

**STUDY OF THE EFFECT OF DIFFERENT CARBON
BLACK COMBINATIONS ON PHYSICO-MECHANICAL
PROPERTIES OF NATURAL RUBBER BASED SOLID
TYRE TREAD COMPOUND**

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DECLARATION OF THE CANDIDATE & SUPERVISOR

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ABSTRACT

The performance and the life-time of a solid tyre depend on the properties of the solid tyre tread compound. Abrasion resistance and rebound resilience are the key parameters of the solid tyre tread compound. Carbon black types used in tread compounds and carbon black ratio in the combined filler are the main contributors for the above two properties. But these two properties behave in contradictory ways such that when carbon black particle size is small, the abrasion resistance is high when rebound resilience is low. Hence most suitable carbon black type and ratio should be selected into solid tyre tread compound to have the optimum abrasion resistance and rebound resilience. In this research, the effect of N220 and N330 carbon black grades and their ratio on solid tyre tread compound was studied. N220: N330 ratio was varied in the combined filler from 0:50 pphr to 50:0 pphr to find the optimum ratio, which provides the best abrasion resistance in solid tyre tread compound. N220:N330 optimum ratio was observed as 30:20 at observed maximum tensile properties and abrasion volume loss was at its lowest point. Further, the highest standard deviation of carbon black aggregate size was observed for this ratio and that ratio has shown the highest reinforcement in the solid tyre tread compound.

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LIST OF ABBREVIATIONS

Abbreviation	Description
6PPD	N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine
ASTM	American Society for Testing and Materials
CTP	N-(cyclohexyl-thio)phthalimide
et al	and others
MDR	Moving Die Rheometer
M_H	Maximum Torque
M_L	Minimum Torque
NR	Natural Rubber
pphr	parts per hundred parts of rubber
PVI	Pre vulcanization inhibitor
rpm	Revolutions per minute
SG	Specific Gravity
SIR	Standard Indonesia Rubber
SMR	Standard Malaysia Rubber
STR	Standard Thai Rubber
t_{90}	Optimum Cure Time
TBBS	N-tert-butyl-2-benzothiazole sulphenamide
TMQ	Polymerized 2,2,4-trimethyl-1,2-dihydroquinoline
t_{s2}	Induction Time
TSR	Technically Specified Rubber
300% modulus	Modulus at 300% elongation

1. INTRODUCTION

1.1 Solid tyre

Sri Lanka is one of the main manufacturers of solid tyres and 25% of the global solid tyre requirement is fulfilled by Sri Lanka. The private sector plays a major role in the solid tyre industry in Sri Lanka [1]. Solid tyres are extremely stable, puncture-resistant, and maintenance-free. They have a high load-carrying capacity in extreme service conditions. Also, it is extremely economical. These features make them ideal for forklift trucks, vehicles used in airport, heavy-duty transport vehicles, pallet trucks, platform trucks, and other industrial vehicles.

Solid tyres can be divided into three main categories, namely cured-on tyres, resilient tyres, and press-on tyres. Also, solid tyres are categorized according to the number of layers in the tyre. Mainly three-layer tyres consist of tread, middle and heel layers.

Another category of solid tyres is the non-marking tyres which is manufactured in three colors; green, white and grey. They have anti-static properties and not contribute on marking on the floor in usage.

1.2 Carbon black as a filler in tread compounds

Tread compound is the main layer of the solid tyre which is contacted with the floor and subjected the wearing of the tyre. Reinforcement cannot be satisfied only from the rubber. Hence reinforcing fillers are used into the rubber compounds and mainly carbon black is the reinforcing filler used in the solid tyre industry. There are different types of carbon black grades in the industry level based on particle size and structure. In the view of the compound cost, performance and manufacturing process, the most suitable carbon black types and their blends should be used. Carbon black loading is prominent for selecting the best formulation for the component [2].

As per the customer, their expectation is a long life for the product. Wearing for the tyre tread is the main factor influenced on life expectations. Abrasion loss is measured to illustrate the wearing properties of the tyre. Improved tyre life can be obtained by

the selection of the optimized formula for each component. Carbon black type and carbon black ratio is the key measure to provide such benefit to the product [3].

The impact of the particle size, structure, and type of the carbon black on physical and mechanical properties has been investigated previously in individual usage. Most of the previous studies have been discussed on the selection of best carbon type and carbon black loading. In this research, two types of carbon blacks which are used for solid tyres have been considered and the optimum ratio of those carbon black types was studied.

1.3 Research objectives

The main objective of this study is;

- To study the effect of different carbon black combinations on the physico-mechanical properties of natural rubber-based solid tyre tread compound.

The specific objectives are;

- To identify the most suitable carbon black combination of N220:N330 with highest abrasion resistance
- To study the effect of particle size standard deviation to the physical and mechanical properties of combined filler tread compound
- To study the effect of the mixing cycle on the physico-mechanical properties

2. LITERATURE REVIEW

2.1 Introduction of solid tyre

Role of the solid tyre is significant not in the high ways but in the off the road. It acts a vital role in enhancing the modern heavy industry. Solid tyres are used in forklift trucks for handling heavy loads and goods. Solid tyres are constructed by using different composite compounds and different layer constructions to achieve various requirements. Steel rings and bands are also used to reinforce the components in solid tyres.

Solid tires are manufactured using different technologies by various manufacturers around the world. The base of the solid tire can be constructed on a frame or metal wheel structure or they can also be fabricated to adequate on rims that are manufactured to assemble directly to the vehicle. Solid tyres applications differ in two ways as material handling and usage in construction sites and design is categorized into three as resilience, press on and cured on. This is basically separated how the tyre is mounted on to the wheel or shaft of the vehicle. Solid tyres are always made to meet the requirements of extremely hard and tough applications. The latest designs of solid tyres are set to compete with modern tyres [4].

The first step of solid tyre manufacturing is blank preparation. This is called as green tire also. It is mainly done by the rolling method supported by two roll mill. Thin layers of rubber compound are constructed onto a metal frame mount and it is pressed through a hydraulic system to the two roll mill. Required dimensions of the blank are assured in this form. These layers are built on a wheel. The blank on the wheel adds the next layer with every full rotation of a wheel turn. Construction and size of the solid tyre decide the required thickness of these layers and the number of layers.

Once the green tire construction is completed as per the requisite dimensions, it will be heated in a mould to completed the vulcanization process. The tread design of the solid tyre is also offered to the surface by the mold during this period. Specific pressure is applied to mould by the hydraulic mounting press to complete the manufacturing process of a solid tire [4].

In order to provide specific features and cost, solid tires are composed of dozens of different raw materials. It contains mainly rubber, carbon, oil, and chemicals. Additional chemicals are added to the compound to expand its lifetime and performance.

The solid tyre is subjected to irregularities in the surface of a road due to its off the road application. So it should be capable enough to tolerate flexible qualities of the bond to help grip the road better while providing higher friction between road and tyre. That provides better handling, dynamic stability and braking capabilities of the tyre as well.

Rubber improves its flexibility as well as durability while it is undergoing the vulcanization process. Tyre made on the rubber is strong and able to withstand the load transferred from the axels of the vehicle properly and able to overcome damages from sharp stones in the road.

Since reinforcing fillers and added chemicals to the rubber will make an already tough product at its highest. Those additives make tires more capable to wear and tear resistance. Added special chemical help to stop tires from melting from excessive heat or surface cracking in different weather conditions. Proper mixing of the fillers with rubber compounds enhances the resistance to wear and tear [5].

2.2 Importance of rubber in solid tyre tread

Rubber products are unique materials having many different features. It has an affinity for deformation but maintains its original dimensions. Rubber molecules are extremely long-chain molecules that can be cross-linked to form a unique network. Vulcanized products that are having proper crosslink density will return to its original unstressed size and shape when the external forces are eliminated. This reversibility is valid even at several times of elongation from the original state. This ability of rubber is called elasticity and is used in many different applications and industries.

The mechanical properties of rubber compounds derived from the molecular chains crosslinked network. In a natural state, the rubber molecular segments are randomly coiled between crosslinks. When the vulcanized rubber compound is subjected to

tensile stress, molecular segments start localized motions and deformation is fulfilled by creating new dimensions to the product. During the deformation, molecules are stressed out in the tensile axis direction. Deformation of rubber vulcanizates is not comparable to that of the well-ordered structure of metal crystal even though endless random molecular segments are involved. This behavior is well explained by the very elegant theory of rubber elasticity. It is founded on a statistical explanation of states of molecular and its relationship with the deformation entropy change [6].

Rubbers compounding is designed with a complex mixture of different additives. Purpose of adding these additives to improve and control the crosslinking efficiency, favorable mechanical properties and prevent degradation due to ultraviolet (UV) irradiation caused by the environment condition.

Carbon black is the most common filler and used as a common additive to expand its service level. By including carbon black to the rubber compound, stiffness and strength of the compound are increased and reduce abrasion loss which is very useful in tires, and it is caused to reduces UV degradation [6].

2.2.1 Natural rubber for solid tyre

Natural rubber obtained from rubber trees as latex by tapping manually. Natural rubber is named as poly-*cis*-1,4 polyisoprene and it contains more than 99.9% of poly-*cis*-1,4 polyisoprene. The most important and commercial source is *Hevea Brasiliensis*. There are several non-isoprene structure units available at the end of the main macromolecules. These functional groups or non-isoprene structures severely affect the properties of the natural rubber. It is significant in the properties comparison between natural rubber and its synthetic equivalent (Isoprene Rubber) [7].

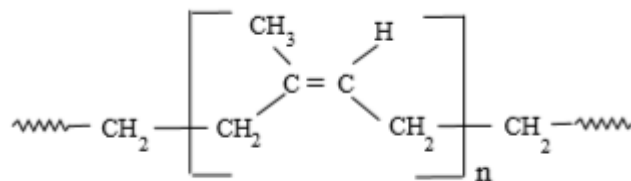


Figure 2-1: Structure of *cis*-1,4 polyisoprene

Natural rubber macromolecules are the long-chain repeated structure that is flexible and linear. So it shows highly elastic properties and spontaneously crystallizes also under influence of deformation forces. The tensile strength of natural rubber filled with reinforcement is greater than 30 MPa. Generally, the mastication step is added to before compounding since molecular weight varies the most in between 10^4 - 10^7 and special NR types with constant viscosity (CV) can be used without mastication since its good processing properties [7].

2.2.2 Technically specified rubbers (TSR) for solid tyre

There were several difficulties and issues with available NR products such as RSS and crepe Rubber such as lack of technical details, poor packing & handling. By the collaboration of both ends, customers and suppliers of NR came out with a solution to accept the above-mentioned facts. Technically Specified Rubber (TSR) was introduced with accepted technical specifications based on grade and polyethylene wrapped bale [3].

Table 2-1: Specifications for TSR grades

Property	Rubber grade				
	L	CV	5	10	20
Max. dirt content on 45-micron sieve %	0.05	0.05	0.05	0.10	0.20
Maximum Ash content %	0.60	0.60	0.60	0.75	1.00
Maximum Nitrogen content %	0.60	0.60	0.60	0.60	0.60
Maximum Volatile matter %	0.80	0.80	0.80	0.80	0.80
Initial plasticity, P ₀ min	30	-	30	30	30
Plasticity retention index, PRI, min %	60	60	60	50	40
Lovibond scale of color, max	6.0	-	-	-	-
Mooney viscosity, ML(1+4) 100° C	-	60± 5	-	-	-
L = Light colour					
CV = constant viscosity					
The numbers 5,10,20 indicate the maximum permeable dirt content in the grade					

TSR overcome existing issues of NR products such as unable to guarantee the important technical parameters, quality consistency, limited space required for storage and easy to handle packing. Typical specifications of TSR are given in Table 2-1.

Specifications of TSR have been revised several times based on the customer requirement since its introduction. Rubber plantation industry and development of TSR were developed parallel due to the mutual benefits of the TSR customer requirements [6].

