	59.32
Modulus at 300% (kg/cm ²)	>=90	99.56	101.22
Elongation at break (%)	>=400	430	410

Table 4.6 indicates that all the physico-mechanical properties of S1 and S7 are within the defined specifications.

4.4 Properties of a Tire

After preparing the compound, a test tire was produced according to the standard procedure. The tire was subjected to the endurance test following the conditions given below to evaluate run time and rolling resistance.

Test conditions:

Rolling resistance: Speed-10 Km/hr, 2 min. run with each load - 25%, 50%, 75% and 100% of load wheel load and average was taken.

Run time: Speed-10 Km/hr, Load-1945 Kg (90.68 % of load wheel load). Tire was run until it blasted and the temperature inside the tire (using drilled holes, at base, center and tread) was tested at each running hour.

Table 4.7 TTM test results

Date :	2018.04.01			Surface temp. when tire blasted (°C)			Details of tire		
Tire P.Plant	Rolling resistance (N)	Total run time when tire blasted (hrs)	Test method	Base	Center	Tread	Tire No.	Mould No.	Test No.
Plant-01	235	1.45	TTM11	43	81	54	A180400415	1	1
Plant-01	229	1.59	TTM11	49	94	59	A180411157	1	7

4.4.1 Rolling resistance

The sample tire which was prepared using the formulation of S7 has a significant lower rolling resistance than the Control (S1). Energy consumed to travel a unit distance of the tire produced with S7 is lower compared to that of the Control. This is probably due to low hysteresis of S7 indicated by higher rebound resilience. Low rolling resistance helps to maintain good fuel economy.

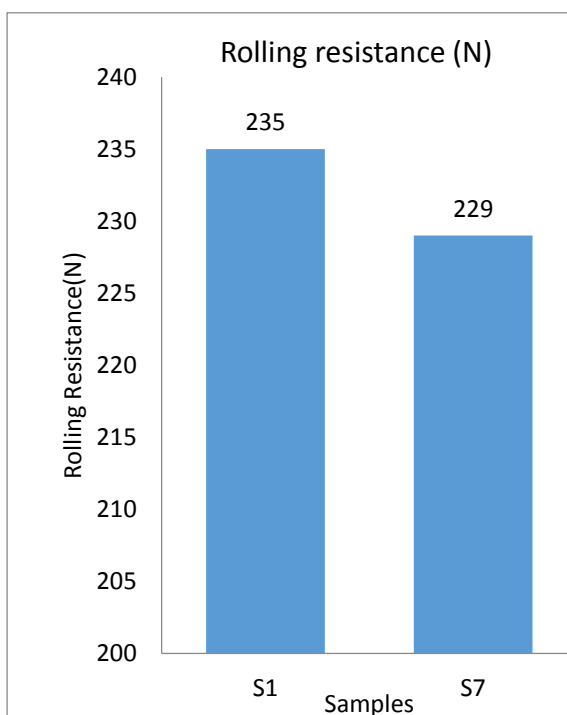


Figure 4.25 Rolling resistance of test tires

4.4.2 Run time

The tire of S7 has a higher run time than that of the Control. This means that the tire of S7 can be used for a long time in an application continuously without any issue. High rebound resilience and anti-reversion properties would impart a better run time, when the tire is subjected to dynamic applications.

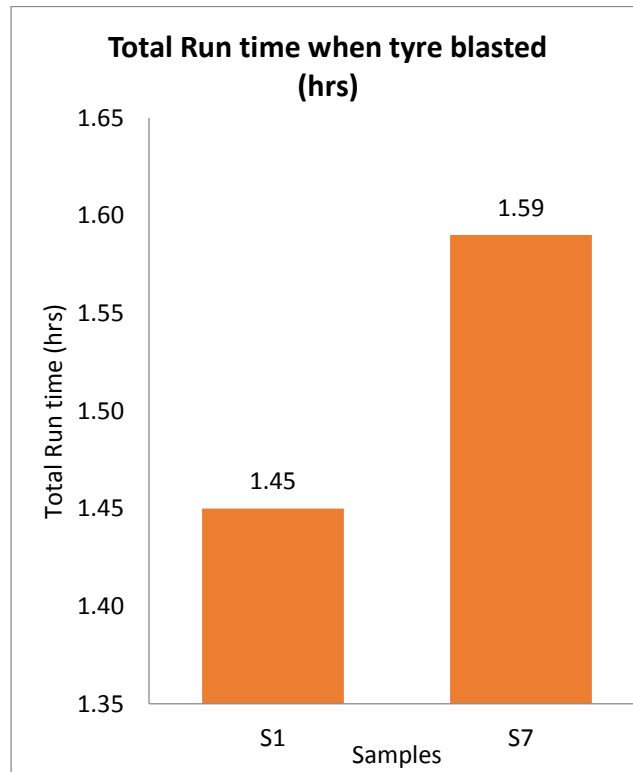


Figure 4.26 Run time of test tires

According to the test results, dynamic performance of the tread compound (S7) is better than that of the Control.