2.2.3 Carbon black

Carbon black is at its top level as reinforcing filler in tyre industry and it increases in tensile strength properties, wear resistance and resistance to fatigue in rubber compound vulcanizates. Fine particles of the Carbon Black anchor the polymer chains and strengths cured compound as in Figure 2-2 [8].

Further carbon black is an excellent UV light absorber due to its black color. Therefore most of the components of ultraviolet sunlight are absorbed by carbon black. Hence it reduces the opportunity of degradation of the product due to oxidation of the rubber.

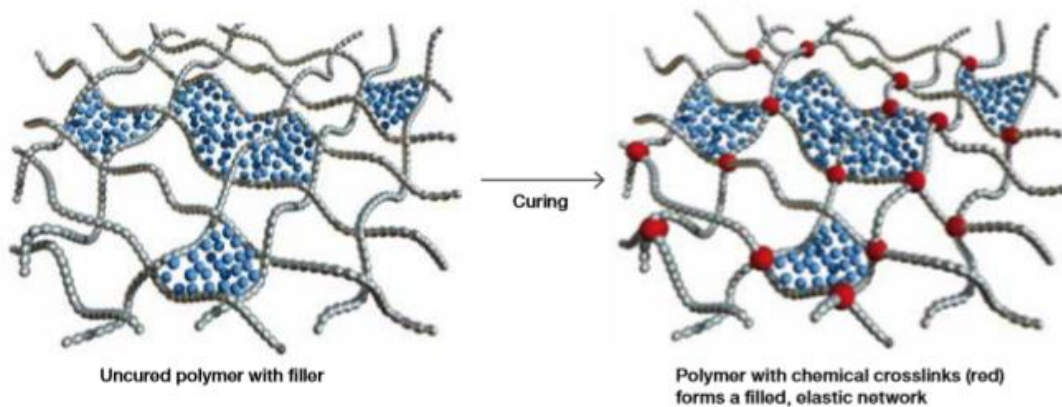


Figure 2-2: Uncured, filled polymer compared with cured rubber [8]

2.3 Rubber compounding

Rubber compounds are prepared in order to achieve defined properties by mixing rubbers, fillers, chemicals, and others. Different chemical types are used as crosslinking agents, accelerators, activators, reinforcements, anti-degradants, and processing aids. By the vulcanization, long-chain polymer chains will be transferred from viscous state to elastic solid by forming a crosslink between the polymer matrix. Further, tensile & tear strength and the modulus are increased and the hysteresis is decreased. Sulphur based vulcanization is widely used in natural rubber based compounds [2].

Reinforcement of the rubber compound is increased with higher the surface area and it act as stress arrestors for the polymer chain. Typical particle size is used smaller than 1µm in size. Carbon black and silica are used as the most widely used reinforcing fillers different other filler types are used non-reinforcing fillers [9].

2.4 Rubber grade carbon black

2.4.1 Basic chemistry

Carbon black is an amorphous molecular arrangement and a basic form of the carbon in the smallest particle size. These amorphous structured microcrystalline groups are compressed as rings. These carbon arrays may appear as ring structure which is condensed layers of another carbon form. It is known as graphite. There is a random orientation in an amorphous mass of arrays. Consequently, a significant amount of arrays display open molecular in their layer planes at the particle surface. These open ends provide chemical activity by the high amount of unsaturated carbon particles. Chemically active particles play a major role in carbon black properties. Carbon black properties, as well as the performance of the finished products, depending on both of their morphological characteristics and surface activity [10].

2.4.2 Carbon black morphology

The smallest individual unit of the carbon black is identified as aggregate in tyre industry. Aggregate is formed by the fusion of carbon black particles together. Other industries such as pigment refer to the smallest identified unit of carbon black as a particle. However, the carbon black industry convention refers to the component parts of aggregates as particles [11].

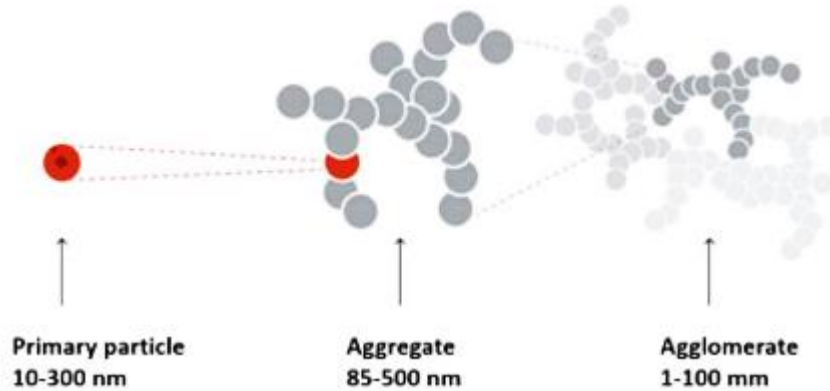


Figure 2-3: Morphological hierarchy of CB [12]

2.4.3 Particle size

The particle size of the carbon black is a very important fact to the reinforcing strength of the compound. As per the ASTM standards, particle size is assessed by the surface area method. Generally, the average particle size of commercially available carbon black grades ranges vary from about 10 to 500 nanometres. A large number of carbon black grades are within the average particle size 60 to 1 spread as shown in Table 2-2. Different size of carbon black types gives intrinsic properties in compounding and unique way of behavior in mixing. In common small particle size carbon black has higher reinforcement and lower cost. The difficulty of the compound mixing is also increased with smaller particle carbon black [12].

Particle size distribution is the second most important thing in particle sizes. Rubber compound properties are influenced by its narrow or broad or even bimodal distribution of particle size. Narrow distributions of a single aggregate in mixture act

as a broader distribution in the grade. Distribution of a different type occurs when a range of particle sizes exists within single aggregates [9].

Table 2-2: Carbon black particle size in different types

Type (abbreviation)	ASTM designation	Particle size(nm)	Typical use in tyre
SRF	N762	61-100	Non-tread components
GPF	N660	49-60	Non-tread components
FEF	N550	40-48	Non-tread components
FF	N475	31-39	Non-tread components
HAF	N330	26-30	Tread and other components
ISAF	N220	20-25	Tread components
SAF	N110	11-19	Tread components

2.4.4 Carbon black aggregates

Carbon black is made up of a solid unit of colloidal carbon titled as aggregates which is less than 1 μm in dimensions. Several particles of carbon black fused together and make random order to build aggregate. The ratio of the effective carbon volume to the total volume of carbon is decided by the arrangement and number of particles in the aggregate, which is entitled as the structure in history. [13].

Aggregate properties that are not represented by the size of the carbon particle have been recognized as structure. Higher structure carbon black aggregates have a higher number of particle count and particles joined together more chain-like bunches to form a narrow core [14].

2.4.5 Carbon black agglomerates

Agglomerates are formed by the attraction of van der Waals forces on individual aggregates. Adequate force is required to break down these agglomerates into small components. Carbon black aggregates are likely to combine with physical agitation.

This propensity to the combination is the distinctive factor that permits the formation of pellets. Agglomerates contain loosely bound aggregates but not fused [10].

2.4.6 Carbon black structure

Structure level is one of the key governing factors for reinforcement potential. Aggregate size and shape distribution have categorized the structure of the carbon black. The high structure represents the higher number of particles per aggregates and indicates by higher stiffness, viscosity or hardness, elastic modulus, conductivity, and make easy to disperse, whereas low swell and tear strength in the compound. Figure 2-4. illustrates the carbon structure changes over the grades [11].

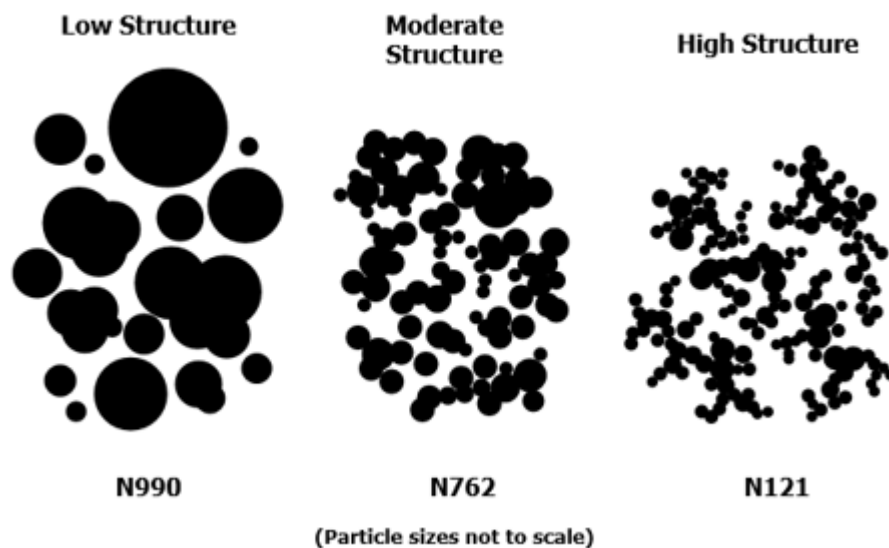


Figure 2-4: Structural representation of CB particle sizes [10]

2.4.7 Surface activity of Carbon black

The third major parameter of carbon black is surface activity. It has been proved that a carbon black is possessed a high reinforcement capacity will lose by some extent of its ability for reinforcing rubber upon being subjected to sufficient heat. Since its morphology change can be considered negligible with this treatment but it may lose surface activity. The reduction of reinforcement is demonstrated by the decrease in the rate of cure, abrasion resistance, tread wear, elastic modulus, tensile strength, and

other physical properties. The severity of the heat treatment decides the degree of change. Since this surface effect, carbon black is not just a filler [10].

2.5 Compound mixing

Materials that should be vulcanized have to undergo compounding before use. It should be a coherent and homogenous mass with numerous additives including curative agents, protective system, reinforcing and non-reinforcing fillers, and processing aids mixed to the polymer or blend of the polymer. Since Rubber is elastic and high viscosity material, power-intensive types of machinery like two roll mills or internal mixers are needed to disperse additives into the polymer matrix. The ingredients are in the form of powders, solid agglomerates or liquids [15].

The mixing of ingredients into the polymer matrix occurs in phases. The following four stages are happened in the mixing as per

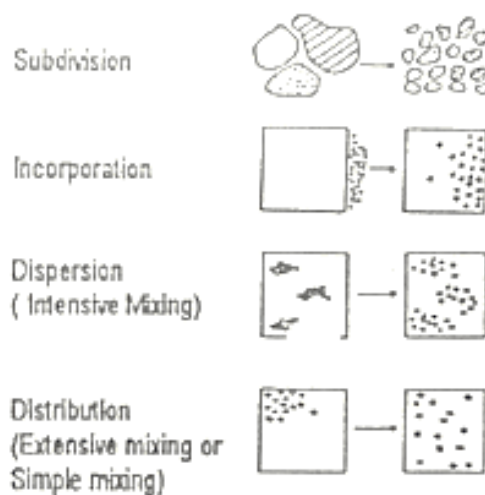


Figure 2-5.

Figure 2-5: CB dispersion progress [16]

During subdivision large agglomerates are broken down into aggregates fit for incorporation into the polymer. Carbon black pellets of the order 250-2000 μm in dimension get broken down into aggregates of the order of 100 μm . During the mixing, aggregates

are incorporated into the coherent mass of rubber. The following actions happen during particle size reduction such as increased surface area, a number of high energy sites, crystal defects, amorphous level and reduces melting point. Since all these actions solubility of the mix is increased [17].

In mixing, shear stress is applied to the rubber mass and carbon black aggregates. Shearing stress imposed by rubber mass applies shear stress on aggregates and reduces its size into their smallest size of the order of about 1 μ m in size. This size reduction is also recognized as intensive mixing at the macromolecular level.

Dispersion of the ingredients is dependent on generated shear stress within the rubber and therefore prolonged mixing is not direct to good dispersion. For optimum performance of the mixture is depended on not only the correct setting for the mixing step time but also the adding order of ingredients to the mixer [8].

Viscosity reduction happens in mixing and is important to have good processability of the stock. The dispersion level of carbon black has an intense impact on the physical properties of the vulcanizates. Undispersed carbon black in the compound acts as gritty particles and these points develop cracks under tension. Important properties like tensile strength, tear strength are reduced and abrasion resistance comes down hence the degree of dispersion comes down [18].

The effort of governing rubber compound temperature throughout the mixing has also influenced the retention of batch processes. Temperature control in mixing is important for the 1st stage mixing efficiency and for minimizing the adverse due to progress of the chemical reactions in 2nd stage mixing, which leads to crosslinking in 2nd stage mixing. A high amount of heat is produced by mixing when the viscosity of the rubber compound is very high. The requirement of the temperature control in the mixer is significant as the volume of the mixer is increased due to the reduction of the contact between cooling channels and rubber compound lump and it also increases as mixer rotor speed is enhanced [18].

2.5.1 Mechanisms of mixing

2.5.1.1 Viscosity reduction

Viscosity reduction of rubber is due to the molecular breakdown happening during the compound mixing. There are several factors that affected the viscosity reduction of the mixing such as polymer chain scission (mastication), temperature raise, flow-induced molecular dis-entanglement [19].

Strain rate increases the viscosity reduction by occurring flow-induced dis-entanglement of rubber molecules. Chain scission makes the permanent breakdown of polymer chains and hence it gives permanent viscosity reduction. But the other two factors, temperature increment and flow-induced changes in viscosity are reversible. Chain scission in natural rubber processing is more critical in all commercial rubber grades hence processability of the compound is totally depends on its viscosity reduction. At 100 °C, chain scission is minimum. But, bellow this point, the rate of chain scission increases due to mechanical breakdown and above this point, the rate of chain scission increases too due to the oxidative breakdown.[19].

2.5.1.2 Incorporation

During the incorporation phase, the rubber compound moves from a separate ingredient to a compact and substantially non-viscous mass that can undergo viscous flow. When only rubber and particulate matter are involved, the transition usually takes three phases to overlap.

- Encapsulation
- Subdivision
- Immobilization

Encapsulation can be achieved between the rotors of an internal mixer or between the rolls of a two-roll mill. It happens due to the pressure and shear stress applied at the rubber granules and combines the with the neighboring material. After this phase change, the particular rubber can be undergoing flow [18].

To have better properties of the rubber compound, uniformity of the composition of the compound should be there. Uniformity of composition at the microscopic level is expressed in the subdivision. The subdivision acts under the shear stress and the elongation flows in the rubber molecules to separate and surround them for permanent deformation. Because of subdivision, the distance between molecules is reduced. Agglomerate is the final particle outcome of the subdivision [18].

Immobilization is another concept that needs to describe incorporation and it is the entrapment of rubber within carbon agglomerates. Reinforced carbon black has internal space, normally it is approximately twice the normal solid material. Entrapped air in these voids is displaced by the rubber during the encapsulation and the subdivision. Due to that, the further flow of rubber molecules is stopped by the rigid filler. During incorporation, the density of the rubber compound is increased gradually and at the end of the incorporation phase, it is reached solid density. Primary aggregate reduction or reduction of internal void volume in carbon black is minimal at the incorporation phase. Viscosity at the end of incorporation can be more than three times that calculated from the filler loading in the rubber compound formulation[19].

Processing aids are one of the important materials that are used in rubber compounding and it has many reasons for the usage of this. The incorporation of the carbon black is enhanced by processing aids by providing lubrication to the system. Processing aids may be oil or plasticizers. To have efficient incorporation, these materials should be absorbed by the filler before the encapsulation. Since the processing aids added to the compound has high mobility, they allow to rubber molecules to enter the internal void volume of filler pellets and agglomerates more quickly. Therefore, plasticizers reduce the void volume available for immobilization of rubber and as a result increasing the viscosity is reduced. Other than this, plasticizers reduce overall incorporation time[19].

2.5.1.3 Dispersion

After the incorporation phase, there is a phase called dispersion which has the highest viscosity. It is happening due to the filling of internal voids of the filler by rubber, oil or plasticizer giving the rubber compound its solid density. Carbon agglomerates are further reduced into the primary aggregates and particles during the dispersion phase [20]. The high viscosity and incompressibility of the rubber compound are shown in the initial phase of the dispersion due to the high tensions that must be generated by the shear and elongation flows. In addition, the large size of the agglomerates makes them very susceptible to fracture, allowing the dispersion to develop rapidly. Embedded immobilized rubber is discharged by the fractured agglomerates and it leads to reduce the viscosity. Completed dispersion is not achieved during the practical mixing process and a small fraction of undispersed filler remaining into the final product. This may lead to batch to batch variation or within the batch variation of its critical properties. [19].

2.5.1.4 Distribution

The distribution of the filler is the phase that completes micro and macro level distributive mixing. There are minor additives used in compound mixing and at the initial stage, these materials are concentrated at the small region of the mixer. Adequate distribution of the minor components of a rubber compound is more than that of the major components such as fillers. Macro-distribution can be explained by the separation of filler agglomerate fragments after fracture during dispersive mixing. Macro-distribution is consists of two mechanisms called as laminar shear mixing and exponential mixing. These two mechanisms can be described by the reduction of the scale of segregation between two components of a rubber compound. The adverse effect of dispersion can be eliminated by further mixing or[18].

2.5.2 Compound properties of carbon black

Carbon black is significantly affected by the rubber compound properties like physical, mechanical and dynamic properties. Qualitative changes of these properties are

depending on the type of carbon black and properties such as particle size, particle size distribution, structure, surface activity affected the compound properties.

Cut growth and fatigue resistance of the rubber compound is increased by the increase in a carbon black aggregate size or structure. A decrease in particle size of the carbon black improves the abrasion and resistance and tear strength while it is negatively affected by the resilience and hysteresis properties. Therefore, carbon black is significantly affected by the properties of the tread compound of the tires and the following are some of the impacts of carbon black type and the loading on the properties of the tread compound [9].

- The increase of carbon black loading rises the rolling resistance, but it increases wear resistance.
- The fineness of the carbon black increases both rolling resistance and traction.
- The broad aggregate size distribution of carbon black reduces rolling resistance
- Performance of tyre improved by selection of most suitable carbon blacks and wet and dry traction, rolling resistance, wear improvement in tyre performance.

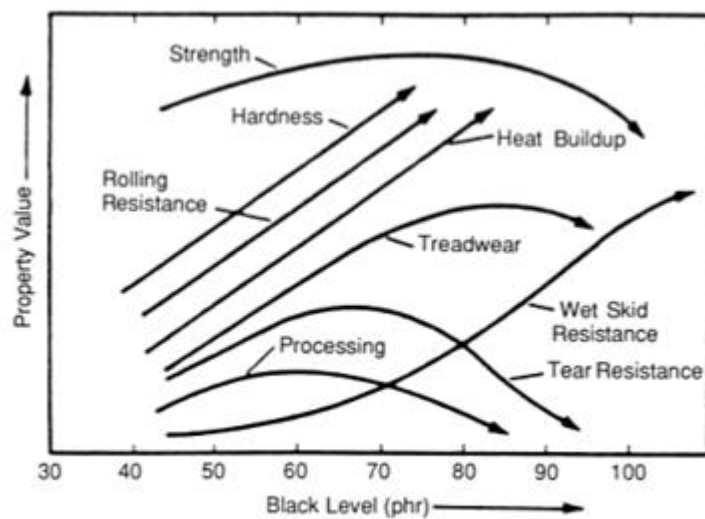


Figure 2-6: Physical and mechanical properties variation with CB loading [21]

Figure 2-6 demonstrates the common tendencies of physical and mechanical properties with carbon black loading for tread grades. With the increase of carbon black loading, tyre hardness and heat build-up of the compound are increased while rolling resistance

and wet traction properties. Tensile strength, tear strength abrasion resistance, and compound processability behavior reach an optimum and then these properties are declined [21].

Physical and mechanical properties behavior with particle size, structure, dispersion, and interaction are shown in Table 2-3.

Table 2-3: Physico-mechanical property variation with filler morphology [22]

Compound property	Properties of filler			
	Particle size (Decreasing)	Structure (Increasing)	Dispersion (Decreasing)	Interaction (Increasing)
Hardness	++	++	-	+
Tensile strength	++	Small	+	+
300% modulus	+	++	Small	++
Elongation at break	-	-	++	-
Tear resistance	++	Small	Small	Small
Hysteresis	++	+	-	-
Abrasion resistance	++	+	++	++

Notes: sign + and ++ shows an enhance of that parameter and sign – shows a reduction. That does not imply the advantages or disadvantages of property. That depends on its particular application. For example, high hardness is an application for the heel, but bad for tread where wearing increases [22].

2.6 Dispersion data point calculation

Carbon black dispersion is tested by the Dispergrade α view test machine which utilizes the analysis method of optical dispersion. Rubber compound with a mixture of carbon black are tested by a reflected light microscope, an image of the fresh surface of the sample cut is used for analyzing the presence of agglomerates as shadow cast. Dispersion is discussed considering four different factors as X value, Y value, Z value, and Dispersion percentage [23].

2.6.1 X- value

In the test piece carbon blacks are showing up as surface bumps or depressions and comparison of the size and frequency between the test piece and reference photographs

refer to as X value. In its initial step reference images were classified with the same calculation algorithms and after that test image was compared with the reference. The value obtained from results ranges from 1 as very poor to 10 as very good [23].

2.6.2 Y-value

Y value is given on a numerical scale from 1 to 10, in here 10 means that there is no agglomerate of 23 μm or more in diameter, and 1 means that a large number of such agglomerates (relate to 19% of the test area). Y value is Calculated according to the equation.

$$Y = 10 - 9 \times \frac{N_w}{0.19 \times N_{tot}} \quad \text{Equation 1}$$

Where,

N_w is the number of white pixels in the test area image due to the following aggregates resulting in particles with an average diameter of 23 μm or more

N_{tot} is the total number of pixels in the image of the test area.

2.6.3 Z- value

Quantification of dispersion simply expressed as Z- Value and It ranges from 0 to 100. 0 represent the poorer mix while 100 represent the perfect mix and that value being proportional to the number of agglomerates (white undispersed zones)

$$Z \text{ value} = 100 - \frac{(100 - \text{Dispersion})}{0.35} \quad \text{Equation 2}$$

2.6.4 Dispersion%

$$\text{Dispersion\%} = 100 - \frac{100}{\text{sum of all image pixes}} \times \text{sum of all agglomerate pixels} \quad \text{Equation 3}$$

That can be applicable for whole agglomerates size ranges from 2 to 62μm.

2.6.5 Average aggregate size and standard deviation

The average particle size (diameter) in μm and the standard deviation of average aggregate size is calculated [23].

2.7 Abrasion related researches

Rattanasom et al studied in lieu of optimum ratio of silica:carbon black in the reinforcement of natural rubber composite while maintaining total filled carbon black content as 50 pphr. The mechanical properties of the vulcanizates were determined in natural rubber with reinforcement of carbon black by heat buildup, rolling resistance, growth of cracks, tear strength and tensile strength. The research outcome concludes that overall mechanical properties are at optimum when the silica content of the vulcanizates is between 20 and 30 pphr in the formulation. The consequence was explained as the better filler dispersion causes the lowest development of filler network in the vulcanizates. And it was shown that silica-containing 20 pphr is more susceptible to processing than 30 pphr silica in compounding. Hence it is easy to incorporate a higher amount of N330 CB into NR than silica does in first stage mixing [24].