4.5 Field test

Performance of the tread compound in real application was determined by conducting a field test. Prepared a 7.00 -12 STD tire by using tread compound (S7) and installed to a forklift as the Front –Left tire, while Control tire was at Front-Right.

Information category	Available Information
Testing Place	Cargills Ware House, Mattakkuliya
Fork Lift Type	GP 25NT
Fork Lift Serial No	CT 17D68332
Load Capacity	2.5 MT
Average Speed	15-20 Km/h
Average Load Lifted	1.5-2.0 MT
Application	Higher Driving speeds with Moderate Loading.

Figure 4.27 Tire information of field test

Performance of the tire was evaluated by calculating the wear rate (Running Hours/worn depth) and measuring running hours and tread depth. Chipping and chunking resistance was monitored. According to the test results, tire prepared from PAH comply tread compound has performed in a manner similar to that of the Control tire in the field.

Table 4.8 Results of field test

Tire Mounted Location	Front-Left	Front-Right
Tire size	7.00-12	7.00-12
Tire Brand	GS WT-RT 20S -T7	GS WT-RT 20S-Con
Tire Serial No.	B171000348	B171000222
Mounted Date	2018.04.03	
Date Demounted	Still Running	
Running hours up to now	437.2	
Remaining Tread Depth (mm)	45.5	45.9
Wear Rate(hrs/mm)	67.26	71.67
Wear Percentage at Present	13%	12%
Performance Difference	6.15%	
Estimated Wear Life (hrs)	3497.6	3726.95082

According to the observation, chipping and chunking, layer separation or any defect was not observed. There was significant improvement in wet and dry traction and grip due to addition of SBR rubber with NR. Improved chipping and chunking resistance are due to blending white reclaimed rubber with NR.



Figure 0.1 Tires for field test

4.6 Cost Analysis

Modern compounding identifies the compound cost as a basic factor other than factors of wear resistance, wet grip and rolling resistance because cost play a major role in compounding. Generally, formulae which have required properties with minimum cost are selected for mass production in industry. Raw material price and cost of each test can be listed as given below. General method has been followed to calculate the cost, considering material dosage and unit price. According to the given market price, as usual, natural rubber has a higher price except chemicals, while synthetic rubber, SBR price is less than NR by 9.31 Rs/kg. Black reclaim rubber is a recycled product and available in the market for a cheaper price. However, White reclaim rubber has a higher price than black reclaim rubber because polymer content and quality of it is higher. It is considered in industry that black reclaim rubber has 50 % polymer content. Polymer content of white reclaim rubber is above 80%. As a result of this, price of the white reclaim rubber is much higher than black reclaim rubber. Similarly, PAH free carbon black, a specially developed product for tire applications is priced as 185 Rs/kg, while conventional carbon black price is less by 10 Rs/kg. Vegetable oil derivatives are available at a cheaper price in the market and present compounders try to use mineral oil in compounding to improve properties and develop eco-friendly products replacing conventional aromatic rubber process oil. Tire crumb and coconut shell powder can be found in the market for a lower price.

Table 4.9 Raw material prices

No	Raw Materials / Chemicals	Price (Rs/kg)
1	Natural Rubber-RSS	262
2	Synthetic Rubber -SBR	252.69
3	Reclaimed Rubber-Black	90.68
4	Reclaimed Rubber-White	100
5	Carbon Black	175
6	Carbon Black-PAH Free	185
7	Precipitated Silica	113.88
8	Rubber Process Oil	148.46
9	Vegetable Oil Derivatives	107.8
10	Tire Crumb 30 Mesh	34
11	Coconut Shell Powder	35
12	Silane Coupling Agent	469.19
13	ZnO 99.5%	378.12
14	Sulphur	52.16

Table 4.10 Compound Prices

Formulation	S1	S2	S3	S4	S5	S6	S7
Compound Cost(Rs/kg)	200.47	202.69	218.36	205.68	214.89	207.07	208.48

Although, carbon black and rubber process oil were removed from S2 (5 phr and 6 phr, respectively), compound price increased by 2.22 Rs/kg due to reduction and removal of low-cost material dosages from formula. S3 has recorded the highest compound cost because natural rubber and carbon black dosages have been increased by 10 phr. Addition of white reclaim rubber for S4 formula reduced the cost. Although white reclaim was introduced to S5, removal of TRC30 from formula increased the compound cost by approximately 9 Rs/kg with respect to S4. Low cost coconut shell powder was added to S6 and S7. However compound cost of S7 slightly increased with respect to S6 due to replacement of carbon black by PAH free carbon black with an increase in the amount by 6phr. PAH comply S7 was prepared without significantly increasing the compound cost with a feasible price for mass production.

5 CONCLUSIONS

1. Reclaimed rubber, crumb rubber, rubber processing oil and carbon black were identified as PAH susceptible materials.
2. By substituting the above materials with PAH comply alternative raw materials, PAH conformity can be achieved.
3. Conventional carbon black has a significant impact on PAH conformity of rubber compounds. However, this can be minimized using newly developed special carbon black grades.
4. Although synthetic materials have a high impact on PAH, biomaterials have a negligible impact.
5. An eco-friendly, PAH comply tread compound (S7) was formulated, and significant property improvement was achieved.

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