Chang et al studied the rate of abrasion and friction of carbon black filled blends of NR, BR and SBR compounds with the particle size and the structure effect. It was revealed that the size of carbon black and agglomerate size and Young's modulus have a linear relationship. There was a relationship between particle size and structure of carbon black. Abrasion resistance is increased with smaller particle size and higher the structure of the carbon black [25].

Savetlana et al studied the variation of mechanical properties of vulcanizates over the carbon black reinforced NR. The experiment was done on carbon black series of N220, N330, N550, and N660. The highest tensile strength was shown in 20% loading for all the above carbon black types between 20% to 30%. Beyond the 20% limit, tensile strength starts decaying. Elastic modulus is proportionate with CB loading and the strain is inversely proportionate to CB. In addition to that, NR and CB interface indicates homogeneous dispersion of NR and CB by SEM images.

Since the agglomeration amount of carbon black increases with its loading, tensile strength is reduced with reinforcements. The carbon black structure affected the tensile strength of the NR and CB composite. According to the SEM images, the higher tensile strength of NR and N220 CB composite shows the lower amount of agglomeration CB. N440 and N550 carbon black aggregates display a large agglomeration in SEM pictures. Large agglomeration in the compound granted lower tensile strength. Although, theoretically, low structure N660 CB has a lower tensile strength while the rest have higher tensile strength was achieved hence CB N660 contains an inadequate amount of agglomerations. The structure and CB loading affected the tensile strength of natural rubber and carbon black-based compounds by this experiment [26].

3. MATERIALS AND METHODOLOGY

3.1 Research plan

The main objective of this research was to study the effect of carbon black grades on abrasion properties of solid tyre tread compounds. Solid tyre tread compound was selected for this study since it uses 100% natural rubber as the polymer. Two different grades of carbon black were selected for the study; N 220 and N 330 which have different morphologies. N220:N330 carbon black ratio was changed from 0:50 to 50:0. Unique mixing sequence and conditions were used for all mixing trials and measured physico-mechanical properties and cure characteristics.

3.2 Materials

The formulation was selected based on the tread compound used in solid tyre manufacturing. The formulation consists of TSR 20 as natural rubber, reinforcing carbon black N 220 and N 330 for all combinations. Stearic acid and 99.5 % zinc oxide were used as activators and N-(1,3-dimethyl butyl)-N'-phenyl-p-phenylenediamine (6PPD) and polymerized 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ) were used as anti-oxidants for the tread compound. The slow curing process was used to incurring by using Sulfur and N-tert-butyl-2-benzothiazole sulfenamide (TBBS). Compound scorch safety was controlled by using N-(cyclohexyl-thio) phthalimide (CTP) as the pre-vulcanization inhibitor. Mixing was carried out in a two-stage process in order to provide proper mixing to the fine carbon black powder particles and 18 hours maturation time was maintained between master batch and final batch mixing.

The formulation used in both the 1st stage and 2nd stage mixing is illustrated in Table 3-1.

Table 3-1: Formulation for tread compound

Material	Function	pphr
TSR 20	Elastomer	100
Carbon Black N220/N330	Reinforcing Filler	00-50
6PPD	Antioxidant	1.5
TMQ	Antioxidant	1
Stearic Acid	Cure activator - Organic	2
Zinc Oxide 99.5%	Cure activator - Inorganic	5
Low PAHs Rubber Process Oil	Processing Aid/Softener	5
Sulphur	Curing agent	2
TBBS	Cure accelerator	1
CTP	Retarder	0.3

Information relevant to the origin of the materials which were used in the compound formulation is shown in Table 3-2.

Table 3-2: Material and origin of materials

Name of the material	Origin/Manufacture
Natural rubber -TSR 20	Thai Hua Rubber Public Co. Ltd, Thailand
Carbon black - N220	Jiangxi Black cat carbon Black Inc. Ltd, China
Carbon black - N330	Jiangxi Black cat carbon Black Inc. Ltd, China
Stearic Acid	Palm oleo sdn bhd, Malaysia
Zinc Oxide 99.5% purity	Agromet Asia (Pvt) Ltd, Sri Lanka
Antioxidant - 6PPD	Shandong Sun Sine Chemical Co. Ltd, China
Antioxidant - TMQ	Shandong Sun Sine Chemical Co. Ltd, China
Sulphur	Salfa chemicals, India
CTP	Changdong Gerec New material Ltd, China

3.3 Rubber compounding

The compounding ingredients, as shown in Table 3-1, were mixed using a Farrel BR1600 laboratory-scale internal mixer with a two-stage mixing technique. The fill factor was set to 0.6 during the mixing and friction ratio of the mixer was 1:1.16. Mixer temperature was controlled at 40 ± 5 °C during mixing by Temperature Control Unit (TCU). The actual dumping temperature was measured by the manual Testo 925 temperature probe.

The mixed compound lump was milled on two-roll mill for 4 turns and sheeted out with 2 mm – 3 mm thickness. Laboratory-scale two-roll mill (size 200 mm x 400 mm) was used with a friction ratio of 1:1.2.

Rubber compounding was done in two stages. They are termed as 1st stage mixing and 2nd stage mixing. Material addition in two stages is listed below.

- 1st stage mixing - Rubber mastication and adding fillers, antioxidants, activators.
- 2nd Stage mixing - 1st stage compound mixed with curing agents, accelerators, retarders.

3.3.1 1st stage mixing

Compounding ingredients were prepared as per Table 3-3 in 1st stage mixing. Carbon black ratio of N220:N330 was changed in A to F formulation as shown in the Table 3-3. Total carbon black loading was kept constant at 50 pphr.

Table 3-3: Compounding ingredients in 1st stage mixing

Material	pphr					
	A	B	C	D	E	F
TSR 20	100	100	100	100	100	100
Carbon Black N330	50	40	30	20	10	0
Carbon Black N220	0	10	20	30	40	50
6PPD	1.5	1.5	1.5	1.5	1.5	1.5
TMQ	1	1	1	1	1	1
Stearic Acid	2	2	2	2	2	2
Zinc Oxide 99.5%	5	5	5	5	5	5
Low PAHs Rubber Process Oil	5	5	5	5	5	5

The following mixing cycle was used to mix 1st stage compound as shown in Table 3-4 for all formulations in an internal mixer.

Table 3-4: 1st stage mixing cycle

Time (Seconds)	Description	rpm
0	TSR 20	90
50	N220 + N330 + 6PPD + TMQ+ Zinc oxide + Stearic acid	80
50	Low PAHs Process Rubber Oil	90
40	Ram Sweep	90
90	Dumping at 150 ± 5 °C	100

Materials were selected for the Second experiment based on the optimum physical and mechanical properties in the first experiment. Two formulations were selected as per Table 3-5. 1st stage mixing was followed by two mixing sequences.

Table 3-5: Compound ingredients for 1st stage mixing in the second experiment

Material	pphr					
	L25 (N220)	M25 (N220)	H25 (N220)	L35 (N220)	M35 (N220)	H35 (N220)
TSR 20	100	100	100	100	100	100
Carbon Black N330	25	25	25	15	15	15
Carbon Black N220	25	25	25	35	35	35
6PPD	1.5	1.5	1.5	1.5	1.5	1.5
TMQ	1	1	1	1	1	1
Stearic acid	2	2	2	2	2	2
Zinc oxide 99.5%	5	5	5	5	5	5
Low PAHs Rubber Process Oil	5	5	5	5	5	5

Mixing cycles were used for 1st stage mixing for the second experiment are shown below in Table 3-6 and Table 3-7. Two mixing cycles used in the second experiment were deviated from the initial mixing cycle by reducing and increasing the last step time. Table 3-6 shows the mixing cycle used for the reduced mixing cycle. At this point, 10 seconds of the last mixing step has been reduced than the initial mixing cycle in Table 3-4.

Table 3-6: 1st stage mixing for the second trial with reduced cycle

Time (s)	Description	rpm
0	TSR 20	90
50	N220 + N330 + 6PPD + TMQ+ zinc oxide + Stearic acid	80
50	Low PAHs process rubber oil	90
40	Ram sweep	90
80	Dumping at 150 ± 5 °C	100

The extended mixing cycle is shown in Table 3-7. The last step of the extended mixing cycle was increased by 10 seconds.

Table 3-7: 1st stage mixing for the second trial with extended cycle

Time (s)	Description	rpm
0	TSR 20	90
50	N330 + N220 + 6PPD + TMQ+ zinc oxide + stearic acid	80
50	Low PAHs process rubber oil	90
40	Ram sweep	90
100	Dumping at 150 ± 5 °C	100

Six different combinations were selected to experiment with the different mixing cycles and slightly deviated the formulation of the optimized formulation of the previous testing.

Table 3-8: 1st stage mixing sequence with formula and mixing cycle

	L25 (N220)	M25 (N220)	H25 (N220)	L35 (N220)	M35 (N220)	H35 (N220)
Sample code						
CB ratio (N220:N330)	(25:25)	(25:25)	(25:25)	(35:15)	(35:15)	(35:15)
Mixing cycle	Lower	Medium	High	Lower	Medium	High

The second experiment was done as per Table 3-8 by varying two different compound formulations selected from the 1st experiment and three different mixing sequences including previous mixing cycle, reduced and increased mixing cycles were used to compare the previous experiment.

3.3.2 2nd stage mixing

Ingredients for the 2nd stage formulations are shown in Table 3-9 and 2nd stage mixing was kept constant for all six formulations by fixing the mixing time. 2nd stage mixing cycle is given in Table 3-10. The mixed compound was followed two roll mill after completing the mixing in an internal mixer.

Table 3-9: Compounding ingredients in 2nd stage mixing

Item	pphr
1st stage compound	164.5
Sulphur	2
TBBS	1
CTP	0.3

2nd stage mixing was done in the same method for all six batches to maintain the consistent for properties

Table 3-10: 2nd stage mixing cycle

Time (seconds)	Description	rpm
0	1st stage compound	80
50	Sulphur + TBBS + CTP	70
100	Dumping at 100 ± 5 °C	70

Physical properties and abrasion samples were prepared for curing when the two-stage mixing completed in the mixing room.

3.4 Preparation of samples

Lab tech Laboratory press was used for sample curing which was used in an electrical heating system. Specific pressure on samples was maintained as 4.5 bar according to match with ASTM requirement (minimum 3.5 bar). Standard curing time was used for sample vulcanization as 30 minutes and the setting temperature of the mold was maintained as 150 ± 5 °C.

3.5 Sample testing

3.5.1 Cure characteristics

MonTech MDR 3000 was used to test the cure characteristics and get the information about processability. MDR was used for testing due to high accuracy then ODR. Nearly 5mg of the second stage compound sample was used for MDR testing. Cavity temperature was maintained at 150 °C. Die is oscillating at 0.5 degrees arc and 100 rpm to 30 minutes according to ASTM D 5289.

Frank GmbH rebound tester was used to test the rebound resilience of the samples. It was done to get an idea about the hysteresis of the compound samples. It was a Schob Type pendulum tester. It evaluates impact resilience and penetration of rubber using a pendulum rebound according to ASTM D7121.

3.5.2 Viscosity

The Mooney viscosity test is used to quantify the viscosity of raw rubber and rubber compounds. Mooney viscosity is the viscosity reached after the rotor rotates for a given time interval (Mooney time setting). MV 3000 MonTec Mooney viscometer used to test the compound viscosity and it specifies measuring the Mooney viscosity four minutes after the preheating one minute time ends.

3.5.3 Mechanical properties

The Geotech tensile machine was used to measure and calculate the physical properties of the samples. The thickness of the sheet was 2 mm and it was vulcanized using a curing press. Dumb-bell shaped samples were cut by standard die cutters according to ASTM D412-A. 24 hours maturing time under room temperature was used and tests performed at room temperature. Tensile strength, 300% modulus, and Elongation at break % were calculated by using the following procedure and results obtained from tensile testing.

- Tensile strength = F/A
- Modulus at 300% elongation = F'/A
- Elongation at break % = $(L-L_0)/L_0 \times 100$

Where;

F - Breaking Force A - Initial Cross-sectional area

L_0 – Initial length L – Length at break

F'- The force required at 300% elongation

3.5.4 Hardness

Durometer hardness tester was used to measure the hardness. The principle of the tester is the resistance of the indentation is proportional to the hardness of the tested piece. ASTM D 2240 test procedure is used for this test and Shore A is the unit of the measurement.

3.5.5 Specific gravity

Electronic Densimeter MD-300S was used to determine the specific gravity of the all different versions. Archimedes' principle is the measuring method under ASTM D 297.

3.5.6 Abrasion resistance

Abrasion resistance was tested by DIN type abrader machine using ASTM D 5963. Molded & drilled specimens from finished products were run on the abrasive surface. The standard test piece was tested in the same condition for the reference test. Abrasion loss is calculated by the following equation.

Abrasion Loss (Derived from ASTM D 5963 Method A)

$$A = \frac{\delta m \times S_0}{d \times S}$$

Where,

A – Abrasion of test sample in mm³

δm – Weight loss of test sample (mg)

d – Density of test sample

S₀ – 200 mg

S – Weight loss of reference rubber (mg)

3.5.7 Rebound resilience

Rebound resilience was tested by Frank GmbH rebound tester. Schob Type pendulum tester was used for the test. It evaluates impact resilience and penetration of rubber using a pendulum rebound according to ASTM D7121.

3.5.8 Carbon black dispersion

Carbon black dispersion was tested by using Alpha dispergrader. Different samples were compared by the images and the values as per the ASTM D7723 standard. X, Y, Z, and Overall figures were measured in the test. In addition to that, aggregate size standard deviation was calculated by using the dispergrader values.

4. RESULTS AND DISCUSSION

This Chapter presents cure characteristics, mechanical, physical, rheological properties and dispersion of the vulcanizates. First, experimental results of N220:N330 ratio change is described and then mixing cycle optimization results are discussed.

4.1 Study of the effect of N220:N330 composition of combined filler on properties of tread compound

4.1.1 Effect on cure characteristics

Cure characteristics of the compound formulations are shown in Table 4-1. M_L and M_H values were gradually increased with N220 loading in the combined filler was increased. It is due to the enhancement of the reinforcement in the compounds with particle surface area is increased. Since smaller particle size N220 contained higher surface energy than N330 which is having larger particle size carbon black.

Table 4-1: Cure characteristics of the different N220:N330 CB ratios

Type of the test	M_L	M_H	t_{s2}	t_{90}
Unit	dNm	dNm	sec	sec
A (00:50)	1.90	14.97	92.22	199.07
B (10:40)	2.00	15.16	94.01	202.34
C (20:30)	2.11	15.75	94.01	203.22
D (30:20)	2.16	15.35	95.21	206.05
E (40:10)	2.24	15.58	95.21	208.50
F (50:00)	2.44	16.33	92.81	208.92

Values of t_{s2} and t_{90} are shown in Table 4-1 and it is not showing a significant difference in the different CB ratios. This may be due to the same loading of CB in all types, even though the ratio is changed. Carbon black used in the experiment are normal curing carbon blacks and they are particle size difference is not much significant in the curing characteristics. Based on the rheological properties all formulations with N330 and N220 show better results.

4.1.2 Effect on Mooney viscosity

As shown in Figure 4-1, Mooney viscosity is gradually increased from 51.9 to 59.9 with N220 content is increased in the compound. Viscosity is increased with reinforcement is increased in the compound since N220 content is enhanced from 0 to 50 while N330 content is reduced. Deviations of the initial viscosity may be due to variations of the natural rubber used for the compound [18].

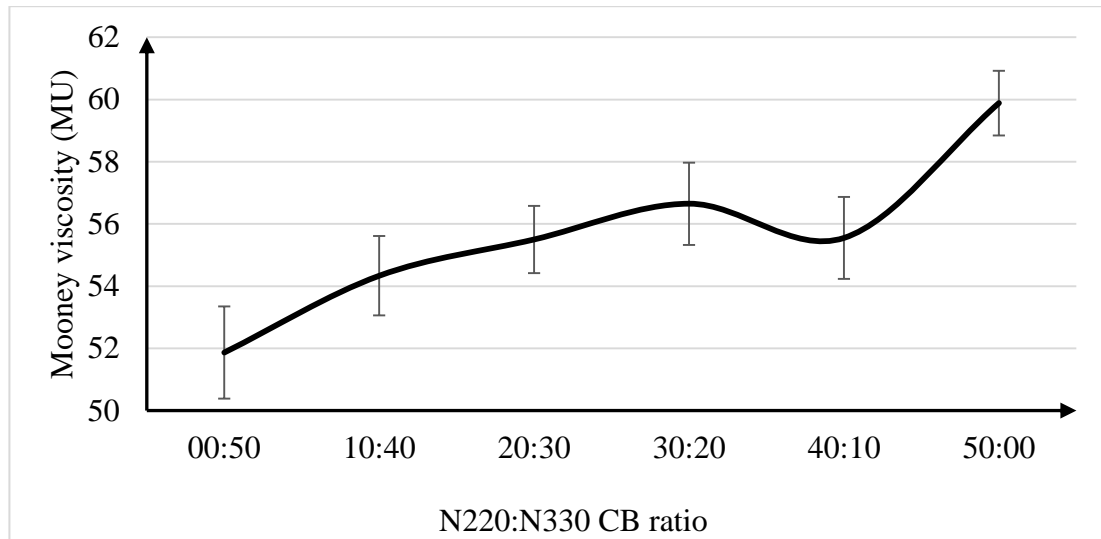


Figure 4-1: Variation of Mooney viscosity with N220:N330 CB ratio

4.1.3 Effect on mechanical and physical properties

The particle size of the carbon black affected the physical properties of the rubber vulcanizates. Different ratios of N220:N330 was used in this experiment and the mechanical and physical properties are discussed in this section. The tensile strength of vulcanizates prepared with different N220:N330 CB ratios are shown in Figure 4-2.

Tensile strength is increased with the increase of N220 and a decrease of N330 contents in the vulcanizates up to 30 pphr of N220. It is due to the smaller particle size of N220 compared to the N330 and this is because smaller particle size increases the surface area of the filler network and hence interactions between the filler and rubber are increased. This helps to increase the tensile strength [26]. After 30 pphr of N220, a slight reduction in tensile strength is observed. When the particle size of the fillers is

reduced, consequently the surface energy is increased. Hence, agglomeration of fillers occur and therefore high energy is required to break these filler agglomerates during mixing to have better filler distribution [27]. After 30 pphr of N220, agglomerations are increased as explained above and therefore higher energy is needed to break the filler agglomerations. Since the same mixing cycles were used during this experiment, the same energy content was given. Therefore breakdown of agglomerations is reduced and rubber to filler interactions is reduced, resulted reduction in tensile strength after 30 pphr of N220.

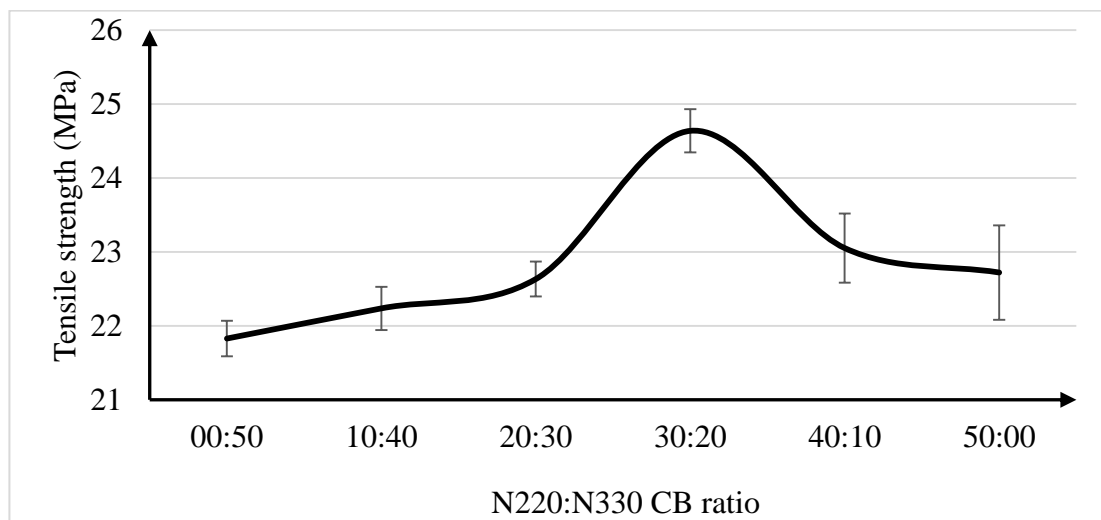


Figure 4-2: Tensile strength variation with N220:N330 CB ratios

According to the results, formulation D (30:20 ratio of N220:N330) shows the highest tensile strength. Both reinforcement, as well as less particle agglomeration, positively contributed to this highest value. High reinforcement is given by the higher amount of N220 and agglomeration of this N220 is deactivated by a lower amount of N330. Therefore blend of N220 and N330 gives the best results in terms of tensile strength. The study conducted by Savetlana et al [26] also illustrated the same observation and explanation.

According to the specifications of a several tyre tread compounds for tensile strength, only samples D, E and F could achieve the minimum tensile strength expected for the product. It shows that minimum tensile strength is 23 MPa and the other three ratios were not matched with the specification.

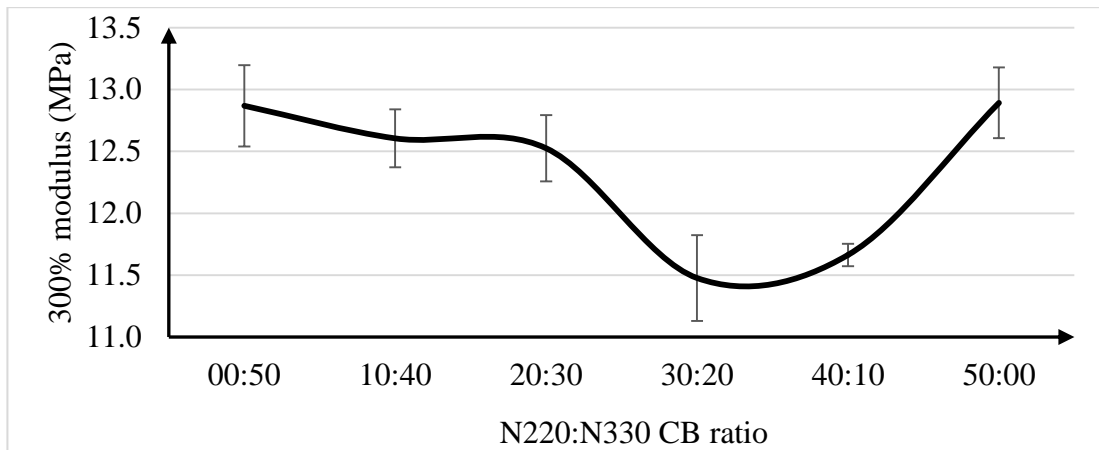


Figure 4-3: 300% modulus with N220:N330 ratios

There is no significant effect on 300% modulus when N220:N330 CB ratio is changed up to 30:20 ratio. Then, increment in 300% modulus is observed with the increase of N220 loading in the combined filler. This is due to the higher reinforcement of the vulcanizates associated with higher N220 loading. The same behavior was observed by Amir A Abdelsalam et al [27]. When the polymer filler interaction is higher, then the resistance of the deformation of the polymer network under stresses is increased.

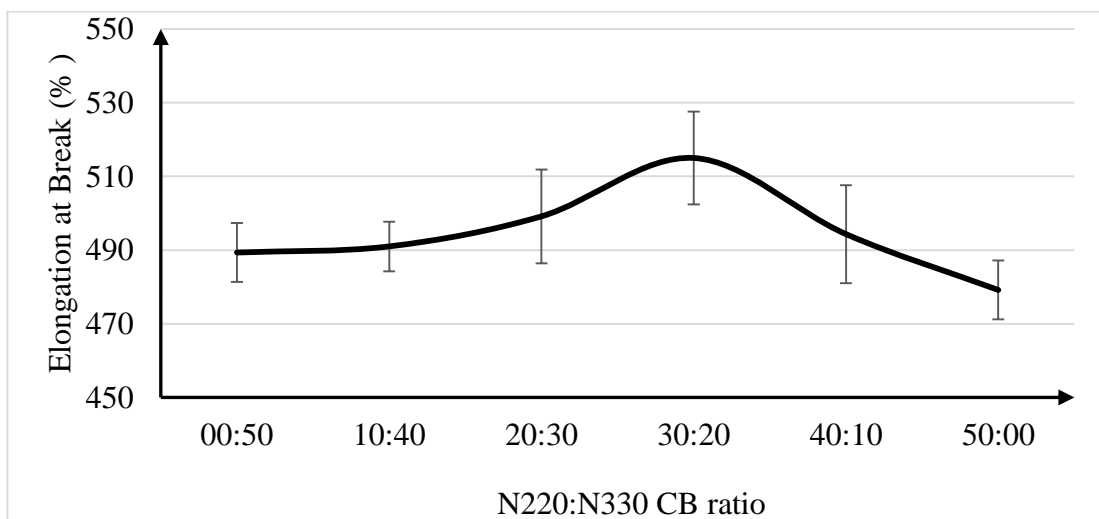


Figure 4-4: Elongation at break variation with N220:N330 CB ratios

In Figure 4-4, elongation at break is plotted against CB ratio and slight improvement is shown with N220 up to 30 pphr. The same reason explained for the tensile strength improvement with the N 220 is caused by the improvement of elongation at break. A

slight reduction of elongation at break after 30 pphr of N220 was already observed in the study conducted by Amir A Abdelsalam et al [27]. This is because of the higher amount of filler agglomeration of the lower particle size CB used for the compounding.

Table 4-2: Physical properties of vulcanizates of different CB ratios

Property	Unit	A (0:50)	B (10:40)	C (20:30)	D (30:20)	E (40:10)	F (50:00)
Hardness	Shore A	66	67	66	67	66	67
Specific Gravity		1.119	1.119	1.119	1.116	1.116	1.117

Hardness and specific gravity of the vulcanizates are shown in Table 4-2. It can be seen that hardness and specific gravity of the vulcanizates are not showing a significant difference in the different CB ratios. This may be due to the same loading of CB in all types, even though the ratio is changed. Based on the physical and mechanical properties Formulation D that has 20 pphr of N330 and 30 pphr of N220 shows better results compared to the other vulcanizates.

4.1.4 Effect on abrasion resistance variation

Abrasion resistance is a key parameter for solid tyre tread compound when the tyre life is calculated. Different ratios of N220 and N330 CB significantly affect the abrasion resistance and it is shown in Figure 4-5. Vulcanizates which have a higher amount of large particle size fillers such as N 330 and a lower amount of small particle size such as N220 show higher abrasion volume loss. This is due to the low reinforcement of polymer networks which is given by the large particle size fillers. When the amount of N330 is reduced, it is noted that abrasion volume loss also gradually decreases up to 20 pphr of N330. While the N330 amount is reduced up to 30 pphr and N220 increases, filler systems and hence reinforcement of the polymer network is increased. This helps to reduce the abrasion volume loss of the vulcanizates. Generally, the fine particle size CB increases the filler aggregation and agglomeration with N220 since a higher amount of fine particle CB. Due to that, filler to rubber interactions may be reduced and it will be directly affected by the abrasion volume loss increment [25]. However, according to the results obtained, abrasion volume loss

reduction is observed up to 30 pphr of N220 CB together with 20 pphr of N330 CB. A low amount of N330 contributes to minimize aggregation and agglomeration of filler system and hence the best abrasion resistance achieved with this filler blend ratio [15].

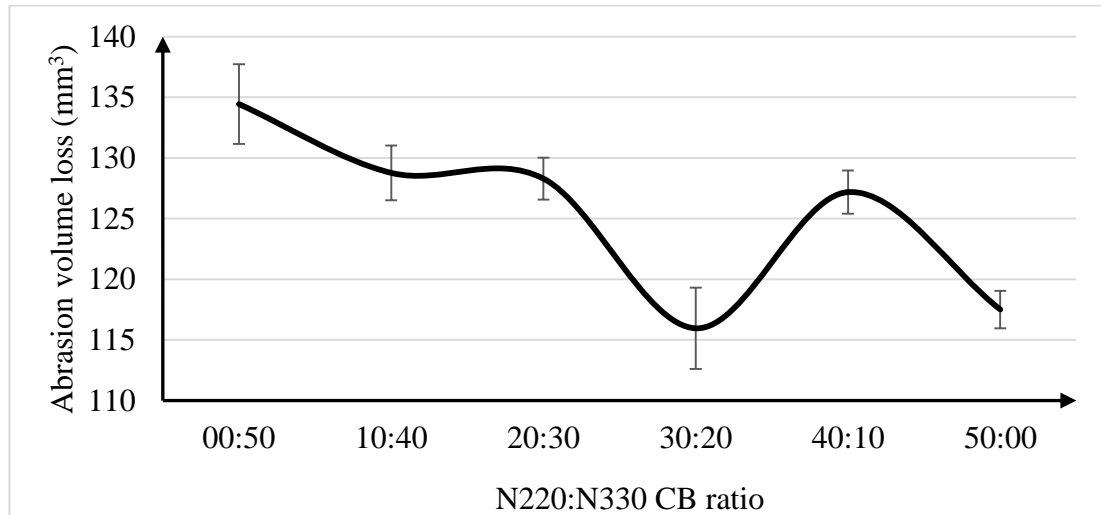


Figure 4-5: Variation of abrasion volume loss with N220:N330 CB ratios

Beyond the 30 pphr of N220 content in the combined filler, a slight increment of abrasion volume loss is noted. These vulcanizates have a higher amount of N220 and less amount of N330. Hence filler aggregation and agglomeration are predominant and therefore rubber to filler interaction is reduced. So that abrasion resistance is increased. Based on the abrasion resistance results, formulation D where N220:N330 ratio is 30:20 has the best filler combination and it shows a significant reduction than the other formulations.

4.1.5 Effect on rebound resilience

Rebound resilience of the vulcanizates is also important for the solid tyre tread compounds, due to its expectations of lower heat generation during the applications.

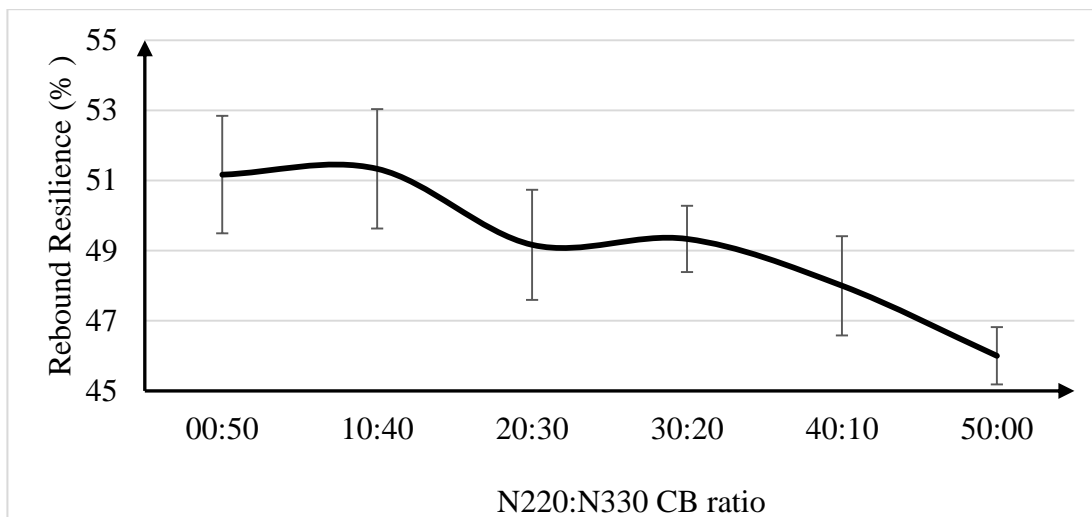


Figure 4-6: Rebound resilience variation with the different N220: N330 CB ratios

As per Figure 4-6 rebound resilience is decreased gradually with N220 CB is increased from 0 to 40 pphr and at the 50 pphr of N220 there is a significant reduction of rebound resilience. A gradual decrease of up to 40 pphr is due to the higher reinforcement with N220. Other than that N330 also there in the vulcanizates. It increases the packing factor of the vulcanizates and minimum free volume is available. Under the dynamic stresses, heat loss due to filler vibration and motion is less [17]. Rebound is an indirect method of vulcanization and therefore the rate of rebound reduction is lower of the vulcanizates which have a combination of N220 and N330.

In formulation F only N220 was used and it has a significant reduction in the rebound. This is due to the higher free volume compared to the other vulcanizates and hence free vibration of free carbon black is higher and therefore rebound is reduced. A high rebound is necessary for solid tyre tread compound and therefore formulation F is not good and blend of carbon black gives the best results.

Since this is a solid tyre tread compound, rebound resilience should be maximum to reduce energy loss during its applications. And this can be caused by higher fuel consumption for the vehicle. In those facts, sample A will be ideal but due to poor performance of the other properties, Sample A can not be selected. Here also, Sample D could maintain a low difference than the Sample and balance the properties.

4.1.6 Effect of carbon black dispersion

Overall dispersion value with X, Y and Z values are shown in Table 4-3. It can be seen that the dispersion of the vulcanizates is not showing a significant difference in the different CB ratios. This may be due to the same loading of CB in all types of formulations and both types of carbon black have adjacent sizes. This also contributes not to show a significant difference in the dispersion. The particle size of the N 220 is from 20 nm to 25 nm and N330 is from 26nm to 30nm. Hence all these compounds were mixed in well-controlled small scale laboratory mixer and all were given constant time, the dispersion may not be significant.

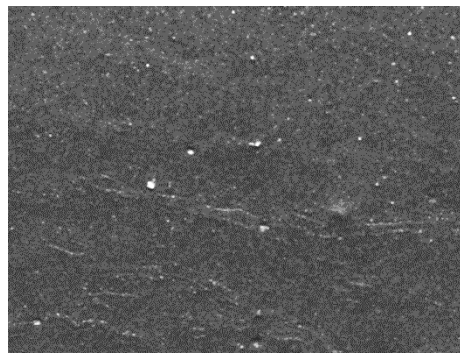
Table 4-3: Dispersion of CB at different N220:N330 ratios

Property	Unit	A (00:50)	B (10:40)	C (20:30)	D (30:20)	E (20:10)	F (50:00)
Overall X value	No units	8.54	8.47	8.27	8.34	8.73	8.10
Overall Y value	No units	9.93	9.95	9.89	9.94	9.96	9.86
Overall Z% value	No units	91.65	91.68	90.86	89.92	93.14	91.87
Overall Dispersion % value	No units	99.28	99.52	98.88	99.35	99.57	98.54

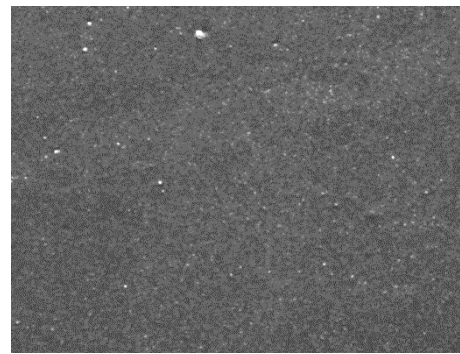
Figure 4-7 shows the images of the dispersion of the vulcanizates. A significant difference can not be observed in the images since all dispersion figures are over 98 level in dispersion.

In Figure 4-8 shows the aggregate size standard deviation is gradually increased up to a maximum of 30 pphr of N220. Since compounds having CB ratio, the difference of the particle size and aggregate size of the CB is increased until its maximum ratio. Here, two vulcanizates are contained maximum ratios of CB blends in C (20:30 ratio of N220:N330) and D (30:20 ratio of N220:N330 ratio). The standard deviation of the aggregate is at its maximum in D (30:20 ratio of N220:N330). It may due to the nature of the N220 aggregate size standard deviation and both N330 and N220 CB are packed well with its 30:20 ratio than the 20:30 ratio. This compact may be effected to enhance

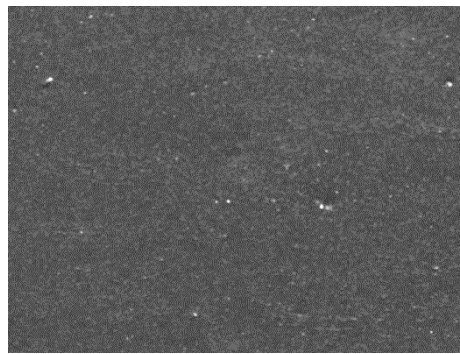
the properties of the vulcanizates such as tensile strength, abrasion, and highest elongation at break and a minimum 300 % modulus.



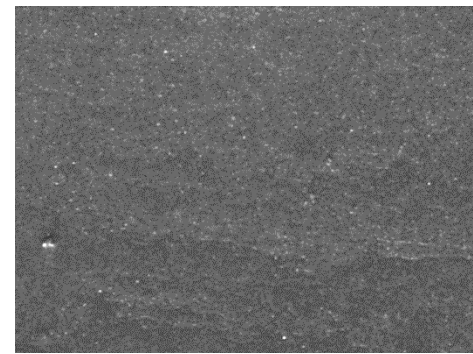
A (00:50)



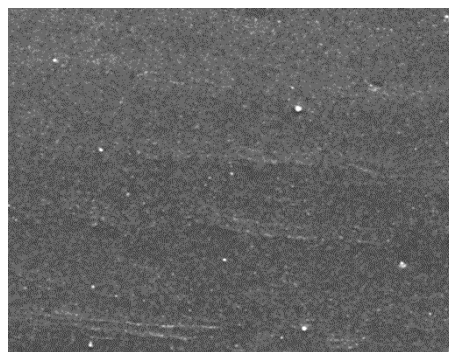
B (10:40)



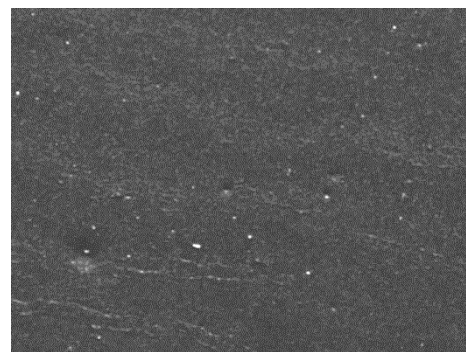
C (20:30)



D (30:20)



E (40:10)



F (50:00)

Figure 4-7: Compound dispersion of the different N220:N330 CB ratios

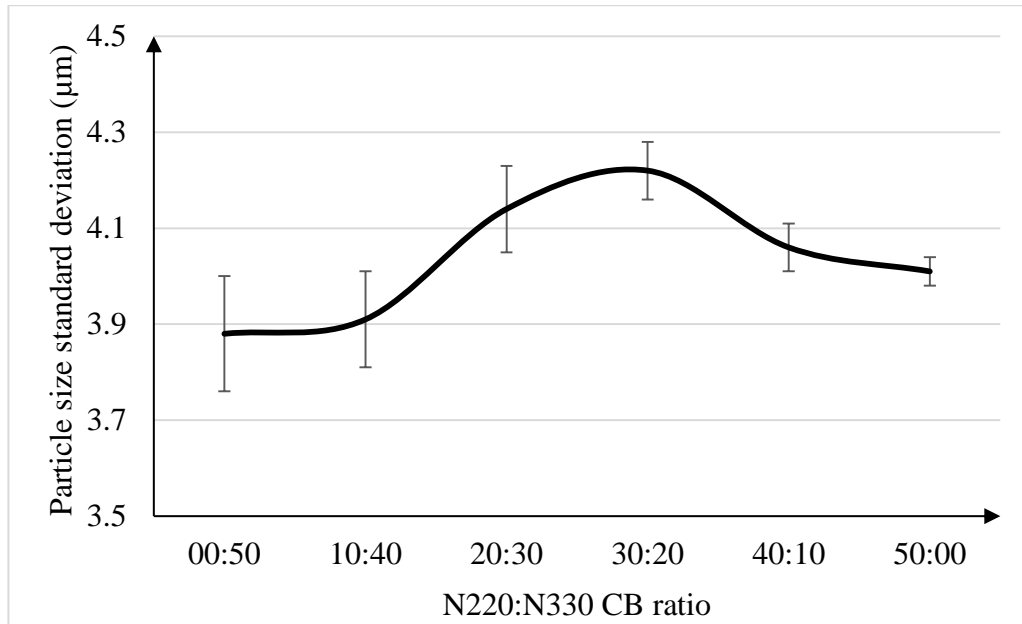


Figure 4-8: Variation of aggregate size standard deviation with N220:N330 CB ratios

4.1.7 Effect on dumping temperature of the mixing

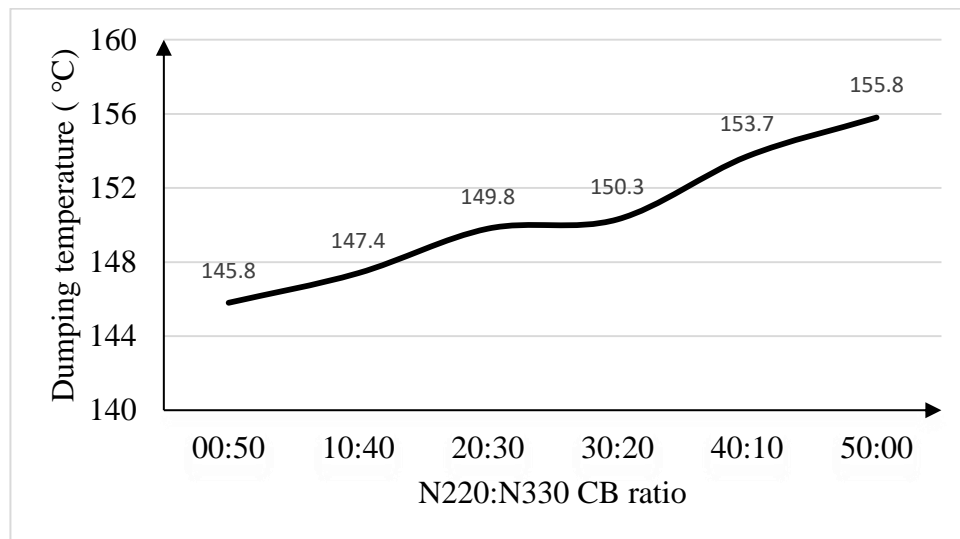


Figure 4-9: Variation of dumping temperature of the compound with N220:N330 CB ratios

The dumping temperature of the mix is increased with the N220 pphr is increased. This is due to the small particles sized CB need extra energy to incorporate into the rubber matrix [18].

4.2 Study of the effect of mixing cycle of N220:N330 ratios on physical and mechanical properties

In the second experiment, two different formulations were selected comparing the results of 1st experiment by considering the mechanical, physical and abrasion properties as per a solid tyre. Six types of different combinations were selected by CB pphr increasing and reducing from the formulation D where N220:N220 ratio is 30:20. For this study, N220:N330 ratio is selected 25:25 and 35:15. Selected CB ratios and changed mixing cycles are summarized in Table 3-8 and samples were coded as per Table 3-8.

4.2.1 Effect on cure characteristics

As indicated in rheological properties are also not shown a significant difference in the values. The same behavior was observed in the first trial with CB ratio is changed. Here, the impact is further reduced since the CB ratio change is minimum.

Table 4-4: Cure characteristics of the compound with N220:N330 ratios of CB and mixing cycles

	M_L	M_H	t_{s2}	t₉₀
Test Type	dNm	dNm	sec	sec
L25(N220)	2.26	14.34	93	194
M25(N220)	2.34	14.32	102	201
H25(N220)	2.20	14.55	101	213
L35(N220)	2.43	14.86	101	213
M35(N220)	2.51	14.94	101	215
H35(N220)	2.42	14.33	99	213

4.2.2 Effect on mechanical and physical properties

As shown in Figure 4-10, 300% modulus is gradually reduced from the lower mixing cycle to a higher mixing cycle in both formulations. This is due to the polymer chains are broken down further in mixing. Since the mixing cycle is extended in the last step polymer chain breakdown is vigorous. 300% modulus is not significant in these two formulae with the carbon content is increased by 10 pphr.

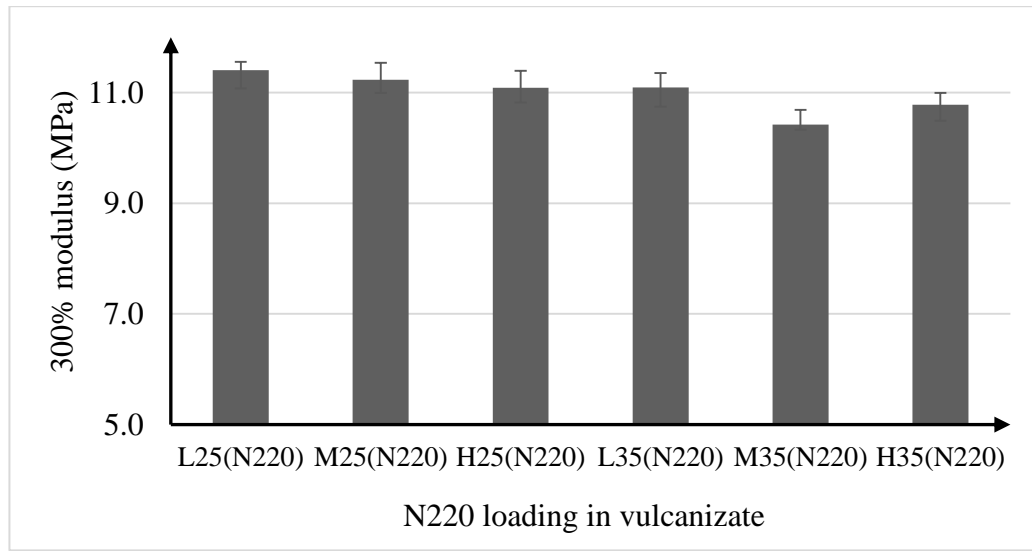


Figure 4-10: 300% modulus with N220:N330 ratios of CB and mixing cycles

Tensile strength in two formulas is shown in Figure 4-11. The medium mixing cycle shows the maximum tensile strength in both cases for two formulas. The medium mixing cycle which was used 90 sec for the last step may be the optimum cycle with respect to the tensile strength. Mixing cycle less time has lower tensile strength because it is not completed its break down of aggregates and incorporation of the CB into the rubber matrix. The higher mixing cycle is having lower tensile strength since it experiences excess break down of polymer and degradation of the compound.

A significant difference was not shown in two peaks which were used different CB ratios but the same mixing cycle. The advantage of CB further mixing was not shown additional improvement than the formulation used in D where N220:N330 ratio is 30:20.

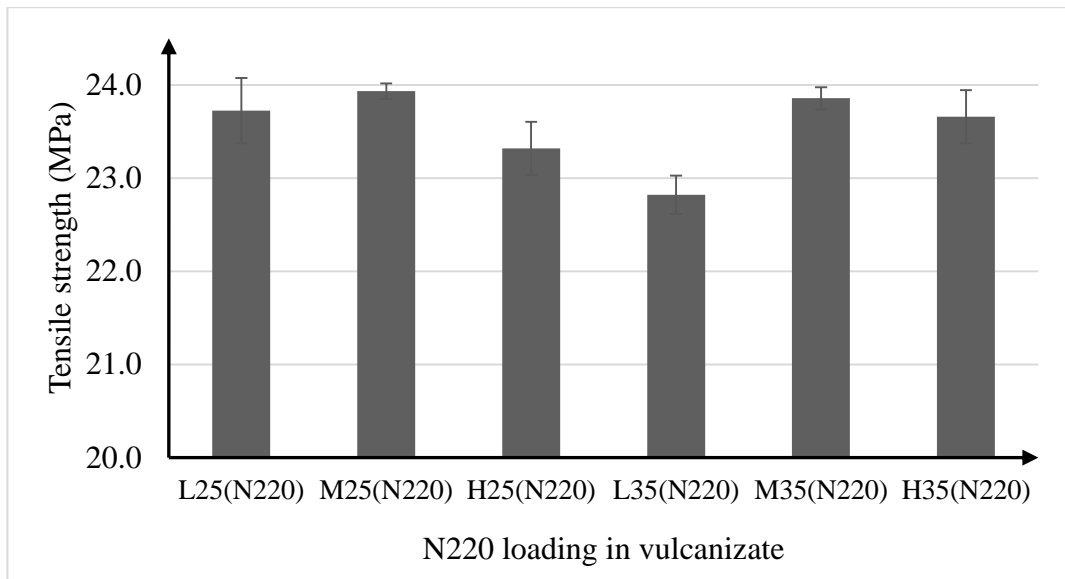


Figure 4-11: Tensile strength with N220:N330 ratios of CB and mixing cycles

Elongation at break is shown in Figure 4-12 and shows no significant difference in two compound recipes and between the mixing cycles. The same effect was discussed in the previous test also.

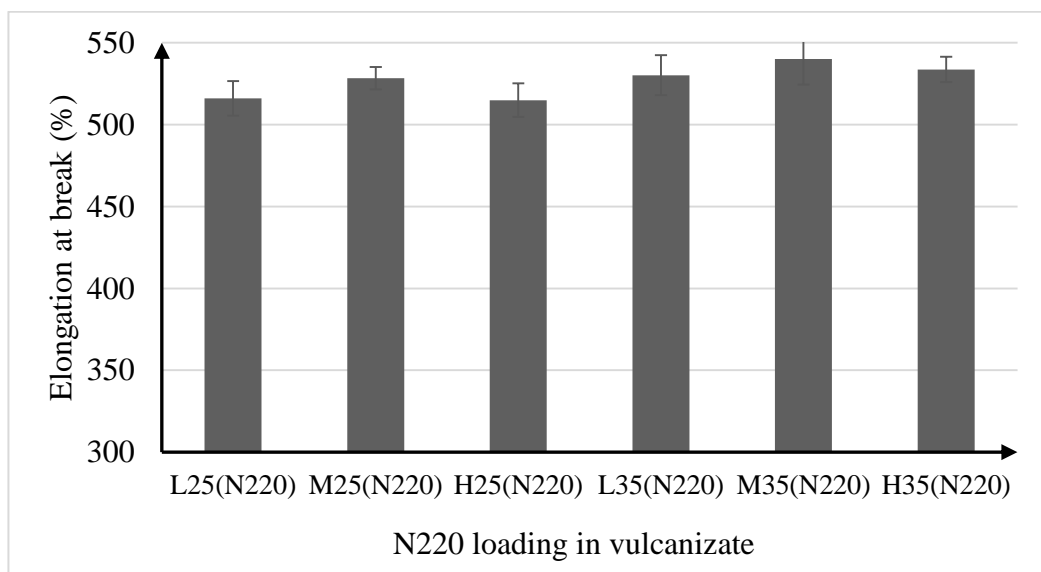


Figure 4-12: Elongation at break with N220:N330 ratios of CB and mixing cycles

Hardness and specific gravity of the vulcanizates are shown in Table 4-5. It can be seen that hardness and specific gravity of the vulcanizates are not showing a significant difference in the different CB ratios as same as the previous trial.

Table 4-5: Physical properties with N220:N330 ratios of CB and mixing cycles

Property	Unit	L25 (N220)	M25 (N220)	H25 (N220)	L35 (N220)	M35 (N220)	H35 (N220)
Hardness	Shore A	67.00	66.00	67.00	68.00	66.00	67.00
Specific Gravity	No units	1.117	1.115	1.118	1.117	1.115	1.119

Based on the physical and mechanical properties there is no significant improvement in the formulation and mixing cycle changes done in L25(N220) to H35(N220). Improvement of the two CB ratios or mixing cycles cannot be observed in the experiments.

4.2.3 Effect on abrasion resistance

Abrasion is the most important feature of this optimization study. Abrasion loss in these six different combinations is shown in Figure 4-13. In both formulas used in this experiment shows that the lowest abrasion is shown in the medium mixing cycle. Deviations from the initial mixing cycles are always shown higher abrasion loss. It is due to the insufficient mixing of the compound used in these compounds. CB aggregates were not given enough energy to break down and bound with the rubber matrix.

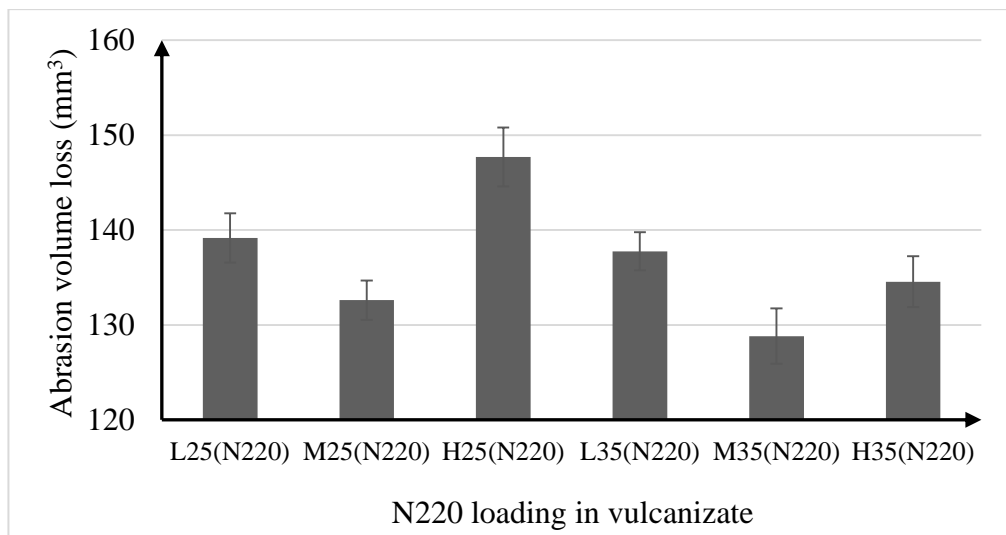


Figure 4-13: Abrasion volume loss with N220:N330 ratios of CB and mixing cycles

In higher mixing cycles is also shown higher abrasion loss. It may be due to the degradation of the polymer matrix. Degradation is caused by excessive breakdown of rubber chains and weaken the polymer by high temperature. Since the compound is exposed to the temperature higher than 155 °C and it is cooled only by natural convection cooling, the affected time for the higher temperature is increased.

In the first experiment, the lowest abrasion of the 115.96 was obtained in formula D is comparatively lower than the values of the second trial. All observed abrasion volume loss values are greater than Formula D where N220:N330 ratio is 30:20. Neither mixing cycles change no formulation change improves the abrasion than the previous trial.

4.2.4 Effect on rebound resilience

As shown in Figure 4-14 rebound resilience is not shown significant differences in mixing cycle changes than CB reinforcement. In the first trail over 20 pphr change also only one unit is changed. So impact from the mixing cycle is not salient in the selected range.

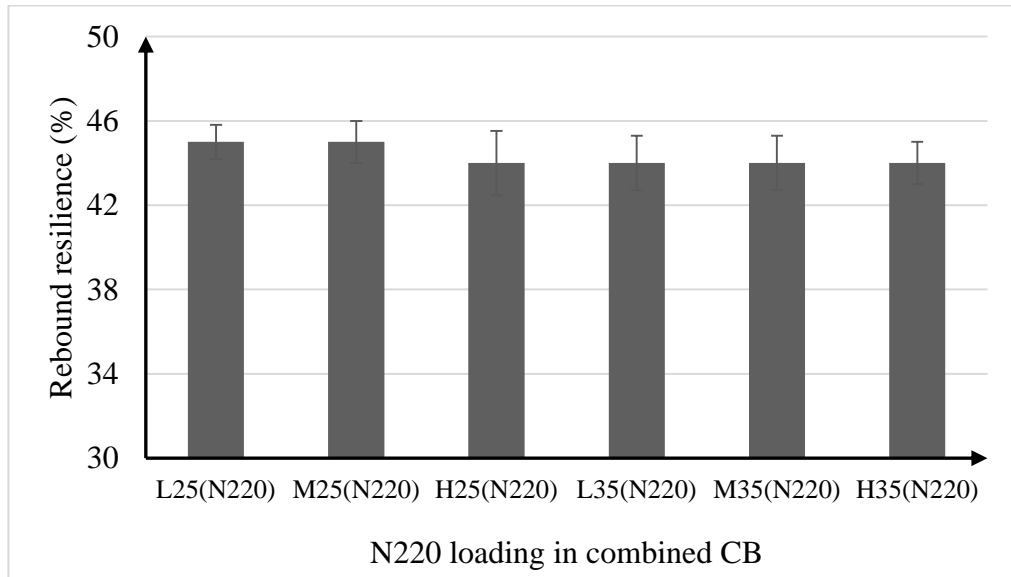


Figure 4-14: Rebound resilience with N220:N330 ratios of CB and mixing cycles

5. CONCLUSIONS

In this research, it was observed the effect of combinations of N220 and N330 carbon black ratios on physico-mechanical properties. Further, it was identified the impact of the mixing cycle of the solid tyre tread compound.

- In this investigation, with increasing N220 content upto 30 pphr, the physical and mechanical properties of the tread compound were improved. From 30 pphr onwards, the corresponding properties were decreased.
- The standard deviation of particle size dispersion in vulcanizates was in maximum level at 30:20 ratio of N220 and N330 carbon blacks.
- Hence, the dispersion was also significant to decide the optimum ratio for better physico-mechanical properties.

Futher, the impact of the mixing cycle was identified using three different mixing sequences as lower, medium and high.

- At the point of optimum filler feeding in to the compound, it was identified the medium mixing cycle had shown the best results for abrasion resistance and highest physico-mechanical properties with rebound resilience was at a moderate level.
- The properties such as hardness and cure characteristics were not shown any significant variation in the experiment.

Based on these facts, selected carbon black ratio 30:20 of N220 and N330 carbon black with medium mixing cycle could be found as the optimum combinations for the solid tyre tread compound formulation.

6. RECOMMENDATIONS

Based on the finding of the present study it is recommended the following studies.

- The effect of the curing system with the change of the combination of carbon black is needed to be considered.
- It is proposed to observe the impact of the optimum carbon black combination on internal heat build-up of the final product through dynamic mechanical analyser (DMA), in order to predict the heat build-up under service condition.
- Physical and mechanical properties were tested in laboratory-scale but it is recommended to conduct a field level product confirmation by set of test tyres.

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